

# Noble Gas Sources, Transport and Groundwater Interaction in Sedimentary Basins

Anran Cheng

St Catherine's College

University of Oxford

*A thesis submitted for the degree of*

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## Abstract

The transport of subsurface fluids is an essential factor for the understanding of natural resource reservoirs and the assessment of environmental projects, such as carbon capture and storage and nuclear waste respiratory. Noble gases, due to their chemical inertness, are a useful suite of tracers for identifying and quantifying physical processes in the subsurface. In this study, numerical models were developed to characterise noble gas migration, aiming to identify hydrogeological events and to quantify crustal degassing processes. Samples from the Williston Basin were analysed for their noble gas concentration and isotopic composition. The excess  $^4\text{He}$  compared to the predicted in-situ production is evidence of cross-formational migration and noble gas flux from the ancient crystalline basement. Numerical simulations enable the quantification of apparent helium basement flux and the identification of hydrogeological units that have experienced  $^4\text{He}$  loss due to water disturbance. Noble gas samples from the Southwestern Ontario Basin were analysed.  $^4\text{He}$  and  $^{40}\text{Ar}$  basement fluxes are estimated with the transport model and are then used to construct basement flux maps. The maps identify flux anomalies in the basin, that are likely caused by compositional and permeability variations in the basement rock. Furthermore, differential equations are derived characterising the water-gas interaction under different degassing processes. Error-weighted, nonlinear inversion matrix models are computed for atmospheric noble gas isotopes to quantify the gas-water volume ratios and the excess Kr and Xe widely observed in sedimentary basins. The modelled results suggest that excess Kr and Xe are likely released from sedimentary grains. Finally, the formation of helium reservoirs in the Williston Basin is investigated and simulated with a one-dimensional diffusion-and-exsolution model, producing modelled results comparable to observations. This aids the understanding of nitrogen-rich helium reservoirs in ancient, stable intracratonic basins. Overall, this thesis explores noble gases applications, by combining measurements from natural systems with numerical and mathematical models, to identify and quantify fluid transport, gas exsolution, and crustal degassing.



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# Declaration

I declare that this thesis is composed by myself and the work has not been submitted for another degree of professional qualification.

Anran Cheng,  
St Catherine's College



# Extended Abstract

Groundwater plays a significant role in subsurface transport; it controls the movement of dissolved materials and influences the chemistry of fluids and solids it contacts. Research on paleo- and present day fluid migration is important for understanding the sources, formation and transport of natural resources, including oil and gas (Meakin and Tartakovsky, 2009). It is also essential for accurate calculation of groundwater residence times and for determining the dominant transport mechanism of fluids, information vital to environmental projects such as carbon capture and storage and nuclear waste repository. With a growing number of investigations on water-rock interactions and fluid residence in the crystalline basement, deep crustal systems appear to be a source for multiple natural resources, including helium, hydrogen, nitrogen and light hydrocarbons (e.g. Sherwood Lollar and Ballentine, 2009; Holland et al., 2013; Warr et al., 2018). The quantification of outgassing from the crystalline basement is not only an essential component required in analysing the hydrogeology of the overlying sedimentary basin but also has an impact on the assessment of helium reservoirs and associated hydrogen as a nutrient source for the deep sedimentary environment.

Noble gases, due to their chemical inertness, are a useful suite of tracers for identifying and quantifying physical processes in the subsurface, including the interactions between different fluids (e.g. Ballentine et al., 2002; Zhou et al., 2005; Gilfillan et al., 2009; Barry et al., 2016) and crustal degassing (e.g. Torgersen and Clarke, 1985; Torgersen, 1989; Torgersen, 2010). Numerical modelling has been used to simulate the transport of groundwater and dissolved substances and to identify hydrogeological events (e.g. Castro et al., 1998b; Mazurek et al., 2011; Hendry et al., 2015). In this study, numerical models from first principles are developed to identify noble gas transport mechanisms in sedimentary basin systems and to quantify crustal degassing processes. The model is based on noble gas data from samples collected from various locations and geological formations in two sedimentary basins, the Williston Basin and the Southwestern Ontario Basin.

The Williston Basin is an intracratonic basin located along the border of the US and Canada. Twenty-six natural gas samples were collected and analysed for their noble gas isotopic and concentration data. Most samples demonstrate air-normalised  $^3\text{He}/^4\text{He}$

( $R_a$ ) values range between 0.08  $R_a$  and 0.36  $R_a$ , higher than the crustal endmember of 0.02  $R_a$ . Mass balance calculations and neutron capture estimates suggest that the excess  $^3\text{He}$  is not likely to be sourced from magma intrusion or localized Li enrichment.  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios of Deadwood samples (contact unit with the basement) fall on a mixing line between air and a radiogenic production endmember which is distinct from the modern crust and has been ascribed to an Archean source (Kendrick et al., 2011; Lippmann-Pipke et al., 2011; Holland et al., 2013), consistent with the Archean-aged basement rock beneath the Deadwood well. The He and Ne signatures can be explained by gas transport between the different sedimentary formations with a deeper input from the crystalline basement. Cross-formational transport of noble gases and crystalline basement flux is further supported by observations of excess  $^4\text{He}$  in relative to that expected from in situ production in the sedimentary units. Deviations from simulated vertical diffusion profiles of  $^4\text{He}$  are shown for the Viking, Mannville and Mississippian formations, indicating  $^4\text{He}$  loss due to water disturbance, likely related to anthropogenic water flooding associated with hydrocarbon production, a common occurrence in these formations of the Williston Basin. The apparent helium flux into the base of the Williston Basin is estimated to be  $0.8\text{--}1.6 \times 10^{-6} \text{ mol/m}^2/\text{yr}$ , comparable to the steady state flux of average continental crust ( $1.47 \times 10^{-6} \text{ mol/m}^2/\text{yr}$ ). The simplifications associated with the model indicate the estimates are minimum values for the basement flux.

The Southwestern Ontario Basin refers to sedimentary strata overlying the Algonquin Arch, which separates the Michigan Basin to the west and the Appalachian Basin to the east. Thirty-three natural gas samples were collected and analysed for their noble gas isotopic and concentration data. Excess  $^4\text{He}$  compared to the calculated in situ radiogenic production is observed in most samples, indicating the presence of an external  $^4\text{He}$  flux and gas transport between different geological units. The comparison of  $^3\text{He}/^4\text{He}$  ratios between Southwestern Ontario Basin and the Michigan Basin, suggest a Pleistocene water migration is unlikely. For a static and diffusion-dominated groundwater, an iterative method is applied to the transport models to estimate the apparent basement fluxes of  $^4\text{He}$  and  $^{40}\text{Ar}$  for each well. The estimated fluxes are used for the construction of basement flux maps. The maps show that the Algonquin Arch separate the Southwestern Ontario Basin into a high flux area on the southeast ( $0.39 \times 10^{-6} \text{ mol } ^4\text{He}/\text{m}^2/\text{yr}$  and  $0.97 \times 10^{-8} \text{ mol } ^{40}\text{Ar}/\text{m}^2/\text{yr}$ ) and a low flux area on the northwest ( $0.10 \times 10^{-6} \text{ mol } ^4\text{He}/\text{m}^2/\text{yr}$  and  $0.32 \times 10^{-8} \text{ mol } ^{40}\text{Ar}/\text{m}^2/\text{yr}$ ). This higher flux can be attributed to compositional or permeability differences in the basement rock. The average modelled  $^4\text{He}$  flux estimated for the Southwestern Ontario Basin is smaller than both the expected crustal production value and the values determined for the Williston Basin. The lower  $^4\text{He}$  flux in the Southwestern Ontario Basin corresponds with less mantle-derived helium and lower

heat flux and stronger decoupling of heat-He. This suggests potential correlations among variables of  $^4\text{He}$  flux,  $^3\text{He}/^4\text{He}$  ratios, heat flux and heat-He-decoupling, which requires further studies to be identified.

With the noble gas data from the Southwestern Ontario Basin, noble gas behaviour during gas-water interaction is further investigated, using the atmospheric isotopes,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$ . In sedimentary basins, these isotopes are usually assumed to be sourced from the atmosphere through groundwater recharging and are useful tools for quantifying subsurface fluid interactions. Differential equations characterizing water-gas interaction under different degassing processes (Barry et al., 2016) are first summarized and derived. Error-weighted, nonlinear inversion matrix models are computed to estimate the gas-water ratios and to quantify excess Kr and Xe using the concentrations and concentration ratios of these isotopes. Different solutions obtained between the concentration and ratio models can be resolved mathematically considering an air contamination or a fluid dilution scenario. The relationship between krypton and xenon enrichment ( $f_{\text{Xe}}$  and  $f_{\text{Kr}}$  in the Southwestern Ontario Basin, and in various basins globally, is comparable to the theoretical ratios estimated from Kr and Xe adsorption on carbon (charcoal),  $0.22 (\text{Kr}/\text{Xe})_{\text{ASW}}$ , the observations from young ocean sediment,  $0.12 (\text{Kr}/\text{Xe})_{\text{ASW}}$  and the observation of siliceous ocean sediments  $0.55 (\text{Kr}/\text{Xe})_{\text{ASW}}$ , suggesting the release of adsorbed krypton and xenon on sedimentary grains is likely the source of excess Kr and Xe observed in the basin systems.

And lastly, the focus is on investigating and simulating the formation of helium reservoirs quiescent and ancient intracratonic basins. The one-dimensional diffusion-and-exsolution model is developed to predict the formation of  $\text{N}_2$  dominant gas phase, which is associated with  $^4\text{He}$  and sourced from the crystalline basement. The model is able to simulate gas compositions comparable to observations in the Cambrian Deadwood Helium reservoir in the Williston Basin, with a basement helium flux compatible with observed concentration gradients and the  $\text{N}_2/^4\text{He}$  basement flux ratio comparable to that observed in helium reservoirs in the sedimentary basins. The model demonstrates the significance of sedimentary basin architecture, basement helium and nitrogen flux, and the timing and size of gas formation, and these factors need to be considered in predicting the generation of economically viable helium fields in similar basin settings.

Overall, the data and interpretations presented in this study explore the application of noble gases as tracer elements for subsurface fluids, especially deep groundwater systems, and establishes new models for the understanding of fluid transport, gas exsolution and crustal degassing.





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# 1

## Introduction

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### 1.1 GROUNDWATER AND FLUID MIGRATION IN SEDIMENTARY BASINS

Groundwater plays a significant role in subsurface transport. Its migration controls the movement of dissolved materials and influences the chemistry of fluids and solids it contacts. Groundwater movement in sedimentary basins has been researched for decades with a broad scope of applications. Fluid migration research can be applied in the exploration and management of water resources and groundwater contamination (e.g. Gorelick, 1983; Werner et al., 2013; Anderson et al., 2015; Gassiat et al., 2013; McIntosh et al., 2018; Gilevska et al., 2019). Groundwater studies also provide crucial information in understanding the sources, formation and transport of natural resources, including oil and gas (e.g. Meakin and Tartakovsky, 2009). The residence time and migration history of groundwater and basinal geophysical and geochemical properties are also vital to environmental projects such as carbon capture and storage (e.g. Gunter et al., 2004) and nuclear waste repositories (e.g. Hendry et al., 2015; Sykes et al., 2011).

### 1.2 CRUSTAL DEGASSING

Fluid residence in the continental crust can be on time scales up to millions and sometimes billions of years (Sherwood Lollar and Ballentine, 2009; Holland et al., 2013; Warr et al., 2018). The resulting products of long-term water-rock interaction, such as hydrogen, can be globally significant (Sherwood Lollar et al., 2014) and released to

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the shallow sedimentary system. Deep crustal fluid systems are increasingly being postulated as a potential source for helium, hydrogen, trace hydrocarbons as well as heat.

Radiogenic helium within the crystalline basement and overlying sedimentary units is produced by uranium and thorium decay chains (Ballentine and Burnard, 2002). Hydrogen can be produced in the continental lithosphere by the radiolysis of water and hydration reactions (Sherwood Lollar et al., 2014). Abiogenic methane is generated by low-temperature water-rock reactions in continental settings (Etiope and Sherwood Lollar, 2013). Heat is stored in the crust as a result of both heat flux from the mantle as well as heat generation from radioactive reactions within the crustal units. The quantification of gas flux from the crystalline basement is an essential component in understanding the geochemistry and biogeochemistry of deep sedimentary systems. This includes the formation of helium and hydrogen resources and sources of electron donors and acceptors that may influence the deep sedimentary biosphere. However, the compositional heterogeneity within the crust results in local and regional deviations in the production rate from the global average. In order to quantify the degassing processes, concentration measurements alongside numerical models and simulations, are required.

### **1.3 HELIUM EXPLORATION IN SEDIMENTARY BASINS**

Helium has a boiling point approaching absolute zero and thus an unreplaceable industrial coolant, especially for medical MRI scanners and Large Hadron Collider. The non-reactive nature also makes helium suitable for applications such as rocket propulsion systems and semiconductor manufacturing.

Helium has been produced mainly as a secondary product of hydrocarbon production. If helium concentrations within hydrocarbon reservoirs are greater than 0.3%, it is economically viable for separation. However, these concentrations are only reached in a limited number of hydrocarbon fields. In natural gas fields that are produced for liquified natural gas (LNG), helium concentrations as low as 0.01% become

#### *1.4. PROJECT OUTLINE*

commercially viable but are then reliant on the market for LNG (Bare et al., 2016; Ballentine, 2017). The coupling between the current helium and hydrocarbon industry results in the helium supply being sensitive to the oil and gas field production. The scarcity and unrenewable nature make it a valuable resource and susceptible to supply shortages. Between 2009 and 2016, the open market price for crude helium in the U.S.A. increased by more than 60% while the price for liquid helium increased by 250% over the same time period (Bare et al., 2016). In 2006, 2013 and again at the time of writing (2019) supply warnings were sent to Europe and US users, stating any demand increase could not be met for those years (Ballentine, 2017).

The distribution and migration of helium from the crystalline basement of the continental crust remain relatively unconstrained. The depletion of current helium reserves and geopolitics of the remaining resource locations has resulted in a greater need to understand helium distribution and migration in sedimentary basins. This is essential to the understanding and discovery of new helium plays. Furthermore, the study of helium systems also aids in the understanding of other basement sourced gases.

#### **1.4 PROJECT OUTLINE**

This project aims to further develop the application of noble gas isotopes to understand groundwater residence and migration in sedimentary basin systems, the degassing fluxes from the underlying crystalline basement and the interaction between different fluid phases. This thesis achieves the aim through the following sections.

1. Providing comprehensive noble gas isotope analysis and simulating the transport of groundwater-dissolved materials with numerical models from first-order principles in both the Williston Basin (Chapter 4) and the Southwestern Ontario Basin (Chapter 5).
2. Quantitatively estimating noble gas flux from the crystalline basement (Chapter 4) and producing basement flux maps (Chapter 5).



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3. Constructing error-weighted non-linear inversion models to characterise reservoir degassing processes and the widely observed Kr and Xe enrichment in basin systems (Chapter 6).
4. Developing the transport model to include solubility to predict the condition under which helium-rich gas reservoirs are formed (Chapter 7).

In addition to the above, numerically model construction are presented in Chapter 3, analytical chapters, field sampling techniques, experimental protocols are included in Appendix A, and overall conclusions and future research potential are outlined in Chapter 8.



# 2

## Literature Review

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## 2.1 INTRODUCTION TO NOBLE GASES

Noble gases are the elements belonging to Group 18 in the Periodic Table. Stable isotopes of He, Ne, Ar, Kr and Xe are considered in this thesis. According to modern atomic theory, their outer electron shells are full, making the formation of covalent bonds unfavourable. Therefore, they are chemically inactive and do not form compounds with other elements, with some exceptions under extreme pressure and temperature conditions (e.g. Lemieux, 2011). They are called ‘the inert gases’, ‘the noble gases’ or ‘rare gases’, reflecting their high volatility and low abundance in geological materials. The analysis of noble gases utilises both the concentrations and variance in elemental and isotopic ratios and is widely used in Earth and solar system research. Noble gases were used to date minerals and to analyse meteorite samples

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from as early as 1900s (Rayleigh, 1933; Strutt, 1908; Strutt, 1933; Dewar, 1908; Dubey and Holmes, 1929; Paneth et al., 1930; Arrol et al., 1942; Reasbeck and Mayne, 1955).

With increased studies and improved knowledge of the noble gas system, researchers quantified the noble gas budget of the atmosphere and oceans, and noble gases are applied to the understanding the Earth's mantle and magma, and the origin, migration, and alteration of crustal fluids.

### **2.2 NOBLE GASES AS GEOCHEMICAL TRACERS**

The fundamental sources/production pathway of terrestrial noble gases can be grouped into three categories: 1) primordial gases trapped in the Earth's interior since planetary accretion; 2) radiogenic, nucleogenic and fissiogenic gases produced from terrestrial radioelements; 3) cosmogenic gases produced by spallation reactions and extraterrestrial gases accumulated from meteorites and interplanetary dust particles.

The primordial gases refer to the elements that originated in the proto-solar nebula – the cloud of dust and gas that the solar system formed from. The well-mixed nature of the solar nebula has resulted in comparable isotopic signatures between all undifferentiated solar system materials, along with similar elemental abundances between primitive meteorites and the sun (Wieler, 2002). However, during the formation of terrestrial planets, noble gases, due to their high volatility and chemical inertness, became depleted in solid phases. The accretion of materials during the formation of the proto-Earth induced devolatilisation of volatile species, including noble gases, into the growing atmosphere. Atmosphere can be lost to space as a result of impact erosion, sputtering, thermal evaporation or hydrodynamic escape (Pepin and Porcelli, 2002; Tucker and Mukhopadhyay, 2014). Primordial gases retained in the mantle are readily transferred to the crust, the hydrosphere and the atmosphere through volcanic and magmatic events (Porcelli and Ballentine, 2002). Primitive noble gases are also proposed to be added during late stage of terrestrial accretion of

## 2.2. NOBLE GASES AS GEOCHEMICAL TRACERS

asteroidal and/or cometary materials to the Earth’s mantle and atmosphere (Holland et al., 2009; Caracausi et al., 2016; Marty et al., 2016; Guillaume Avice et al., 2017).

Another significant contributor to the global noble gas budget is production from radioactive decay. Such reactions are functions of radioelement concentration, element distribution in the minerals and reaction time, which will be described further in the following sections.

Cosmogenic noble gases are produced at the Earth’s surface by the interaction between cosmic rays and target nuclei, mostly by spallation reactions (Samuel Niedermann, 2002). However, the low production rates make this an insignificant contribution to the Earth’s noble gas budget (Ballentine and Burnard, 2002). Interplanetary dust particles (IDP), extra-terrestrial materials with diameters between  $1\ \mu\text{m}$  -  $1\text{ mm}$ , are argued to be the primary source of extra-terrestrial  $^3\text{He}$  today (e.g. Farley, 1995). While entering the Earth’s atmosphere, IDPs experience various amounts of heating, and consequently, different degrees of gas loss, based on the particle size, entry angle and their original orbital properties (Flynn, 1989). Extra-terrestrial noble gas flux varies geographically and temporally (e.g. Takayanagi and Ozima, 1987; Farley, 1995; Marcantonio et al., 2001; Chavrit et al., 2016; Schmitz et al., 2019). While demonstrating high abundance in some marine/ocean sediments, noble gases from IDPs are not considered a significant contribution to the global noble gas budget or terrestrial sedimentary systems. Therefore, when considering crustal fluids, noble gases from cosmogenic and IDP sources are not considered further in this study.

After accretion, the Earth differentiated into four main geosphere reservoirs – the core, mantle, crust, and atmosphere. Over time, these reservoirs developed distinctive elemental and isotopic noble gas signatures, depending on the relative contributions of primordial and radiogenic noble gases. While the signature of the core remains poorly known, the noble gases in the mantle, crust, and atmosphere are increasingly well characterised. Because these elements are chemically inert, the end-member ratios

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for each reservoir can be used to understand the physical processes and conditions (pressure, temperature) influencing crustal fluids.

### **2.2.1 Naturally Occurring Noble Gas Stable Isotopes**

Helium is the lightest noble gas, with two stable isotopes,  $^3\text{He}$  and  $^4\text{He}$ .  $^4\text{He}$  has the highest radiogenic production rate in the Earth compared to the other noble gases and formed as part of the decay chains from U and Th (Ballentine and Burnard, 2002). Helium is readily lost to space and difficult to be recycled back into the mantle (Ballentine and Holland, 2008). The residence time of He in the atmosphere is approximately one to ten million years (Graham, 2002), which leaves the atmosphere with a relatively low He abundance. Radiogenic production of  $^3\text{He}$  within the earth forms a minor contribution to terrestrial systems, and therefore, most  $^3\text{He}$  is primordial and preserved within the Earth's mantle since the formation of the Earth.

The three stable isotopes of neon are  $^{20}\text{Ne}$ ,  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$ .  $^{21}\text{Ne}$  is readily produced by nucleogenic reactions (Wetherill, 1954; Ballentine and Burnard, 2002). Crustal production of  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  in young and shallow crustal systems is low relative to  $^{21}\text{Ne}$ , and, in sedimentary basin systems, these two isotopes are dominated by atmospherically-derived sources (Ballentine and Burnard, 2002; Ballentine et al., 2002).

There are three stable isotopes of argon:  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$  and  $^{40}\text{Ar}$ . The other isotopes include  $^{37}\text{Ar}$ ,  $^{39}\text{Ar}$ ,  $^{41}\text{Ar}$  and  $^{42}\text{Ar}$ , but are produced either cosmogenically or synthetically in nuclear reactors. These synthetic isotopes are used in  $^{40}\text{Ar}/^{39}\text{Ar}$  dating or for tracing surface water circulation with high-sensitivity accelerator mass spectrometry. Since they do not exist in natural crustal fluids in concentrations detectable by standard noble gas mass spectrometry, these unstable isotopes are not considered further. The contribution of  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  from nucleogenic production routes in the crust and the mantle is small relative to the atmospheric sources (Wetherill, 1954; Ballentine and Burnard, 2002). The presence of these two isotopes in mantle samples is usually interpreted as an atmospheric component recycled into the mantle via

## 2.2. NOBLE GASES AS GEOCHEMICAL TRACERS

subduction, or a primordial component retained since the accretion of the proto-Earth, or a combination of the two (Ballentine and Holland, 2008). Although some are primordial,  $^{40}\text{Ar}$  in the atmosphere is dominated by radiogenic  $^{40}\text{Ar}$  produced from  $^{40}\text{K}$  decay that has degassed from the mantle and crust (Allège et al., 1996; Porcelli and Ballentine, 2002). Unlike  $^4\text{He}$ ,  $^{40}\text{Ar}$  does not escape the atmosphere and this isotope is the most abundant noble gas in the modern atmosphere.

There are six naturally occurring stable isotopes of krypton:  $^{78}\text{Kr}$ ,  $^{80}\text{Kr}$ ,  $^{82}\text{Kr}$ ,  $^{83}\text{Kr}$ ,  $^{84}\text{Kr}$  and  $^{86}\text{Kr}$ .  $^{79}\text{Kr}$  and  $^{81}\text{Kr}$  are synthetic radioisotopes, and  $^{85}\text{Kr}$  is a trace radioisotope with a half-life of 10.76 years. The isotopic composition of krypton of oceanic basalt is dominated by that of the modern air (Desmond B Patterson et al., 1990; Graham, 2002), with trace signals of a primordial component found in some  $\text{CO}_2$  well gases (Holland et al., 2009). Only a minor amount of krypton is produced from fission reactions (Ballentine and Burnard, 2002).

There are thirteen xenon isotopes (70 to 82 neutrons) in total, but only nine of them ( $^{124}\text{Xe}$ ,  $^{126}\text{Xe}$ ,  $^{128}\text{Xe}$ ,  $^{129}\text{Xe}$ ,  $^{130}\text{Xe}$ ,  $^{131}\text{Xe}$ ,  $^{132}\text{Xe}$ ,  $^{134}\text{Xe}$  and  $^{136}\text{Xe}$ ) are stable isotopes that exist naturally and are considered in this study. Xenon can also be produced through fission reactions (Ballentine and Burnard, 2002; Graham, 2002). The differences between  $^{129}\text{Xe}/^{130}\text{Xe}$  and  $^{136}\text{Xe}/^{130}\text{Xe}$  in the mid-ocean ridge basalts and the air are used as evidence for an early separation of the atmosphere and the upper mantle (Thomsen, 1980; Staudacher and Allège, 1982; Graham, 2002). Pujol et al. (2011) proposed the model of Xe isotopic fractionation during the Archean. Noble gases trapped in Archean quartzite indicates the Paleo-atmospheric Xe in 3.0-3.3 Ga is mass-dependently fractionated by  $12.9 \pm 2.4\text{‰ } amu^{-1}$  relative to the modern atmosphere, enriched in light isotopes and depleted in heavy ones (Guillaume Avice et al., 2017; Bekaert et al., 2018). The composition slowly evolved to modern compositions at approximately 2.1 Ga (Avice et al., 2018). The distinct isotopic composition of Xe comparing to Solar or Chondritic endmember is proposed as the result of the cometary Xe input at the last stages of Earth accretion (Guillaume Avice et al., 2017).



## *2. Literature Review*

### **2.2.2 Sources of Noble Gases in Sedimentary Basins**

In crustal systems, noble gases can help to differentiate the input from different reservoirs (e.g. Ballentine et al., 2002; Castro et al., 2005; Ballentine and Holland, 2008; Holland et al., 2013; Barry et al., 2016; David J Byrne et al., 2018), quantify the interaction between different fluids (e.g. Ballentine et al., 1991; Pinti and Marty, 1995; Zhou et al., 2005; Gilfillan et al., 2009; Barry et al., 2018a; D. Byrne et al., 2018; Heard et al., 2018; Warr et al., 2018; Karolyté et al., 2019), reveal mechanisms controlling crustal degassing (e.g. Torgersen and Clarke, 1985; Torgersen, 1989; Ballentine et al., 1991; Elliot et al., 1993; Bender et al., 2008; Sherwood Lollar and Ballentine, 2009; Torgersen, 2010; Lowenstern et al., 2014; Aggarwal et al., 2015) and identify fluid passage from mantle to the crust (e.g. Ballentine et al., 1991; Ballentine and O’Nions, 1992; Sherwood Lollar et al., 1994a; Palcsu et al., 2014; Broadley et al., 2016; Amaral et al., 2017).

In sedimentary basins, noble gases are sourced from the atmosphere, the crust and the mantle. Atmospheric gases dissolve in meteoric water at the earth’s surface and become incorporated into crustal fluids when that water enters the crust, either as formation water during burial, or via recharge. Such waters acquire their atmospheric noble gas contents as dissolved components by equilibrating with the atmosphere at recharge; dissolved concentrations are functions of temperature, pressure and salinity. With time, atmospheric signatures in crustal waters are altered by the addition of radiogenic noble gases, either in situ from the sedimentary sequence or via flux from the crystalline basement. Mantle gases can also be transported into the crust by magmatic intrusions and volcanic activity.

### **2.2.3 Atmospheric Noble Gases**

The noble gas composition of the atmosphere is well constrained in terms of elemental abundance and isotopic ratios and is listed in Table 2.1.

## 2.2. NOBLE GASES AS GEOCHEMICAL TRACERS

Atmospheric noble gases dissolved in the groundwater in equilibrium with the atmosphere can be calculated following Henry's law, which characterises phase partitioning between the amount of dissolved gases in the liquid and the partial pressure in the gas phase in equilibrium with the liquid. The proportionality constant is called Henry's constant. For gas  $i$ , the molar fraction in gas and water phase can be expressed with Henry's constant:

$$\phi_i p_i = \gamma_i K_i^{pressure} x_i. \quad (2.1)$$

$\phi$  and  $\gamma$  are gas-phase fugacity and liquid-phase activity coefficients, respectively;  $p$  is the partial pressure and is equal to the total gas pressure multiplied by the mole fraction of gas  $i$  in the bulk gas.  $K^{pressure}$  is Henry's constant between water and gas in units of pressure and  $x_i$  is the mole fraction of gas  $i$  in the water phase. Noticeably, Henry's constant can be expressed in multiple units depending on the units of the other parameters.

Gas activity at the ground surface is similar to the ideal gas system with the gas-phase fugacity ( $\phi$ ) equal to 1. In an ideal gas system, particles are moving randomly and the only interactions are elastic collisions. Noble gas partitioning demonstrates significant deviations from ideality in extreme conditions, such as a  $\text{CO}_2$  - water system with high  $\text{CO}_2$  density (Warr et al., 2015).

The non-ideal behaviour of noble gases ( $\gamma_i$ ) in the water phase is controlled by temperature and electrolyte concentration. The relationship is mathematically summarised by the Setchenow equation (Ballentine et al., 2002)

$$\gamma_i = \frac{S_i^0(T)}{S_i^{Na}(T)} = e^{N_{aki}(T)}, \quad (2.2)$$

where  $S_i^0(T)$  and  $S_i^{Na}(T)$  represent the solubility of the non-electrolyte  $i$  in pure water and saline solution of salinity  $Na$  respectively at temperature  $T$ . Setchenow coefficients can be calculated with the equation and constants listed in Table 2.2.

## 2. Literature Review

**Table 2.1:** Noble gas isotopic composition and abundance in the atmosphere. (Modified from Porcelli and Ballentine (2002) and reference therein.  $^{40}\text{Ar}/^{36}\text{Ar}$  is updated by J. Y. Lee et al. (2006), volume mixing ratios are calculated using elemental abundance and relative isotopic abundance, with propagated errors)

| Constituent/Isotopes | Relative abundance                 | Volume Mixing Ratio                |
|----------------------|------------------------------------|------------------------------------|
| Dry air              |                                    | 1                                  |
| Helium               |                                    | $(5.24 \pm 0.05) \times 10^{-6}$   |
| $^3\text{He}$        | $(1.399 \pm 0.013) \times 10^{-6}$ | $(7.34 \pm 0.07) \times 10^{-12}$  |
| $^4\text{He}$        | $\equiv 1$                         | $(5.24 \pm 0.05) \times 10^{-6}$   |
| Neon                 |                                    | $(1.818 \pm 0.004) \times 10^{-5}$ |
| $^{20}\text{Ne}$     | $9.8 \pm 0.08$                     | $(1.645 \pm 0.004) \times 10^{-5}$ |
| $^{21}\text{Ne}$     | $0.0290 \pm 0.08$                  | $(4.872 \pm 0.011) \times 10^{-8}$ |
| $^{22}\text{Ne}$     | $\equiv 1$                         | $(1.678 \pm 0.004) \times 10^{-6}$ |
| Argon                |                                    | $(9.34 \pm 0.01) \times 10^{-3}$   |
| $^{36}\text{Ar}$     | $\equiv 1$                         | $(3.14 \pm 0.003) \times 10^{-5}$  |
| $^{38}\text{Ar}$     | $0.1880 \pm 0.0004$                | $(5.90 \pm 0.006) \times 10^{-6}$  |
| $^{40}\text{Ar}$     | $298.56 \pm 0.31$                  | $(9.30 \pm 0.010) \times 10^{-3}$  |
| Krypton              |                                    | $(1.14 \pm 0.01) \times 10^{-6}$   |
| $^{78}\text{Kr}$     | $0.6087 \pm 0.0020$                | $(3.95 \pm 0.03) \times 10^{-9}$   |
| $^{80}\text{Kr}$     | $3.9599 \pm 0.0020$                | $(2.57 \pm 0.02) \times 10^{-8}$   |
| $^{82}\text{Kr}$     | $20.217 \pm 0.004$                 | $(1.31 \pm 0.01) \times 10^{-7}$   |
| $^{83}\text{Kr}$     | $20.136 \pm 0.021$                 | $(1.31 \pm 0.01) \times 10^{-7}$   |
| $^{84}\text{Kr}$     | $\equiv 100$                       | $(6.50 \pm 0.06) \times 10^{-7}$   |
| $^{86}\text{Kr}$     | $30.521 \pm 0.025$                 | $(1.98 \pm 0.02) \times 10^{-7}$   |
| Xenon                |                                    | $(8.7 \pm 0.1) \times 10^{-8}$     |
| $^{124}\text{Xe}$    | $2.337 \pm 0.008$                  | $(8.3 \pm 0.10) \times 10^{-11}$   |
| $^{126}\text{Xe}$    | $2.180 \pm 0.011$                  | $(7.7 \pm 0.09) \times 10^{-11}$   |
| $^{128}\text{Xe}$    | $47.15 \pm 0.07$                   | $(1.7 \pm 0.02) \times 10^{-9}$    |
| $^{129}\text{Xe}$    | $649.6 \pm 0.9$                    | $(2.3 \pm 0.03) \times 10^{-8}$    |
| $^{130}\text{Xe}$    | $\equiv 100$                       | $(3.5 \pm 0.04) \times 10^{-9}$    |
| $^{131}\text{Xe}$    | $521.3 \pm 0.8$                    | $(1.8 \pm 0.02) \times 10^{-8}$    |
| $^{132}\text{Xe}$    | $660.7 \pm 0.5$                    | $(2.3 \pm 0.03) \times 10^{-8}$    |
| $^{134}\text{Xe}$    | $256.3 \pm 0.4$                    | $(9.1 \pm 0.10) \times 10^{-9}$    |
| $^{136}\text{Xe}$    | $217.6 \pm 0.3$                    | $(7.7 \pm 0.09) \times 10^{-9}$    |

## 2.2. NOBLE GASES AS GEOCHEMICAL TRACERS

**Table 2.2:** Constants for calculating Setchenow coefficients,  $k_i$  (Smith and Kennedy, 1983).

| Species | G1       | G2      | G3     |
|---------|----------|---------|--------|
| He      | -10.081  | 15.1068 | 4.8127 |
| Ne      | -11.9556 | 18.4062 | 5.5464 |
| Ar      | -10.6951 | 16.7513 | 4.9551 |
| Kr      | -9.9787  | 15.7619 | 4.6181 |
| Xe      | -14.5524 | 22.5255 | 6.7513 |

$k_i(T) = G_1 + \frac{G_2}{0.01T} + G_3 \ln(0.01T)$ , where temperature is expressed in Kelvin. The equation constants are valid for temperature between 273 to 337 K, and salinity between 0 to 5.2 Molar. The experimental data are obtained from the NaCl solution, and little study has done on examining the effect of multi-electrolyte solutions. The impact of other dissolved non-electrolytes can be different but is also unknown.

**Table 2.3:** Coefficients for calculating Henry's constant in units of pressure,  $K_i^{pressure}$  (Ballentine et al., 2002).

| Species | A0       | A1       | A2       | A3        |
|---------|----------|----------|----------|-----------|
| He      | -0.00953 | 0.107722 | 0.001969 | -0.043825 |
| Ne      | -7.259   | 6.95     | -1.3826  | 0.0538    |
| Ar      | -9.52    | 8.83     | -1.8959  | 0.0698    |
| Kr      | -6.292   | 5.612    | -0.8881  | -0.0458   |
| Xe      | -3.902   | 2.439    | 0.3863   | -0.221    |

He values are obtained from Smith (1985). Ne, Ar, Kr and Xe values are derived from Crovetto et al. (1982). For Ne, Ar, Kr and Xe,  $\ln(K_i^{pressure}) = A_0 + \frac{A_1}{0.001T} + \frac{A_2}{(0.001T)^2} + \frac{A_3}{(0.001T)^3}$  where  $K^{pressure}$  is in GPa and T is the temperature in Kelvin. For He,  $\ln(F_{He}) = A_0 + \frac{A_1}{0.001T} + \frac{A_2}{(0.001T)^2} + \frac{A_3}{(0.001T)^3}$ , where  $F_{He}$  is relative fractionation of He to Ar, i.e.  $F_{He} = \frac{(X_{He}/X_{Ar})_{liquid}}{(X_{He}/X_{Ar})_{gas}} = \frac{(X_{Ar})_{gas}/(X_{Ar})_{liquid}}{(X_{He})_{gas}/(X_{He})_{liquid}} = K_{Ar}/K_{He}$ .

The solubility of noble gases is studied for different temperature ranges (e.g. Benson and Krause Jr, 1976; Potter and Clynnne, 1978; Crovetto et al., 1982; Smith, 1985). The empirical equations of Henry's constant are summarised by Ballentine and Hall (1999) (Table 2.3) and Ballentine et al. (2002) (Table 2.4) with units in atm and Gpa, respectively.

As mentioned above, Henry's constant can be expressed in multiple units, including a dimensionless form,  $K_i^d$ , or in units of molality,  $K_i^m$ , and are defined with the following equations, respectively:

$$C_i^{gas} = K_i^d C_i^{water}, \quad (2.3)$$

and

$$\phi_i P_i = K_i^m n_i^{water}, \quad (2.4)$$

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**Table 2.4:** Coefficient for calculating  $K_i^{pressure}$  and  $\beta_i^{pressure}$  (Ballentine and Hall, 1999).

| Species                      | A        | B       | C       | Reference                          |
|------------------------------|----------|---------|---------|------------------------------------|
| Ne                           | -52.8573 | 61.0494 | 18.9157 | IUPAC (Battino and Clever, 1979b)) |
| Ar                           | -57.6661 | 74.7627 | 20.1398 | IUPAC (Battino and Clever, 1979a)  |
| Kr                           | -66.9928 | 91.0166 | 24.2207 | IUPAC (Clever, 1979)               |
| Xe                           | -74.7398 | 105.21  | 27.4664 | IUPAC (Clever, 1979)               |
| <hr/>                        |          |         |         |                                    |
| Bunsen coefficient $\beta_i$ |          |         |         |                                    |
| Ne                           | -39.1971 | 51.8013 | 15.7699 | Ray F Weiss, 1971                  |
| Ar                           | -55.6578 | 82.0262 | 22.5929 | Ray F Weiss, 1971                  |

IUPAC coefficients are fit to the equation  $\ln(K_i^{pressure}) = A + \frac{B}{0.01T} + C\ln(0.01T)$ .  $K_i^{pressure}$  presents mole fraction solubility of noble gas i at 1 atm partial pressure, while Bunsen coefficient,  $\beta_i$ , is the volume of gas (standard temperature and pressure) dissolved per unit volume of water at 1 atm partial pressure.  $\ln(\beta_i^{pressure}) = A + \frac{B}{0.01T} + C\ln(0.01T)$ . For both equations, temperatures are expressed in Kelvin.

where  $C_i^{gas}$  and  $C_i^{water}$  are the concentration of species i in the gas and water phases, expressed as the amount of i per unit volume.  $n_i^{water}$  is the number of moles of i per kilogram of water. The different formats of Henry's constant are interchangeable:

$$K_i^d = \frac{Mr(H_2O)T^0}{V_m^{STP}T\rho_{H_2O}} \frac{\gamma_i}{\phi_i} K_i^{pressure}, \quad (2.5)$$

and

$$K_i^d = \frac{1000T^0}{V_m^{STP}T\rho_{H_2O}} \frac{\gamma_i}{\phi_i} K_i^m, \quad (2.6)$$

where  $Mr(H_2O)$  represents the molar mass of  $H_2O$ ;  $T^0$  is the standard temperature expressed in K;  $V_m^{STP}$  is the molar volume of gas at standard temperature and pressure. 1000 is the conversion factor from per gram to per kilogram.

### Crustal and mantle noble gases

The decay of radioactive parent elements is the pathway for radiogenic noble gas production. The continental crust contains about 40% of the terrestrial radioelement budget (Rudnick and Fountain, 1995). The concentration of radiogenic noble gases in the crustal fluid system is a combined result of radioactive decay, and the release of the daughter isotopes from the mineral hosting the radioelements into the surrounding fluid regime (Ballentine et al., 2002; Warr et al., 2018). Reliable quantification of these processes can, for example, help to resolve mean groundwater residence ages,

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**Table 2.5:** Natural isotopic abundance, decay constant and production yield for dominant alpha decay parents (Ballentine and Burnard, 2002).

|                   | $X_R$  | $\lambda_R(yr^{-1})$   | $yield_R$ |
|-------------------|--------|------------------------|-----------|
| $^{238}\text{U}$  | 0.9928 | $1.55 \times 10^{-10}$ | 8         |
| $^{235}\text{U}$  | 0.0072 | $9.85 \times 10^{-10}$ | 7         |
| $^{232}\text{Th}$ | 1.0000 | $4.95 \times 10^{-11}$ | 6         |

which is controlled by the three-dimensional transport of an age mass, the product of age and mass (Bethke and Johnson, 2002).

### Helium

$^4\text{He}$  is primarily produced by radioactive alpha decay, which is controlled by the abundance of  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$ . The stabilised alpha particles become  $^4\text{He}$ . Radiogenic  $^4\text{He}$  abundance can be calculated as a function of time (Ballentine and Burnard, 2002):

$$^4\text{He atoms per unit mass of rock} = \frac{X_R[R] \times 10^{-6}}{M_R} N_A (e^{\lambda_R t} - 1) yield_R \quad (2.7)$$

where  $X_R$  is the fractional natural abundance of isotope R,  $[R]$  is the present concentration of R (ppm);  $M_R$  is the molecular mass of R (g/mol),  $N_A$  is Avogadro's number,  $yield_R$  is the production of  $\alpha$ -particles per decay,  $\lambda_R$  is the decay constant ( $yr^{-1}$ ) and  $t$  is the number of years. The corresponding constants for each radioelement can be found in Table 2.5.

Nearly all terrestrial  $^3\text{He}$  is primordial. Crustal production of  $^3\text{He}$  is dominantly through thermal neutron capture by  $^6\text{Li}$  in the reaction  $^6\text{Li}(n, \alpha)^3\text{H}(\beta^-)^3\text{He}$  (Ozima and Podosek, 2002; Porcelli et al., 2002), with its rate proportional to the subsurface thermal neutron density, the number of neutrons that reach the thermal energy level and the fraction of neutrons that can be captured by Li. It is generally assumed 80% of neutrons reach the required thermal energy level, although it can be as high as 100% for a rock matrix enriched in light elements (Morrison and Pine, 1955; Andrews,

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1985; Ballentine and Burnard, 2002). The fraction of total neutrons in the matrix that can be captured by Li varies between different types of rocks depending on the availability of other neutron accepting elements. This fraction can be estimated from neutron capture cross-sections and element abundance, according to Equation 2.8.

$$F_{Li} = \sigma_{Li}N_{Li} / \sum_i^n \sigma_i N_i \quad (2.8)$$

where  $\sigma_i$  and  $N_i$  refer to the neutron capture cross-sections (barns) of  $i$  and its abundance in moles, respectively. Estimates of the fraction of neutrons captured by Li, in different rock types, are presented in Table 2.6.  $^3\text{He}$  production can then be calculated following the equations summarised by Ballentine and Burnard (2002):

$$\begin{aligned} ^3\text{He} = & 0.8 \times \{0.01[U] \times (13.8[Na] + 5.4[Mg] + 5.0[Al] + 1.31[Si] + 2.0[C]) \\ & + 0.01[Th] \times (6.0[Na] + 2.45[Mg] + 2.55[Al] + 0.56[Si] + 0.83[C]) \\ & + 0.4788[U]\} \times F_{Li} \end{aligned} \quad (2.9)$$

where [U] and [Th] are in ppm, and the concentrations of the other elements are in %. The crustal production  $^3\text{He}/^4\text{He}$  value is two to three magnitudes lower than the atmospheric ratio of  $1.4 \times 10^{-6}$ . Theoretically, rock bodies with high lithium concentration can generate higher  $^3\text{He}/^4\text{He}$  ratios. The spatial distribution and type of minerals as well as the release mechanisms can result in fractionation between the two different isotopes.

Gravitational escape from the atmosphere makes the recycling of degassed helium back into the Earth interior extremely hard, maintaining the mantle with a pristine and unique isotopic ratio (Graham, 2002). The average  $^3\text{He}/^4\text{He}$  ratio observed from the mid-ocean ridge basalts (MORB), originate in the upper, asthenospheric mantle, is  $8.75 \pm 2.14$  times greater than the atmospheric ratio (Graham, 2002), while the oceanic island basalts Ocean island basalts (OIB) derived from mantle plumes can be as high as 50 times greater than the atmospheric ratio (Stuart et al., 2003). Phenocrysts and

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**Table 2.6:** Composition of different rock types, focusing on elements most relevant to neutron capture and  $^3\text{He}$  production. \* average crust elemental abundance from Rudnick and Fountain (1995); \*\* rock composition from Parker and Fleischer (1967); \*\*\* oil shale composition from Fu et al. (2015).

| Neutron<br>Capture<br>Elements | Cross-<br>section<br>(barns) | Elemental Abundance (ppm) |                 |                       |                 |                        |                 |                  |
|--------------------------------|------------------------------|---------------------------|-----------------|-----------------------|-----------------|------------------------|-----------------|------------------|
|                                |                              | Upper<br>crust *          | Sandstone<br>** | Carbonate<br>rocks ** | Syenites<br>**  | Clays and<br>Shales ** | Shale<br>**     | Oil Shale<br>*** |
| <b>Li</b>                      | 71                           | 20                        | 15              | 5                     | 28              | 60                     | 66              | 13.9             |
| <b>B</b>                       | 755                          | 9.56                      | 35              | 20                    | 9               | 100                    | 100             | 0                |
| <b>Na</b>                      | 0.534                        | 28900                     | 3300            | 400                   | 40400           | 6600                   | 9600            | 805.2            |
| <b>Mg</b>                      | 0.064                        | 13300                     | 7000            | 47000                 | 5800            | 13400                  | 15000           | 8444.1           |
| <b>Al</b>                      | 0.232                        | 80400                     | 25000           | 4200                  | 88000           | 104500                 | 80000           | 16349.5          |
| <b>Si</b>                      | 0.16                         | 309000                    | 368000          | 24000                 | 291000          | 238000                 | 73000           | 22307.4          |
| <b>Cl</b>                      | 32.6                         | 232                       | 10              | 150                   | 520             | 160                    | 180             | 0                |
| <b>K</b>                       | 2.07                         | 28200                     | 10700           | 2700                  | 48000           | 22800                  | 26600           | 4661.5           |
| <b>Ca</b>                      | 0.44                         | 30000                     | 39100           | 302300                | 18000           | 25300                  | 22100           | 281554.6         |
| <b>Ti</b>                      | 6.1                          | 3000                      | 1500            | 400                   | 3500            | 4500                   | 4600            | 768.2            |
| <b>Cr</b>                      | 3.1                          | 35                        | 35              | 11                    | 2               | 100                    | 90              | 27.7             |
| <b>Mn</b>                      | 13.3                         | 620                       | 50              | 1100                  | 850             | 670                    | 850             | 407.8            |
| <b>Fe</b>                      | 2.56                         | 31500                     | 9800            | 3800                  | 36700           | 33000                  | 47200           | 21256            |
| <b>Co</b>                      | 37.5                         | 10                        | 0.3             | 0.1                   | 1               | 20                     | 19              | 13.2             |
| <b>Ni</b>                      | 4.54                         | 20                        | 2               | 20                    | 4               | 95                     | 68              | 75.8             |
| <b>Sm</b>                      | 5820                         | 4.5                       | 10              | 1.3                   | 18              | 6.5                    | 6.4             | 1.2              |
| <b>Gd</b>                      | 49000                        | 3.8                       | 10              | 1.3                   | 18              | 6.5                    | 6.4             | 1.3              |
| $\sum \text{F}$                |                              | 0.009411                  | 0.010167        | 0.006303              | 0.016141        | 0.016224               | 0.016062        | 0.005415         |
| F(Li)                          |                              | <b>0.02174</b>            | <b>0.015091</b> | <b>0.008115</b>       | <b>0.017745</b> | <b>0.03783</b>         | <b>0.042033</b> | <b>0.026255</b>  |
| Other Elements                 |                              |                           |                 |                       |                 |                        |                 |                  |
| <b>U</b>                       |                              |                           |                 |                       |                 |                        |                 |                  |
| (ppm)                          |                              | 2.8                       | 1.7             | 1.7                   | 13              | 11                     | 12              | 4.5              |
| <b>Th</b>                      |                              |                           |                 |                       |                 |                        |                 |                  |
| (ppm)                          |                              | 10.7                      | 0.45            | 2.2                   | 3               | 3.2                    | 3.7             | 2.4              |
| <b>C (%)</b>                   |                              | 0.324                     | 0               | 0                     | 0               | 1                      | 0               | 10.2             |

xenoliths from the subcontinental lithosphere also suggest an endmember enriched in  $^3\text{He}$  but more radiogenic than the convecting upper mantle or the upwelling mantle (less than 6.0 times greater than the atmospheric ratio) (Dunai and Porcelli, 2002; Day et al., 2015; Gilfillan and Ballentine, 2018). In either case, addition of mantle helium to a crustal fluid will elevate the  $^3\text{He}/^4\text{He}$  values above that of the crustal endmember (Ballentine and Burnard, 2002), and this can be used to quantify the flux of mantle-derived volatiles in continental regions (Sano et al., 1986; Martel et al., 1989; Stute et al., 1992; Kipfer et al., 1994; Aeschbach-Hertig et al., 1996; Aeschbach-Hertig et al., 2000).



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**Table 2.7:** Nucleogenic routes of neon isotopes (Wetherill, 1954; Yatsevich and Honda, 1997; Ballentine and Burnard, 2002).

| Isotope          | Nucleogenic routes                                                                                                                               |
|------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| $^{20}\text{Ne}$ | $^{17}\text{O}(\alpha, n)^{20}\text{Ne}, ^{23}\text{Na}(n, \alpha)^{20}\text{Ne}$                                                                |
| $^{21}\text{Ne}$ | $^{18}\text{O}(\alpha, n)^{21}\text{Ne}, ^24\text{Mg}(n, \alpha)^{21}\text{Ne}$                                                                  |
| $^{22}\text{Ne}$ | $^{19}\text{F}(\alpha, n)^{22}\text{Ne}(\beta^+)^{22}\text{Ne}, ^{25}\text{Mg}(n, \alpha)^{22}\text{Ne}, ^{19}\text{F}(\alpha, p)^{22}\text{Ne}$ |

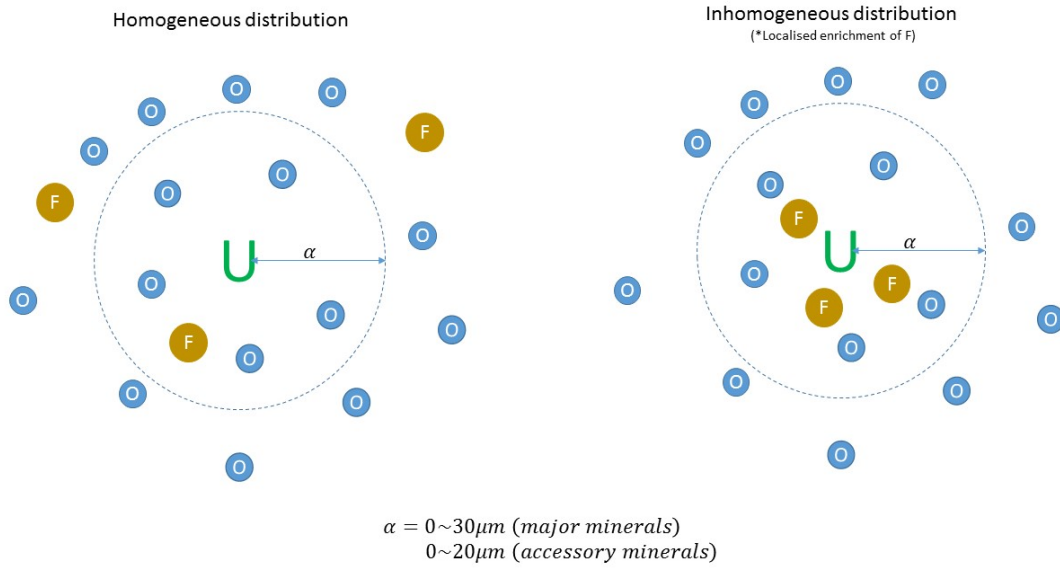
## Neon

Subsurface Ne production is entirely attributed to nucleogenic reactions (Ballentine and Burnard, 2002).  $^{21}\text{Ne}$  derived from this route is readily observed while the production of  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  is an order of magnitude lower (Ballentine and Burnard, 2002; Ballentine and Holland, 2008). Production routes for neon isotopes are listed in Table 2.7.

The nucleogenic parents of neon isotopes would suggest that  $^{21}\text{Ne}/^{22}\text{Ne}$  production ratio in the crust depends on the O/F ratio of the rock mass. The average O/F values of the Earth's crust and crystalline shield are 752 and 1140, respectively, corresponding to production  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios of 3.51 and 5.18 (Ballentine and Burnard, 2002). Neon isotope signatures in free fluids and fluid inclusions from old crystalline basement demonstrate a  $^{21}\text{Ne}/^{22}\text{Ne}$  production ratio of  $3.3 \pm 0.2$  (Lippmann et al., 2003; Holland et al., 2013; Warr et al., 2018), comparable to that expected from the average crust.

In contrast,  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios observed in natural gas samples define the endmember production ratio considerably lower at approximately 0.469. Such production ratios correspond to a lower apparent O/F value of 113 (Kennedy et al., 1990). . The second hypothesis suggests the siting of O and F could be a contributor. Since oxygen is a ubiquitous element the variation in  $^{21}\text{Ne}/^{22}\text{Ne}$  is thought to be associated with the distribution of the element F in the minerals and rocks (Figure 2.1). The major alpha-neutron production pathway requires the Ne parent isotopes to be within the effective distance from alpha-emitters (e.g. U, Th). Therefore, the O/F ratios within this effective distance control the value of produced  $^{21}\text{Ne}/^{22}\text{Ne}$ . Localised enrichment of F in proximity to alpha emitters, relative to a homogeneous distribution can generate

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**Figure 2.1:** Schematic demonstration of the effect of the distribution of F and the effective distance from alpha-emitters (e.g. U, Th). Localised enrichment in F in proximity to alpha emitters could generate neon ratios with lower  $^{21}\text{Ne}/^{22}\text{Ne}$  relative to a homogeneous distribution. For major minerals, the effective distance is less than  $\sim 30 \mu\text{m}$ ; and for accessory minerals, this is less than  $\sim 20 \mu\text{m}$ .

lower  $^{21}\text{Ne}/^{22}\text{Ne}$  (Kennedy et al., 1990; Ballentine and Burnard, 2002). Fluorine is an incompatible element and preferably resides in accessory minerals, where the alpha generators are also most concentrated. The much higher  $^{21}\text{Ne}/^{22}\text{Ne}$  production ratios in fluid inclusion samples from the Archean terrains are suggested to represent the metamorphic fluid component  $>2\text{Ga}$  during the last period of regional metamorphism (Lippmann-Pipke et al., 2011) which results in mineral assemblages with a higher concentration of F in accessory minerals. This global scale mineral formation is possibly related to the Great Oxidation Event at around 2.4 Ga. Explosive growth in the diversification of minerals was the result of the increase in partial pressure of oxygen which allowed elements to occur in various oxidised forms (Sverjensky and N. Lee, 2010). F could have been incorporated within the minerals sitting in the vicinity of alpha-emitters, resulted in localised depletion in O/F and produces higher  $^{22}\text{Ne}$  and those lower  $^{21}\text{Ne}/^{22}\text{Ne}$ .

The mantle has higher ratios of  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  relative to atmospheric

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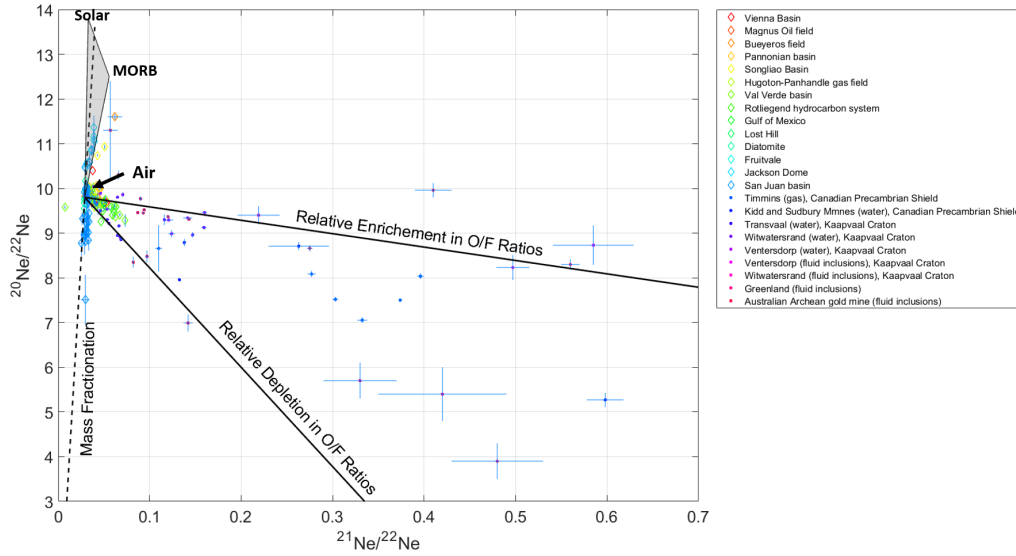
and continental nucleogenic production values (Dunai and Porcelli, 2002; Graham, 2002; C. D. Williams and Mukhopadhyay, 2019). Neon isotopes in a crustal system can, therefore, be elevated with the addition of mantle component. Neon isotopes can also be altered by mass fractionation (Zhou et al., 2005), and need to be carefully distinguished from a mantle input (Figure 2.2). The relationship between  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  can, therefore, be used to trace the sources of neon within a sedimentary fluid.

### Argon

Nucleogenic  $^{36}\text{Ar}$  and  $^{38}\text{Ar}$  production in the crust and mantle is small compared to their concentrations in the mantle and atmosphere. Within the continental crust, concentrations introduced from the atmosphere dissolved in groundwater are similarly dominated by the atmospheric isotopic composition (Ballentine and Burnard, 2002; Kipfer et al., 2002). Except for systems containing very old fluids (e.g. Holland et al., 2013; Warr et al., 2018).  $^{38}\text{Ar}/^{36}\text{Ar}$  in crustal fluids is usually indistinguishable from that of the atmosphere but could be affected by mass-dependent fractionation (e.g. Zhou et al., 2005). MORB and OIB samples have  $^{38}\text{Ar}/^{36}\text{Ar}$  ratios comparable to the atmospheric ratios (Graham, 2002; Pepin and Porcelli, 2002).  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios for samples representative of MORB are variable, mostly due to atmospheric contamination. Reported ratios range from those indistinguishable from the modern air (Ballentine and Holland, 2008) up to 40,000 (Burnard et al., 1997).

The primordial  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in the solar system is low, around  $10^{-4}\sim 10^{-3}$  (Begemann et al., 1976; Pepin and Porcelli, 2002). The current atmospheric value of 298.56 is considerably higher, indicating that a considerable amount of radiogenic  $^{40}\text{Ar}$  has accumulated in the atmosphere.  $^{40}\text{Ar}$  production is dominated by  $^{40}\text{K}$  decay. The majority of  $^{40}\text{K}$  produces  $^{40}\text{Ca}$  by beta decay and only a small fraction produces  $^{40}\text{Ar}$  by electron capture. The decay constant for beta decay and electron capture factor are  $\lambda_{\beta} = 4.962 \times 10^{-10} \text{yr}^{-1}$  and  $\lambda_C = 0.581 \times 10^{-10} \text{yr}^{-1}$ , respectively (Steiger and Jäger, 1977; Ballentine and Burnard, 2002). Therefore, the total decay constant for  $^{40}\text{K}$  is

## 2.2. NOBLE GASES AS GEOCHEMICAL TRACERS



**Figure 2.2:**  $^{20}\text{Ne}/^{22}\text{Ne}$  VS  $^{21}\text{Ne}/^{22}\text{Ne}$  demonstrating endmember mixing trends overlain with published data. Solar  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  are 13.8 and 0.0328, respectively (Graham, 2002). MORB  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  are 12.5 and 0.0558 (Ballentine et al., 2005). Extrapolated OIB endmembers of Iceland and Loihi lie in between the solar and MORB endmembers. O/F enrichment and depletion lines are plotted following Holland et al. (2013). Diamonds represent fluids samples from basin settings, and circles are fluids and inclusion samples from the crystalline basement. Data sources: Vienna Basin (Ballentine and O’Nions, 1992); Magnus oil field (Ballentine et al., 1996); Bueyeros field (Phinney et al., 1978); Pannonian basin (Sherwood Lollar et al., 1994a); Songliao Basin (Xu et al., 1995); Hugoton-Panhandle gas field (Ballentine and Sherwood Lollar, 2002); Val Verde basin (Ballentine et al., 2001); Rotliegend hydrocarbon system (Barry et al., 2017); Gulf of Mexico (Barry et al., 2018a); Lost Hill (Barry et al., 2018b); Diatomite (Barry et al., 2018b); Fruitvale (Barry et al., 2018b); Jackson Dome (Zhou et al., 2012); San Juan basin (Zhou et al., 2005); Timmins (Holland et al., 2013); Kaapvaal Craton (Lippmann-Pipke et al., 2011); Greenland (Zadnik and Jeffery, 1985); Australian Archean gold mine (Kendrick et al., 2011). The plot demonstrates the air mixing trend with four different endmembers: Solar, Mid-Ocean Ridge Basalt and crustal production lines (O/F enrichment and depletion lines).  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$  are produced dominantly from O and F respectively.  $^{21}\text{Ne}/^{22}\text{Ne}$  is, therefore, controlled by the relative O/F ratios of the bulk rock as well as their distribution and proximity to alpha-emitters. Samples so far collected from precambrian terrains lie on the trend line corresponds to a higher  $^{21}\text{Ne}/^{22}\text{Ne}$  endmember ratio, while samples collected from younger sediments follow the mixing trend to a lower  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio.

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$\lambda_K = \lambda_\beta + \lambda_C$ , and the fraction of  $^{40}\text{K}$  that decays to  $^{40}\text{Ar}$  can be described as  $\frac{\lambda_C}{\lambda_K} = \frac{\lambda_C}{\lambda_\beta + \lambda_C}$ . The equation describing the production of  $^{40}\text{Ar}$  can, therefore be written as

$$^{40}\text{Ar atoms } g^{-1} = \frac{X_K[K] \times 10^{-6}}{M_K} N_A \frac{\lambda_C}{\lambda_K} (e^{\lambda_K t} - 1) \text{yield}_K, \quad (2.10)$$

where,  $X_K$ , the fractional natural abundance of  $^{40}\text{K}$ , is  $1.167 \times 10^{-4}$ ,  $M_K$ , the molar mass of  $^{40}\text{K}$ , is 39.964 g/mol, and yield, the number of  $^{40}\text{Ar}$  atoms produced through one electron-capture event, is 1 (Ballentine and Burnard, 2002).

High  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are observed in the Canadian Shield. Holland et al. (2013) observed ratios up to 44000 for free fluid sampled at 2.4 km depth in the Timmins Mine. Deeper samples collected are later found values in excess of 125000, the highest value yet reported for a crustal fluid (Warr et al., 2018). Resampling of fluids from the same locality demonstrated a noticeable reduction in  $^{40}\text{Ar}/^{36}\text{Ar}$ , showing mixing with less radiogenic fluids (Heard et al., 2018; Warr et al., 2018). High  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are also observed in hydrocarbon samples from deep sedimentary units approaching the crystalline basement (Hiyagon and Kennedy, 1992).

## Krypton and xenon

Production of  $^{80}\text{Kr}$ ,  $^{82}\text{Kr}$  and  $^{124}\text{Xe}$ ,  $^{126}\text{Xe}$ ,  $^{128}\text{Xe}$ ,  $^{130}\text{Xe}$  in the crust is insignificant, and the other stable isotopes are dominantly produced by fission of  $^{238}\text{U}$  (Ballentine and Burnard, 2002). Spontaneous fission of  $^{232}\text{Th}$  and thermal or fast neutron-induced fission of  $^{235}\text{U}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$  have been considered. Estimates of crustal production of the different Kr and Xe isotopes are usually based on that of  $^{136}\text{Xe}$ , and scaled according to expected production ratios (Ballentine and Burnard, 2002). In sedimentary fluid systems, the isotopic ratios of Kr and Xe are usually similar to that of the atmosphere, but can show significant fissiogenic contributions in ancient fluid systems (e.g. Holland et al., 2013; Warr et al., 2018).  $^{129}\text{Xe}$  could be produced by decay reactions of crustal and sediment  $^{129}\text{I}$  (half-life  $t_{1/2} = 15.7$  Myr).  $^{129}\text{I}$  can also be sourced cosmogenically and concentrated in carbon-rich sediments (Santos et al., 2007). Alternatively,  $^{129}\text{Xe}$  could be supplied from the mantle, and in such

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cases, a correlation between  $^{129}\text{Xe}$  and  $^{124}\text{Xe}$  would be expected. Deviations from the mantle  $^{129}\text{Xe}/^{124}\text{Xe}$  of  $1640 \pm 209$  (Holland and Ballentine, 2006) can be used to estimate the mantle contribution of  $^{129}\text{Xe}$ .

### Release of radiogenic noble gases from mineral phases

Radiogenically produced noble gases are released from their host minerals through diffusion, recoil and chemical transformation (Ballentine and Burnard, 2002). Diffusive loss is the underlying releasing mechanism for all noble gas species and occurs when a compositional gradient is present between minerals and the surrounding fluids. The diffusion rate is controlled by temperature, size of diffusing elements, and the matrix through which the element is diffusing. The fraction of diffusive loss from the mineral is summarised by Mussett (1969) for grains with various geometries. For a spherical grain, the fraction of diffusive loss can be approximated as:

$$F_L = \frac{6}{\pi^{3/2}} \left[ \pi^2 \left( \frac{D}{a^2} \right) t \right]^{1/2} - \frac{3}{\pi^2} \left[ \pi^2 \left( \frac{D}{a^2} \right) t \right], \quad (2.11)$$

where  $D$  and  $t$  represent the diffusion coefficient and time;  $a$  is the diffusive length scale or domain size, and in this case, it is the radius of the spherical grain. For most of the simple geometries, the diffusive loss is a function of  $\frac{D}{a^2}$ .

Diffusivity in a mineral is commonly expressed following the Arrhenius equation and assuming there is no anisotropy in diffusivity in different dimensions, diffusivity in a mineral can be shown as:

$$D = D_o e^{-E_a/RT} \quad (2.12)$$

where  $D_o$  is the frequency factor in  $\text{m}^2/\text{s}$  and  $E_a$  is the activation energy in  $\text{KJ/mol}$ .  $R$  is the gas constant  $= 8.314 \times 10^{-3} \text{ KJ mol}^{-1} \text{ K}^{-1}$  and  $T$  is the temperature in Kelvin.  $\frac{D}{a^2}$  is easier to be characterised during mineral release experiments. The diffusion coefficient can be calculated with a reasonable estimation of the  $a$  value. However, assigning a value to  $a$  can be challenging. The most common practice is to take the average of the macroscopic dimensions of a crystal. This is built on implied

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assumptions that the initial distribution of the parent element is uniform in the crystal, and there is no anisotropy in diffusivity in different dimensions (Baxter, 2010). Smaller domains presented within a crystal are often associated with fast pathways for diffusive loss; in such cases, the effective length scale is unrepresentative by its macroscopic crystal domains (Baxter, 2010).

Frequency factors,  $D_o$ , and activation energy,  $E_a$ , of different gas species vary in different types of minerals and are reviewed by Ballentine and Burnard (2002) and Baxter (2010) and summarised in Table 2.8.

Recoil describes the process when the daughter isotope of a radioactive reaction is ejected from the site of its parent isotope. The ejection distance depends on the kinetic energy obtained by the daughter particle during the reaction. Stabilized alpha particles,  $^4\text{He}$ , have the most significant recoil distance among all other species. The recoil distance of  $^4\text{He}$  depends on the chemistry of the mineral, the density of the mineral grain and grain sizes (J. F. Ziegler, 1977). Recoil loss is significant when the grain has a large surface area compared to its volume (Martel et al., 1990; Farley et al., 1996; Ballentine and Burnard, 2002). This implies that an increase in grain size, as may happen with higher metamorphic grade, usually results in less recoil loss. However, chemical breakdown and significant redistribution of U on grain boundaries will increase the influence of recoil loss (Torgersen, 1980; Torgersen and Clarke, 1985; Andrews et al., 1989; Ballentine and Burnard, 2002). Fissionogenic xenon isotopes also experience a small recoil loss in fine-grained U-bearing minerals (Ballentine and Burnard, 2002). Experiments on Ba glass suggest  $\sim 30\%$  loss of  $^{126}\text{Xe}$  produced in silicon carbide of  $1\text{ }\mu\text{m}$ , and the spallation composition changes with the size of grains (Ott et al., 2005).

Due to their incompatible nature, noble gases can also be released from a mineral lattice through chemical alterations. Such alterations can be caused by processes such as diagenesis and metamorphism and are not associated with significant elemental

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**Table 2.8:** Frequency factors ( $D_o$ ) and activation energy ( $E_a$ ) of different minerals, modified from Baxter (2010). \* indicates the average calculated from reported values for the same mineral.

| Mineral                 | Gas | $E_a(KJ/mol)$ | $D_o(m^2/s)$ | $D_{298K}(m^2/s)$ | $D_{373K}(m^2/s)$ |
|-------------------------|-----|---------------|--------------|-------------------|-------------------|
| Garnet                  | He  | 660           | 3.98E+11     | 8.10E-105         | 1.48E-81          |
| Hematite (botryoidal) * | He  | 173.8         | 7.36E-01     | 2.52E-31          | 3.37E-25          |
| Magnetite               | He  | 220           | 3.98E-01     | 1.09E-39          | 6.17E-32          |
| Goethite *              | He  | 170.6         | 1.57E-01     | 1.96E-31          | 2.02E-25          |
| Monazite *              | He  | 202           | 1.25E-02     | 4.88E-38          | 6.43E-31          |
| Diopside                | He  | 290           | 1.26E-02     | 1.85E-53          | 3.07E-43          |
| Apatite *               | He  | 138           | 3.16E-03     | 2.04E-27          | 1.49E-22          |
| Quartz *                | He  | 90.9          | 2.61E-03     | 3.04E-19          | 4.86E-16          |
| Titanite *              | He  | 174           | 8.77E-04     | 2.77E-34          | 3.76E-28          |
| Olivine *               | He  | 259.3         | 6.67E-04     | 2.35E-49          | 3.24E-40          |
| Langbeinite             | He  | 126           | 7.59E-05     | 6.22E-27          | 1.72E-22          |
| Zircon *                | He  | 164           | 1.95E-05     | 3.49E-34          | 2.10E-28          |
| Augite *                | He  | 120           | 4.62E-06     | 4.26E-27          | 7.23E-23          |
| Hornblende *            | He  | 112           | 3.43E-07     | 7.99E-27          | 7.08E-23          |
| Nepheline *             | He  | 116.7         | 1.15E-07     | 4.02E-28          | 5.22E-24          |
| Muscovite               | He  | 87            | 1.15E-08     | 6.46E-24          | 7.53E-21          |
| Sanidine                | He  | 86            | 1.11E-08     | 9.34E-24          | 1.00E-20          |
| Hematite (specular) *   | He  | 128.3         | 7.03E-10     | 2.28E-32          | 7.57E-28          |
| Ilmenite                | He  | 46.2          | 5.01E-15     | 3.99E-23          | 1.70E-21          |
| Diamond                 | He  | 103.5         | 6.31E-18     | 4.54E-36          | 2.02E-32          |
| Quartz                  | Ne  | 153.7         | 1.49E+00     | 1.70E-27          | 4.45E-22          |
| Olivine                 | Ne  | 87.9          | 3.00E-14     | 1.17E-29          | 1.47E-26          |
| Ilmenite                | Ne  | 62.8          | 1.95E-15     | 1.91E-26          | 3.13E-24          |
| Muscovite *             | Ar  | 264           | 0.00023      | 1.22E-50          | 2.45E-41          |
| Plagioclase *           | Ar  | 168           | 0.000142     | 5.05E-34          | 4.22E-28          |
| Biotite *               | Ar  | 197           | 7.50E-06     | 2.20E-40          | 1.93E-33          |
| Hornblend *             | Ar  | 276           | 6.00E-06     | 2.50E-54          | 1.34E-44          |
| K feldspar *            | Ar  | 177           | 1.84E-07     | 1.73E-38          | 3.00E-32          |
| Ilmenite                | Ar  | 92.4          | 1.00E-14     | 6.36E-31          | 1.15E-27          |
| Quartz *                | Ar  | 43            | 3.10E-19     | 8.99E-27          | 2.95E-25          |
| Olivine                 | Ar  | 42            | 7.20E-20     | 3.13E-27          | 9.45E-26          |
| Enstatite               | Ar  | 32            | 1.30E-20     | 3.20E-26          | 4.29E-25          |
| Corundum                | Ar  | 33            | 1.20E-20     | 1.97E-26          | 2.87E-25          |

or isotopic fractionation. Such processes can induce large scale degassing of noble gases from the solid crust into crustal fluids (Torgersen, 1989).

Dilatant fracturing, microfractures caused by the inelastic failure of brittle rocks that occurs during compressional loading, also assists noble gas liberation from the parental minerals (Ballentine and Burnard, 2002). These microfractures reduce the distance from the formation sites to the interface of the minerals with surrounding fluids and reduce the time for diffusive loss.



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### Resolving different noble gas components

The endmember isotopic and elemental ratios in the atmosphere, crust and mantle reservoirs allow the determination of the relative contribution from these three reservoirs. Helium isotopic ratios can be corrected for atmospheric contamination assuming  $^{20}\text{Ne}$  is entirely atmospheric (Craig et al., 1978; Ballentine et al., 2002),

$$\left(\frac{^3\text{He}}{^4\text{He}}\right)_c = \frac{\left(\frac{^3\text{He}}{^4\text{He}}\right)_s f\left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_{\text{air}} - \left(\frac{^3\text{He}}{^4\text{He}}\right)_{\text{air}}}{f\left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_{\text{air}} - 1} \quad (2.13)$$

where  $f\left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_{\text{air}} = \frac{\left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_s}{\left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_{\text{air}}}$ . The air-corrected, measured, and air ratios are denoted with subscripts c, s and air, respectively. The correction is usually negligible for many old fluid systems where  $\frac{^4\text{He}}{^{20}\text{Ne}}$  is large. For systems with low  $\frac{^4\text{He}}{^{20}\text{Ne}}$ , error propagation is critical and can be calculated following equations summarised by Mackintosh and Ballentine (2012).

The corrected  $\frac{^3\text{He}}{^4\text{He}}$  ratio represents a result of mixing between helium from the crust and the mantle and can, therefore, be used to resolve the respective amount of helium sourced from these two reservoirs.

$$[^4\text{He}]_{\text{crust}} = [^4\text{He}]_T \left[ \left(\frac{^3\text{He}}{^4\text{He}}\right)_{\text{mantle}} - \left(\frac{^3\text{He}}{^4\text{He}}\right)_{\text{crust}} \right] \quad (2.14)$$

where the subscripts T represents the total in the sample, and subscripts mantle and crust represents concentrations and ratios for mantle and crust endmembers. If the system is assumed to be a two-component mixture between endmember 1 and endmember 2, the contribution from each of the sources can be calculated following the generalised equation:

$$[i]_{\text{endmember 1}} = [i]_T \left[ 1 - \frac{(i)_{\text{endmember 2}}}{(i)_T} \right] \quad (2.15)$$

where [i] represents the concentrations and (i) represents the isotopic ratio, respectively. Subscripts endmember 1 and 2 represents concentrations and ratios for the two endmembers.

## 2.3 TRANSPORT OF NOBLE GASES

Noble gases are produced in mineral grains in trace quantities and are partially retained within the mineral lattice. The gases that escape the minerals are not sufficient to form a free-flowing phase on their own but dissolve in pore fluids surrounding the grains and in fractures. The most common solvent in a sedimentary basin is groundwater. Most of the other carrier fluids, such as hydrocarbons and CO<sub>2</sub>, will experience different degrees of interaction with the groundwater system. As a result, the distribution of noble gases depends on the transport of groundwater and the interaction between subsurface fluid phases. The transport of noble gases, therefore, depends on the hydrogeology in the basin. The two fundamental transport mechanisms for subsurface fluids in a sedimentary basin are advection and diffusion. While advection is driven by pressure gradients and gravity, diffusion is a much slower process caused by differences between concentrations. Diffusion is the underlying transport mechanism in static water bodies. Advective transport occurs through veins and fractures or permeable aquifers when there is enough hydraulic pressure to produce fluid flow.

### 2.3.1 Degassing of the Deep Continental Crust

A steady-state basement flux refers to a crustal degassing model where the noble gas is released into overlying sedimentary units at the same rate as it is produced from the entire volume of the crystalline basement (Torgersen and Clarke, 1985; Torgersen, 1989; Ballentine and Burnard, 2002). This basement flux can be estimated from radiogenic production rate based on radioelement concentrations and the thickness of the crystalline basement. A steady-state helium flux can be calculated from an average continental crust composition as  $1.47 \times 10^{-6}$  mol <sup>4</sup>He/m<sup>2</sup>/yr (Torgersen and Clarke, 1985). Such a model has been used to explain noble gas concentrations in sedimentary units higher than that produced from in situ production and accumulation, including the Great Artesian Basin, Australia (Torgersen and Clarke, 1985; Torgersen, 1989;

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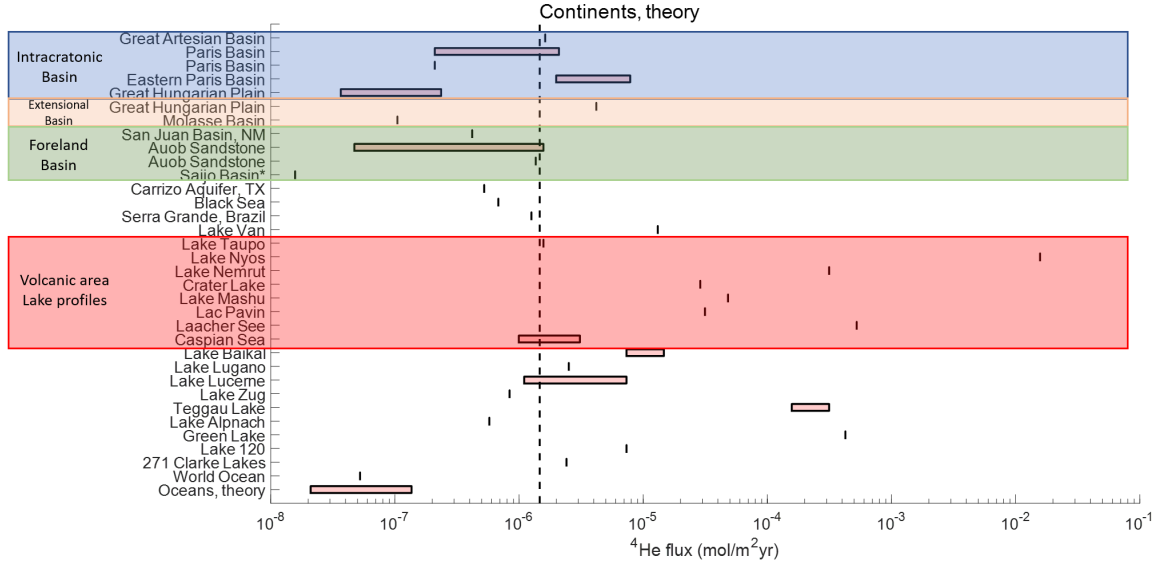
Torgersen et al., 1992), the Paris Basin, France (Castro et al., 1998a; Castro et al., 1998b), and the San Juan Basin, New Mexico (Zhou et al., 2005).

The noble gas flux through the crust can also be tectonically controlled (Ballentine and Burnard, 2002). The noble gas content in the overlying sedimentary basins has been observed to be higher than can be explained with a steady-state model, for example in the Pannonian Basin (Ballentine et al., 1991) and Uranian Basin (Winckler et al., 1997). In both cases, the researchers proposed an advective mechanism for transporting noble gases that have accumulated at depth. The high emission rate of  $^4\text{He}$  in Yellowstone is suggested to be the result of hundreds of millions of years crustal accumulation in the Archean and a liberation induced by hotspot over the past two million years, demonstrating the extremes of temporal variation for crustal fluxes (Lowenstern et al., 2014). It has been argued that diffusive transport of noble gases from the deep crust is not significant, nor is it continuous or widespread, and the rate of noble gas loss from the deep system is more strongly associated with tectonic activities which trigger regional metamorphism, fluid mobilization and regional degassing (Ballentine and Burnard, 2002). Study of noble gases in mines reveals variations both temporally and spatially, and fracture networks in the crustal systems are crucial factors that will affect noble gas distribution and residence time in the crystalline basement (Lippmann et al., 2003; Holland and Ballentine, 2006; Warr et al., 2018).

A global statistical average of basement  $^4\text{He}$  flux has been calculated as  $2.19 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  from estimations reported and calculated in different geological settings, including intracratonic basins, foreland basins and volcanic areas (Torgersen, 2010) (Figure 2.3). Ranges of  $^4\text{He}$  flux values are observed globally with high  $^4\text{He}$  flux mostly observed in Volcanic areas.

Quantitative estimation of noble gas flux from the basement is significant for the simulation of noble gas migration, the outgassing of noble-gases and other associated components and the exploration of helium reservoirs. However, the large variability

### 2.3. TRANSPORT OF NOBLE GASES



**Figure 2.3:**  $^4\text{He}$  flux reported for different geological settings (Torgersen, 2010 and reference therein, Saijo Basin - Takahata and Sano, 2000). The localities reported can be grouped (shaded in colours) into intracratonic basins, extensional basins, foreland basins, volcanic areas and lakes. Saijo Basin locates in a non-volcanic front arc area. A steady-state helium flux calculated from an average continental crust composition ( $1.47 \times 10^{-6}$  mol  $^4\text{He}$ /m<sup>2</sup>/yr) is demonstrated as the dashed vertical line in the plot for comparison (Torgersen and Clarke, 1985).

of flux in different systems suggests further studies are required for understanding the different regional processes controlling deep crustal degassing.

#### 2.3.2 Transport of Heat and Mantle Fluids through the Crust

As a product of radioactivity, terrestrial  $^4\text{He}$  is accompanied by heat generation, resulting in a consistent  $^4\text{He}$ /Heat production ratios through the crust and mantle (Graham, 2002). In a low permeability environment, conduction and diffusion are the dominant transport mechanism for heat and helium, respectively, from the mantle and through the crust. Such mechanisms induce fractionation between heat and helium due to the much higher dissipation rate of heat (Ballentine and Burnard, 2002).

$^3\text{He}$  is almost entirely primordial, with well-constrained high  $^3\text{He}/^4\text{He}$  ratios from the mantle, distinct from crustal production (Graham, 2002 and references therein).  $^3\text{He}$  and  $^3\text{He}/^4\text{He}$  ratios are therefore useful tracers of mantle fluids. Given that high

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$^3\text{He}/^4\text{He}$  ratios suggest effective transport of mantle fluids, it is consequently expected that high  $^3\text{He}/^4\text{He}$  is associated with high heat flow. Mathematical correlation between  $^3\text{He}/^4\text{He}$  and heat flux was proposed by Polyak and Tolstikhin (1985). Burnard et al. (1999) demonstrated a positive relationship between  $^3\text{He}/^4\text{He}$  isotopic ratios and heat flux from fluid inclusions collected from a gold mine, that has experienced mantle fluid mixing. But such correlations cannot be applied to advection systems where advective helium transport is much faster than heat transport (Bach et al., 1999). High heat flow can also be associated with low  $^3\text{He}/^4\text{He}$  ratios due to the low permeability in the crust and long residence times for radiogenic  $^4\text{He}$  production that dilute  $^3\text{He}/^4\text{He}$  ratios in the fluids (Aeschbach-Hertig et al., 2002).

If this correlation between  $^3\text{He}/^4\text{He}$  isotopic ratios, helium flux and heat flux can be observed in more basin systems, and eventually be numerically simulated, the relationship would provide a practical and easy method for the estimation of basement outgassing and the analysis of transport in the crystalline basement.

### **2.3.3 Transport through Sedimentary Units**

Understanding the controls on migration of noble gases through sedimentary units is essential for being able to use the noble gases to understand fluid transport mechanisms and any resulting estimation of element budget and storage in sedimentary basins.

A qualitative understanding of vertical connectivity between sedimentary sequences can be achieved through the comparison of noble gas signatures between different geological units; similarly, the same method as analysing aqueous geochemistry, e.g. the distribution of the salt type, total dissolved solid concentration and conservative tracers (e.g.  $\text{Br}^-$  and  $\text{Cl}^-$ ) (e.g. Weaver et al., 1995; Bachu and Hitchon, 1996; Worden et al., 1999).

Numerical modelling is widely used for the quantification of transport and related parameters. Helium has been used to evaluate the relative importance between advection and diffusion (Marty et al., 1993; Marty et al., 2003) and to investigate

## 2.4. PARTITIONING OF NOBLE GASES BETWEEN DIFFERENT FLUIDS

diffusion transport in various shale units (William Payton Gardner et al., 2011; Clark et al., 2013; Hendry et al., 2015). Both helium and argon have been applied in constructing a basin-scale hydrogeological model of the Paris basin (Castro et al., 1998a; Castro et al., 1998b). Due to the uncertainties involved in various model parameters, comparison among modelling results of other tracer elements, including anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ) and water isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), can give a better understanding of the system (Hendry and Harrington, 2014; Hendry et al., 2015). Quantitative numerical modelling of the transport of noble gases is the focus of this thesis and will be applied to two different basin systems, with the aim of inspecting the basement and cross-formational flux of noble gases and identifying hydrogeological events.

### 2.4 PARTITIONING OF NOBLE GASES BETWEEN DIFFERENT FLUIDS

The initial noble gas composition of the groundwater, which is usually the air saturated water corresponding to its recharging condition, is modified by re-equilibration with gas and/or oil phases (Zartman et al., 1961; Bosch and Mazor, 1988; Ballentine et al., 2002; Barry et al., 2016; Barry et al., 2018a). The different solubilities among noble gas species result in elemental fractionation. Noble gas partitioning at an equilibrated interface between a fixed volume of gas and groundwater is summarised by Ballentine et al. (2002) using a dimensionless Henry's constant,  $K_i^d$ :

$$[i]_g = [i]_T \left( \frac{V_l}{V_g K_i^d} + 1 \right)^{-1} \quad (2.16)$$

where  $[i]_T$  represents the total amount of  $i$  in both the water and gas phases. The partitioning between elements  $i$  and  $n$ , can be written as:

$$\left( \frac{[i]}{[n]} \right)_g = \left( \frac{[i]}{[n]} \right)_T \frac{\left( \frac{V_g}{V_l} + \frac{1}{K_n^d} \right)}{\left( \frac{V_g}{V_l} + \frac{1}{K_i^d} \right)} \quad (2.17)$$

when there is a constant removal of the gas phase formed, the process can be expressed by the Rayleigh fractionation law:

$$\left( \frac{[i]}{[n]} \right)_w = \left( \frac{[i]}{[n]} \right)_o p^{\alpha-1} \quad (2.18)$$

## 2. Literature Review

where  $\left(\frac{[i]}{[n]}\right)_o$  is the initial ratio in the water phase and  $p$  is the fraction of the initial amount of substance  $n$  remaining in the water phase;  $\alpha$  is the fractionation between element  $i$  and  $n$  at any instance, which can be estimated as  $\frac{K_i^d}{K_n^d}$ ; and  $\left(\frac{[i]}{[n]}\right)_w$  is the resulted ratio in the water phase after Rayleigh loss.

Barry et al. (2016) analysed four degassing scenarios in gas and oil reservoirs, corresponds to different close and open systems. By introducing variables  $\frac{G}{W}$ , the gas to water volume ratio for each degassing step, and  $d$ , the number of degassing steps, Barry et al. (2016) provided mathematical solutions for the overall gas-water volume ratio, i.e. the ratio between volume of gas and the volume in contact with per volume of groundwater. In this thesis, differential equations are derived from calculating the gas-water volume ratios from noble gas concentrations and elemental ratios for different degassing processes. Processes such as re-solution, effervescence and interaction of multiple fluids may add another degree of complexity (Ballentine et al., 2002) and the derived equations make the simulation of such processes possible in future studies.

### 2.5 EXCESS KRYPTON AND XENON

Excess Kr and Xe are observed in fluids from multiple basins (e.g. Hiyagon and Kennedy, 1992; Torgersen and Kennedy, 1999; Zhou et al., 2005; Barry et al., 2016; Györe et al., 2017). There are two hypotheses for such observations: one is related to elemental fractionation caused by diffusive transport and multi-step dissolution of excess air during groundwater recharge (Heaton and Vogel, 1981; Kipfer et al., 2002); another hypothesis is the diffusive release of adsorbed krypton and xenon from organic carbon (Torgersen et al., 2004). The adhering of Kr and Xe on carbon particle surface is proposed to be related to their high adsorption rates and the release could be caused by temperature increase or a concentration gradient and related to hydrocarbon formation and expulsion (Torgersen and Kennedy, 1999; Kennedy et al., 2002). Heating of deep ocean sediments also shows adsorption of excess Kr and Xe but is correlated with the silica contents in the matrix (Matsuda and Nagao, 1986). Failure to quantify excess

## 2.6. SAMPLE ANALYSIS

Kr and Xe in a system can result in spurious interpretations of fluid interactions with these heavy noble gases (see Barry et al. (2016) for discussion). In this study, excess Kr and Xe are calculated with error-weighted, nonlinear inversion matrix models, which can help with the understanding of sources of excess Kr and Xe in sedimentary basins as well as better constrain the processes involved in crustal fluid interactions.

## 2.6 SAMPLE ANALYSIS

In this project, gas samples (mostly natural gas samples, see Chapters 4 and 5) are collected in duplicate or triplicate from wellheads for major gas composition and noble gas determination. The two sets of samples require different sampling procedures. Gas compositions ( $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{N}_2$ ) are analysed at the University of Toronto by a thermal conductivity detector and gas chromatography isotopic ratio mass spectrometry. Sample collection and analysis of major gas compositions were described by Ward et al. (2004) and Sherwood Lollar et al. (2006). Noble gas samples were analysed with noble gas mass spectrometers at the noble gas laboratory at the University of Oxford.

Noble gas samples are collected in a cold-welded internally polished, refrigeration-grade copper tubing (Weiss, 1968). Sampling setups are illustrated in Appendix I.1. The sample tubes are mounted on an all-stainless steel Ultra-High Vacuum system for gas purification. Hydrocarbon and other reactive gases are removed chemically by exposing gas samples to a titanium getter (Stout and Gibbons, 1955), a hot getter (SAES GP-50) at  $250^\circ\text{C}$  and a cold getter (SAES NP-10) at room temperature. To avoid overloading or contaminating the mass spectrometer, a primary indication of gas composition is analysed by isolating an aliquot of the sample and measuring with a Hiden Analytical HAL-201 (quadrupole mass spectrometer) (Warr et al., 2015). Moisture content is further removed with stainless-steel water traps held at 250 K and 180 K respectively. Noble gases are separated based on their differential absorption using two cryogenic traps cooled by a helium adiabatic expansion module each. Adsorption temperatures



## *2. Literature Review*

are manipulated to release the desired elements from the traps for measurement. He is measured using Helix SFT and Ne, Ar, Kr and Xe using Argus VI.

Full procedural blanks are run once per week and are corrected from sample signals.  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  are corrected for doubly-charged  $^{40}\text{Ar}^{++}$  and  $\text{CO}_2^{++}$  if needed following the method described by Niedermann et al. (1993). Air-standards are analysed weekly for sample calibration. The air standards are collected in the University Parks, Oxford, UK on November 24, 2014 (297 K, 1.01 atm, 95% humidity). Internal ‘running’ standards are run at least once every night following sample analysis to confirm machine stability. Detailed laboratory configuration and experimental procedures are described in Appendix A.



# 3

## Mathematical Models of Transport

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### 3.1 INTRODUCTION

The transport of noble gases through water column can be mathematically calculated and numerically simulated for more complicated scenarios. In this section, we discuss the 1D transport equations for a solute in porous media and the relevant mathematical models. This chapter includes an introduction of the conservation equations and the Flick's law of diffusion (Blunt, 2017), and the numerical meshes and related matrix and boundary settings in the models. The model's calculation is then validated by comparing with published profiles.

### 3.2 CONSERVATION EQUATIONS

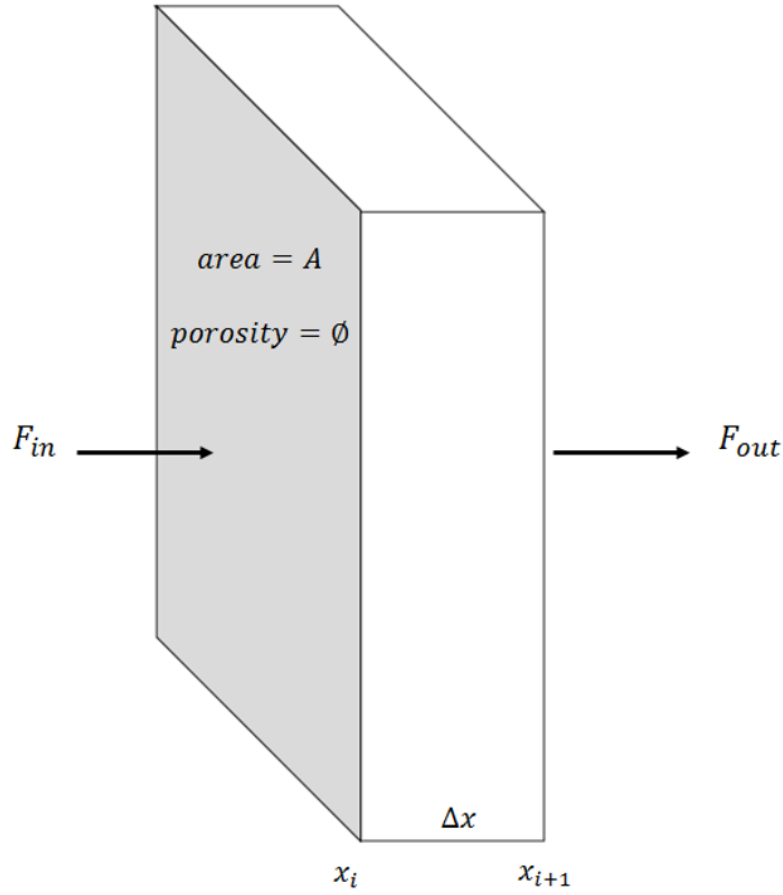
#### 3.2.1 Diffusive Transport in Porous Media

Assuming during an infinitely small-time interval  $\Delta t$ , there is a flux of solute entering ( $F_{in}$ ) and leaving ( $F_{out}$ ) a box (with the dimension of mass of solute per unit area per unit time) with area  $A$ , porosity  $\phi$  and width  $\Delta x$  (Figure 3.1).

At time  $t = t_n$ , the time at the start of transport, the mass of solute in this box ( $m$ ) is:

$$m(t_n) = C(t_n)A\Delta x\phi \quad (3.1)$$

### 3. Mathematical Models of Transport



**Figure 3.1:** Schematic box model for illustrating flux in and out.  $F_{in}$  and  $F_{out}$  represent flux in and out of the box.  $\Delta x$  represents the width of the box, i.e. the distance for substance transport, between node  $i$  and  $i+1$ .

where  $C$  represent the concentration of solute.

At time  $t = t_n + \Delta t = t_{n+1}$ , where  $\Delta t$  represents the time allowed for transport, the mass of solute in the box is:

$$m(t_{n+1}) = C(t_{n+1})A\Delta x\phi. \quad (3.2)$$

During this time interval,  $\Delta t$ , the mass of solute entering the box at  $x = x_i$ ,

$$m(x_i) = F(x_i)A\Delta t. \quad (3.3)$$

The mass leaving the box at  $x = x_{i+1}$ , is:

$$m(x_{i+1}) = -F(x_{i+1})A\Delta t \quad (3.4)$$

### 3.2. CONSERVATION EQUATIONS

with the negative sign indicating flux loss from the box.

Diffusive flux can be expressed in different formats depending on the definition of parameters, as summarised extensively by Shackelford and Moore (2013). The following definition is applied in this thesis which is consistent with tortuosity estimations reported by Boving and Grathwohl (2001):

$$F = -D_e \frac{\delta C}{\delta x}. \quad (3.5)$$

In the equation,  $F$  is also denoted as  $J$  in many other publications.  $D_e$  is the effective diffusion coefficient that considers tortuosity and porosity. The negative sign indicates a flux loss from high concentration to low concentration. Equation 3.1 and 3.2 can, therefore, be rewritten as

$$m(t_n) = -D_e \left( \frac{\delta C}{\delta x} \right)_x A \Delta t, \quad (3.6)$$

and

$$m(t_{n+1}) = -D_e \left( \frac{\delta C}{\delta x} \right)_{x+1} A \Delta t \quad (3.7)$$

Considering conservation of mass: mass in at  $x_i$  – mass out at  $x_{i+1}$  = mass at time  $t_{k+1}$  – mass at time  $t_k$ , the equation can be rearranged as

$$\frac{C(t_{n+1}) - C(t_n)}{\Delta t} = \frac{\frac{D_e}{\phi} \left[ (\delta C / \delta x)_{x_{i+1}} - (\delta C / \delta x)_{x_i} \right]}{\Delta x}. \quad (3.8)$$

As  $\Delta t$  and  $\Delta x \rightarrow 0$ :

$$\frac{\delta C}{\delta t} = \frac{D_e}{\phi} \frac{\delta^2 C}{\delta x^2}. \quad (3.9)$$

#### 3.2.2 Diffusive-Advective Transport in Porous Media

Advection in porous media can be expressed by Darcy's law:

$$q = -\frac{K}{\mu} \frac{\delta P_x}{\delta x}, \quad (3.10)$$

### 3. Mathematical Models of Transport

where  $q$  is the Darcy velocity, which quantifies the volume of fluid passing through per unit area per unit time (m/s).  $P$  is the resulting pressure of both fluid and gravity in the direction of flow.

$$P = P_f + P_g = P_f + \rho g_x x \quad (3.11)$$

where  $g_x$  is the component of the gravitational force along the direction of flow. For advection flow to occur, the overall pressure  $P \neq 0$ , indicating an overpressure or under-pressure hydraulic status. Similarly, we can derive the diffusion-advection equation with the box model using the Darcy velocity,  $q$ . The combined flux of advection and diffusion,  $F$ , can be expressed as

$$F = -D_e \frac{\delta C}{\delta x} + qC, \quad (3.12)$$

And the transport equation can, therefore, be written in the following format

$$\phi \frac{\delta C}{\delta t} + q \frac{\delta C}{\delta x} = D_e \frac{\delta^2 C}{\delta x^2} \quad (3.13)$$

### 3.3 SOLVING 1-D DIFFUSION-ADVECTION EQUATION

The concentration along a 1D profile changes according to both the position and time allowed for transport. The partial differential equation (Equation 3.13) can be solved analytically for simple systems. However, as complexity increases, with the occurrence of multiple layers and variation of parameters, it is more efficient to simulate the transport numerically. Numerical analysis solves mathematical problems with numerical approximation. The finite difference method expresses functions by their values at specific grid points and derivatives are approximated through differences in these values.

We consider  $C(x, t)$ , the concentration at a transport distance of  $x$  and at a transport time of  $t$ , where  $0 \leq x \leq a, 0 \leq t \leq T$ , and  $a$  is the total thickness of the unit and  $T$  is the full time for transport. The discretised spatial variable  $x$  is divided into

### 3.3. SOLVING 1-D DIFFUSION-ADVECTION EQUATION

$k$  meshes, and  $k + 1$  nodes (i.e., there is a node at  $x = 0$ ), with  $i$  representing the node of choice. We obtain the following equations

$$\Delta x = \frac{a}{k} \quad (3.14)$$

and therefore, the distance at node  $i$  can be expressed as

$$x_i = (i - 1)\Delta x, 1 \leq i \leq k + 1. \quad (3.15)$$

The discrete temporal variable  $t$  is divided into  $m$  meshes, and  $m$  nodes (i.e., there is no node at  $t = 0$ ), with  $n$  representing the node of choice. We obtain similar equations

$$\Delta t = \frac{T}{m}, \quad (3.16)$$

and therefore, the time at node  $n$  can be expressed as

$$t_n = n\Delta t, 0 \leq n \leq m. \quad (3.17)$$

The produced distance-time 2D meshes are illustrated in Figure 3.2.

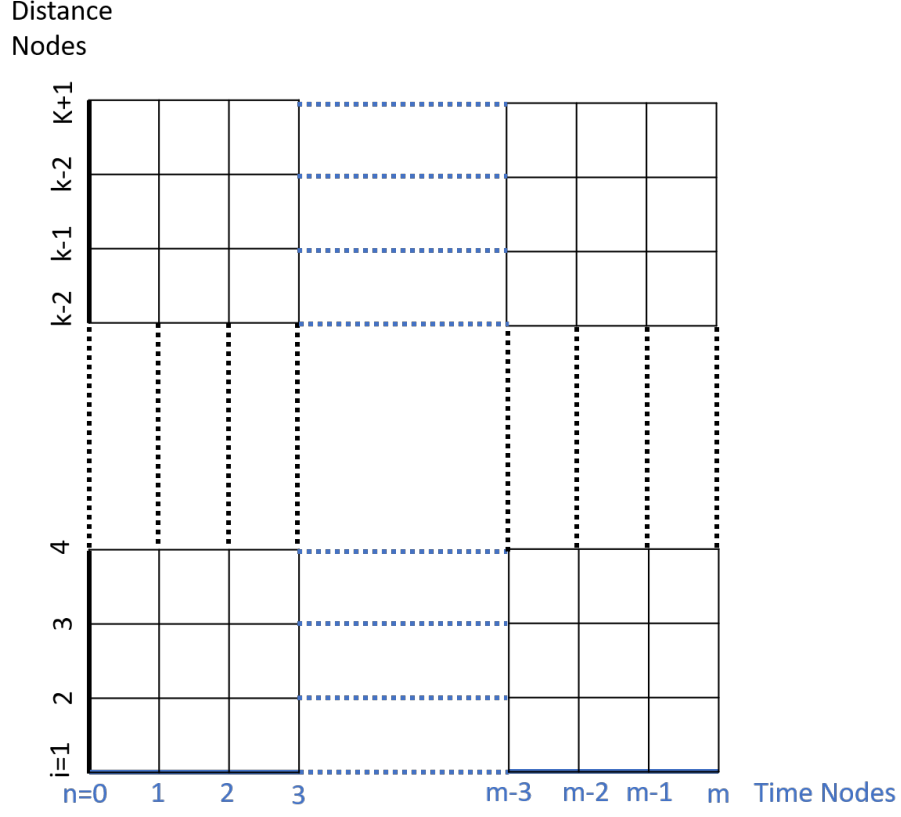
The concentration at the  $n^{th}$  time step (at time  $n\Delta t$ ) and  $i^{th}$  spatial step (at a distance of  $(i - 1)\Delta x$  is expressed as  $C_i^n = C(x_i, t_n)$ .

This equation can be solved explicitly by applying the Forward Euler Method or implicitly using the Backward Euler Method. Explicit and implicit methods are approaches used in numerical analysis for obtaining numerical approximations to the solutions of time-dependent ordinary and partial differential equations. Explicit methods calculate the state of a system at a later time step from the state of the system at the current time, and the diffusion equation can be expressed as

$$C_i^{m+1} - C_i^m = -\frac{q\Delta t}{\phi\Delta x} (C_{i+1}^m - C_i^m) + \frac{D_e\Delta t}{\phi\Delta x^2} \left[ \left( \frac{\delta C}{\delta x} \right)_{i+1}^n - \left( \frac{\delta C}{\delta x} \right)_i^n \right]. \quad (3.18)$$



### 3. Mathematical Models of Transport



**Figure 3.2:** Distance-time 2D meshes. The time is presented on the  $x$ -axis and the distance on the  $y$ -axis.  $i$  and  $n$  represent the nodes of choice. Time is divided into  $m$  nodes ( $0 \leq n \leq m$ ), and distance is divided into  $k + 1$  nodes ( $1 \leq i \leq k + 1$ ).

Derivatives can be approximated following one of the expansion equations of the Taylor's series,

$$f(x + \Delta x) = f(x) + \Delta x \frac{df}{dx} + \frac{\Delta x^2}{2!} \frac{d^2 f}{dx^2} + \frac{\Delta x^3}{3!} \frac{d^3 f}{dx^3} + \dots = f(x) + \Delta x \frac{df}{dx} + O(\Delta x^2), \quad (3.19)$$

and therefore  $C_i^n$  can approximate as

$$C_i^n = C_{i-1}^n + \Delta x \left( \frac{\delta C}{\delta x} \right)_i^n + O(\Delta x^2), \quad (3.20)$$

which can be rearranged as

$$\left( \frac{\delta C}{\delta x} \right)_i^n = \frac{C_i^n - C_{i-1}^n}{\Delta x}. \quad (3.21)$$

Similarly,

$$\left( \frac{\delta C}{\delta x} \right)_{i+1}^n = \frac{C_{i+1}^n - C_i^n}{\Delta x}. \quad (3.22)$$

### 3.3. SOLVING 1-D DIFFUSION-ADVECTION EQUATION

Therefore, the difference of the two derivatives can be approximated as

$$\left(\frac{\delta C}{\delta x}\right)_i^n - \left(\frac{\delta C}{\delta x}\right)_{i+1}^n = \frac{(C_{i-1}^n - 2C_i^n + C_{i+1}^n)}{\Delta x}. \quad (3.23)$$

By substituting Equation 3.23 to the explicit equation (Equation 3.18),

$$C_i^{n+1} - C_i^n = -\frac{q\Delta t}{\phi\Delta x} (C_{i+1}^n - C_i^n) + \frac{D_e\Delta t}{\phi\Delta x^2} (C_{i-1}^n - 2C_i^n + C_{i+1}^n). \quad (3.24)$$

By assigning  $s = \frac{D_e\Delta t}{\phi\Delta x^2}$  and  $r = \frac{q\Delta t}{\phi\Delta x}$ , Equation 3.24 can be written as

$$C_i^{n+1} - C_i^n = -r(C_{i+1}^n - C_i^n) + s(C_{i-1}^n - 2C_i^n + C_{i+1}^n). \quad (3.25)$$

By rearranging, the solution for the concentration at the next time step is

$$C_i^{n+1} = sC_{i-1}^n + (r - 2s + 1)C_i^n + (s - r)C_{i+1}^n. \quad (3.26)$$

A faster computational speed can be achieved by setting bigger spatial and temporal steps. However, this causes a sacrifice of accuracy. Furthermore, forward Euler is no longer stable if  $s < 0$  or  $s > 0.5$  (Hindmarsh et al., 1984), which suggests a trade-off between processing speed and stability. If we set  $\Delta x = 1$  to ensure a proper vertical resolution, a porosity of 0.5 (which is an unrealistic upper limit in our study area) and a minimum diffusion coefficient of  $10^{-12}$  m<sup>2</sup>/s, the maximum time step that can be taken is 8000 yrs. Since we are monitoring a system from Cambrian to present, which is about 500 Myrs, a minimum of 62500 steps is therefore required for calculation. Constraints on time steps are non-existent for implicit backward Euler as it is unconditionally stable. This method finds a solution by solving an equation involving both the current state of the system and the later one. The implicit equation can be obtained by rearranging Equation 3.25,

$$C_i^n = -sC_{i-1}^{n+1} + (1 + 2s - r)C_i^{n+1} - (s - r)C_{i+1}^{n+1}. \quad (3.27)$$

$C_{i=2}$  and  $C_{i=k}$  can be calculated with Equation 3.27 with the following matrix equation:

### 3. Mathematical Models of Transport

$$\begin{aligned}
C_{i=2,3,4\dots k}^m = & \begin{bmatrix} 1+s_1+s_2-r_1 & -(s_2-r_2) & 0 & \cdots & 0 & 0 & 0 \\ -s_1 & 1+s_1+s_2-r_1 & -(s_2-r_2) & \cdots & 0 & 0 & 0 \\ 0 & -s_1 & 1+s_1+s_2-r_1 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 1+s_1+s_2-r_1 & -(s_2-r_2) & 0 \\ 0 & 0 & 0 & \cdots & -s_1 & 1+s_1+s_2-r_1 & -(s_2-r_2) \\ 0 & 0 & 0 & \cdots & 0 & -s_1 & 1+s_1+s_2-r_1 \end{bmatrix} \\
& \times C_{i=2,3,4\dots k}^{m+1} + \bar{b},
\end{aligned} \tag{3.28}$$

where  $\bar{b}$  is the boundary vector with a columnar matrix with  $k-1$  elements influences  $C_{i=2}$  and  $C_{i=k}$ , which will be defined in the later section. Let  $U^n = C_{i=2,3,4\dots k}^n$ , and  $A$  equals the sparse diagonal matrix, and the equation can be re-written as

$$U^n = AU^{n+1} + \bar{b}. \tag{3.29}$$

By rearranging the equation, we can calculate concentrations of the next time step from the current step using the inverse matrix of  $A$ , i.e.

$$U^{n+1} = A^{-1}(U^n - \bar{b}). \tag{3.30}$$

$C_{i=1}$  and  $C_{x=k+1}$  represent concentrations at the bottom and top boundaries and controls the boundary vector  $\bar{b}$ . Different boundary conditions are discussed in the following section.

#### 3.3.1 Initial Conditions and Boundary Conditions

Setting Initial conditions ( $C^0$ ): The formation water trapped in pore spaces during sediment deposition can be assumed to be air saturated water; therefore, noble gas concentrations at  $t = 0$  can be calculated from Henry's law with recharging temperature, pressure and salinity. Setting boundary conditions: There are different types of

### 3.3. SOLVING 1-D DIFFUSION-ADVECTION EQUATION

boundary conditions to be considered, including a specified constant concentration, a specified flux, whether it is perfectly absorbing (explained in the following), or a mixture of them. A specified constant concentration boundary can be applied when the concentration does not change with time:

$$C_{at\ the\ boundary} = constant . \quad (3.31)$$

A perfectly absorbing boundary indicates a complete escape of the substance at the boundary and that

$$C_{at\ the\ boundary} = 0 . \quad (3.32)$$

A specified flux boundary has a specified flux per unit area across the boundary,

$$F = -D_e \frac{\delta C}{\delta x} + qC . \quad (3.33)$$

For modelling the vertical transport of groundwater, we can assume that the upper boundary has a constant concentration of air saturated water, i.e.,

$$C_{k+1} = C_{ASW} . \quad (3.34)$$

According to Equation 3.27,

$$C_k^n = -sC_{k-1}^{m+1} + (1 + 2s - r)C_k^{m+1} - (s - r)C_{ASW} . \quad (3.35)$$

Since the first two terms are included in matrix A (Equation 3.3), the third term for constraining  $C_k^n$  needs to be included in  $\bar{b}$ , i.e., the last term for  $\bar{b}$ ,

$$\bar{b}_{k-1} = -(s - r)C_{ASW} . \quad (3.36)$$

For the bottom boundary, the interface of the sedimentary basin and the crystalline basement, we can model a constant flux boundary:

$$F_1^n = -D_e \left( \frac{\delta C}{\delta x} \right)_1^n + qC_1^m . \quad (3.37)$$

### 3. Mathematical Models of Transport

A better estimation for the derivative can be calculated by summing Equations 3.22 and 3.23,

$$\left(\frac{\delta C}{\delta x}\right)_i^n + \left(\frac{\delta C}{\delta x}\right)_{i+1}^n = \frac{C_{i+1}^n - C_{i-1}^n}{\Delta x}, \quad (3.38)$$

which can be rearranged as

$$\left(\frac{\delta C}{\delta x}\right)_i^n \approx \frac{C_{i+1}^n - C_{i-1}^n}{2\Delta x} \approx \frac{C_{i+2}^n - C_i^n}{2\Delta x}. \quad (3.39)$$

Substituting Equation 3.39 into Equation 3.37, the bottom flux can be expressed as

$$F_1^n = -D_e \frac{C_3^n - C_1^n}{2\Delta x} + qC_1^n, \quad (3.40)$$

which can be rearranged as

$$C_1^n = \frac{2\Delta x F + D_e C_3^n}{D_e + 2q\Delta x}. \quad (3.41)$$

According to Equation 3.27,

$$C_2^n = -sC_1^{n+1} + (1 + 2s - r)C_2^{n+1} - (s - r)C_3^{n+1}. \quad (3.42)$$

Substitute Equation 3.41 to Equation 3.42, the following equation is obtained:

$$C_2^n = -s \left( \frac{2F\Delta x + D_e C_3^n}{D_e + 2q\Delta x} \right) + (1 + 2s - r)C_2^{n+1} - (s - r)C_3^{n+1}, \quad (3.43)$$

which can be rearranged:

$$C_2^n = -s \left( \frac{2F\Delta x}{D_e + 2q\Delta x} \right) + (1 + 2s - r)C_2^{n+1} - \left[ \left( \frac{D_e}{D_e + 2q\Delta x} + 1 \right) s - r \right] C_3^{n+1}. \quad (3.44)$$

Matrix A and boundary vector  $\bar{b}$  need to be corrected for the constant flux boundary as

$$A(1, 2) = - \left[ \left( \frac{D_e}{(D_e + 2q\Delta x)} + 1 \right) s - r \right] \quad (3.45)$$

and

$$\bar{b}_1 = -s \frac{2F_1^n \Delta x}{D_e} = -s \frac{2F\Delta x}{D_e}. \quad (3.46)$$

If the system is a closed system with solid boundary, i.e. flux is 0, the boundary can be set as  $F_k^n = 0$ .

### 3.4. VALIDATION OF THE NUMERICAL MODEL

For a vertical transport model assuming a constant concentration upper boundary and a constant flux boundary at the bottom, the concentrations for  $C_1$  (bottom/basement) and  $C_k$  (top/contact to atmosphere) are defined by Equation 3.36 and Equation 3.41, respectively. The columnar matrix  $\bar{b}$  has the first element ( $\bar{b}_1$ ) and the last element ( $\bar{b}_{k-1}$ ) defined by Equation 3.46 and 3.36, respectively, and all the other elements as zeros.

### 3.4 VALIDATION OF THE NUMERICAL MODEL

Fluid transport is governed by well-known equations. In order to tailor the simulation to particular problems and to better understand the different parameters, numerical models are coded with MATLAB<sup>®</sup>. The model is also validated by comparing the modeling result of a commercial software published by Hendry et al. (2013) My model can be validated if the same results are derived by inputting the same parameters run with the commercial model by Hendry et al. (2013).

In Hendry et al. (2013)'s paper, porewater samples from drilling wells in the Williston Basin in North America are analysed for their  $\delta^{18}\text{O}$  to produce high-resolution vertical  $\delta^{18}\text{O}$  profiles across the Cretaceous, the Mississippian and the upper Devonian units.  $\delta^{18}\text{O}$  values decrease from -13‰ at 3m BG in the glacial till to -15‰ and -17‰ in the till-shale contact. An increasing trend is shown until the 2nd White Specks unit of -12‰ and -9‰ but follows by a decrease to between 16‰ and -19‰ at the shale-Mannville contact. Uniform values of 16.1‰ are observed in the Mannville formation. Values as high as -0.5‰ to -2‰ are found in the Devonian Duperow units. The high resolution samples in the Cretaceous units are pore water samples collected from freshly drilled wells in 2009. The samples below the Mannvilles are mostly seepage inflows in mine shafts collected by between 1985 and 2004.

Transport of  $\delta^{18}\text{O}$  is analysed by simulating with the finite element model CTRANW. The general trend excluding the negative excursion around the Mannville is compared with 15, 20 and 25 Ma diffusive transport from the Prairie Evaporite of +5‰. The

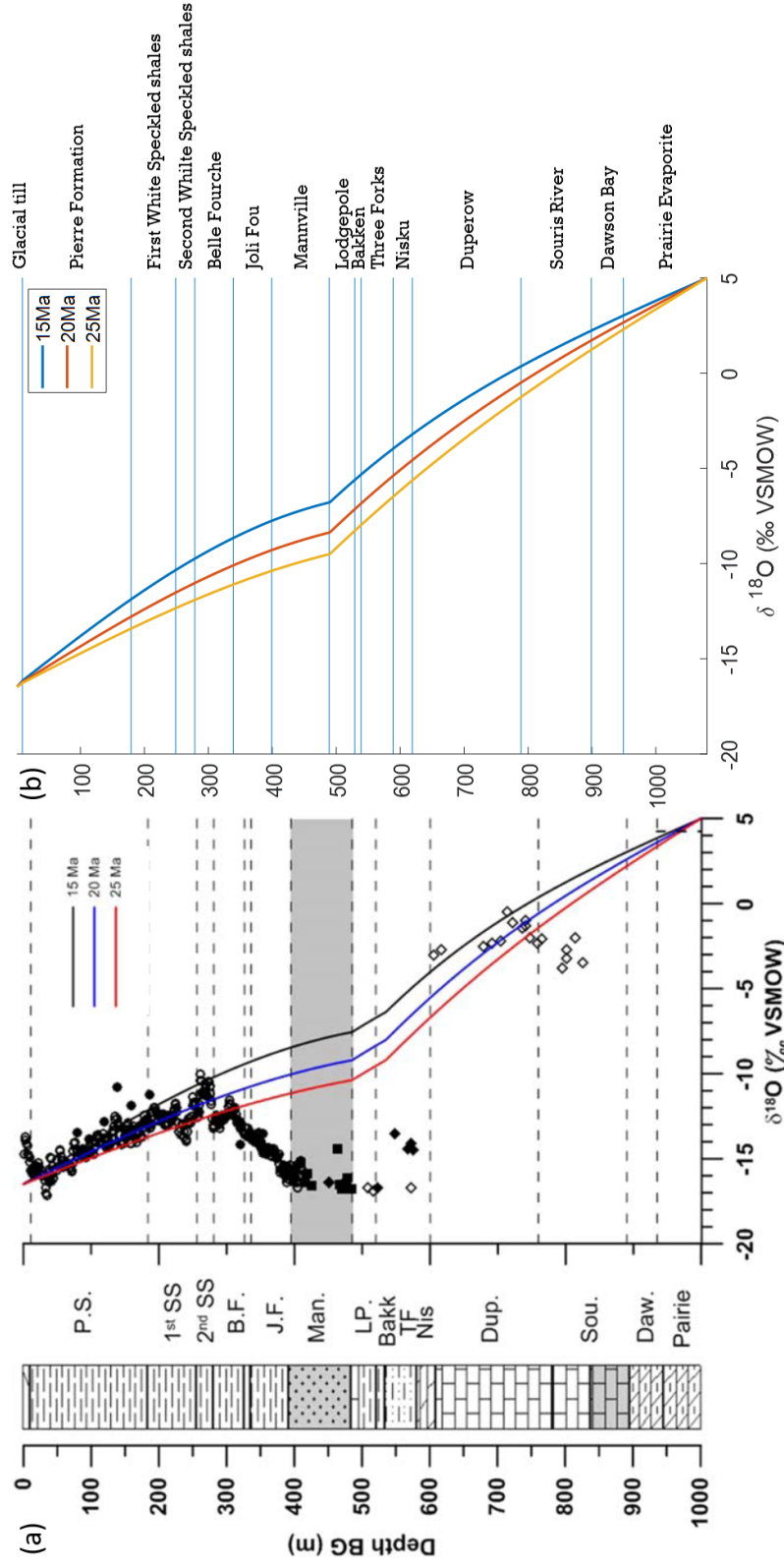
### 3. Mathematical Models of Transport

**Table 3.1:** Parameters for reconstructing  $\delta^{18}\text{O}$  transport model reported by Hendry et al. (2013)

| Units                        | $\phi$ | $D'_e \times 10^{-10} \text{ m}^2/\text{s}$ | $D_e \times 10^{-10} \text{ m}^2/\text{s}$ | Thickness m |
|------------------------------|--------|---------------------------------------------|--------------------------------------------|-------------|
| Glacial till                 | 0.24   | 2.3                                         | 0.552                                      | 11          |
| Pierre Formation             | 0.33   | 2.3                                         | 0.759                                      | 173         |
| First White Speckled shales  | 0.33   | 2.3                                         | 0.759                                      | 72          |
| Second White Speckled shales | 0.33   | 2.3                                         | 0.759                                      | 25          |
| Belle Fourche                | 0.33   | 2.3                                         | 0.759                                      | 55          |
| Joli Fou                     | 0.33   | 2.3                                         | 0.759                                      | 56          |
| Mannville                    | 0.34   | 2.3                                         | 0.782                                      | 93          |
| Lodgepole                    | 0.1    | 2.1                                         | 0.21                                       | 37          |
| Bakken                       | 0.1    | 2.1                                         | 0.21                                       | 12          |
| Three Forks                  | 0.1    | 2.1                                         | 0.21                                       | 48          |
| Nisku                        | 0.1    | 2.1                                         | 0.21                                       | 27          |
| Duperow                      | 0.1    | 2.1                                         | 0.21                                       | 172         |
| Souris River                 | 0.1    | 2.1                                         | 0.21                                       | 114         |
| Dawson Bay                   | 0.1    | 2.1                                         | 0.21                                       | 51          |
| Prairie Evaporite            | 0.1    | 2.1                                         | 0.21                                       | 130         |

negative excursion is compared with simulations of Pleistocene horizontal flushing events. The successful reproduction of the vertical  $\delta^{18}\text{O}$  distribution suggests a long-term diffusion superimposed with Pleistocene glacial flushing to the Mannville aquifer. Such hydrogeological interpretation is also supported by other geochemical evidence (Grasby et al., 2000; Grasby and Betcher, 2002; Grasby and Zhouheng Chen, 2005; Ferguson et al., 2007) and the simulation of  $\text{Cl}^-$  profiles (Hendry and Harrington, 2014).

### 3.4. VALIDATION OF THE NUMERICAL MODEL



**Figure 3.3:** Validation of the numerical transport model. (a) Modelled results reported by Hendry et al. (2013); (b) Modelled results with models constructed from the first principle in this study using MATLAB®.



### 3. Mathematical Models of Transport

In their model, the effective diffusive coefficient,  $D_e$ , is defined as

$$F = -\phi D'_e \frac{\delta C}{\delta x}, \quad (3.47)$$

which is different from that defined in this study (Equation 3.5) and the symbol  $D'_e$  is used to differentiate between the two.  $D_e$  used in this thesis is, therefore, the product of porosity and  $D'_e$ . The parameters required for modelling are summarised in Table 3.1, and modelled results are illustrated in Figure 3.3.

To test the mathematical functions in the model developed in MATLAB<sup>®</sup>, the same parameters are used to simulate the long-term diffusion transport of the mixing between Prairie Evaporite brine with freshwater at the surface. The reproduced diffusion profiles of 15 Ma, 20 Ma and 25 Ma are plotted in Figure 3.3 alongside simulation results from Hendry et al. (2013). Noticeably, the simulated results do not match the sample measurement since the horizontal flushing events are simulated in this validation step. However, the model developed in this thesis reproduces the diffusion profiles reported by Hendry et al. (2013), indicating the diffusion calculations in our model is robust.

In addition to diffusive transport, other processes like horizontal and vertical advection can also affect subsurface fluid migration. By developing and focusing in this work on exploring a 1D model, we use this as a reference model which considers the smallest number of model parameters in a complex system, and where this cannot fit the observed data. The extent and form of data misfit informs us about the magnitude and type of process that must be, in addition to diffusion, controlling the helium distribution of dissolved gases considered here.



# 4

## Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin

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## ABSTRACT

Understanding subsurface fluid migration within sedimentary basins is crucial for the exploration of natural resources as well as building safety cases for environmental projects such as carbon sequestration and nuclear waste repositories. Noble gases, due to their chemical inertness, are useful tools to identify and quantify subsurface physical processes and provide a quantitative understanding of sedimentary fluid origin, residence times and transport mechanisms. The Williston Basin is an intracratonic basin with Cambrian to Pleistocene multi-layered aquifers and aquitards. Twenty-eight natural gas samples collected from different locations and geological formations and their noble gas isotopic and concentration data are presented here. Except for Bakken Weyburn samples, which are crustal dominated, air-normalised  $^3\text{He}/^4\text{He}$  ( $R_a$ ) varies between 0.08  $R_a$  to 0.36  $R_a$ , higher than the crustal endmember of  $\sim 0.02$

#### *4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin*

$R_a$  and consistent with a resolvable mantle  $^3\text{He}$  component. By plotting the  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios against each other, the Ne ratios of the Deadwood samples (contact unit with the basement) fall on a mixing line between air and a radiogenic production endmember which is distinct from modern sedimentary sources and has been ascribed to an old Precambrian source (Kendrick et al., 2011; Lippmann-Pipke et al., 2011; Holland et al., 2013).

The radiogenic  $^4\text{He}$  concentration in the groundwater associated with the sampled natural gas can be estimated from the gas  $^4\text{He}/^{20}\text{Ne}$  ratio (Ballentine et al., 2002; Ballentine and Sherwood Lollar, 2002). Compared to calculated in situ radiogenic production,  $^4\text{He}$  is in excess in shallower units and depleted in deeper units and is evidence of both gas transport between the different sedimentary formations and a deeper input from the crystalline basement. Cross-formational transport of noble gases and a crystalline basement flux is further supported by the mantle-derived  $^3\text{He}$  observed in various units and the Ne signature of Precambrian basement in the Deadwood Formation, which overlies an Archean crystalline basement complex. A vertical scale diffusional model has been constructed to estimate the basement  $^4\text{He}$  flux into the basin. The reference models assume that the groundwater column is static and that the noble gas transport is dominated by diffusion. Deviation from modelled diffusion profiles is observed for the Viking, Mannville and Mississippian formations, and interpreted to indicate  $^4\text{He}$  loss due to water disturbance, likely related to anthropogenic water flooding in the oil industry, common in these formations of the Williston. To fit the observed  $^4\text{He}$  profile, the apparent He flux into the base of the Williston Basin is estimated to be between  $0.8\text{-}1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ . The estimation is comparable to the steady-state flux estimated for the average continental crust ( $1.47 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ ), suggesting diffusion can play a dominant role in the transport of helium in stable sedimentary basin systems. This work shows that the helium flux into any single aquifer or lithological unit is, critically, controlled by the flux from the lithological unit directly underlying the aquifer of interest. The development of basin architecture and hydrogeological events need to be considered when making the assumption of  $^4\text{He}$  steady-state flux in  $^4\text{He}$  groundwater dating applications.

## 4.1 INTRODUCTION

Understanding the sources of fluids in sedimentary basins, their mass, residence times and migration mechanisms are fundamental to the exploration of natural resources, such as hydrocarbon, and developing safety cases for environmental projects such as carbon storage (e.g. Gunter et al., 2004; Celia and Nordbotten, 2009; Lemieux, 2011) and nuclear waste repositories (e.g. Tóth and Sheng, 1996; Schwartz, 2009; Sykes et al., 2011; Joyce et al., 2014; Hendry et al., 2015).

Geochemical tracers are useful tools in analysing basin hydrogeology; for example, the comparison of TDS (total dissolved solids) distribution among different geological formations can be used to qualitatively evaluate cross-formational connectivity (Bachu and Hitchon, 1996); the mixing trends of cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^{+}$ ) can be used to identify endmember salt compositions (Ferguson et al., 2007); and the correlation between  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  and global and local meteoric water can be used to identify the sources of groundwater (Weaver et al., 1995). Quantitative numerical models of these tracers enable the identification of the dominant mechanism of transport and hydrogeological events (Mazurek et al., 2011; Hendry et al., 2013; Hendry and Harrington, 2014; Hendry et al., 2015). However, uncertainties associated with hydrogeological and geochemical properties, including initial conditions, boundary conditions, porosity and permeability make the determination of a unique transport model difficult. It is, therefore, necessary to compare the interpretations of different tracer profiles (Hendry et al., 2015).

Noble gases, due to their chemical inertness, serve as useful tools for identifying and quantifying physical processes in the subsurface. Noble gases which originate from different terrestrial reservoirs (i.e., atmosphere, crust and mantle) possess distinct elemental and isotopic end-member ratios. Deviations from these ratios help to differentiate the sources of input as well as identify and quantify the physical processes controlling fluid migration (e.g. end-member mixing, phase separation, and mass fractionation) (Ballentine and Burnard, 2002; Zhou et al., 2005; Barry et al., 2016).

#### *4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin*

Noble gases have been used to identify the mechanism and interactions between different fluids (Ballentine et al., 1991; Pinti and Marty, 1995; Zhou et al., 2005; Gilfillan et al., 2008; Gilfillan et al., 2009; Barry et al., 2016), to estimate groundwater mean residence times (Lippmann et al., 2003; Holland et al., 2013; Aggarwal et al., 2015; Warr et al., 2018) and quantify crustal degassing (Torgersen and Clarke, 1985; Torgersen, 1989; Torgersen, 2010; Aggarwal et al., 2015). Numerical modelling has the potential to quantify the basement and cross-formational flux of noble gases and hydrogeological events on a basin scale. Such a model requires well-constrained basinal hydrogeological properties and an extensive selection of samples both laterally and vertically in the basin for verification. Basin-scale numerical models describing noble gas observations have previously been applied in, for example, the Great Hungarian Plain (Stute et al., 1992), and the Paris basin with good effect (Castro et al., 1998b). As the understanding of water-rock interactions and fluid residence in the crystalline basement improves, it has become clear that these deep crustal systems may act as a source for helium, hydrogen, nitrogen and light hydrocarbons with subsequent impact on helium and hydrogen resource assessment, and electron donor and electron acceptor sources for the deep subsurface biosphere (Sherwood Lollar and Ballentine, 2009; Holland et al., 2013; Warr et al., 2018).

External helium flux has been argued to be negligible in some sedimentary units (e.g. Tolstikhin et al., 2011), while it is also required in multiple aquifers and surface water systems (Torgersen and Clarke, 1985; Torgersen et al., 1992; Torgersen, 2010; Aggarwal et al., 2015). He flux has also been argued to be associated with tectonics and volcanisms (Oxburgh and O’Nions, 1987; Martel et al., 1989). However, compared to advection, the significance of diffusive transport vertically across sedimentary basins is less well understood. The quantification of diffusive flux in sedimentary basin systems is a significant component that inherent in radiogenic U-Th-<sup>4</sup>He dating. The goal of the study is to understand the role of the crystalline basement on the basinal noble gas inventory within a stable intracratonic basin and identify subsequent transport mechanisms within the basin with the help of a numerical model. Natural gas samples

## 4.2. REGIONAL GEOLOGY AND HYDROGEOLOGY

from multiple hydrogeological units within the Williston Basin were collected and analysed for their noble gas abundance and isotopic composition to this end.

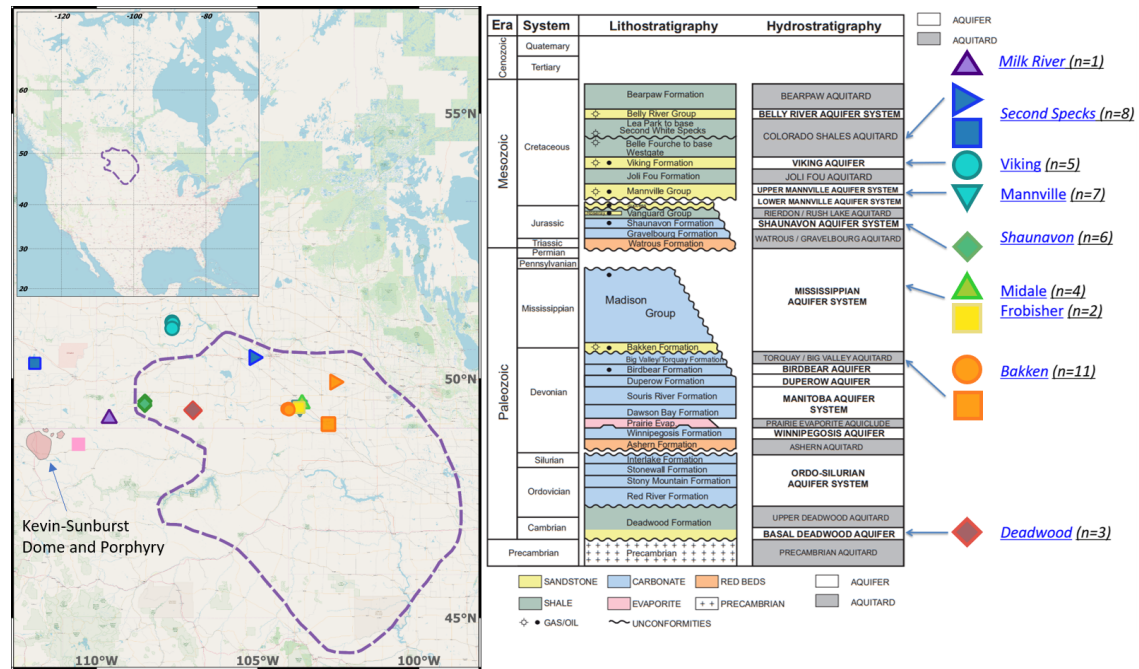
### 4.2 REGIONAL GEOLOGY AND HYDROGEOLOGY

The Williston Basin is an oval intracratonic basin that stretches across the border of the United States and Canada (Figure 4.1). Erosion of the Precambrian basement and subsequent cooling and contraction led to lithosphere thinning and subsidence (Ahern and Mrkvicka, 1984; Ahern and Ditmars, 1985; Crowley et al., 1985; Crowley and Kuhlman, 1988). Major subsidence and sediment filling started in the Middle Ordovician (Pollastro et al., 2013; EERC, 2016), followed by episodic subsidence in through Palaeozoic (Zhu and Hajnal, 1993; Osadetz et al., 2002). Cycles of sea-level changes connected the basin to the proto-Pacific ocean to the west (Bachu, 1993) and deposited successions of marine carbonates and evaporites during the Cambrian to the Middle Jurassic. Progressive uplift of the Precambrian Shield in the Late Jurassic and the pre-Aptian Cretaceous transformed the Williston Basin into a clastic, shale-dominated foreland basin succession. Foreland folding and thrusting during the Laramide orogeny in the late Paleocene to early Eocene led to a significant erosional event, but was terminated by regional extension during the Early and Middle Eocene (Price, 1994; Wright et al., 1994).

Modern basin-scale groundwater flow has been explained by a gravity-driven model: this recharges at northwest-southeast-trending topographic highs in the western United States, flows lateral southwest to northeast across the basin and discharges along the Manitoba lowlands Palaeozoic outcrop belt (Bachu and Hitchon, 1996; Iampen and Rostron, 2000). Both the stratigraphic and hydrostratigraphic columns are presented in Figure 4.1. Later studies indicated that Pleistocene glaciation temporarily changed flow directions and recharged the basin (e.g. Grasby et al., 2000; Grasby and Betcher, 2002; Ferguson et al., 2007). Although flow direction and recharge changed, the preservation of dense brines in the centre of the basin suggests the deep formations have



#### 4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin



**Figure 4.1:** The left panel shows the location (inset) and outer margin of the Williston Basin (USGS, 2013) as well as the locations of the sampling wells. The right panel shows the lithological and hydrogeological stratigraphy (Melnik, 2012). The samples were collected from the marked geological formations, and these symbols are used throughout this paper. The pink square is the location of the Red River sample reported by Danabalan (2017). The Deadwood well that was reported by Danabalan (2017) is either the same well or in close approximate to the Deadwood well collected in this study, and is marked as pink diamonds throughout the study.

not been disturbed (Grasby et al., 2000). Extensive water injection and enhanced oil recovery (EOR) activities during hydrocarbon production in the Williston Basin over the last century also need to be considered when analysing the groundwater system.

Petrogeology studies revealed 10 total petroleum systems (TPS) in the US part of the basin (Anna, 2013). Many of them are self-contained, i.e. the hydrocarbon is generated and preserved in a closed system, with no external sources or sinks (Anna, 2013). Therefore, most samples represent the producing formation. The formations targeted in this study include Milk River, Second White Specks, Viking, Mannville, Shaunavon, Midale, Frobisher, Bakken and Deadwood (Figure 4.1). While most formations produce gas or gas bubbles at the wellhead, Mannville wells produce a gas-liquid mixture. Samples from the Midale formation are proximal to a CO<sub>2</sub>-EOR project, and recycled gas used in the carbon capture and storage project is sampled.

### 4.3. METHODOLOGY

The Frobisher well is an observation well for the EOR project, and Viking wells are newly drilled wells with low flow rate during sample collection.

The reservoir pressure can be estimated with an average pressure gradient of 10.8 Kpa/m that is obtained from the Cambro-Ordovician Saline System (Peck et al., 2013). The value is comparable to the hydrostatic pressure of seawater but significantly lower than lithostatic pressure of that is usually greater than 20 KPa/m (Pashin, 2008). An internal geothermal gradient map demonstrates that the Williston Basin has a thermal gradient between 20~40°C /km (Bachu, 1993).

### 4.3 METHODOLOGY

Two sets of gas samples were collected for different analysis either directly from the wellhead or through a gas separator for a produced gas-fluid mixture (Appendix B.1). For compositional and stable isotope analysis, gases are collected in evacuated glass serum bottles with gas-tight stoppers fixed with mercuric chloride to inhibit any microbially-generated changes post-collection. For noble gases, samples were collected in a cold-welded internally polished, refrigeration-grade copper tubing. Gas compositions and stable isotopes are measured in the University of Toronto. Twenty-nine noble gas samples were analysed by a commercial institute, and seventeen duplicates were analysed by the noble gas laboratory at the University of Oxford. For duplicates, samples that demonstrate stronger crustal signatures are selected, details are explained in the following section and Appendix B.2.

The measurement protocol at the University of Oxford is summarised. The sample tubes were mounted on an all-stainless steel Ultra-High Vacuum system for gas purification. Hydrocarbon and other reactive gases were removed chemically by exposing gas samples to a titanium getter, a hot getter (SAES GP-50) and a cold getter (SAES NP-10). Moisture was further removed by passing through a stainless-steel water traps held at 250K and 180K respectively. Noble gases are separated based on their differential absorption using two cryogenic traps cooled by He compressors. He is

#### *4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin*

measured using Helix SFT and Ne, Ar, Kr and Xe using Argus VI. Detailed laboratory configuration and experimental procedures are described by Barry et al. (2016).

Full procedural blanks were run once per week. The average blank to sample signal ratios of  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  were 0.0001%, 0.01%, 0.35%, 0.10% and 0.05% respectively.  $^{20}\text{Ne}$  was corrected for doubly-charged  $^{40}\text{Ar}^{++}$  following the method described by Niedermann et al. (1993). Signal size for  $\text{CO}_2^{++}$  was not distinguishable from the blank and no  $\text{CO}_2^{++}$  corrections were applied to  $^{22}\text{Ne}$ . Air-standards were analysed weekly for sample calibration. The air standards were collected in the University Parks, Oxford, UK on November 24, 2014 (297 K, 1.01 atm, 95% humidity). Internal ‘running’ standards were run at least once every night following sample analysis to confirm machine stability. Signal variations ( $1\sigma$ ) for the ‘running’ standards are 1.2%, 0.3%, 0.5%, 0.4%, 0.4%  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  respectively. The calculated isotopic concentrations and ratios are presented at  $1\sigma$  uncertainty.

## **4.4 RESULTS**

### **4.4.1 Major Gas Compositions**

The major gases compositions reported include  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{C}_{2+}$  (hydrocarbon species with more than one carbon atom in each molecule). The concentrations are normalised if samples demonstrate a sum higher than 100% and are shown in Table 4.1. The Deadwood sample is mainly composed of  $\text{N}_2$  with a minor amount of the other gases. The highest  $\text{C}_{2+}$  is seen in the Bakken and Midale samples, ranging from 23.1% to 43.7%. However, the two Midale samples demonstrate large concentration differences of the other gas components. Samples from the Frobisher, Mannville and Second White Specks (Belle Plaine) formations are enriched in  $\text{N}_2$ , but with higher  $\text{CO}_2$  contents observed in the Mannville samples. The other samples are dominated by methane gas.

Table 4.1: Major gas composition of collected samples.

| Sample name                            | Distance Above Basement (m) | Depth Below Surface (m) | CH <sub>4</sub> % | N <sub>2</sub> % | C <sub>2+</sub> % | CO <sub>2</sub> % |
|----------------------------------------|-----------------------------|-------------------------|-------------------|------------------|-------------------|-------------------|
| <i>Milk River</i>                      |                             |                         |                   |                  |                   |                   |
| 14-8-3-27W3                            | 1733                        | 553                     | 92                | 3.8              | 0.1               | <0.1              |
| <i>2nd White Specks (Belle Plaine)</i> |                             |                         |                   |                  |                   |                   |
| 11-9-17-23W2                           | 1567                        | 700                     | 37.3              | 61.9             | 0.1               | <0.1              |
| <i>2nd White Specks (Alderson)</i>     |                             |                         |                   |                  |                   |                   |
| 8-31-15-14W4                           | 1490                        | 745                     | 88.9              | 5.2              | 0.2               | <0.1              |
| 5-31-15-14W4                           | 1490                        | 761                     | 88                | 6.5              | 0.2               | <0.1              |
| 14-31-15-14W4                          | 1490                        | 757                     | 89.4              | 6.5              | 0.2               | <0.1              |
| <i>Viking</i>                          |                             |                         |                   |                  |                   |                   |
| 1-7-25-12W3                            | 1357                        | 706                     | 61.7              | 26.4             | 7.6               | 0.2               |
| 7A-1-32-24-12W3                        | 1412                        | 684                     | 65                | 32.9             | 1.6               | <0.002            |
| 16-30-23-12W3                          | 1325                        | 794                     | 73.7              | 20.9             | 5.2               | <0.1              |
| <i>Mannville</i>                       |                             |                         |                   |                  |                   |                   |
| 16-28-5-13W2 a                         | 1764                        | 1107                    | 0.5               | 87.5             | <0.01             | 6.3               |
| 5-16-6-13W2(#6) b                      | 1764                        | 1083                    | 0.6               | 89.4             | <0.1              | 6.9               |
| 5-16-6-13W2(#8) c                      | 1764                        | 1083                    | 2.3               | 78.9             | 0.3               | 8.2               |
| 16-28-5-13W2 d                         | 1764                        | 1107                    | 0.3               | 74.6             | <0.1              | 3.3               |
| 5-16-6-13W2(#3) e                      | 1764                        | 1083                    | 0.3               | 86.6             | <0.1              | 5.4               |
| 5-16-6-13W2(#6) f                      | 1764                        | 1083                    | 0.6               | 88.6             | <0.1              | 5.4               |
| 5-16-6-13W2(#8) g                      | 1764                        | 1083                    | 4.2               | 81.8             | 0.1               | 5.3               |
| 16-28-5-13W2 h                         | 1764                        | 1107                    | 0.6               | 87.4             | <0.1              | 4.9               |
| 5-16-6-13W2(#3) i                      | 1764                        | 1083                    | 0.5               | 87.5             | <0.1              | 5.6               |
| 5-16-6-13W2(#6) j                      | 1764                        | 1083                    | 0.6               | 84.9             | <0.1              | 5.7               |
| 5-16-6-13W2(#8) k                      | 1764                        | 1083                    | 2.9               | 83.8             | 0.2               | 5.8               |
| <i>Shanavon</i>                        |                             |                         |                   |                  |                   |                   |
| 15-10-7-19W3                           | 993                         | 1424                    | 84.5              | 9.4              | 4.8               | 0.2               |
| 4C-15-9-6-19W3                         | 990                         | 1435                    | 85.7              | 10.7             | 3                 | 0.6               |
| 2B-3-28-6-19W3                         | 980                         | 1425                    | 81.5              | 11               | 4.8               | 0.8               |
| <i>Midale</i>                          |                             |                         |                   |                  |                   |                   |
| 8-25-6-13W2                            | 1364                        | 1457                    | 1.6               | 0                | 40.1              | <0.1              |
| 2-25-6-13W2                            | 1360                        | 1447                    | 26.8              | 26               | 43.9              | 3.3               |
| <i>Frobisher</i>                       |                             |                         |                   |                  |                   |                   |
| 2-32-5-13W2                            | 1313                        | 1557                    | 18.6              | 73.7             | 6.7               | 1                 |
| <i>Bakken (Weyburn)</i>                |                             |                         |                   |                  |                   |                   |
| 13-24-5-16W 2                          | 717                         | 2313                    | 31.2              | 12.7             | 43.7              | 5.9               |
| 1-21-5-16W2                            | 1181                        | 1849                    | 54.1              | 14.9             | 28.7              | 2.3               |
| 16-12-5-16W2                           | 980                         | 2059                    | 47                | 26.8             | 23.1              | 0.1               |
| <i>Bakken (Estevan)</i>                |                             |                         |                   |                  |                   |                   |
| 13-31-1-6W2                            | 981                         | 1926                    | 56.6              | 9.9              | 29.2              | 0.3               |
| 11-31-1-6W2                            | 996                         | 1911                    | 60.8              | 4.4              | 34.1              | 0.7               |
| 4-6-2-6W2                              | 1000                        | 1922                    | 64.9              | 3.5              | 30.8              | 0.8               |
| <i>Deadwood</i>                        |                             |                         |                   |                  |                   |                   |
| 10-3-5-8W3                             | 0                           | 2462                    | 1.6               | 96.1             | 0.1               | <0.1              |

4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin

Table 4.2: He, Ne and Ar concentration and isotopic ratios for selected samples

| Sample name                            | $^4\text{He} \times 10^{-5}$<br>$\text{cm}^3 \text{ STP}/\text{cm}^3$ | $^{20}\text{Ne} \times 10^{-8}$<br>$\text{cm}^3 \text{ STP}/\text{cm}^3$ | $^{40}\text{Ar} \times 10^{-6}$<br>$\text{cm}^3 \text{ STP}/\text{cm}^3$ | R/R <sub>a</sub> | $^{20}\text{Ne}/^{22}\text{Ne}$ | $^{21}\text{Ne}/^{22}\text{Ne}$ | $^{40}\text{Ar}/^{36}\text{Ar}$ | $^{38}\text{Ar}/^{36}\text{Ar}$ |
|----------------------------------------|-----------------------------------------------------------------------|--------------------------------------------------------------------------|--------------------------------------------------------------------------|------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| <i>Milk River</i>                      |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 14-8-3-27W3                            | 96.2 ± 2.89                                                           | 2.7 ± 0.17                                                               | 214.0 ± 6.42                                                             | 0.15 ± 0.015     | 9.75 ± 0.044                    | 0.0304 ± 0.00033                | 388.3 ± 3.88                    | 0.188 ± 0.0019                  |
| <i>2nd White Specks (Belle Plaine)</i> |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 11-9-17-23W2                           | 14.5 ± 0.43                                                           | 46.6 ± 2.83                                                              | 3570.0 ± 107.10                                                          | 0.08 ± 0.008     | 9.80 ± 0.044                    | 0.0289 ± 0.00032                | 319.6 ± 3.20                    | 0.186 ± 0.0019                  |
| <i>2nd White Specks (Alderson)</i>     |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 8-31-15-14W4                           | 190.0 ± 2.15                                                          | 8.8 ± 0.80                                                               | 149.0 ± 13.70                                                            | 0.16 ± 0.022     | 9.71 ± 0.079                    | 0.0369 ± 0.00038                | 586.6 ± 1.38                    | 0.187 ± 0.0008                  |
| 5-31-15-14W4                           | 200.0 ± 2.22                                                          | 9.0 ± 0.82                                                               | 153.0 ± 14.00                                                            | 0.16 ± 0.022     | 9.69 ± 0.079                    | 0.0369 ± 0.00038                | 584.0 ± 1.44                    | 0.187 ± 0.0009                  |
| 14-31-15-14W4                          | 170.0 ± 1.90                                                          | 8.9 ± 0.81                                                               | 150.0 ± 13.70                                                            | 0.15 ± 0.020     | 9.69 ± 0.079                    | 0.0369 ± 0.00038                | 584.0 ± 1.44                    | 0.187 ± 0.0009                  |
| <i>Viking</i>                          |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 1-7-25-12W3                            | 26.6 ± 0.80                                                           | 13.2 ± 0.80                                                              | 376.0 ± 11.28                                                            | 0.28 ± 0.028     | 9.70 ± 0.044                    | 0.0292 ± 0.00032                | 346.0 ± 3.46                    | 0.198 ± 0.0020                  |
| 7A-1-32-24-12W3                        | 10.2 ± 0.12                                                           | 25.4 ± 2.33                                                              | 407.0 ± 37.20                                                            | 0.30 ± 0.042     | 9.76 ± 0.080                    | 0.0299 ± 0.00031                | 332.9 ± 0.69                    | 0.186 ± 0.0006                  |
| 16-30-23-12W3                          | 31.9 ± 0.96                                                           | 13.4 ± 0.82                                                              | 411.0 ± 12.33                                                            | 0.27 ± 0.026     | 9.88 ± 0.044                    | 0.0294 ± 0.00032                | 367.0 ± 3.67                    | 0.195 ± 0.0020                  |
| <i>Mannville</i>                       |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 5-16-6-13W2(#6) b                      | 2050.0 ± 61.50                                                        | 207.6 ± 12.59                                                            | 7600.0 ± 228.00                                                          | 0.27 ± 0.026     | 9.70 ± 0.044                    | 0.0300 ± 0.00033                | 407.0 ± 4.07                    | 0.189 ± 0.0019                  |
| 5-16-6-13W2(#8) c                      | 2020.0 ± 60.60                                                        | 273.3 ± 16.58                                                            | 7490.0 ± 224.70                                                          | 0.26 ± 0.025     | 9.59 ± 0.043                    | 0.0298 ± 0.00033                | 397.1 ± 3.97                    | 0.188 ± 0.0019                  |
| 16-28-5-13W2 d                         | 1610.0 ± 48.30                                                        | 1574.6 ± 95.54                                                           | 9870.0 ± 296.10                                                          | 0.16 ± 0.016     | 9.72 ± 0.044                    | 0.0292 ± 0.00032                | 317.8 ± 3.18                    | 0.186 ± 0.0019                  |
| 5-16-6-13W2(#3) e                      | 1610.0 ± 48.30                                                        | 583.9 ± 35.42                                                            | 7860.0 ± 235.80                                                          | 0.19 ± 0.018     | 9.78 ± 0.044                    | 0.0299 ± 0.00033                | 381.3 ± 3.81                    | 0.188 ± 0.0019                  |
| 5-16-6-13W2(#6) f                      | 2020.0 ± 60.60                                                        | 198.4 ± 12.04                                                            | 8140.0 ± 244.20                                                          | 0.20 ± 0.019     | 9.92 ± 0.045                    | 0.0298 ± 0.00033                | 391.9 ± 3.92                    | 0.189 ± 0.0019                  |
| 5-16-6-13W2(#8) g                      | 2840.0 ± 85.20                                                        | 196.4 ± 11.91                                                            | 7980.0 ± 239.40                                                          | 0.22 ± 0.021     | 9.77 ± 0.044                    | 0.0297 ± 0.00033                | 387.8 ± 3.88                    | 0.184 ± 0.0018                  |
| 16-28-5-13W2 h                         | 2020.0 ± 60.60                                                        | 1391.7 ± 84.43                                                           | 14700.0 ± 441.00                                                         | 0.19 ± 0.019     | 9.87 ± 0.044                    | 0.0286 ± 0.00031                | 348.3 ± 3.48                    | 0.188 ± 0.0019                  |
| <i>Shawnavon</i>                       |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 15-10-7-19W3                           | 38.0 ± 0.42                                                           | 6.4 ± 0.58                                                               | 246.0 ± 22.50                                                            | 0.21 ± 0.029     | 9.73 ± 0.079                    | 0.0334 ± 0.00035                | 657.9 ± 1.36                    | 0.188 ± 0.0006                  |
| 4C-15-9-6-19W3                         | 43.3 ± 0.49                                                           | 6.3 ± 0.57                                                               | 210.0 ± 19.20                                                            | 0.20 ± 0.028     | 9.75 ± 0.080                    | 0.0336 ± 0.00035                | 615.9 ± 1.28                    | 0.187 ± 0.0006                  |
| 2B-3-28-6-19W3                         | 54.8 ± 0.61                                                           | 8.0 ± 0.73                                                               | 247.0 ± 22.60                                                            | 0.20 ± 0.028     | 9.77 ± 0.080                    | 0.0333 ± 0.00034                | 638.3 ± 1.32                    | 0.188 ± 0.0006                  |
| <i>Midale</i>                          |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 8-25-6-13W2                            | 2.8 ± 0.09                                                            | 0.5 ± 0.03                                                               | 9.9 ± 0.30                                                               | 0.21 ± 0.021     | 9.87 ± 0.044                    | 0.0316 ± 0.00035                | 583.3 ± 5.83                    | 0.198 ± 0.0020                  |
| 2-25-6-13W2                            | 22.6 ± 0.68                                                           | 229.4 ± 13.92                                                            | 1410.0 ± 42.30                                                           | 0.16 ± 0.016     | 9.68 ± 0.044                    | 0.0292 ± 0.00032                | 335.3 ± 3.35                    | 0.187 ± 0.0019                  |
| <i>Frobisher</i>                       |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 2-32-5-13W2                            | 30.3 ± 0.34                                                           | 23.0 ± 1.59                                                              | 212.0 ± 14.60                                                            | 0.15 ± 0.017     | 9.80 ± 0.080                    | 0.0307 ± 0.00032                | 332.4 ± 2.62                    | 0.183 ± 0.0013                  |
| <i>Bakken (Weyburn)</i>                |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 13-24-5-16W 2                          | 146.0 ± 4.38                                                          | 7.4 ± 0.45                                                               | 156.0 ± 4.68                                                             | 0.16 ± 0.016     | 9.90 ± 0.045                    | 0.0324 ± 0.00036                | 445.0 ± 4.45                    | 0.189 ± 0.0019                  |
| 1-21-5-16W2                            | 299.0 ± 8.97                                                          | 21.4 ± 1.30                                                              | 814.0 ± 24.42                                                            | 0.28 ± 0.027     | 9.69 ± 0.044                    | 0.0317 ± 0.00035                | 304.6 ± 3.05                    | 0.186 ± 0.0019                  |
| 16-12-5-16W2                           | 70.9 ± 1.15                                                           | 3.6 ± 0.33                                                               | 126.0 ± 11.60                                                            | 0.11 ± 0.016     | 9.67 ± 0.079                    | 0.0389 ± 0.00041                | 426.0 ± 1.35                    | 0.182 ± 0.0013                  |
| <i>Bakken (Esteron)</i>                |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 13-31-1-6W2                            | 59.1 ± 1.77                                                           | 0.8 ± 0.05                                                               | 75.9 ± 2.28                                                              | 0.01 ± 0.001     | 9.61 ± 0.043                    | 0.0385 ± 0.00042                | 433.8 ± 4.34                    | 0.190 ± 0.0019                  |
| 11-31-1-6W2                            | 38.2 ± 0.66                                                           | 1.6 ± 0.13                                                               | 72.5 ± 6.03                                                              | 0.01 ± 0.001     | 9.66 ± 0.079                    | 0.0398 ± 0.00042                | 425.9 ± 1.15                    | 0.187 ± 0.0007                  |
| 4-6-2-6W2                              | 28.8 ± 0.49                                                           | 1.2 ± 0.10                                                               | 61.9 ± 5.15                                                              | 0.01 ± 0.001     | 9.65 ± 0.079                    | 0.0400 ± 0.00042                | 427.9 ± 1.15                    | 0.186 ± 0.0007                  |
| <i>Deadwood</i>                        |                                                                       |                                                                          |                                                                          |                  |                                 |                                 |                                 |                                 |
| 10-3-5-8W3                             | 1390.0 ± 94.00                                                        | 11.6 ± 0.88                                                              | 2300.0 ± 175.00                                                          | 0.15 ± 0.026     | 9.73 ± 0.079                    | 0.0722 ± 0.00094                | 7563.8 ± 26.90                  | 0.191 ± 0.0017                  |
| <i>Air</i>                             | 0.5 ± 0.01                                                            | 1645.3 ± 3.62                                                            | 9302.6 ± 9.96                                                            | 9.80 ± 0.080     | 9.80 ± 0.080                    | 0.0290 ± 0.00030                | 295.5 ± 0.50                    | 0.189 ± 0.0004                  |
| <i>Air saturated water*</i>            | 0.0 ± 0.00                                                            | 13.2 ± 0.00                                                              | 221.6 ± 0.00                                                             | 1.00 ± 0.066     | 9.80 ± 0.080                    | 0.0290 ± 0.00030                | 295.5 ± 0.50                    | 0.189 ± 0.0004                  |

\*Air saturated water is calculated from Henry's constant providing a temperature of 297K, salinity of 35‰, and a pressure of 1 atmosphere.

Table 4.3: Kr and Xe concentrations and isotopic ratios. All data reported here are duplicates measured at Oxford

| Sample name                        | $^{84}\text{Kr} \times 10^{-12} \text{ cm}^3 \text{ STP} / \text{cm}^3$ | $^{132}\text{Kr} \times 10^{-12} \text{ cm}^3 \text{ STP} / \text{cm}^3$ | $^{86}\text{Kr} / ^{84}\text{Kr} \times 10^{-3}$ | $^{132}\text{Xe} / ^{130}\text{Xe}$ |
|------------------------------------|-------------------------------------------------------------------------|--------------------------------------------------------------------------|--------------------------------------------------|-------------------------------------|
| <i>2nd White Specks (Alderson)</i> |                                                                         |                                                                          |                                                  |                                     |
| 8-31-15-14W4                       | 7250.0 $\pm$ 665.00                                                     | 421.0 $\pm$ 38.80                                                        | 308.1 $\pm$ 0.76                                 | 6.734 $\pm$ 0.1447                  |
| 5-31-15-14W4                       | 7380.0 $\pm$ 676.00                                                     | 431.0 $\pm$ 39.70                                                        | 308.6 $\pm$ 0.82                                 | 6.472 $\pm$ 0.1443                  |
| 14-31-15-14W4                      | 7290.0 $\pm$ 669.00                                                     | 420.0 $\pm$ 38.70                                                        | 308.3 $\pm$ 0.85                                 | 6.588 $\pm$ 0.1541                  |
| <i>Viking</i>                      |                                                                         |                                                                          |                                                  |                                     |
| 7A-1-32-24-12W3                    | 42800.0 $\pm$ 3930.00                                                   | 2840.0 $\pm$ 261.00                                                      | 305.7 $\pm$ 0.51                                 | 6.567 $\pm$ 0.0471                  |
| <i>Shanavon</i>                    |                                                                         |                                                                          |                                                  |                                     |
| 15-10-7-19W3                       | 16400.0 $\pm$ 1500.00                                                   | 1680.0 $\pm$ 155.00                                                      | 306.6 $\pm$ 0.53                                 | 6.623 $\pm$ 0.0454                  |
| 4C-15-9-6-19W3                     | 16200.0 $\pm$ 1480.00                                                   | 1830.0 $\pm$ 168.00                                                      | 306.7 $\pm$ 0.54                                 | 6.612 $\pm$ 0.0443                  |
| 2B-3-28-6-19W3                     | 17300.0 $\pm$ 1580.00                                                   | 2010.0 $\pm$ 185.00                                                      | 306.4 $\pm$ 0.51                                 | 6.641 $\pm$ 0.0459                  |
| <i>Middle</i>                      |                                                                         |                                                                          |                                                  |                                     |
| 8-25-6-13W2                        | 1640.0 $\pm$ 114.00                                                     | 574.0 $\pm$ 40.20                                                        | 306.0 $\pm$ 0.78                                 | 6.572 $\pm$ 0.0596                  |
| 2-25-6-13W2                        | 117000.0 $\pm$ 8150.00                                                  | 6350.0 $\pm$ 445.00                                                      | 304.4 $\pm$ 0.77                                 | 6.623 $\pm$ 0.0523                  |
| <i>Frobisher</i>                   |                                                                         |                                                                          |                                                  |                                     |
| 2-32-5-13W2                        | 14500.0 $\pm$ 1010.00                                                   | 1080.0 $\pm$ 75.80                                                       | 305.5 $\pm$ 0.78                                 | 6.612 $\pm$ 0.0823                  |
| <i>Bakken (Weyburn)</i>            |                                                                         |                                                                          |                                                  |                                     |
| 16-12-5-16W2                       | 18200.0 $\pm$ 1690.00                                                   | 3460.0 $\pm$ 322.00                                                      | 309.5 $\pm$ 0.71                                 | 6.611 $\pm$ 0.0650                  |
| <i>Bakken (Esteron)</i>            |                                                                         |                                                                          |                                                  |                                     |
| 11-31-1-6W2                        | 12300.0 $\pm$ 1030.00                                                   | 1920.0 $\pm$ 161.00                                                      | 306.6 $\pm$ 0.51                                 | 6.630 $\pm$ 0.0547                  |
| 4-6-2-6W2                          | 13800.0 $\pm$ 1160.00                                                   | 2420.0 $\pm$ 204.00                                                      | 306.4 $\pm$ 0.51                                 | 6.631 $\pm$ 0.0548                  |
| <i>Deadwood</i>                    |                                                                         |                                                                          |                                                  |                                     |
| 10-3-5-8W3                         | 7720.0 $\pm$ 588.00                                                     | 398.0 $\pm$ 30.70                                                        | 307.8 $\pm$ 1.80                                 | 7.234 $\pm$ 0.4239                  |
| <i>Air</i>                         |                                                                         |                                                                          |                                                  |                                     |
|                                    | 649800.0 $\pm$ 5700.00                                                  | 23394.3 $\pm$ 268.90                                                     | 305.2 $\pm$ 0.25                                 | 6.607 $\pm$ 0.0050                  |
| <i>Air saturated water*</i>        |                                                                         |                                                                          |                                                  |                                     |
|                                    | 27641.4 $\pm$ 0.00                                                      | 1658.9 $\pm$ 0.00                                                        | 305.2 $\pm$ 0.25                                 | 6.607 $\pm$ 0.0050                  |

\*Air saturated water is calculated from Henry's constant providing a temperature of 297K, salinity of 35‰, and a pressure of 1 atmosphere.

#### 4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin

**Table 4.4:** Calculated crustal He, estimated He in groundwater prior to degassing and excess Ne and Ar and their elemental ratios

| Sample name                              | ${}^4\text{He}_{\text{crust}} \times 10^{-6}$<br>$\text{cm}^3 \text{ STP/cm}^3$ | ${}^{21}\text{Ne}_{\text{excess}} \times 10^{-12}$<br>$\text{cm}^3 \text{ STP/cm}^3$ | $\frac{{}^4\text{He}_{\text{crust}}}{{}^{21}\text{Ne}_{\text{excess}}} \times 10^6$ | $\frac{{}^{20}\text{Ne}}{{}^{36}\text{Ar}} \times 10^{-2}$ | ${}^{40}\text{Ar}_{\text{excess}} \times 10^{-5}$<br>$\text{cm}^3 \text{ STP/cm}^3$ | $\frac{{}^4\text{He}_{\text{crust}}}{{}^{40}\text{Ar}_{\text{excess}}}$ | ${}^4\text{He}_{\text{water}} \times 10^{-4}$<br>$\text{cm}^3 \text{ STP/cm}^3 \text{ H}_2\text{O}$ | Close system<br>He age (Ma) |
|------------------------------------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|-----------------------------|
| <i>Milk River</i>                        |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 14-8-3-27W3                              | 9.4 ± 0.81                                                                      | 3.9 ± 0.25                                                                           | 241.0 ± 25.88                                                                       | 5.0 ± 0.34                                                 | 5.1 ± 5.11                                                                          | 18.5 ± 1.69                                                             | 41.3 ± 2.74                                                                                         | 270                         |
| <i>2nd White Specks (Belle Plaine)</i>   |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 11-9-17-23W2                             | 1.4 ± 0.12                                                                      |                                                                                      |                                                                                     | 4.2 ± 0.29                                                 | 26.9 ± 26.92                                                                        | 0.5 ± 0.05                                                              | 0.4 ± 0.02                                                                                          | 2                           |
| <i>textbf2nd White Specks (Alderson)</i> |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 8-31-15-14W4                             | 18.6 ± 1.99                                                                     | 71.6 ± 6.73                                                                          | 26.0 ± 3.71                                                                         | 34.6 ± 4.49                                                | 7.4 ± 7.39                                                                          | 25.2 ± 3.56                                                             | 25.4 ± 2.15                                                                                         | 168                         |
| 5-31-15-14W4                             | 19.6 ± 2.10                                                                     | 73.2 ± 6.87                                                                          | 26.8 ± 3.81                                                                         | 34.2 ± 4.43                                                | 7.6 ± 7.56                                                                          | 26.0 ± 3.65                                                             | 26.3 ± 2.22                                                                                         | 173                         |
| 14-31-15-14W4                            | 16.7 ± 1.77                                                                     | 72.7 ± 6.82                                                                          | 23.0 ± 3.25                                                                         | 34.7 ± 4.48                                                | 7.4 ± 7.41                                                                          | 22.5 ± 3.15                                                             | 22.5 ± 1.89                                                                                         | 149                         |
| <i>Viking</i>                            |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 1-7-25-12W3                              | 2.6 ± 0.25                                                                      | 2.7 ± 0.17                                                                           | 94.4 ± 10.89                                                                        | 12.1 ± 0.83                                                | 5.5 ± 5.49                                                                          | 4.7 ± 0.47                                                              | 2.4 ± 0.16                                                                                          | 22                          |
| 7A-1-32-24-12W3                          | 1.0 ± 0.12                                                                      | 23.4 ± 2.21                                                                          | 4.2 ± 0.64                                                                          | 20.8 ± 2.69                                                | 4.6 ± 4.57                                                                          | 2.1 ± 0.32                                                              | 0.5 ± 0.04                                                                                          | 4                           |
| 16-30-23-12W3                            | 3.1 ± 0.29                                                                      | 5.4 ± 0.35                                                                           | 56.7 ± 6.48                                                                         | 12.0 ± 0.82                                                | 8.0 ± 8.01                                                                          | 3.9 ± 0.38                                                              | 2.8 ± 0.19                                                                                          | 27                          |
| <i>Mannville</i>                         |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 5-16-6-13W2(#6) b                        | 198.2 ± 18.79                                                                   | 214.0 ± 13.76                                                                        | 92.6 ± 10.61                                                                        | 11.1 ± 0.76                                                | 208.2 ± 208.21                                                                      | 9.5 ± 0.95                                                              | 10.7 ± 0.74                                                                                         | 101                         |
| 5-16-6-13W2(#8) c                        | 195.7 ± 18.35                                                                   | 228.0 ± 14.66                                                                        | 85.8 ± 9.76                                                                         | 14.5 ± 0.99                                                | 191.6 ± 191.64                                                                      | 10.2 ± 1.01                                                             | 8.0 ± 0.55                                                                                          | 76                          |
| 16-28-5-13W2 d                           | 157.8 ± 13.71                                                                   | 324.0 ± 20.83                                                                        | 48.7 ± 5.26                                                                         | 50.7 ± 3.47                                                | 69.3 ± 69.26                                                                        | 22.8 ± 2.11                                                             | 1.1 ± 0.07                                                                                          | 11                          |
| 5-16-6-13W2(#3) e                        | 157.4 ± 13.93                                                                   | 537.3 ± 34.54                                                                        | 29.3 ± 3.20                                                                         | 28.3 ± 1.94                                                | 176.9 ± 176.87                                                                      | 8.9 ± 0.84                                                              | 3.0 ± 0.20                                                                                          | 29                          |
| 5-16-6-13W2(#6) f                        | 197.2 ± 17.62                                                                   | 160.0 ± 10.29                                                                        | 123.3 ± 13.57                                                                       | 9.6 ± 0.65                                                 | 200.2 ± 200.23                                                                      | 9.8 ± 0.93                                                              | 11.1 ± 0.75                                                                                         | 105                         |
| 5-16-6-13W2(#8) g                        | 276.6 ± 25.10                                                                   | 140.7 ± 9.05                                                                         | 196.6 ± 21.86                                                                       | 9.5 ± 0.65                                                 | 189.9 ± 189.93                                                                      | 14.6 ± 1.40                                                             | 15.7 ± 1.07                                                                                         | 149                         |
| 16-28-5-13W2 h                           | 197.3 ± 17.56                                                                   |                                                                                      |                                                                                     | 33.0 ± 2.26                                                | 222.8 ± 222.84                                                                      | 8.9 ± 0.84                                                              | 1.6 ± 0.11                                                                                          | 15                          |
| <i>Shanavon</i>                          |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 15-10-7-19W3                             | 3.7 ± 0.41                                                                      | 28.7 ± 2.69                                                                          | 12.9 ± 1.88                                                                         | 17.0 ± 2.19                                                | 13.6 ± 13.55                                                                        | 2.7 ± 0.39                                                              | 7.5 ± 0.65                                                                                          | 72                          |
| 4C-15-9-6-19W3                           | 4.2 ± 0.47                                                                      | 29.6 ± 2.78                                                                          | 14.3 ± 2.07                                                                         | 18.4 ± 2.38                                                | 10.9 ± 10.92                                                                        | 3.9 ± 0.56                                                              | 8.7 ± 0.75                                                                                          | 83                          |
| 2B-3-28-6-19W3                           | 5.3 ± 0.59                                                                      | 35.4 ± 3.32                                                                          | 15.1 ± 2.19                                                                         | 20.8 ± 2.69                                                | 13.3 ± 13.26                                                                        | 4.0 ± 0.58                                                              | 8.6 ± 0.74                                                                                          | 82                          |
| <i>Middle</i>                            |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 8-25-6-13W2                              | 0.3 ± 0.03                                                                      | 1.2 ± 0.08                                                                           | 22.7 ± 2.52                                                                         | 27.4 ± 1.88                                                | 0.5 ± 0.49                                                                          | 5.7 ± 0.55                                                              | 7.9 ± 0.54                                                                                          | 189                         |
| 2-25-6-13W2                              | 2.2 ± 0.19                                                                      | 47.4 ± 3.05                                                                          | 4.7 ± 0.50                                                                          | 54.6 ± 3.73                                                | 16.7 ± 16.74                                                                        | 1.3 ± 0.12                                                              | 0.1 ± 0.01                                                                                          | 3                           |
| <i>Frobisher</i>                         |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 2-32-5-13W2                              | 3.0 ± 0.25                                                                      | 39.9 ± 2.89                                                                          | 7.5 ± 0.83                                                                          | 36.1 ± 3.53                                                | 2.4 ± 2.35                                                                          | 12.6 ± 1.39                                                             | 1.8 ± 0.12                                                                                          | 44                          |
| <i>Bakken (Weyburn)</i>                  |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 13-24-5-16W 2                            | 5.9 ± 0.44                                                                      | 8.1 ± 0.52                                                                           | 72.6 ± 7.16                                                                         | 4.7 ± 0.32                                                 | 2.4 ± 2.42                                                                          | 24.4 ± 1.98                                                             | 109.5 ± 6.93                                                                                        | 112                         |
| 1-21-5-16W2                              | 3.8 ± 0.33                                                                      | 17.3 ± 1.49                                                                          | 22.0 ± 2.71                                                                         | 9.1 ± 1.07                                                 | 2.2 ± 2.22                                                                          | 17.2 ± 2.08                                                             | 36.4 ± 2.75                                                                                         | 37                          |
| 16-12-5-16W2                             | 2.9 ± 0.25                                                                      | 13.3 ± 1.15                                                                          | 21.6 ± 2.66                                                                         | 8.1 ± 0.95                                                 | 1.9 ± 1.92                                                                          | 15.0 ± 1.82                                                             | 36.9 ± 2.80                                                                                         | 38                          |
| <i>Bakken (Esteron)</i>                  |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 13-31-1-6W2                              | 10.8 ± 0.96                                                                     | 56.2 ± 4.13                                                                          | 19.2 ± 2.21                                                                         | 41.6 ± 4.13                                                | 4.0 ± 3.98                                                                          | 27.1 ± 3.07                                                             | 13.6 ± 0.92                                                                                         | 14                          |
| 11-31-1-6W2                              | 28.9 ± 2.76                                                                     | 59.7 ± 3.84                                                                          | 48.4 ± 5.57                                                                         | 8.0 ± 0.55                                                 | 2.4 ± 2.43                                                                          | 118.8 ± 11.94                                                           | 20.1 ± 1.39                                                                                         | 20                          |
| 4-6-2-6W2                                | 7.0 ± 0.74                                                                      | 37.1 ± 3.51                                                                          | 18.9 ± 2.68                                                                         | 12.2 ± 1.60                                                | 3.9 ± 3.86                                                                          | 18.1 ± 2.54                                                             | 28.3 ± 2.40                                                                                         | 29                          |
| <i>Deadwood</i>                          |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| 10-3-5-8W3                               | 136.5 ± 18.43                                                                   | 514.9 ± 40.88                                                                        | 26.5 ± 4.15                                                                         | 38.2 ± 4.11                                                | 221.0 ± 221.03                                                                      | 6.2 ± 0.96                                                              | 166.3 ± 17.48                                                                                       | 477                         |
| <i>Air</i>                               |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
| <i>Air saturated water*</i>              |                                                                                 |                                                                                      |                                                                                     |                                                            |                                                                                     |                                                                         |                                                                                                     |                             |
|                                          |                                                                                 |                                                                                      |                                                                                     | 52.3 ± 0.16                                                |                                                                                     |                                                                         |                                                                                                     |                             |
|                                          |                                                                                 |                                                                                      |                                                                                     | 17.4 ± 0.03                                                |                                                                                     |                                                                         |                                                                                                     |                             |

\*Air saturated water is calculated from Henry's constant providing a temperature of 297K, salinity of 35‰, and a pressure of 1 atmosphere.

${}^4\text{He}_{\text{crust}}$  and  ${}^{21}\text{Ne}_{\text{excess}}$  represent crustal radiogenic helium and nucleogenic  ${}^{21}\text{Ne}$  respectively;  ${}^4\text{He}_{\text{water}}$  represents  ${}^4\text{He}$  concentration in the groundwater

### 4.4.2 Noble gases

#### Data selection

Twenty-eight samples were collected in 2012 and 2013 by the University of Toronto and were sent out for commercial He, Ne and Ar analysis. Seventeen samples have their duplicates measured by the University of Oxford in 2016 for He, Ne, Ar, Kr and Xe isotopes. Not all duplicates measured in Oxford reproduce the commercial measurements.  $^{21}\text{Ne}/^{22}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are compared as indications of stronger crustal signals and less air contamination. Most samples measured in Oxford demonstrate similar or higher  $^{21}\text{Ne}/^{22}\text{Ne}$ , suggesting the commercial lab may suffer from air contamination. Sample  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are further compared and thirteen Oxford duplicates are selected to represent the noble gas composition of the sampled wells as they demonstrate either higher or similar ratios compared to the commercial ones (Appendix B.2). The measured geochemical information of the selected samples is reported in Table 4.2, 4.3 and 4.4.

#### Helium

Measured He concentrations range from  $2.8 \times 10^{-5} \text{ cm}^3 \text{ }^4\text{He STP}/\text{cm}^3$  for the Midale to  $2.84 \times 10^{-2} \text{ cm}^3 \text{ }^4\text{He STP}/\text{cm}^3$  for the Mannville. The minimum concentration obtained for the Mannville samples is  $1.61 \times 10^{-2} \text{ cm}^3 \text{ }^4\text{He STP}/\text{cm}^3$ .  $^4\text{He}$  and  $^3\text{He}/^4\text{He}$  are air-corrected (Craig et al., 1978) with appropriate propagated uncertainty (Mackintosh and Ballentine, 2012).

$^4\text{He}/^{20}\text{Ne}$  of most samples ranges from 310 to 119830. One Midale sample is as low as 98.5. High ratios are mostly observed in aquitard units. Since all ratios are much higher compared to the air ratio of 0.318, or air saturated water ratio of 0.277 (for seawater at 297K), and assuming all  $^{20}\text{Ne}$  is air-derived, air-corrections for  $^3\text{He}/^4\text{He}$  are insignificant.  $^3\text{He}/^4\text{He}$  ratios are normalised to the atmospheric ratio ( $^3\text{He}/^4\text{He} = 1.4 \times 10^{-6}$ , and denoted as  $R/R_a$  (Ballentine and Burnard, 2002). Apart from Bakken



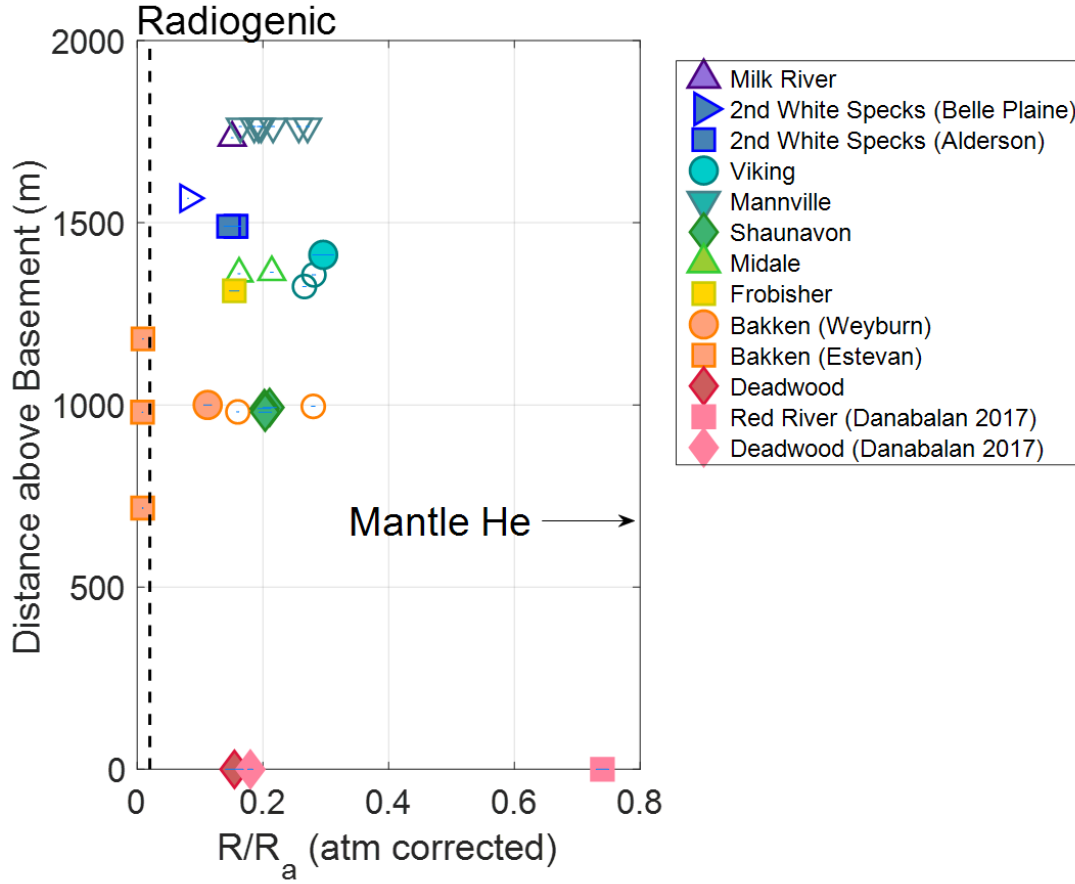
#### *4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin*

Estevan showing values of  $\sim 0.01$ ,  $R/R_a$  values in all other samples vary between 0.08 (Bakken Estevan) and 0.36 (Bakken Weyburn). There is no apparent correlation with the distance from the basement (Figure 4.2). If  $R/R_a$  values for crustal radiogenic production and continental lithospheric mantle are taken as 0.02 and 6 respectively (Ballentine and Burnard, 2002; Dunai and Porcelli, 2002), mantle contribution to the total  $^4\text{He}$  range from unresolvable for Bakken Estevan samples to 4.6% for Bakken Weyburn. High helium concentrations (along with high concentrations of the other noble gases) are observed from Mannville samples. This is likely to be attributed to their collection method (Appendix: B.1) which allows greater extent of noble gas degassing from liquid at lower pressure.

#### **Neon**

$^{20}\text{Ne}$  concentrations observed in the natural gas samples are between  $4.63 \times 10^{-9}$  and  $1.57 \times 10^{-5} \text{ cm}^3 \text{ }^{20}\text{Ne STP/cm}^3$  measured from the Midale and Mannville formations, respectively. The lower end  $^{20}\text{Ne}$  concentrations are within the range reported from other basin systems (e.g. San Juan Basin (Zhou et al., 2005), West Texas Permian Basin (Ballentine et al., 2001)). The maximum  $^{20}\text{Ne}$  concentration is observed from the Mannville formations and approaches the atmospheric concentration of  $1.65 \times 10^{-5} \text{ cm}^3 \text{ }^{20}\text{Ne STP/cm}^3$ .

Nucleogenic and radiogenic contributions to  $^{20}\text{Ne}$  in crustal systems are insignificant (Ballentine and Burnard, 2002),  $^{20}\text{Ne}$  can, therefore, be assumed to be atmospherically sourced. In most cases, it is introduced to the subsurface environment dissolved in groundwater at recharge. It can also be an injected artefact found in reservoirs associated with enhanced oil recovery (Barry et al., 2016), or occasionally represents air contamination due to inappropriate sample collection and handling procedures. There is no clear trend between  $^{20}\text{Ne}$  concentrations with depth, but samples collected from aquitard layers, such as the Milk River and Bakken Estevan Formations, have lower  $^{20}\text{Ne}$  concentrations when compared with those from aquifers, such as Mannville, Midale and Frobisher.



**Figure 4.2:**  $(R/R_a)_c$ , air normalised  $^3\text{He}/^4\text{He}$  ratios (air-corrected), are plotted against distance above the basement. Error bars smaller than the plotted symbols. The Bakken Estevan samples have ratios of 0.01.  $(R/R_a)_c$  values for the other samples are between 0.08 and 0.36. No apparent correlation with the distance from the basement can be observed. The two samples with pink symbols are those reported by Danabalan (2017). Solid samples represent samples measured by the University of Oxford, and hollow symbols are samples measured by the commercial institute.

In a plot of  $^{20}\text{Ne}/^{22}\text{Ne}$  vs  $^{21}\text{Ne}/^{22}\text{Ne}$ , samples lie both below and above the atmospheric value, on a trend consistent with mass fractionation (Figure 4.3). Samples collected from Bakken and Deadwood, the two deepest formations, and Second White Specks (Alderson), the shallower Colorado Shale group, show resolvable nucleogenic  $^{21}\text{Ne}$  ( $^{21}\text{Ne}^*$ ). Neglecting the effect of mass fractionation,  $^{21}\text{Ne}^*$  can be calculated with equations summarised by Ballentine et al. (2002). The proportion of  $^{21}\text{Ne}^*$ , reflecting the crustal and mantle Ne input, varies from 0.7% (Viking, Mannville and Midale) to 59.8% (Deadwood).  $^4\text{He}/^{21}\text{Ne}^*$  ranges from  $4.2 \times 10^6$  to  $241 \times 10^6$ , showing different

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degrees of fractionation relative to an average crustal value of  $\sim 17.1 \times 10^6$  (Ballentine and Burnard, 2002).

### **Argon**

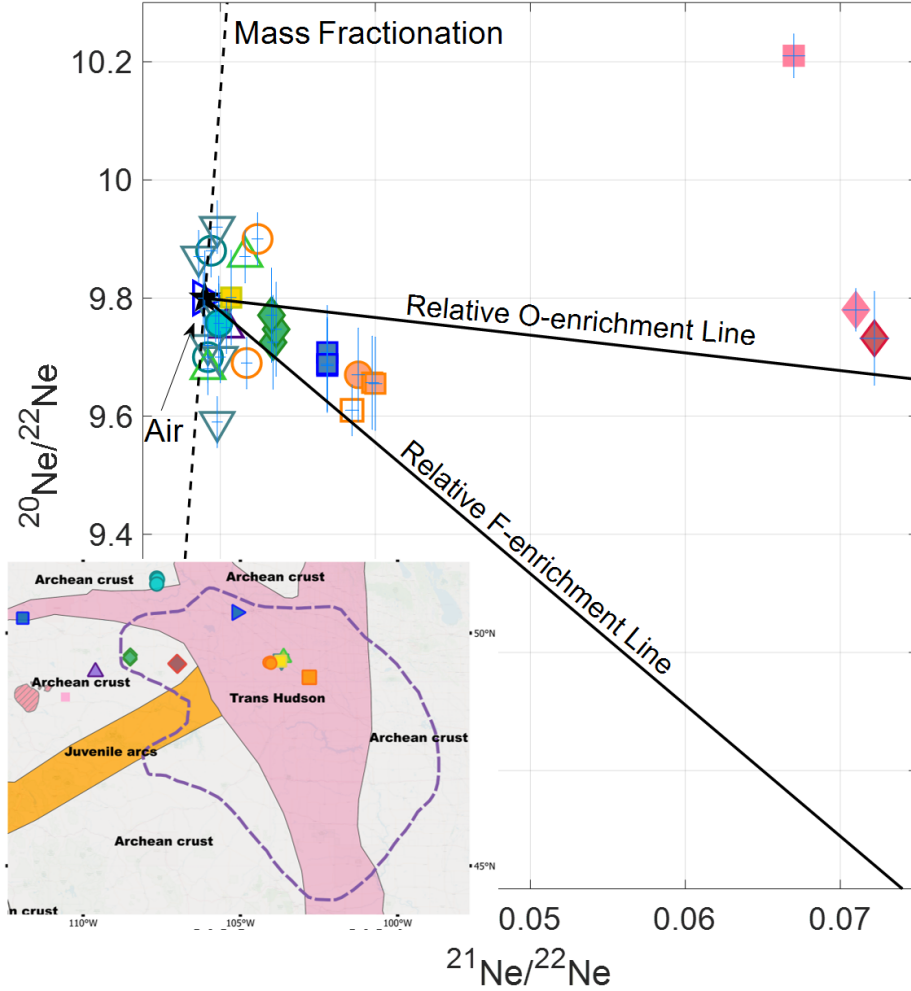
$^{40}\text{Ar}/^{36}\text{Ar}$  ratios range from 304 (Bakken Estevan) to 7580 (Deadwood). High  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are mostly observed in aquitards and share a similar pattern with  $^4\text{He}/^{20}\text{Ne}$ . Shaunavon aquifer samples also exhibit high  $^{40}\text{Ar}/^{36}\text{Ar}$ .  $^{38}\text{Ar}/^{36}\text{Ar}$  ratios show small deviations both above and below the atmospheric value of 0.188, ranging from  $0.182 \pm 0.0013$  to  $0.198 \pm 0.0020$ . It is unlikely that these are due to nucleogenic contributions to either isotope (Ballentine and Burnard, 2002) and may reflect a small amount of mass fractionation. Such mass-dependent fractionation is also observed in the Ne isotopic system (Figure 4.3).

Excess  $^{40}\text{Ar}$  relative to the atmosphere  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio,  $^{40}\text{Ar}^*$ , varies from  $0.5 \times 10^{-5}$  to  $513.5 \times 10^{-5} \text{ cm}^3 \text{ }^{40}\text{Ar}^* \text{ STP/cm}^3$ , suggesting the sources of  $^{40}\text{Ar}$  vary from almost entirely atmospheric (3% excess  $^{40}\text{Ar}$ ) to entirely crustal (96.1% excess  $^{40}\text{Ar}$ ).  $^4\text{He}_{\text{crust}}/^{40}\text{Ar}^*$  ratios range from 0.5 to 118.8 and similar to  $^4\text{He}/^{21}\text{Ne}^*$  fall both above (66% of samples) and below the average crustal value of 5.7 (Ballentine and Burnard, 2002).

### **Krypton and Xenon**

Where determined, concentrations of  $^{84}\text{Kr}$  range from  $1.64 \times 10^{-9}$  to  $1.17 \times 10^{-7} \text{ cm}^3 \text{ }^{84}\text{Kr STP/cm}^3$  (both from Midale) and  $^{132}\text{Xe}$  range from  $3.98 \times 10^{-10}$  (Cambrian) to  $6.35 \times 10^{-9} \text{ cm}^3 \text{ }^{132}\text{Xe STP/cm}^3$  (Midale).

Apart from the Deadwood sample, the others all have isotopic Kr and Xe ratios indistinguishable from that of air.  $^{86}\text{Kr}/^{84}\text{Kr}$  ratios range from  $0.3044 \pm 0.00077$  (Midale) to  $0.3095 \pm 0.00071$  (Bakken - Estevan) and  $^{132}\text{Xe}/^{130}\text{Xe}$  ratios range from



**Figure 4.3:**  $^{20}\text{Ne}/^{22}\text{Ne}$  vs  $^{21}\text{Ne}/^{22}\text{Ne}$  for all samples analysed. The ‘Relative F-enrichment Line’, which is also referred to as ‘the typical radiogenic crustal endmember’ (Holland et al., 2013), has  $^{21}\text{Ne}/^{22}\text{Ne}$  production of 0.47 (Holland et al., 2013), which corresponds to an O/F ratio of 113 for the rock matrix (Ballentine and Burnard, 2002). Such Ne ratios are typically observed from sedimentary basin systems (Kennedy et al., 1990). The ‘Relative O-enrichment Line’ has a  $^{21}\text{Ne}/^{22}\text{Ne}$  intercept of  $\sim 3.3$  when  $^{20}\text{Ne}/^{22}\text{Ne}$  is zero (Holland et al., 2013), corresponding to an apparent crustal O/F ratio of 752 (Ballentine and Burnard, 2002). Literature samples observed following this mixing line are from Precambrian basement (Lippmann-Pipke et al., 2011; Kendrick et al., 2011). Basinal Precambrian basement map modified from Whitmeyer and Karlstrom (2007) is shown on the bottom left corner superimposed by the locations of sampling wells. The Deadwood sample which sits on the Archaean basement province demonstrates an O-enriched Ne signature, representing an influx from the Precambrian basement to the overlying sedimentary units. The Eocene Kevin-Sunburst Dome and Porphyry are also plotted.

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6.472±0.1443 (2nd White Specks Alderson) to 6.734±0.423 (Deadwood), not significantly fractionated from the atmospheric ratios of 0.3052 and 6.607, respectively. The Deadwood samples, however, although demonstrating an atmospheric like  $^{86}\text{Kr}/^{84}\text{Kr}$  value,  $^{132}\text{Xe}/^{130}\text{Xe}$  ratio is noticeably higher, suggesting an input of fissionogenic Xe.

### 4.5 DISCUSSION

#### 4.5.1 $^4\text{He}$ Concentration in Groundwater Estimated from the $^4\text{He}/^{20}\text{Ne}$ ratio

To analyse noble gas transport in the groundwater, the investigation is focused on  $^4\text{He}$ .  $^4\text{He}$  is predominantly sourced from radiogenic production. It has very low dissolved air background levels in groundwater, making the crustal contribution readily resolvable. It also has a high diffusivity compared with other noble gases. Here  $^4\text{He}$  and  $^{20}\text{Ne}$  concentrations measured in the gas phase are used to determine the  $^4\text{He}$  concentrations dissolved in the groundwater associated with the produced gas.

Due to the low concentration of  $^4\text{He}$  and  $^{20}\text{Ne}$ , it is reasonable to assume that both isotopes were originally dissolved in the groundwater and that the  $^{20}\text{Ne}$  is entirely air-derived from when the groundwater last equilibrated with the atmosphere. Since He and Ne have similar Henry's constants between in water, there is negligible solubility induced fractionation upon gas-phase formation. The groundwater supplying the observed amount of noble gases has its original  $^4\text{He}$  concentration estimated as

$$^4He_{\text{groundwater}} = ^{20}Ne_{\text{asw}} \times \left( \frac{^4He}{^{20}Ne} \right)_g, \quad (4.1)$$

where  $^4He_{\text{groundwater}}$  is the concentration of  $^4\text{He}$  in groundwater before degassing,  $^{20}Ne_{\text{asw}}$  is the concentration in air saturated seawater, and  $\left( \frac{^4He}{^{20}Ne} \right)_g$  is the ratio measured from gas samples.

During the Palaeozoic, North America was located at tropical latitudes (Der Voo, 1988). The basin is also periodically connected to the proto-Pacific ocean to the west from Cambrian to Jurassic (Bachu and Hitchon, 1996). The porewater is

#### 4.5. DISCUSSION

assumed to be originated from seawater (salinity 35‰) at 298K at one-atmosphere pressure. The  $^{20}\text{Ne}$  concentration in this water can be calculated from Henry's law as  $1.33 \times 10^{-7} \text{ cm}^3 \text{ }^{20}\text{Ne STP}/\text{cm}^3 \text{ H}_2\text{O}$ . Recharge is assumed to be unchanged throughout geological time. Notably, later uplift of Precambrian basement may allow fresh water instead of seawater to recharge through subaerial outcrops occurring in Cretaceous and younger stratigraphic units. A lower salinity air saturated water is more enriched with atmospheric noble gases and leads to higher  $^4\text{He}$  estimations in the groundwater. Therefore, the estimated  $^4\text{He}$  concentration in water represent a minimum for Cretaceous and younger stratigraphic units.

#### 4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin

**Table 4.5:** Parameters of hydrogeological units estimated. Radioelement concentrations are estimated from well log provided from the industry. Porosity estimations are made based on literature review and lithology (Appendix B.3).

| Hydrogeological Units     | U (ppm) | Th (ppm) | age (Myr) | Total Porosity (%) | Effective Porosity (%) |
|---------------------------|---------|----------|-----------|--------------------|------------------------|
| Post Belly river aquitard | 12      | 12       | 72        | 0.6                | 0.3                    |
| Belly river aquifer       | 5.5     | 11       | 86        | 0.45               | 0.45                   |
| Colorado Shale aquitard   | 12      | 12       | 100       | 0.4                | 0.1                    |
| Viking aquifer            | 5.5     | 11       | 106       | 0.33               | 0.33                   |
| Mannville aquifer         | 5.5     | 11       | 145       | 0.33               | 0.33                   |
| Rierdon aquitard          | 12      | 12       | 166       | 0.3                | 0.1                    |
| Shaunavon aquifer         | 3.5     | 5        | 168       | 0.3                | 0.3                    |
| Watrous aquitard          | 12      | 12       | 252       | 0.3                | 0.1                    |
| Mississippian aquifer     | 1       | 1        | 360       | 0.1                | 0.1                    |
| Bakken Formation          | 12      | 12       | 370       | 0.05               | 0.05                   |
| Devonian Complex          | 1       | 1        | 420       | 0.1                | 0.1                    |
| Ordo-Silurian Aquifer     | 1       | 1        | 480       | 0.1                | 0.1                    |
| Deadwood Upper aquitard   | 5.5     | 11       | 495       | 0.05               | 0.05                   |
| Deadwood Basal aquifer    | 5.5     | 11       | 500       | 0.08               | 0.08                   |

**Table 4.6:** Salinity estimation of the groundwater where the samples were collected, extracted from salinity maps constructed by Melnik (2012) and Bachu and Hitchon (1996).

| Formation                          | Salinity (TDS mg/cm <sup>3</sup> ) |
|------------------------------------|------------------------------------|
| Milk River                         | 25~50                              |
| Second White Specks (Belle Plaine) | 10~25                              |
| 2nd White Specks (Alderson)        | 10~25                              |
| Viking                             | 10~25                              |
| Mannville                          | 25~50                              |
| Shaunavon                          | 25~50                              |
| Midale                             | 50~100                             |
| Frobisher                          | 100~200                            |
| Bakken (Weyburn)                   | 200~300                            |
| Bakken (Estevan)                   | ~200                               |
| Deadwood                           | ~50                                |

### 4.5.2 Minor Air Entrapment

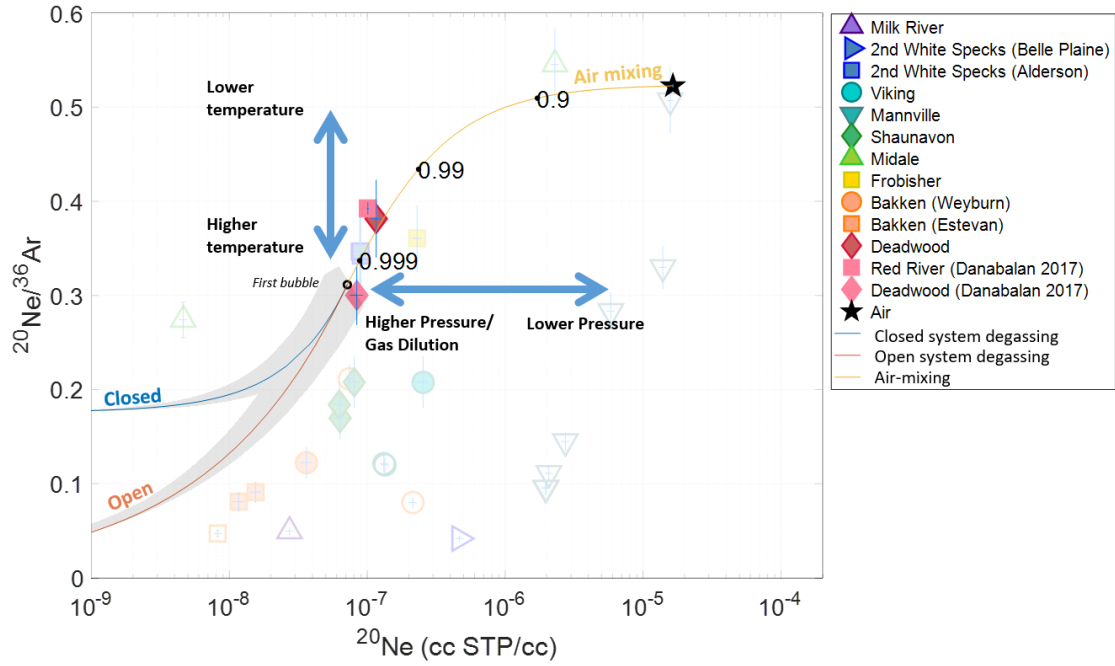
Atmospheric  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  can be used to examine the hypothesised groundwater degassing relation between  $^4\text{He}$  and  $^{20}\text{Ne}$  (Figure 4.4), in which the  $^{20}\text{Ne}$  is originally assumed to be only sourced from air saturated groundwater. The concentration of  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  in the gas phase can be mathematically modelled for a closed system in which gas and liquids with fixed volumes reach equilibration, and for an open system that has instant gas loss after gas-phase generation described as a Rayleigh fractionation process (Barry et al., 2016). Variations in degassing conditions result in different degassing models regarding their noble gas concentrations and elemental ratios; for example, a lower temperature or lower salinity increases elemental fractionation of the first gas-phase formed, and a higher reservoir pressure corresponds to more significant expansion at the ground surface and thus affects the concentration expressed in standard temperature and pressure (STP). The models also depend on the original composition of the groundwater, which in turn correlates with the recharge condition.

Figure 4.4 is an example of the predicted  $^{20}\text{Ne}/^{36}\text{Ar}$  and  $^{20}\text{Ne}$  concentrations in the gas phase during degassing processes for the deep Deadwood samples. This figure highlights the Deadwood sample (red diamond), the Red River (pink square) and the Deadwood (pink diamond) samples reported by Danabalan (2017). The degassing models are constructed based on reservoir conditions of the Deadwood Formation. Both Deadwood samples deviate from the predicted degassing trajectory. The samples highlighted are consistent with an air component mixing with the composition expected for a subsurface gas formation.

Air mixing signatures can also be observed in a plot of  $^{21}\text{Ne}^*/^{40}\text{Ar}^*$  plotted against  $^{20}\text{Ne}/^{36}\text{Ar}$  (Figure 4.5), where crustal and atmospheric Ne and Ar are expected to fractionate on a linear trend after mixing. The shaded area represents the range of ratios that resulted from different recharging conditions (from 273K freshwater to 298K seawater). Assuming the groundwater was initially recharged as 298K seawater, elemental fractionation of the crustal and atmospheric noble gases should sit on



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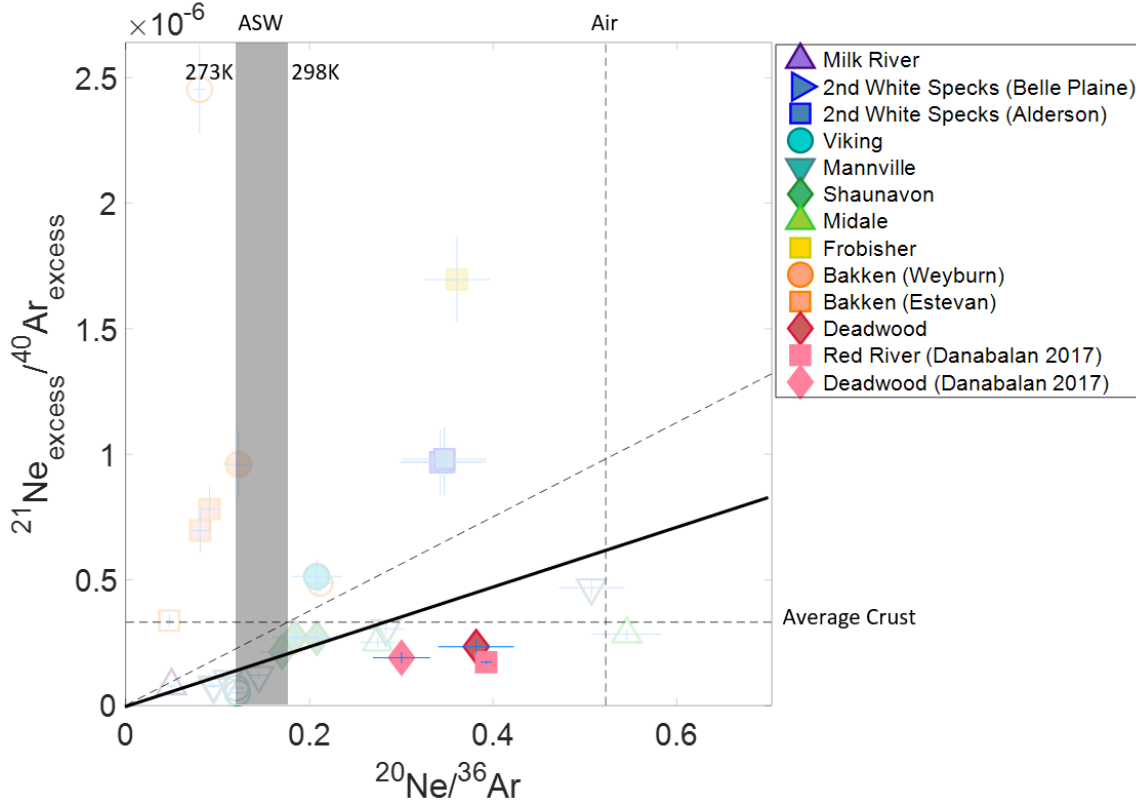


**Figure 4.4:** Modelled  $^{20}\text{Ne}$  and  $^{20}\text{Ne}/^{36}\text{Ar}$  for the closed (yellow) and open (green) degassing system modelled with estimated temperature, salinity and pressure of the Deadwood water. Deadwood samples are highlighted in the plot. Changes in temperature and pressure, as well as the addition of diluting gas, can shift the modelled degassing curves, see arrows. The air mixing line (purple) demonstrate the resulted concentration and elemental ratio of a mixture between gas formed from water exsolving and addition of air. The proportions of exsolved gas in the mixtures is tick marked along the mixing line. The shaded area represents the variability of models considering the temperature change of  $\pm 15\text{K}$ , pressure change of  $\pm 5$  bar and variation of salinity between 0 to 100.

the plotted slope. The elevated  $^{20}\text{Ne}/^{36}\text{Ar}$  ratios compared to the co-fractionation line can also be explained by air mixing. The Deadwood well is an abandoned well, and air mixing is not unexpected. An air mixing signature is also observed for the Red River sample (Ordovician). Irrespective of the source, the air component can be resolved and removed to estimate the initial concentrations in the reservoir (Appendix B.4). The air correction (which is the same for a closed or an open system) does not change the observed He concentration in the gas phase substantially, but the high Ne content indicates a significant underestimation of  $^4\text{He}/^{20}\text{Ne}$  before correction. The corrected He concentration for Deadwood sample in groundwater is increased by about 2 times for a closed system.

Since anthropogenic water flooding distorts noble gas signatures in the groundwater,

#### 4.5. DISCUSSION



**Figure 4.5:**  $^{21}\text{Ne}^*/^{40}\text{Ar}^*$  plotted against  $^{20}\text{Ne}/^{36}\text{Ar}$  with Deadwood and Red River samples highlighted. The horizontal dashed lines represent  $^{21}\text{Ne}^*/^{40}\text{Ar}^*$  of average crustal production (Ballentine and Burnard, 2002). The shaded area represents the range of  $^{20}\text{Ne}/^{36}\text{Ar}$  values for air saturated water recharged by 273K freshwater to 298K seawater. The vertical dashed line represents the air  $^{20}\text{Ne}/^{36}\text{Ar}$  ratio. The dashed slope represents the expected fractionation of groundwater that was recharged by 298K seawater and possesses an average crustal  $^{21}\text{Ne}^*/^{40}\text{Ar}^*$  ratio. The deviations of the samples from the slope suggest they could be the resulted of air-addition or significant fractionation with little gas-water volume ratio.

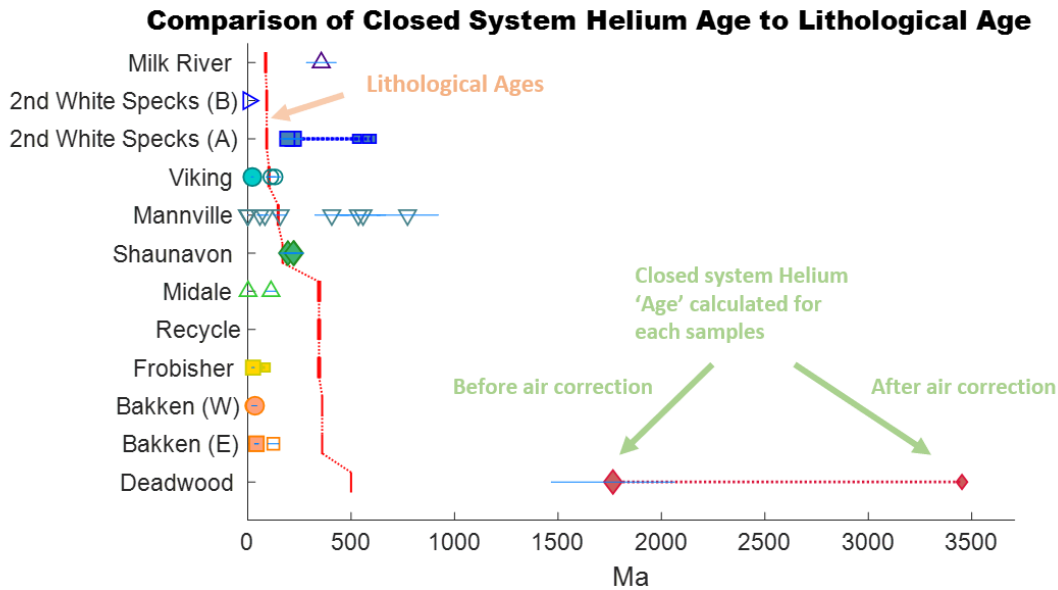
only formations/wells that have not been affected by water flooding are analysed (Appendix B.5). 2nd White Specks (Alderson) samples are corrected with a closed system degassing model. The Frobisher sample is corrected for an open system representing an upper limit. Many other samples sit below the degassing lines, possibly representing a pressure drop relative to the pristine system modelled value caused by drilling and production. Absence of pressure information makes it hard to construct the appropriate degassing lines and impossible to identify and correct for air component. Therefore, those samples represent the lower limit of the groundwater  $^4\text{He}$  concentration estimation.

#### *4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin*

##### **4.5.3 He Residence Age – A Closed System Reference Model**

The estimated  $^4\text{He}$  concentration in the groundwater can be used to quantify He residence time in each stratigraphic unit. The ‘closed system reference’ assumes that all He within the groundwater is produced by uranium and thorium decay in situ within the lithological units and is released completely from the minerals into the water occupying the porosity due to the small sediment grain size in sedimentary units (Ballentine and Burnard, 2002; Tolstikhin et al., 2011). The closed system ages required for the lithological units to produce the estimated He in the groundwater can be calculated following equations summarised by Ballentine and Burnard (2002). The lithological unit porosities (Appendix B.3), as well as the U and Th concentrations (from U and Th logs), are estimated for each stratigraphic unit and presented in Table 4.5. A comparison of the closed system reference He age against the actual lithological ages can be compared to test the degree to which a system is not closed (Figure 4.6): an older He age indicates an external supply of He and a younger He age suggests He loss from the sedimentary unit. For such non-closed systems, noble gas transport between sedimentary formations occurred.

While some samples demonstrate closed-system helium ages comparable to the lithological ages, the majority of samples demonstrate discrepancies. The comparison suggests that the closed system reference model is not able to explain the observed He profile in most formations. Younger and shallower formations, Milk River and Second White Specks (Alderson), both show closed system He ages older than the lithological ages, demonstrating that an external source of He must have been transported into these units. Coal beds have been reported in the Milk River formation. Researches reported U and Th concentrations range from 0.07-7.5 ppm and 0.3-11.0 ppm in Lower Cretaceous coals in two different sites in Canada (Van Der Flier and Fyfe, 1985). Another study examined the Jurassic-Cretaceous coal in British Columbia and found U and Th concentrations less than 4 ppm and 10 ppm respectively (Goodarzi and Fuel, 1987). These values are comparable to those estimated for Cretaceous shale, the model therefore already considers the formation of a far greater volume than any



**Figure 4.6:** The closed system He ages compared with the lithological age. Each sample point represents the amount of time required for the lithological unit to produce the observed  $^4\text{He}_{\text{groundwater}}$  radiogenically from U and Th concentrations of the rock matrix alone, i.e. in a closed system. The calculation assumes no external He sources or sinks and a complete release of  $^4\text{He}$  from sediment grains. The error bars are constructed assuming  $\pm 20\%$  uncertainty associated with the U and Th concentrations. The lithological ages are represented by the red boxes. If the sedimentary units are closed systems, the closed system He ages are expected to match the lithological ones. Multiple units demonstrate He ages younger than the lithological ones, suggesting a substantial amount of He loss. An older He age is observed for the Deadwood sample, suggesting an external He source, likely to be the basement. Older He ages are also observed for some shallow samples, indicating the presence of external He supply and cross-formational He migration.

individual coal with equal or higher U and Th concentrations. Other formations, including some deeper and older ones, have younger He age estimates than their lithological ages, requiring various degrees of He loss, either vertically or horizontally.

This indicates that the geological units investigated here should be considered as open systems with respect to noble gases and that the migration of He must be considered. It is important to note that the Deadwood sample, from the basement contact unit, has a He age significantly older than the lithological age, which means the  $^4\text{He}$  preserved in this formation also requires a considerable amount of external He input. Flux from the Precambrian basement is most likely the source of excess He supplying this basal unit. Basement He input and cross-formational He migration need to be considered and are discussed in the following sections.

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The calculation is sensitive to porosity and it is well acknowledged that porosity varies, especially if obtained from individual rock samples. However, the gas samples collected are exsolved from large volumes of water instead of a single pore, and therefore represent water mixture from pores of various sizes. As such, the average reservoir porosities are good estimates of the reservoir conditions.

The estimate of the closed system He age also depends on the U and Th concentrations in each lithological unit. The U and Th concentrations are estimated from U and Th logs of well 1-15-33-26W2 (Jim M. Hendry, personal communication) where uncertainties are hard to be determined due to the limited log data available. An arbitrary 20% U and Th error is used to demonstrate the significance of radioelement concentration accuracy. Noticeably, the U and Th estimations from well-logs are considerably higher than those reported by Parker and Fleischer (1967) for similar lithologies. If applying Parker and Fleischer (1967)'s U and Th concentrations, older closed system He ages will be obtained (Appendix B.6), and the evidence for an open system and basement flux is further strengthened.

##### **4.5.4 Evidence for Basement Noble Gas Flux from Ne and Ar Isotopes**

The contribution of noble gases from the basement is also evident from Ne and Ar isotopes. Subsurface production of  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$  are mainly through nucleogenic reactions with O and F, respectively (Yatsevich and Honda, 1997). As a result,  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  vary as a function of O/F ratios within effective distance from alpha-emitters, e.g. U and Th. Ne isotopic ratios observed in most sedimentary basin systems usually correspond to O/F ratio of 113 (Kennedy et al., 1990; Ballentine and Burnard, 2002; David J Byrne et al., 2018), lower than the average crustal ratio of 752 (Ballentine and Burnard, 2002). This is likely to be caused by inhomogeneous distribution of O and F with a concentrated F in minerals containing the radioelements (Ballentine and Burnard, 2002). Ne isotopic ratios calculated with the average crustal O/F ratio, possibly related to a potential homogeneous elemental distribution, are observed in fluid inclusions and fracture fluids in Archean basement (Lippmann-Pipke

## 4.5. DISCUSSION

et al., 2011; Holland et al., 2013; Warr et al., 2018). The Deadwood formation, which is in direct contact with the Archean basement, have its sample lie on the trend of nucleogenic Ne production typical of Archean rocks (Figure 4.3). Such Ne ratios cannot be produced by the Cambrian or overlying sedimentary units but require a flux from the crystalline basement (Figure 4.3).

The  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio observed in the Deadwood sample,  $>7000$ , also supports the presence of noble gas flux from the basement. The value is abnormally high for sedimentary basins, but not for the crystalline basement. Groundwater with a residence age of 1.0-2.2 Ga collected from Kidd Creek mines, 2.4 and 2.9 km deep in the Canadian Shield, shows average  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of 15100 and 102000 respectively (Warr et al., 2018). Such old water could also be preserved in the basement beneath the Williston Basin, supplying a gas flux enriched in radiogenic  $^{40}\text{Ar}$ .  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios up to more than 6000 have also been reported from sedimentary units in the Alberta Basin Hiyagon and Kennedy, 1992. In the Alberta Basin, an increasing trend of  $^{40}\text{Ar}/^{36}\text{Ar}$  is observed approaching the Precambrian basement, which is also considered to be evidence for a basement supply. Higher  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are observed in Shaunavon aquifer than seen in most other lithologies except the Deadwood samples in contact with the basement. The  $^4\text{He}/^{40}\text{Ar}^*$  within these samples is nevertheless within the range of the other lithologies. A simple explanation for this observation through either diffusion dominated control (reference model), lateral input of high  $^{40}\text{Ar}/^{36}\text{Ar}$  fluids, or an aquifer that may have been affected by phase separation, reducing its atmosphere-derived  $^{36}\text{Ar}$  dissolved content and being locally susceptible to small amounts of  $^{40}\text{Ar}^*$  input generating high  $^{40}\text{Ar}/^{36}\text{Ar}$ .

### 4.5.5 The Requirement for Basement Noble Gas Evident from $^3\text{He}$

The observed  $(\text{R}/\text{R}_a)_c$  values ranging from 0.08 and 0.36 (apart from Bakken Estevan) represents an additional source of  $^3\text{He}$  other than radiogenic production ( $\sim 0.02 \text{ R}_a$ ). High  $(\text{R}/\text{R}_a)_c$  is not unique to the Williston Basin but also observed in other basins. Resolvable amount of mantle He is observed from groundwater samples from

#### *4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin*

the Rhine Graben, the Rhenish Massif and the Black Forest Massif, with the high mantle component observed coincides with the distribution of Cenozoic volcanoes (Griesshaber et al., 1992). It has also been observed in the Pannonian basin which is associated with extension and volcanism in middle Miocene (Oxburgh and O’Nions, 1987; Martel et al., 1990; Ballentine et al., 1991). Oxburgh and O’Nions (1987) concluded that, apart from young volcanoes, the different degrees of excess/primordial  $^3\text{He}$  observed in sedimentary basin systems could also be attributed to active extension and normal faulting. The observation of excess  $^3\text{He}$  in a much wider area than the surface volcanism also proposed to be sourced by a small degree of mantle melt in the lower crust (Oxburgh and O’Nions, 1987; Martel et al., 1989).  $^3\text{He}/^4\text{He}$  ratios between 0.3 and 0.4  $R_a$  are observed in the eastern Morongo Basin. Various amount of mantle He is also resolved from samples collected from hot springs and groundwater in Southwest U.S (Newell et al., 2005 and reference therein). Newell et al. (2005) suggested that samples with high mantle component are likely collected from the youngest and most active tectonic regions with lowest mantle p-velocity.  $^3\text{He}/^4\text{He}$  values approximately 0.2  $R_a$  are also observed extensively in North America along with large faulting systems (Hunt et al., 2016). Mantle He could flux into the near-surface environment through fractures and rifting. The basement of the Williston Basin is far from simple and has undulating topography from faults and erosion (Wright et al., 1994). The faults experienced reactivation in response to regional stress fields. Early Eocene extension after orogeny may open basement fractures and reactivated existing faults, providing conduits for fluids with mantle  $^3\text{He}$ .

The alternative source for magmatic input is through igneous intrusions. Sedimentary units are exposed to igneous intrusions in the Williston Basin around the Kevin-Sunburst Dome (Foley, 1972; Wright et al., 1994). The intrusion is thought to be caused by regional extension during Early and Middle Eocene, which terminates the growth of the foreland thrust and fold belt (Price, 1994; Wright et al., 1994). Dating of dykes in the Sweetgrass Hills and Pinhorn Butte confirms early Eocene magmatic events in the area (M. Y. Williams and Dyer, 1930; Marvin et al., 1980; Wright et al., 1994). These magmatic intrusions could be potential sources of the observed  $^3\text{He}$ .

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Horizontal and vertical diffusion and basin-scale groundwater flow could transport the excess  $^3\text{He}$  to different geological formations laterally in the basin (D. Byrne et al., 2019). High  $^3\text{He}/^4\text{He}$  ratio is also observed from a Red River sample collected closer to the Kevin Sunburst Dome (Danabalan, 2017). However, the estimated volume of the magma body required to supply the excess  $^3\text{He}$  is far more extensive than the actual size of the volcanic domes (Appendix B.7) suggesting that a single igneous intrusion is insufficient to supply the observed regional  $^3\text{He}$  excess. This is further supported by the lack of apparent  $^3\text{He}/^4\text{He}$  gradient around the dome area observed from the  $^3\text{He}/^4\text{He}$  maps generated for the Alberta Basin and the Williston Basin (Figure 4.7).

Other sources of  $^3\text{He}$ , including cosmic rays, interplanetary dust particles (IDP) and localised Li enrichment, are considered, but can be excluded as significant sources of regional  $^3\text{He}$  on mass balance grounds (Appendix B.7). Similar observations have been made in extensional systems around the world and ascribed to a regional deep emplacement of small melt fractions (Ballentine, 1997), from which the near-surface intrusions represent only a small mass component. A regional basement flux enriched in crustal noble gases with excess  $^3\text{He}$  is considered in our models here.

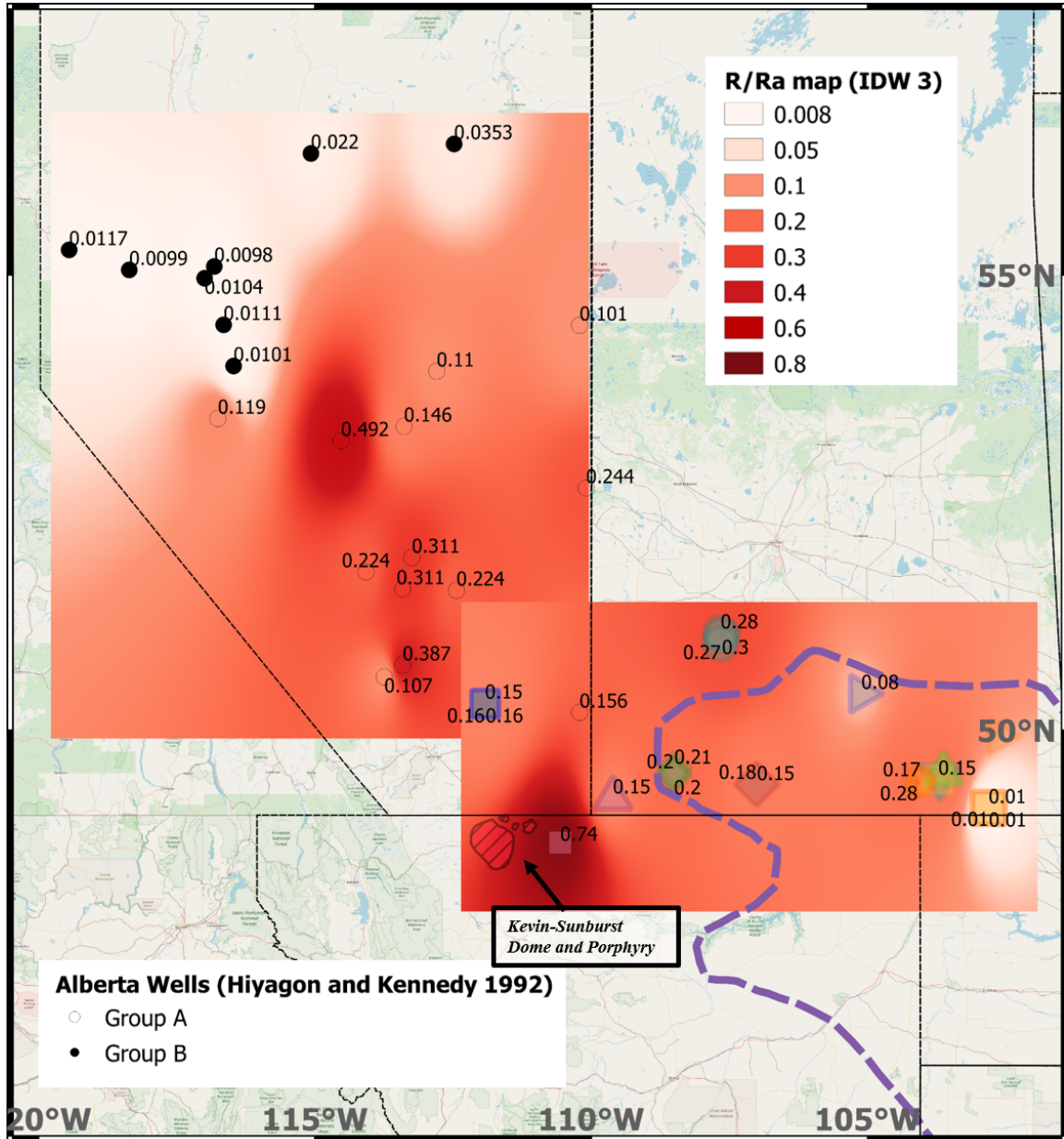
#### 4.6 HELIUM SIMULATION

The analysis above suggests that the Williston Basin exhibits internal cross-formational transport of noble gases and external input from the basement. The two principal transport mechanisms of solvents in groundwater are advection and diffusion. Advection is driven by the pressure gradient and gravity. Cross formation advection mostly takes place along veins and fractures. Diffusion is a much slower process and the dominant transport mechanism for dissolved substances in static water bodies (Hendry et al., 2013; Hendry et al., 2015).

To investigate the significance of cross formational gas migration, a simplified 1-D model is constructed from first principles. Helium is modelled due to its high diffusivity (Jähne et al., 1987). Each stratigraphic unit is constructed in turn and the dissolved



4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin



**Figure 4.7:**  $R/R_a$  (air normalised  $^3\text{He}/^4\text{He}$ ) maps constructed for the Alberta Basin and the Williston Basin. Data for the Alberta Basin are reported by Hiyagon and Kennedy (1992). The Red River sample close to the Dome indeed shows the highest observed  $R/R_a$  value. However, no obvious gradient can be seen radiating from the dome area, suggesting the dome is not likely to be a point source of the excess  $^3\text{He}$ .

#### 4.6. HELIUM SIMULATION

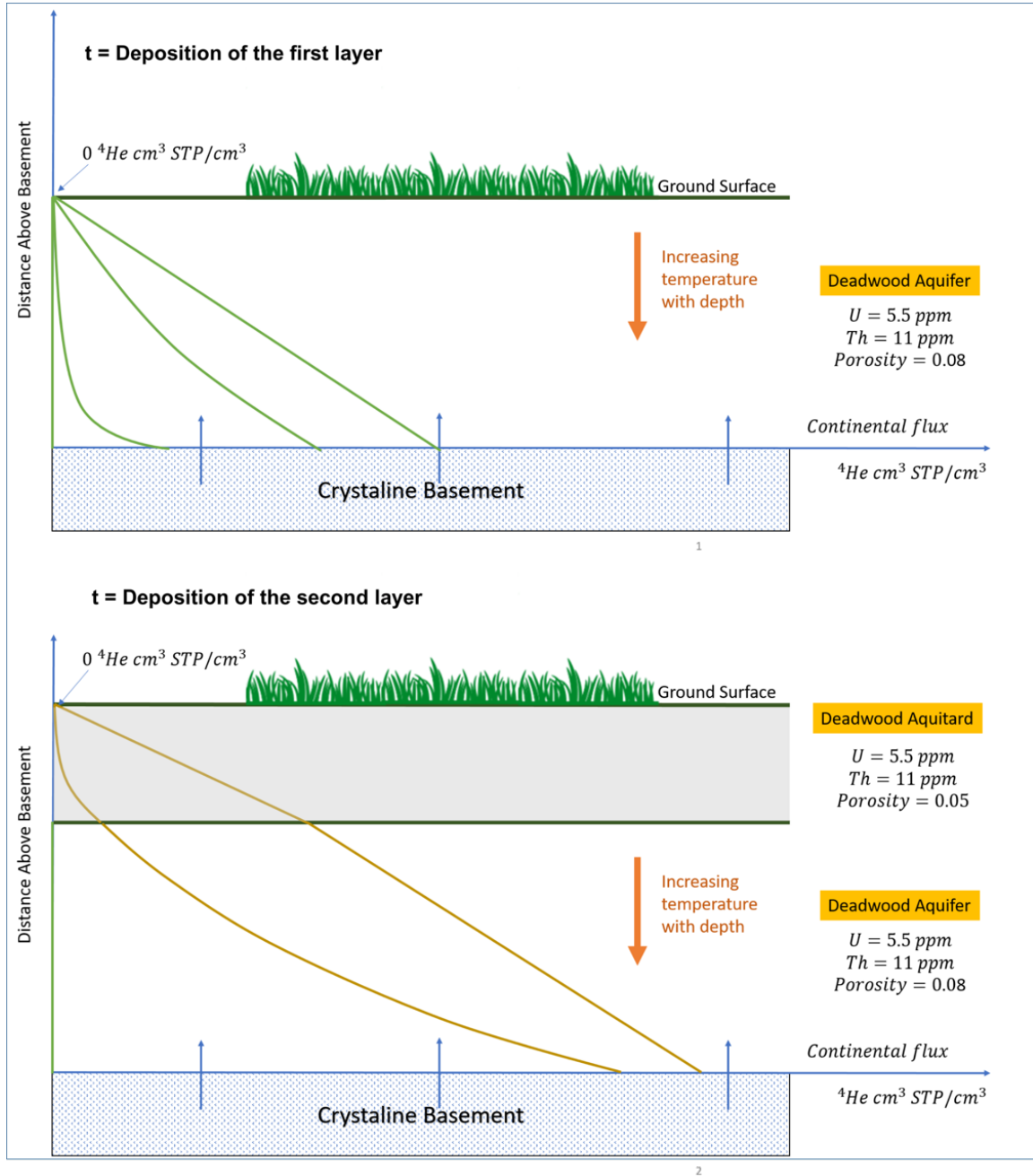
He concentration in the pore space is evolved as a function of depth within each unit through time. Sediments are assumed to be deposited as an entire unit at the start of the formation age. Two sources of crustal He are accounted; a  $^4\text{He}$  flux from the Precambrian basement into the base of the lowest lithology and the in situ radiogenic production from U and Th concentrations within all lithological units following the closed system reference model. The flux from the Precambrian basement in the model is assumed to be constant. In the first instance, the deepest stratigraphic horizon is formed, and it initially contains no dissolved He within its pore space. In situ  $^4\text{He}$  production and a basal  $^4\text{He}$  flux start at the time of its deposition and the He distribution within the unit pore space evolves through diffusion and/or advection loss at its upper surface (Figure 4.8a) following the transport equations detailed below. The next deepest lithology is then instantaneously formed over the first, again containing no initial  $^4\text{He}$ . The He concentration profile in the newest unit develops according to the  $^4\text{He}$  flux determined by the He concentration gradient now established in the first/deepest lithological unit, and its own in situ  $^4\text{He}$  production. Subsequent units are formed in turn and their He profile calculated as a combination of the He flux determined by the previous He accumulation and loss history of the underlying units and in situ production (Figure 4.8b). Groundwater at the air-water contact is assumed to be equilibrated with the atmosphere, i.e. the top boundary has an air saturated water concentration ( $3.7 \times 10^{-8} \text{ cm}^3 \text{ } ^4\text{He}_{crust} \text{ STP/cm}^3 \text{ H}_2\text{O}$ ), which for the purposes of the model is approximated to be  $0 \text{ cm}^3 \text{ } ^4\text{He}_{crust} \text{ STP/cm}^3 \text{ H}_2\text{O}$ . Each lithologic unit has its own porosity, U, Th and effective diffusion length scale also detailed below.

$^4\text{He}$  transport is governed by the following equation,

$$\phi \frac{\delta C}{\delta t} + q \frac{\delta C}{\delta z} = D_e \frac{\delta^2 C}{\delta z^2} + \phi p \quad (4.2)$$

where  $\phi$  is the rock porosity, C is the mass concentration of the solute and t is time. z is the distance from the crystalline basement and p is the production rate per volume of pore water. q is the average linear velocity, for diffusion only scenarios, q=0.  $D_e$  is

#### 4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin



**Figure 4.8:** Illustration of the hydrogeological conceptual model constructed for He diffusion transport. (a) The creation of the first, deepest, stratigraphic unit. (b) The creation of the second stratigraphic unit, overlying the first one. Each unit is deposited as an entire unit at the start of the formation and contains no dissolved He within its pore space. In situ  ${}^4\text{He}$  production and a basal  ${}^4\text{He}$  flux start at the time of its deposition and the He distribution within the unit evolves through diffusion and/or advection loss at its upper surface and a He flux into its basal surface. Groundwater at air-water contact is always equilibrated with the atmosphere, i.e. the top boundary has an air saturated water concentration and is approximated by assuming  $0 \text{ cm}^3 {}^4\text{He}_{\text{crust}} \text{ STP/cm}^3 \text{ H}_2\text{O}$ . Each lithologic unit has its own porosity,  $U$ ,  $Th$  and effective diffusion length scale also detailed below. Subsequent units are formed in turn and their He profile calculated as a combination of the He flux determined by the previous He accumulation and loss history of the underlying units and in situ production.

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the effective diffusion coefficient and is defined according to Fick's first law,

$$J_d = -D_e \frac{\delta C}{\delta z}, \quad (4.3)$$

where  $J_d$  is the diffusive mass flux rate. More detailed equations used for building the numerical model are described in Appendix B.8.

Helium diffusion in pure water is a function of temperature (Ohsumi and Horibe, 1984),

$$D_{He}^{water} = 2.309 \times 10^{-2} e^{-1706/T}, \quad (4.4)$$

where the diffusion coefficient  $D_{He}^{water}$  is expressed in  $\text{cm}^2/\text{s}$ , and temperature  $T$  in K.

Since the thermal gradients in the Williston Basin vary between 20~40 °C (Bachu, 1993), a median value of 30°C is taken to calculate the reservoir temperatures.

However, migration is slower in porous media because of the chemical and physical retardation of grains, pore geometry and connectivity. The diffusive transport of He is controlled by the effective diffusion coefficients or in other words, the retardation coefficients. With a stronger retardation effect, i.e. lower effective diffusion coefficient, more He accumulates at the base of the units. On the contrary, a weaker effect allows a higher helium flux through individual lithological unit. Tortuosity has been derived theoretically but these idealised scenarios are found to deviate from experimental values (Shen and Zhangxin Chen, 2007). Many studies have demonstrated the relationship between the retardation and pore geometry (e.g. Archie, 1942; Van Brakel et al., 1974; Shen and Zhangxin Chen, 2007). Empirical models have been described in power law, linear and logarithm equations (Shen and Zhangxin Chen, 2007). Among which, the power law is analogous to Archie's Law and shown to match experimental values, especially for rock samples with porosity >20% (e.g. Archie, 1942; Boving and Grathwohl, 2001; Grathwohl, 2012; Shen and Zhangxin Chen, 2007; Peng et al., 2012). In Boving and Grathwohl (2001)'s study, the power law model is derived from diffusion coefficients of iodide measured in limestone and sandstone collected from different sites and geological formations. The equation is adapted to determine the

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retardation for limestone and sandstone aquifers which constitute a large proportion of sediments in the Williston Basin.

$$D_e = \phi^{2.2} D_{water} \quad (4.5)$$

where  $\phi$  is the total porosity. However, for tighter sedimentary units with smaller pore size, the exponent is found to be larger (Peng et al., 2012). Therefore, for aquitard units with poor pore connectivity with closed pore-spaces, effective or the through-diffusion porosity is used in the equation (Shackelford and Moore, 2013). In the Williston Basin, the effective porosity for shale has been estimated as 0.1 (Table 4.5), suggesting an tortuosity of 0.0063 following the above equation. This is comparable to tortuosity values reported for shale units in the Southwestern Ontario Basin ranging between 0.0073 and 0.016 (Queenston, Georgian Bay and Blue Mountain formations (Sykes et al., 2011).

The values of  $\phi$ , total porosity, and effective porosity are estimated data provided by IHS Accumap (2018) and other published research (Table 4.5, detailed descriptions included in Appendix B.3). Porosities are not constant values but change over time associated with compaction and cementation. Ignoring the effects of cementation, the compaction history of the Williston Basin is adopted for porosity evolution and is integrated into the transport model (Appendix B.9). Without considering porosity compaction through geological time, He transport through the sedimentary units could be underestimated. It is further assumed that the excessive water due to pore reduction moves laterally along the formation instead of vertically, so that there is no vertical advection caused by compaction.

<sup>4</sup>He concentration in the porewater is heavily dependent on  $z$ , the distance from the crystalline basement. Accurate estimations of the thickness of the geological formations are therefore necessary for modelling. Since the samples are collected from different wells, models are constructed and tailored to each well based on the thickness of the local geological isopach extracted from Geological Atlas of the West Canadian Sedimentary basin Mossop and Shetsen (1994) (Appendix B.10).

## 4.6. HELIUM SIMULATION

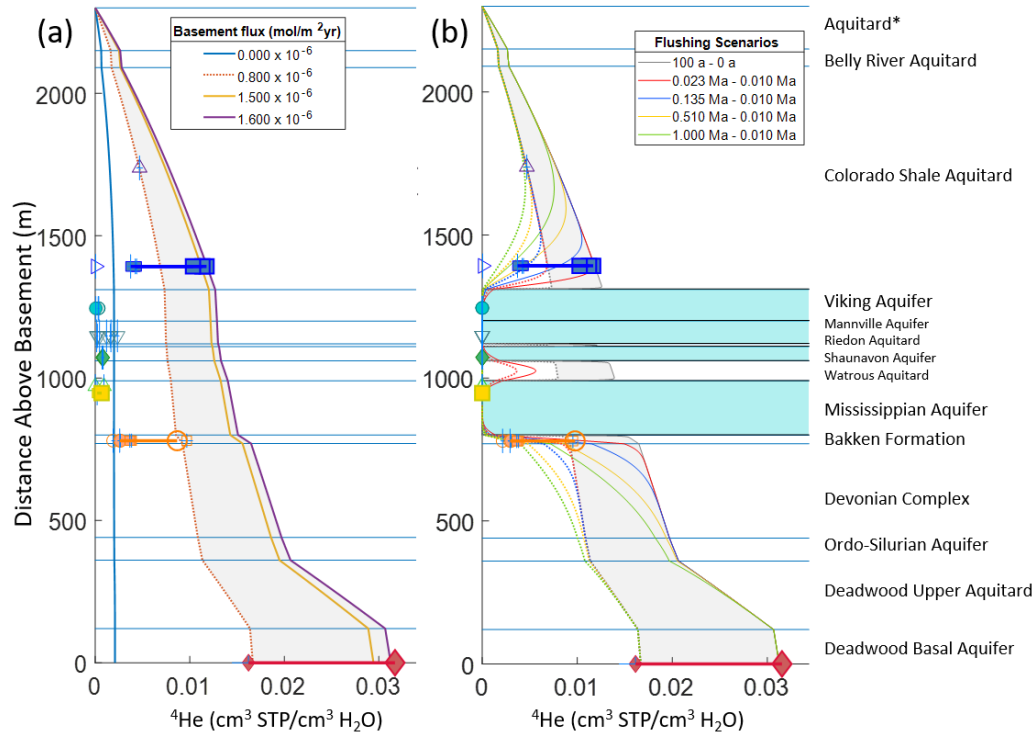
The simple model provides a reference to be compared with sample observations. Deviations are expected and these will be due to processes not considered in the reference model. Where deviations occur and the magnitude of these provide an insight into the basin fluid history.

### 4.6.1 Dominant Basin Scale Migration and He Loss

Previous studies demonstrate that the distribution of anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ) and water isotopes ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) in the Williston Basin is dominantly controlled by diffusion and more recently has been disturbed by Pleistocene glaciation (e.g. Hendry et al., 2013; Hendry and Harrington, 2014). Assuming a static water column with little vertical or horizontal advection component, the reconstructed relative sample concentrations are demonstrated in Figure 4.9 (Appendix B.11). The assumption of a constant  $^4\text{He}$  input from the basement provides a reference model to which the observed data can be tested. The high He samples observed from 2nd White speck, Bakken and Cambrian units can be explained with a constant basement flux of between  $0.7\text{--}0.9 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (Figure 4.9a). The corrected groundwater He profile is illustrated in Figure 4.9(b), and require a higher basement flux of  $1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ . Though horizontal or vertical advection of He-enriched groundwater cannot be disregarded for individual sites, by considering the least number of transport parameters, the diffusive reference model can explain the highest groundwater  $^4\text{He}$  concentrations observed in different lithological units in the basin.

Where the observed data cannot fit the model, other models need to be considered. Though the concentrations observed in some lithological units can be explained by diffusive transport with the estimated amount of basement flux, other samples show discrepancies from the modelled reference profile. Multiple lithological units have significantly lower concentrations. Some of these concentrations are even lower than the simulated profile of a zero-flux scenario, implying significant He depletion without sufficient time for recovery. These depleted units are aquifers which are susceptible

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**Figure 4.9:** Modelled  $^4\text{He}_{\text{crust}}$  profiles compared with reconstructed sample points demonstrating the relative depletion or enrichment to the models. (a) Modelled profiles assume the vertical transported is dominated by diffusion. The higher concentrations observed can be attributed to a basement flux between  $0.8\text{--}1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ . The thick lines connect to the corresponding corrected concentrations with the corrected values on the right end of the lines marked in transparent symbols. (b) Modelled profiles assuming a basement flux of  $0.8 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and horizontal flushing in the aquifer units shown in blue, during four different periods in the Pleistocene.

to advective flow. The two events that can alter groundwater He concentrations are Pleistocene glaciation and anthropogenic water flooding during oil and gas production.

During cycles of advance and retreat, most of the Williston Basin was covered by thick continental ice sheets during Pleistocene glaciation, which provided sufficient hydraulic pressure to reverse groundwater flow (Grasby et al., 2000). Mixing between glacial water and deep basin brine is shown by water samples collected from the Ordovician, Devonian and Mississippian aquifers around the northeast margin of the basin (Grasby et al., 2000; Grasby and Betcher, 2002; Ferguson et al., 2007). Glacial recharge events are also shown to reset the Mannville aquifer in areas closer to the north-east of basin margin (Hendry et al., 2013; Hendry and Harrington, 2014).

#### 4.6. HELIUM SIMULATION

**Table 4.7:** Injection and disposal wells within 5 km to the sampling wells and the injected water volume

| ID                                     | Number of Injection & Disposal Wells within 5 km | Number of Injection and Disposal Wells in the Same Unit as Target Well | Closest Injection or Disposal Well (m) |
|----------------------------------------|--------------------------------------------------|------------------------------------------------------------------------|----------------------------------------|
| <i>Milk River</i>                      |                                                  |                                                                        |                                        |
| 14-8-3-27W3                            | -                                                | -                                                                      | -                                      |
| <i>2nd White Specks (Belle Plaine)</i> |                                                  |                                                                        |                                        |
| 11-9-17-23W2                           | 1                                                | 0                                                                      | 4170                                   |
| <i>2nd White Specks (Alderson)</i>     |                                                  |                                                                        |                                        |
| 8-31-15-14W4                           | -                                                | -                                                                      | -                                      |
| 5-31-15-14W4                           | -                                                | -                                                                      | -                                      |
| 14-31-15-14W4                          | 1                                                | 0                                                                      | 4873                                   |
| <i>Viking</i>                          |                                                  |                                                                        |                                        |
| 1-7-25-12W3                            | -                                                | -                                                                      | -                                      |
| 7A-1-32-24-12W3                        | -                                                | -                                                                      | -                                      |
| 16-30-23-12W3                          | -                                                | -                                                                      | -                                      |
| <i>Mannville</i>                       |                                                  |                                                                        |                                        |
| 16-28-5-13W2                           | 116                                              | 3                                                                      | 551                                    |
| 5-16-6-13W2(#3)                        | 144                                              | 1                                                                      | 402                                    |
| <i>Shaunavon</i>                       |                                                  |                                                                        |                                        |
| 15-10-7-19W3                           | 9                                                | 10                                                                     | 3008                                   |
| 4C-15-9-6-19W3                         | 3                                                | 2                                                                      | 2751                                   |
| 2B-3-28-6-19W3                         | 9                                                | 7                                                                      | 1274                                   |
| <i>Midale</i>                          |                                                  |                                                                        |                                        |
| 8-25-6-13W2                            | 21                                               | 18                                                                     | 2061                                   |
| 2-25-6-13W2                            | 30                                               | 27                                                                     | 1805                                   |
| <i>Frobisher</i>                       |                                                  |                                                                        |                                        |
| 2-32-5-13W2                            | 115                                              | 0                                                                      | 409                                    |
| <i>Bakken (Estevan)</i>                |                                                  |                                                                        |                                        |
| 13-31-1-6W2                            | 4                                                | 4                                                                      | 3047                                   |
| 11-31-1-6W2                            | 4                                                | 4                                                                      | 2505                                   |
| 4-6-2-6W2                              | 4                                                | 4                                                                      | 3430                                   |
| <i>Bakken (Weyburn)</i>                |                                                  |                                                                        |                                        |
| 13-24-5-16W2                           | 12                                               | 0                                                                      | 2050                                   |
| 1-21-5-16W2                            | 2                                                | 0                                                                      | 1820                                   |
| 16-12-5-16W2                           | 5                                                | 0                                                                      | 3854                                   |
| <i>Deadwood</i>                        |                                                  |                                                                        |                                        |
| 10-3-5-8W3                             | -                                                | -                                                                      | -                                      |
| 12-10-5-8W3                            | -                                                | -                                                                      | -                                      |

The Williston Basin, as one of the most well-known gas and oil production fields, has been heavily ‘flooded’. The flooding history around the sampling wells IHS (Accumap, 2018) is summarised in Table 4.7. Produced saline water, is usually rested in a pound, equilibrated with the atmosphere and will have lost its dissolved crustal noble gas signature, before it is re-injected and, likely, dilutes the subsurface He concentration. Such activities started extensively since the 20th century in this basin. Human activities are more localised and recent compared to natural flushing events. Figure 4.9b demonstrates the effect of Pleistocene flushing as well as water flooding on He distribution.

With the available dataset, it is hard to distinguish between these two events. However, the simulation of flushing events indicates that the He profiles in the basin can be



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explained with an estimated basement flux between  $0.8\text{-}1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and horizontal aquifer flushing.

#### **4.7 HELIUM FLUX**

Rolandone et al. (2002) studied the heat flux across different Precambrian provinces and measured U, Th, K and rock density. The study covers Trans-Hudson Orogen, where the thickness of the upper crust is estimated to be approximately 12 km and at least 28 km for the lower crust. Radioelement concentration from the upper crust is measured from 236 samples and is shown in Table 4.8. No measurements are available from the lower crust due to sampling difficulties. By assuming that the basement crust is an open system and the rate of loss equals the rate of production, the steady-state He flux can be estimated from crustal production (Torgersen and Clarke, 1985). The calculated production rate of the upper crust (12 km), if released to the surface at a steady-state averages  $0.44 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ , ranging from  $0.10\text{-}1.15 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  due to variation in U and Th concentration in the samples. If global average U and Th concentration values are taken for the lower crust (Ballentine and Burnard, 2002), this production similarly translates to a flux  $0.19 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  for the lower 28 km. The combined flux of the upper and lower crust is then  $0.64 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ , ranging from  $0.29\text{-}1.34 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ . Noticeably, heat production in the Trans-Hudson is reported to be the lowest compared to the surrounding Precambrian provinces (Perry et al., 2006). Since heat production most generated through  $\alpha$  -decay and is coupled with helium production in the Earth crust, the lower heat flux in the Trans-Hudson area indicates that a basement He flux in the Williston Basin higher than these values are not unexpected. In comparison, the steady-state flux calculated from radiogenic production rate based on average U and Th concentration in the continental crust is  $1.47 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (Torgersen and Clarke, 1985).

The 1D transport model presented here combined with  $^4\text{He}/^{20}\text{Ne}$  observed in natural gases from different basin formations provides a new method to estimate He flux in

## 4.7. HELIUM FLUX

**Table 4.8:** Uranium and thorium concentration for estimating basement He flux.

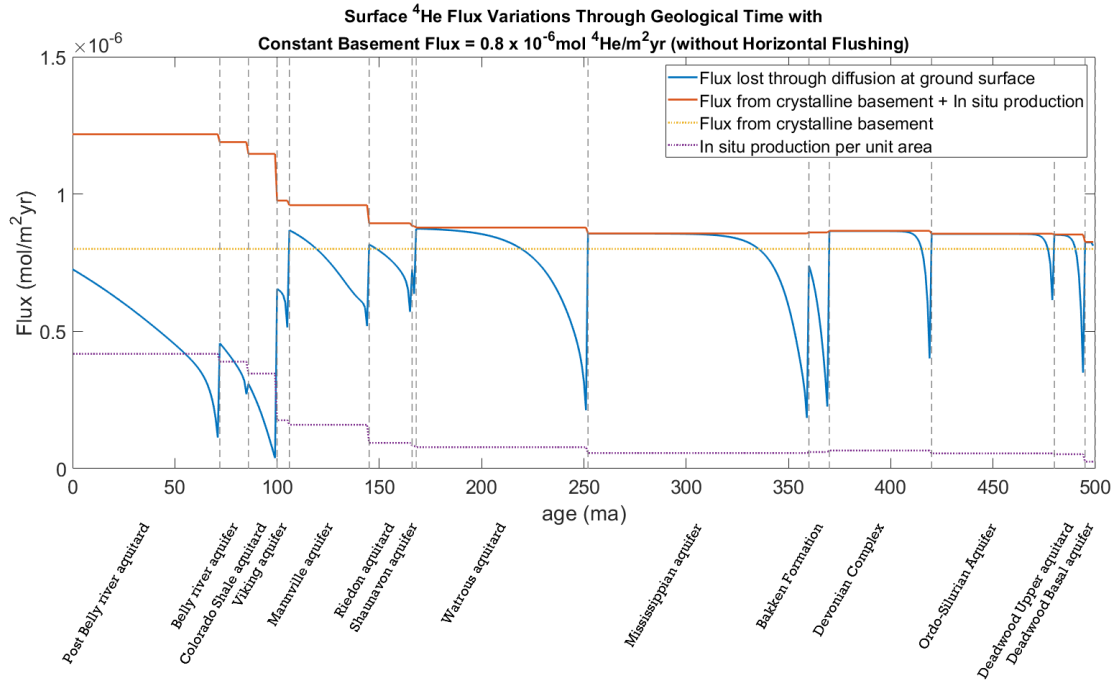
| Sample Number                                                 | U<br>(ppm) | Th<br>(ppm) | Rock<br>density<br>(g/cm <sup>3</sup> ) | Thickness<br>(km) |
|---------------------------------------------------------------|------------|-------------|-----------------------------------------|-------------------|
| Global average for lower crust (Ballentine and Burnard, 2002) | 0.2        | 1.2         | 3.3                                     |                   |
| Global average for upper crust (Ballentine and Burnard, 2002) | 2.8        | 10.7        | 2.6                                     |                   |
| Upper crust (Torgersen and Clarke, 1985)                      | 2.8        | 10.6        | 2.6                                     | 16                |
| Lower Crust (Torgersen and Clarke, 1985)                      | 0.28       | 1.064       | 3.3                                     | 20                |
| Trans-Hudson 236 (Rolandone et al., 2002)                     | 1.52       | 4.52        | 2.6                                     |                   |

sedimentary basins. Apparent flux in the Williston Basin derived here is between  $0.8\text{-}1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and is comparable to the range of steady-state flux estimate calculated based on radioelement concentrations of the Trans-Hudson crust and that of the average continental crust. The estimated helium flux range also lies within the range of other intracratonic basin systems, for example, the Paris Basin and the Great Artesian basin, which have He flux range from  $0.2\text{-}7.9 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and  $0.9\text{-}1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  respectively (Torgersen, 2010 and reference therein)

The apparent He flux simulated from the model assumes the groundwater to be stable, and the turnover of groundwater is negligible; therefore, the modelled value represents the lower limit of flux estimation. The good match of the flux values estimated from a diffusion transport model and the calculated steady-state values and the range of values of similar geological settings provides confidence that the modelling approach adopted is reasonable, that diffusion is the dominant He transport mechanism in the Williston Basin, and that diffusive transport may play a significant role in the transport of associated gases from the crystalline basement across the sedimentary strata over the geological development of intracratonic basins.

Being able to quantify basement and cross-formational He flux is essential when using  $^4\text{He}$  as a dating tool. No helium loss is usually an assumption when calculating water ages. This is to assume all the substances measured is the sum of in situ production and external flux input. By modelling the accumulation of sediments, it is observed that the cross-formational diffusive helium flux changes in response to the addition of sedimentary units, as demonstrated in Figure 4.10. In this simple diffusive model,  $^4\text{He}$  input, i.e. the sum of basement influx and in situ radiogenic production, increases when an additional sediment unit is deposited on top of the previous ones. As diffusion

#### 4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin



**Figure 4.10:** Variation of surface  $^4\text{He}$  flux modelled from the reference model with a constant basement flux of  $0.8 \times 10^{-6} \text{ mol } ^4\text{He}/\text{m}^2/\text{yr}$  for the Deadwood well. The sudden increase of in situ production flux is the combined result of thicker sediment deposit and a decrease in porosity with time. The flux is compared to the constant basement flux (red) applied in the model. The plot suggests that cross-formational diffusive helium flux changes in response to the addition of sedimentary units. A steady state is reached when flux lost through diffusion at ground surface equals to the sum of basement flux and in-situ production. At current stage, the sedimentary column experiences helium loss lower than the sum of basement flux and in situ production: a steady-state is approached but has not been reached.

progresses through time, the entire sedimentary units slowly approach steady-state. This model suggests  $^4\text{He}$  steady state has not been reached in the sedimentary column since approximately 150 Ma ago. Mathematically speaking, once a steady state is reached, no temporal information will be further recorded. If dating with helium assuming no loss from the unit, the water body is likely to be overestimated and resulted in younger ages calculated. Furthermore, horizontal flushing events (Figure 4.9b) reduces helium concentration in the aquifer units and could even change the direction of cross formational flux in the overlying units. Helium flux into any single aquifer or lithological unit is, critically, controlled by the flux from the lithological unit directly underlying the aquifer of interest. It is therefore important in considering the architecture development and hydrogeological events of the basin.

## 4.8 CONCLUSIONS

Noble gas concentrations and isotopic compositions determined in natural gas samples representative of different lithological units in the Williston Basin provide us with an opportunity to investigate cross formational gas transport within a classic intracratonic sedimentary basin.

From the well-constrained concentration of  $^{20}\text{Ne}$  in groundwater,  $^4\text{He}/^{20}\text{Ne}$  ratios in the gas phase can be used to reconstruct the formation groundwater  $^4\text{He}$  concentration. The derived groundwater He concentrations are not consistent with simple in situ production from radioelements with some sample requiring an external helium source. It is, therefore, inadequate to describe each lithological unit as an individual closed system. Basement supply of noble gases is evident from Ne isotopic ratios that are consistent with an Archean rather than basin sediment source as well as the high  $^{40}\text{Ar}/^{36}\text{Ar}$  preserved in the Cambrian Deadwood formation. Basement flux is further supported with the observation of excess mantle-derived  $^3\text{He}$  observed in different formations in the basin compared to crustal  $^3\text{He}/^4\text{He}$  production ratios.

The cross formational migration of He is explored with a 1D transport model which considers He input from both in situ production and the crystalline basement. The model suggests the  $^4\text{He}$  profile can be explained by a diffusive migration throughout geological history, with an apparent basement flux of  $0.8\text{--}1.6 \times 10^{-6} \text{ mol } ^4\text{He}/\text{m}^2/\text{yr}$  and provides a reference for further exploring other hydrogeological events in the basin. He loss in some aquifer units suggests a disturbance of the model-assumed static water body in the basin; the model is unable to distinguish at this stage between lateral water recharging during Pleistocene glaciation or anthropogenic water flooding during oil and gas production. The estimated flux range overlaps with that estimated from the steady-state flux calculated from the composition of the Trans-Hudson crust and that reported from other intracratonic basins (Torgersen et al., 1992; Torgersen, 2010) and is also indistinguishable from steady-state He flux  $1.47 \times 10^{-6} \text{ mol } ^4\text{He}/\text{m}^2/\text{yr}$  calculated from average U and Th concentrations of continental crust (Torgersen et al.,

#### *4. Identifying Cross-formation Helium Migration and Quantifying Basement Flux in the Williston Basin*

1992; Torgersen, 2010). This suggests the helium profile can be explained with a dominant diffusion transported in the Williston Basin and diffusive transport can play a significant role in transporting substances from the basement across sedimentary units in old and stable sedimentary basins. Though horizontal or vertical advection of  $^4\text{He}$  rich water can play an important role at individual sites, it is not a necessary process to account for the He dissolved in the groundwater of this sedimentary basin. The 1D diffusion model also highlights the importance of the basin architecture development and hydrogeological events in determining the  $^4\text{He}$  flux into the different lithological units and illustrates the need to consider this factor when making the assumption of  $^4\text{He}$  steady state flux in  $^4\text{He}$  groundwater dating applications.



# 5

## Quantifying and Modelling Basement He and Ar fluxes into Sedimentary Basins: A Case Study on the Southwestern Ontario Basin

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## ABSTRACT

A quantitative understanding of the role of groundwater in controlling gas migration is crucial for the exploration of natural resources (e.g. traditional petroleum hydrocarbons and natural gas and He exploration) in sedimentary basin systems worldwide. Thirty-three natural gas samples collected from different locations and geological formations in the Southwestern Ontario Basin and their noble gas isotopic and concentration data are presented. Geochemical researches suggest the intermediate-deep groundwater systems are stable over geological time, which is further supported by the different  $^3\text{He}/^4\text{He}$  ratios observed in the Southwestern Ontario Basin comparing to those reported in the Michigan Basin. The scenario of a diagenetic and stable groundwater is then investigated.

The samples are first corrected for their air component based on  $^{20}\text{Ne}$  and  $^{20}\text{Ne}/^{36}\text{Ar}$ .



## *5. Quantifying and Modelling Basement He and Ar fluxes into Sedimentary Basins: A Case Study on the Southwestern Ontario Basin*

$^{20}\text{Ne}$  and  $^{36}\text{Ar}$  in the natural gases are derived predominantly from groundwater. Hence  $^4\text{He}/^{20}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios allow the radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$  concentrations in the groundwater before gas-phase formation to be determined. Calculations show excess  $^4\text{He}$  compared to calculated in situ radiogenic production in most samples, indicating the presence of an external  $^4\text{He}$  flux and noble gas transport between different geological units. 1D Diffusional profiles  $^4\text{He}$  and  $^{40}\text{Ar}$  are constructed from the first-order transport equations for each well. The optimum basement fluxes are simulated for each sample using an iterative approach, which are used to interpolate basement flux maps. The average modelled  $^4\text{He}$  flux estimated for the basin is smaller than both the expected crustal production value and values determined for comparable localities such as the Williston Basin in Western Canada. Variations of  $^4\text{He}$  and  $^{40}\text{Ar}$  flux are observed separated by the Algonquin Arch, and areas with elevated values can be identified closer to the Appalachian Basin. The basement flux variations could be attributed to compositional or permeability differences in the basement rock. The lower  $^4\text{He}$  flux in the Southwestern Ontario Basin comparing to the Williston Basin corresponds with less mantle-derived He and a higher degree of He-heat decoupling, suggesting a potential qualitative correlation among the three parameters ( $^4\text{He}$  flux,  $^3\text{He}/^4\text{He}$  and the degree of He-heat decoupling) which requires further investigation.

### **5.1 INTRODUCTION**

Sedimentary basins are reservoirs of various fluids sourced from or migrated through the Earth's crust. The crystalline basement underlying sedimentary systems as well as the deeper mantle provide both heat and chemical elements for geochemical and biological reactions within the sedimentary basins, including the formation of minerals, hydrocarbons and hydrogen. Another valuable resource produced and concentrated within the crust is radiogenic He ( $^4\text{He}$ ); a non-renewable but crucial resource used in various industries and science research frontiers. The quantification of the elemental flux from the crystalline basement, the 'basement flux' is, therefore, of great economic importance, especially within sedimentary basin environments.

## 5.1. INTRODUCTION

Besides the exploration for natural resources, an understanding of the basement flux can improve our interpretation of subsurface fluid migration in basin systems, which is critical for environmental projects, such as geological storage of CO<sub>2</sub> and nuclear waste repository (e.g. Gunter et al., 2004; Hendry et al., 2015). Numerical modelling is widely used in simulating the transport of geochemical tracers and their associated fluids in order to verify the conceptual hydrogeological models (e.g. Hendry et al., 2013; Hendry and Harrington, 2014; Al et al., 2015). It also provides a quantitative tool to estimate the natural flux from the crystalline basement (Chapter 4).

Geochemical tracers include salt (Bachu and Hitchon, 1996), Br<sup>-</sup>, Cl<sup>-</sup>,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopes (Sykes et al., 2011; Al et al., 2015). Noble gases provide another set of tools in hydrogeological studies, with some unique properties. They are unreactive chemically but can preserve signatures from physical processes, such as fluid mixing (Ballentine and O’Nions, 1992; Ballentine and Burnard, 2002) or degassing (Zhou et al., 2005; Barry et al., 2016), groundwater recharge conditions (Ballentine and Hall, 1999; Aeschbach-Hertig et al., 2002; Kipfer et al., 2002) and fluid residence (Holland et al., 2013; Aggarwal et al., 2015; Tolstikhin et al., 2017; Warr et al., 2018).

The transport of He has been modelled focusing on aquitard units, including the Opalinus Clay of Mont Terri, Switzerland (Mazurek et al., 2011), Boom clay in the Campin Basin, Belgium (Mazurek et al., 2011) and Bulldog Shale in the Great Artesian Basin, Australia (W Payton Gardner et al., 2012). These argillaceous formations demonstrate He migration across the thickness of the units is dominantly controlled by diffusive transport. Basin-scale modelling has been applied to the Paris Basin by Castro et al. (1998b) and the excess amount of crustal noble gases compared to sediment production is attributed to flux from the basement. In the Williston Basin, North America, it has been found that He distribution can be explained with a diffusion dominated transport of basement flux across the sedimentary units (Chapter 4).

In this study, we explore the noble gas content in the Southwestern Ontario Basin, and by applying numerical transport models to each individual sample, we try to

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quantify  $^4\text{He}$  and  $^{40}\text{Ar}$  flux from the crystalline basement and to explain flux variation in the basin.  $^4\text{He}$  flux is further compared with that obtained from the Williston Basin (Chapter 4) and other literature to gain some understanding about the controlling factors of the crystalline basement degassing processes.

### **5.2 GEOLOGICAL BACKGROUND**

The Southwestern Ontario Basin refers to sedimentary successions lying on a Precambrian topographic high, the Algonquin Arch, which separates the Michigan Basin to the west and the Appalachian Basin to the east (Figure 5.1). The Algonquin Arch plunges and reappears as Findlay Arch to the south, forming a structural depression, the Chatham Sag, in between. Both arches are north extensions of a broad basement uplift, the Cincinnati Arch, which formed during late Precambrian and was intermittently active during Palaeozoic (Sanford et al., 1985; K. Ziegler and Longstaffe, 2000b). During the Cambrian to Mississippian, the region was located at a tropical latitude (Der Voo, 1988). Periodic transgression of the inland sea formed different facies throughout time and across the basins. Regression and structural uplift resulted in erosional surfaces and unconformities.

The Southwestern Ontario Basin preserves less than 1500 m of Palaeozoic sediments, from the upper Cambrian to Devonian/Mississippian, which rest unconformably on the Precambrian crystalline basement (Sanford et al., 1985). The sedimentary units are much thinner compared to the 4800 m thickness at the centre of the intracratonic Michigan Basin, and up to 13 km thickness recorded in the siliciclastic dominant foreland basin, the Appalachian Basin (K. Ziegler and Longstaffe, 2000b). The Cambrian unit is composed of fine to coarse sandstone and sandy to argillaceous dolostone (Hamblin, 1998) but pinches out on both limbs of the arch. The Middle Ordovician Limestone (Black River and Trenton Groups) is formed with a variety of carbonate facies, from supratidal to lagoonal, shallow offshore to the deep shelf (Brookfield and Brett, 1988; Haeri-Ardakani et al., 2013). These carbonate deposits

### 5.3. HYDROGEOLOGY BACKGROUND

mark one of the most significant sea level rises (Brookfield and Brett, 1988). The later Taconic Orogeny resulted in deepening of the basin during the Late Ordovician and accumulated shale dominant thick layers (Queenston, Georgian Bay and Blue Mountain Formations), which continued into the Lower Silurian (Manitoulin, Cabot Head Formation). During the middle to late Silurian, the Southwestern Ontario and Michigan Basins were covered by warm shallow seas, ideal for the development of pinnacle reefs in deep waters towards the centre of the Michigan Basin and reefal complexes in shallow water on the rim. The Acadian Orogeny during the Late Silurian resulted in arch uplift and subsidence of the Michigan Basin, and changed the region to a more restricted depositional environment, forming cyclic units of carbonate, evaporites and argillaceous sediments in the Appalachian, the Michigan and the Southwestern Ontario Basins (Salina Group). These regional units are overlain by Devonian carbonate deposited under an arid and restricted marine environment (Birchard et al., 2004). The current landscape was shaped during the Pleistocene glaciation.

### 5.3 HYDROGEOLOGY BACKGROUND

In the Southwestern Ontario Basin, groundwater is conceptually divided into two domains defined by their major ion compositions and salinity (Hobbs et al., 2011). The shallow system, less than 200 m below ground surface, has fresh through brackish water and is mainly composed of the Quaternary drift and Devonian sediments (Hobbs et al., 2011; Sykes et al., 2011). During the period of Pleistocene glaciation, the thick continental ice sheet covered the entire area of the Michigan Basin, the Southwestern Ontario Basin and Northwest part of the Appalachian Basin (McIntosh et al., 2011). The ice sheet not only provided sources for water recharge but locally may have opened up the fracture network to facilitate downward water migration (Martini et al., 1998; McIntosh et al., 2011). In the Michigan Basin, geochemical studies on Devonian Antrim gas samples and formation water samples provide evidence of halite-dissolution and glacial water recharge (modern to 20 ka) (Martini et al., 1998). Glacial recharge

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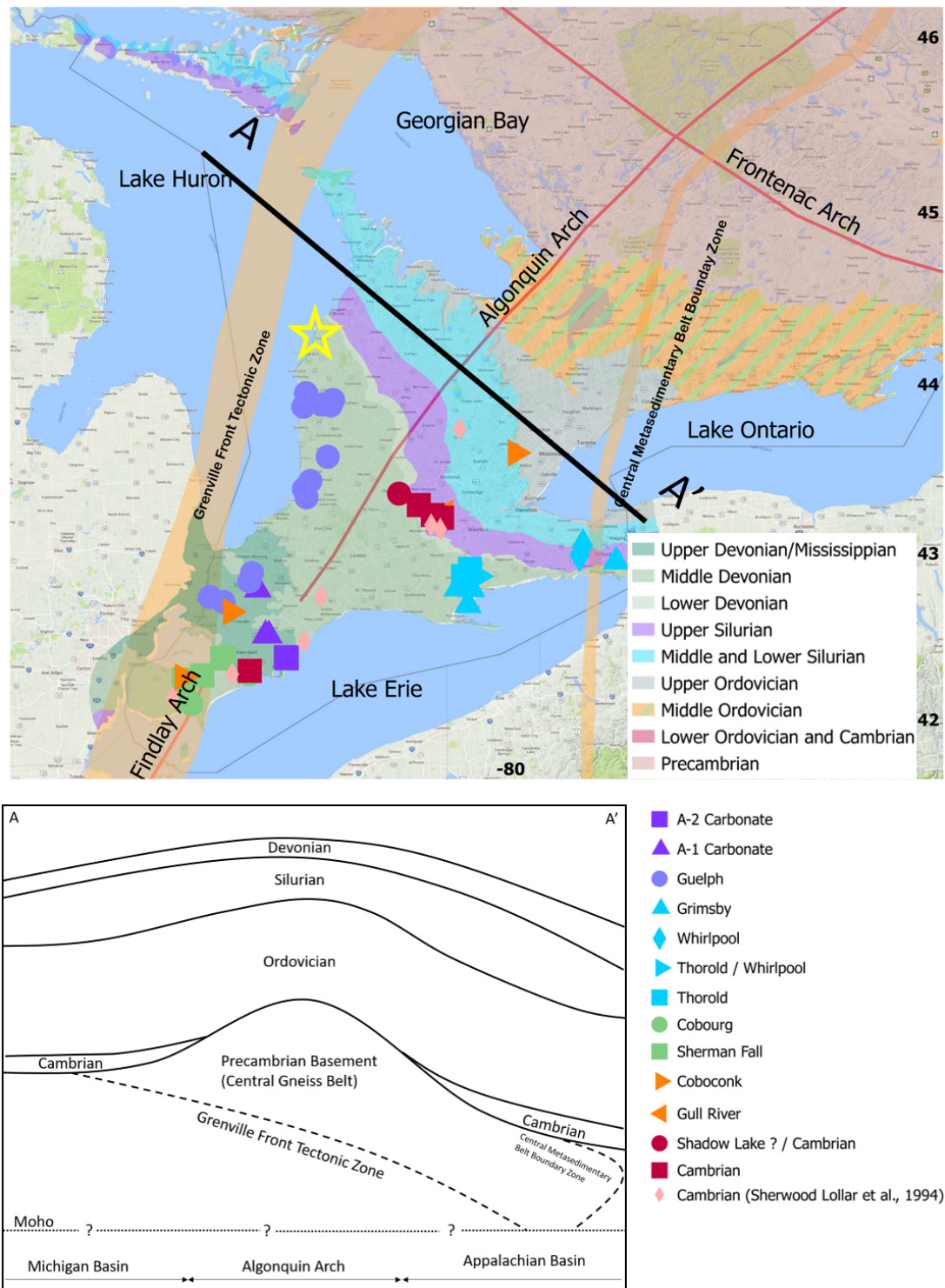
is also suggested for Carboniferous units based on the low salinity and  $\delta^{18}\text{O}$  values (Kolak et al., 1999). Such recharge impacted up to a depth of 300 m in the Michigan Basin, but dilution is not observed for the same shale formation in the Southwestern Ontario Basin (Hobbs et al., 2011). Stable isotopic compositions of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in Southwestern Ontario Basin also demonstrate a mixing of saline waters with dilute meteoric and glacial waters, but the maximum depth of freshwater penetration is 140 m below ground surface (Weaver et al., 1995; Hobbs et al., 2011).

In contrast, the intermediate to deep waters in Southwestern Ontario are predominantly brines associated with hydrocarbons. The low topography gradient and the high salinity of deeper waters prevent the penetration of the recharged meteoric and glacial water (Hobbs et al., 2011). The vertical profiles of  $^{18}\text{O}$  and  $\text{Cl}^-$  measured from drilled cores (marked in Figure 5.1) suggest a static deep and intermediate water system and dominated by diffusion (Al et al., 2015).

To comply with the observed geochemical features, Hobbs et al. (2011) suggested that the waters might have evolved in situ from evaporated seawater or they are the remnants of hydrothermal fluids that migrated from deeper along permeable pathways. The similarity in both salinity and water type between groundwater and dolomitizing fluids suggests the water is likely to be diagenetic in origin (Coniglio et al., 2003; Hobbs et al., 2011). In most models of fluid emplacement, the driving force is thought to be associated with tectonic or orogenic events.

The oldest regional scale fluid migration recorded by geochemical tracers,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , and mineral alteration at the Precambrian-Palaeozoic boundary was related to the Taconic Orogeny during the Late Ordovician (Harper et al., 1995; K. Ziegler and Longstaffe, 2000a; K. Ziegler and Longstaffe, 2000b). The orogeny facilitated sediment loading in the current Appalachian Basin and has been suggested to have transported connate water up-dip to the west (Oliver, 1986; Bethke and Marshak, 1990; Harper et al., 1995; K. Ziegler and Longstaffe, 2000b).

### 5.3. HYDROGEOLOGY BACKGROUND



**Figure 5.1:** A regional geological map of the Southwestern Ontario Basin (modified from AECOM and Canada (2011)) with a schematic cross-section plot across the Algonquin Arch (modified from Sherwood Lollar et al., 1994b). The locations of sampling wells are plotted on the map. Cambrian wells reported by Sherwood Lollar et al., 1994b are marked with pink diamonds. The yellow star shows the area of drilling boreholes that have been researched by AECOM and Canada (2011), Hobbs et al. (2011), Sykes et al. (2011), Clark et al. (2013) and Al et al. (2015).

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The timing of the second regional groundwater movement is not well constrained. In the Michigan Basin, it is thought to be related to the reactivation of Mid-Continental estimated to have occurred between 350 Ma (Haeri-Ardakani et al., 2013). REE<sub>SN</sub> patterns and  $\delta^{18}\text{O}$  suggests cross-formational fluid migration from the Cambrian to Silurian Salina units within the Michigan Basin and possible interaction with the crystalline basement (Haeri-Ardakani et al., 2013). The estimated homogenization temperatures of dolomite and calcite in the Michigan Basin are significantly higher than their burial rift temperature in a typical intracratonic basin (Hogarth and Sibley, 1985). The decrease of homogenization temperature and the absence of fracture-related replacive and saddle dolomite eastward away from the Michigan Basin centre has been used to argue for a thermally-induced buoyancy-driven migration of dolomitizing fluids radially from the basin centre to the margin (Barnes et al., 2008; Haeri-Ardakani et al., 2013). While a heat anomaly was found in the Michigan Basin, low-temperature meteoric water entered groundwater system at the subaerial exposure of Findlay-Algonquin Arches, formed as a result of intermittent uplift during the Acadian (410-360 Ma, Osberg et al., 1989) and Alleghanian (327-266 Ma, Secor JR et al., 1986) (K. Ziegler and Longstaffe, 2000a; K. Ziegler and Longstaffe, 2000b). This is recorded by secondary illite formed at approximately 40°C to 50°C along Precambrian-Palaeozoic unconformity on the Appalachian side of the Southwestern Ontario Basin (K. Ziegler and Longstaffe, 2000a; K. Ziegler and Longstaffe, 2000b).

More recent fluid migration in intermediate and deep water systems have been proposed by Khader and Novakowski (2014). They modelled porewater pressure and captured the under-pressure in Ordovician and Silurian formations through cycles of glacial loading. They interpreted the overpressure in the Cambrian units likely to be the result of density-driven flow from the Michigan Basin centre to the edge caused by deglaciation. Al et al. (2015) modelled vertical profiles of  $^{18}\text{O}$  and  $\text{Cl}^-$  measured from drilled cores marked in Figure 5.1, and suggested a deep brine intrusion from the Michigan Basin along the Cambrian sandstone approximately 2.6 Ma ago to explain the offset of observations from the diffusion model. Neither of these interpretations

## 5.4. METHODOLOGY

has been widely accepted as both are based primarily on modelling with significant uncertainty in some of the end-members anchoring the models.

Overall, there are two major hypotheses with the intermediate to deep groundwater: 1) the water is stable over geological time scale, either as being diagenetic produced and evolved in situ or mixed with migrated water driven by ancient tectonic. 2) During Pleistocene, deep Michigan water migrated margin-wards to the Southwestern Ontario Basin. In this thesis, an extensive suite of noble gas signatures is used to investigate the hypotheses and the role of basement noble gases in the Southwestern Ontario Basin.

### 5.4 METHODOLOGY

Gas samples were collected from natural gas wells producing from different geological units (Figure 5.1) following the procedures outlined in R. Weiss (1968) and stored in the cold welded internally polished, refrigeration-grade copper tubing for noble gas determination. Thirty-three samples were analysed at the University of Oxford for He, Ne, Ar, Kr and Xe abundance and isotopic composition. Gas compositions were measured at the Stable Isotope Laboratory of the University of Toronto after the methods described by Ward et al. (2004) and Sherwood Lollar et al. (2006). The noble gas isotopic and compositional measurement protocol at the University of Oxford is summarised in Chapter 4 and Appendix A and described in detail by Barry et al. (2016). The sample tubes were mounted on a stainless steel Ultra-High Vacuum system. An aliquot of the sample was expanded to a calibrated volume at known pressure and temperature. The known volume of gas was itself exposed to a titanium getter, a hot getter (SAES GP-50) and a cold getter (SAES NP-10) to chemically remove hydrocarbons and other reactive gases. Noble gases were trapped on two cryogenic traps, containing a charcoal and stainless steel substrate respectively, and selectively released by raising the temperature of the traps. He was measured using a Thermo Helix SFT mass spectrometer and Ne, Ar, Kr and Xe using Thermo Argus VI mass spectrometer. First, the charcoal trap containing He and Ne was heated



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to 31 K to release He which was subsequently measured. Then the same trap was heated to room temperature to release Ne which was then measured. Following this the stainless steel trap was heated to 200 K to release all gases and from which an aliquote was used for Ar measurement. The steel cryotrap was then cooled to 52 K to re-adsorb the Kr and Xe and to allow removal of the Ar. Finally, the trap was heated to 300 K to release Kr and Xe, which were measured at the same time.

Full procedural blanks were run once per week. The average blank to average sample signal ratios of  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  were 0.004%, 0.05%, 0.88%, 0.04% and 0.07% respectively.  $^{20}\text{Ne}$  was corrected for doubly-charged  $^{40}\text{Ar}^{++}$  following the method described by Niedermann et al. (1993). Air-standards were analysed weekly for system calibration. The air samples were collected in the University Parks, Oxford, UK on November 24, 2014 (297 K, 1.01 atm, 95% humidity). Internal ‘running’ standards were run at least once every night following sample analysis to confirm machine stability. The maximum overnight variations ( $1\sigma$ ) for these separate runs were 1.6%, 0.6%, 1.3%, 1.2%, 1.0% for  $^4\text{He}$ ,  $^{20}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  respectively. The calculated isotopic concentrations and ratios are presented at  $1\sigma$  level of confidence (Table 5.2 & 5.3).

## **5.5 RESULTS**

### **5.5.1 Major Gas Components**

The gases are mainly composed of  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{C}_{2+}$  (the sum of  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$ ). All samples are normalised to 100% composition, assuming that gas contributions other than those are negligible. Major gas compositions are presented in Table 5.1. Measured samples all have a considerable amount of  $\text{CH}_4$ , ranging from 39% (Guelph and A1 Carbonate) to 89.3% (Guelph). Most samples have  $\text{N}_2$  content  $<10\%$ ; but for those samples with  $\text{CH}_4 < 50\%$ ,  $\text{N}_2$  greater than 40% is reported. No apparent trends can be observed for any of these major gas compositions ( $\text{CH}_4$ ,  $\text{N}_2$ ) against other variables such as depth, distance to the basement, ages of the formation

## 5.5. RESULTS

or hydrogeological properties. All samples have  $\text{CO}_2 < 4\%$  and  $\text{H}_2 < 2\%$ , and both gases are not further discussed for the purpose of this study.

Noble gas concentrations and isotopic ratios are presented in Table 5.2 and 5.3. The two A-1 carbonate samples and the Shadow Lake sample have their noble gas concentrations and elemental and isotopic ratios similar to the atmospheric values and are therefore likely to be heavily contaminated and are disregarded in the following analysis.

### 5.5.2 He

$^4\text{He}$  concentrations in the gas sample range from  $3.7 \times 10^{-4} \text{ cm}^3 \text{ STP/cm}^3$  for Guelph to  $4.9 \times 10^{-3} \text{ cm}^3 \text{ STP/cm}^3$  for Grimsby.  $^4\text{He}/^{20}\text{Ne}$  ratios for the other samples range from 3064 to 83305, suggesting these samples have negligible atmospheric He contamination. Air normalised  $^3\text{He}/^4\text{He}$ , denoted as  $R/R_a$  ( $R_a = 1.4 \times 10^{-6}$ ) is a good indicator of He sources (Ballentine and Burnard, 2002). The sample  $^3\text{He}/^4\text{He}$  ratios range between  $0.0086 R_a$  to  $0.056 R_a$ , close to the crustal radiogenic production of  $0.02 R_a$ . Because of the low concentrations of He in the air, coupled with the crustal  $^3\text{He}/^4\text{He}$  and high  $^4\text{He}/^{20}\text{Ne}$  ratios, all  $^4\text{He}$  is considered to have been sourced in the subsurface (i.e. no air correction needed). Ordovician and Cambrian samples, which are closer to the basement, demonstrate a small increase in  $R/R_a$ , i.e. the  $^3\text{He}/^4\text{He}$  (Figure 5.2).

### 5.5.3 Ne

The minimum and maximum  $^{20}\text{Ne}$  concentrations are  $1.2 \times 10^{-8} \text{ cm}^3 \text{ STP/cm}^3$  (Cobourg) and  $1.62 \times 10^{-7} \text{ cm}^3 \text{ STP/cm}^3$  (Guelph). There is no apparent trend between  $^{20}\text{Ne}$  concentrations with depth. Figure 5.3 plots the samples in the  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  space. The Post Archean Mixing Line is defined with an endmember  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio of 0.475 widely observed in many sedimentary basin systems (Kennedy et al., 1990; Ballentine and Burnard, 2002; David J Byrne et al., 2018). Fluid inclusions and fracture fluids in Archean basement corresponds to a higher endmember  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio of 3.3 and is marked as the Archean Neon Mixing Line (Lippmann-Pipke et al.,

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**Table 5.1:** Major gas composition of collected samples.

| Sample name                     | Distance Above Basement (m) | Depth (m) | CH <sub>4</sub> % | N <sub>2</sub> % | C <sub>2+</sub> % | CO <sub>2</sub> % |
|---------------------------------|-----------------------------|-----------|-------------------|------------------|-------------------|-------------------|
| <b>A-2 Carbonate</b>            |                             |           |                   |                  |                   |                   |
| T008636                         | 770                         | 495       |                   |                  |                   |                   |
| <b>A-1 Carbonate</b>            |                             |           |                   |                  |                   |                   |
| T008633                         | 699                         | 510       | 43                | 50.3             | 6.7               | <0.002            |
| T008634                         | 700                         | 502       |                   |                  |                   |                   |
| <b>Guelph</b>                   |                             |           |                   |                  |                   |                   |
| T002556                         | 612                         | 412       |                   |                  |                   |                   |
| T003899                         | 585                         | 615       | 45                | 46.2             | 5.3               | 3.5               |
| T004918                         | 454                         | 509       | 69                | 3.3              | 25.5              | 2.2               |
| T007415                         | 685                         | 467       | 85.7              | 1.3              | 13.1              | <0.002            |
| T008468                         | 679                         | 550       | 76.4              | 6                | 13.5              | 4                 |
| T008657                         | 702                         | 388       | 78.6              | 8.9              | 12.1              | 0.4               |
| T009602                         | 642                         | 484       | 63.1              | 5.6              | 29.9              | 1.4               |
| T010097                         | 678                         | 469       | 73.6              | 5.6              | 19.1              | 1.7               |
| T011560                         | 607                         | 399       | 79.4              | 12.6             | 7.7               | 0.3               |
| <b>Thorold</b>                  |                             |           |                   |                  |                   |                   |
| T011554                         | 630                         | 317       |                   |                  |                   |                   |
| T011584                         | 657                         | 282       | 82.1              | 10.1             | 7.9               | <0.002            |
| <b>Thorold / Whirlpool</b>      |                             |           |                   |                  |                   |                   |
| T011280                         | 659                         | 298       | 81.3              | 10.6             | 7.3               | 0.7               |
| <b>Grimsby</b>                  |                             |           |                   |                  |                   |                   |
| T002374                         | 630                         | 360       |                   |                  |                   |                   |
| T003188                         | 726                         | 380       | 83.2              | 12               | 4.8               | <0.002            |
| T012287                         | 749                         | 181       | 84.4              | 4.5              | 10                | 1.2               |
| <b>Whirlpool</b>                |                             |           |                   |                  |                   |                   |
| T008194                         | 745                         | 152       |                   |                  |                   |                   |
| T009877                         | 764                         | 165       |                   |                  |                   |                   |
| <b>Cobourg</b>                  |                             |           |                   |                  |                   |                   |
| T007357                         | 247                         | 938       | 83.6              | 6.3              | 9.8               | 0.3               |
| T008358                         | 268                         | 774       | 79.8              | 2.7              | 16.6              | 1                 |
| <b>Sherman Fall</b>             |                             |           |                   |                  |                   |                   |
| T007793                         | 225                         | 904       | 64                | 26.1             | 9.5               | 0.4               |
| T007954                         | 239                         | 843       | 79.2              | 3.8              | 17.1              | <0.002            |
| T008057                         | 235                         | 861       | 82.2              | 5.3              | 10.8              | 1.7               |
| <b>Coboconk</b>                 |                             |           |                   |                  |                   |                   |
| T0011596                        | 51                          | 555       | 83.8              | 6.6              | 8.4               | 1.2               |
| T006907                         | 131                         | 1041      | 87.2              | 0.1              | 11.7              | 1                 |
| T008313                         | 153                         | 928       | 76.2              | 4                | 18.3              | 1.6               |
| <b>Gull River</b>               |                             |           |                   |                  |                   |                   |
| T008974                         | 13                          | 840       | 49.6              | 41.2             | 9.2               | <0.002            |
| <b>Shadow Lake ? / Cambrian</b> |                             |           |                   |                  |                   |                   |
| T008532                         | 0                           | 919       |                   |                  |                   |                   |
| <b>Cambrian</b>                 |                             |           |                   |                  |                   |                   |
| T007369                         | 20                          | 1152      | 79.6              | 6.6              | 10                | 3.9               |
| T007956                         | 7                           | 879       | 75.7              | 6.8              | 17.6              | <0.002            |
| T008094                         | 3                           | 877       | 77.8              | 5                | 16.2              | 1                 |
| Willey 29*                      | 7                           |           |                   |                  |                   |                   |
| Innerkip 30*                    | 1                           |           | 86.7              | 2.6              | 10.7              | <0.002            |
| Innerkip 31*                    | 3                           |           | 85.5              | 5.2              | 9.3               | <0.002            |
| Innerkip 32*                    | 6                           |           | 86.4              | 6.2              | 7.4               | <0.002            |
| Innerkip 33*                    | 5                           |           | 85.7              | 6.3              | 8                 | <0.002            |
| Clearville 34*                  | 26                          |           | 87.5              | 5.6              | 6.8               | 0.1               |
| Clearville 35*                  | 28                          |           | 84.1              | 4                | 11.6              | 0.2               |
| Gobles 36*                      | 0                           |           |                   |                  |                   |                   |
| Raleigh 37*                     | 15                          |           | 84.8              | 4.7              | 10                | 0.4               |
| Raleigh 38*                     | 14                          |           | 82.9              | 6.1              | 10                | 1                 |
| Arthur 39*                      | 7                           |           | 83.7              | 5.4              | 10.5              | 0.4               |
| North Gosfield 40*              | 0                           |           | 75.3              | 16.4             | 8.2               | 0.1               |
| North Gosfield 41*              | 0                           |           | 84.6              | 7.7              | 7.7               | <0.002            |

\*Cambrian samples reported by Sherwood Lollar et al. (1994b); the distance above basement for this samples are estimated from figure 11b in Sherwood Lollar et al. (1994b)'s paper

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**Table 5.2:** Noble gas concentrations and He isotopic ratios.

| Sample name                     | $^4\text{He} \times 10^5$<br>cm <sup>3</sup> STP/cm <sup>3</sup> | $^{20}\text{Ne} \times 10^9$<br>cm <sup>3</sup> STP/cm <sup>3</sup> | $^{40}\text{Ar} \times 10^5$<br>cm <sup>3</sup> STP/cm <sup>3</sup> | $^{84}\text{Kr} \times 10^9$<br>cm <sup>3</sup> STP/cm <sup>3</sup> | $^{132}\text{Xe} \times 10^{10}$<br>cm <sup>3</sup> STP/cm <sup>3</sup> | R/R <sub>a</sub><br>(air corrected) |
|---------------------------------|------------------------------------------------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------|-------------------------------------------------------------------------|-------------------------------------|
| <b>A-2 Carbonate</b>            |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T008636                         | 52.30±0.53                                                       | 46.58±0.20                                                          | 12.02±0.04                                                          | 7.12±0.07                                                           | 5.77±0.07                                                               | 0.018±0.001                         |
| <b>A-1 Carbonate</b>            |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T008633                         | 0.50±0.01                                                        | 18644.00±115.22                                                     | 1040.00±6.06                                                        | 724.42±7.68                                                         | 267.91±3.59                                                             | 1.145±0.499                         |
| T008634                         | 0.24±0.00                                                        | 16594.00±118.48                                                     | 950.00±4.60                                                         | 664.63±6.64                                                         | 250.54±3.18                                                             | 0.991±0.091                         |
| <b>Guelph</b>                   |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T002556                         | 280.00±2.95                                                      | 105.39±0.75                                                         | 46.05±0.27                                                          | 11.75±0.12                                                          | 9.00±0.12                                                               | 0.021±0.002                         |
| T003899                         | 120.00±1.20                                                      | 65.22±0.47                                                          | 19.71±0.09                                                          | 8.77±0.09                                                           | 7.40±0.09                                                               | 0.014±0.001                         |
| T004918                         | 120.00±1.23                                                      | 23.63±0.20                                                          | 13.42±0.06                                                          | 7.46±0.07                                                           | 7.98±0.10                                                               | 0.019±0.002                         |
| T007415                         | 350.00±3.53                                                      | 88.36±0.84                                                          | 26.11±0.26                                                          | 11.65±0.13                                                          | 8.44±0.12                                                               | 0.018±0.001                         |
| T008468                         | 37.29±0.37                                                       | 29.54±0.21                                                          | 25.54±0.12                                                          | 25.33±0.32                                                          | 43.20±0.54                                                              | 0.009±0.001                         |
| T008657                         | 280.00±3.04                                                      | 72.64±0.45                                                          | 28.77±0.26                                                          | 9.87±0.10                                                           | 8.27±0.11                                                               | 0.023±0.001                         |
| T009602                         | 140.00±1.50                                                      | 92.44±0.51                                                          | 25.33±0.13                                                          | 10.37±0.11                                                          | 7.78±0.10                                                               | 0.018±0.001                         |
| T010097                         | 320.00±3.17                                                      | 69.57±0.50                                                          | 25.96±0.12                                                          | 9.42±0.09                                                           | 7.71±0.10                                                               | 0.024±0.002                         |
| T011560                         | 150.00±1.47                                                      | 161.61±1.15                                                         | 56.59±0.26                                                          | 15.93±0.16                                                          | 12.63±0.16                                                              | 0.041±0.004                         |
| <b>Thorold</b>                  |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T011554                         | 250.00±2.49                                                      | 36.87±0.23                                                          | 24.64±0.12                                                          | 7.94±0.08                                                           | 5.55±0.07                                                               | 0.020±0.002                         |
| T011584                         | 260.00±2.55                                                      | 33.60±0.21                                                          | 19.57±0.06                                                          | 8.19±0.08                                                           | 4.92±0.06                                                               | 0.018±0.002                         |
| <b>Thorold / Whirlpool</b>      |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T011280                         | 190.00±2.11                                                      | 66.26±0.36                                                          | 28.42±0.14                                                          | 7.48±0.08                                                           | 4.50±0.06                                                               | 0.016±0.001                         |
| <b>Grimsby</b>                  |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T002374                         | 140.00±1.54                                                      | 53.75±0.29                                                          | 24.50±0.13                                                          | 7.07±0.07                                                           | 5.09±0.07                                                               | 0.019±0.001                         |
| T003188                         | 490.00±4.98                                                      | 62.81±0.60                                                          | 17.95±0.09                                                          | 6.48±0.07                                                           | 3.65±0.05                                                               | 0.014±0.001                         |
| T012287                         | 140.00±1.50                                                      | 28.68±0.16                                                          | 14.08±0.07                                                          | 3.36±0.03                                                           | 2.76±0.04                                                               | 0.014±0.001                         |
| <b>Whirlpool</b>                |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T008194                         | 180.00±1.85                                                      | 23.37±0.10                                                          | 18.34±0.07                                                          | 4.94±0.05                                                           | 3.51±0.04                                                               | 0.015±0.001                         |
| T009877                         | 130.00±1.36                                                      | 29.95±0.15                                                          | 17.79±0.08                                                          | 4.50±0.05                                                           | 3.45±0.04                                                               | 0.016±0.001                         |
| <b>Cobourg</b>                  |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T007357                         | 130.00±1.27                                                      | 66.08±0.28                                                          | 18.84±0.06                                                          | 4.67±0.04                                                           | 3.38±0.04                                                               | 0.023±0.001                         |
| T008358                         | 81.74±0.83                                                       | 11.54±0.11                                                          | 13.21±0.13                                                          | 4.04±0.04                                                           | 5.11±0.07                                                               | 0.033±0.002                         |
| <b>Sherman Fall</b>             |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T007793                         | 96.72±0.98                                                       | 11.61±0.11                                                          | 11.73±0.12                                                          | 2.83±0.03                                                           | 3.40±0.05                                                               | 0.023±0.001                         |
| T007954                         | 42.59±0.43                                                       | 12.08±0.05                                                          | 17.66±0.05                                                          | 5.23±0.05                                                           | 5.94±0.07                                                               | 0.043±0.002                         |
| T008057                         | 200.00±2.01                                                      | 30.25±0.29                                                          | 21.72±0.22                                                          | 4.64±0.05                                                           | 3.78±0.05                                                               | 0.030±0.001                         |
| <b>Coboconk</b>                 |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T0011596                        | 200.00±2.18                                                      | 78.95±0.42                                                          | 40.36±0.20                                                          | 9.52±0.10                                                           | 8.32±0.11                                                               | 0.033±0.001                         |
| T006907                         | 92.19±0.99                                                       | 52.15±0.27                                                          | 20.21±0.10                                                          | 4.58±0.05                                                           | 3.17±0.04                                                               | 0.026±0.001                         |
| T008313                         | 45.06±0.45                                                       | 147.06±0.54                                                         | 21.27±0.07                                                          | 8.75±0.08                                                           | 6.54±0.08                                                               | 0.052±0.003                         |
| <b>Gull River</b>               |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T008974                         | 130.00±1.31                                                      | 26.90±0.11                                                          | 23.45±0.08                                                          | 2.54±0.02                                                           | 2.48±0.03                                                               | 0.031±0.001                         |
| <b>Shadow Lake ? / Cambrian</b> |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T008532                         | 0.37±0.00                                                        | 16251.00±188.94                                                     | 900.00±9.94                                                         | 630.75±5.93                                                         | 233.96±2.93                                                             | 1.167±0.256                         |
| <b>Cambrian</b>                 |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| T007369                         | 86.43±0.87                                                       | 52.65±0.20                                                          | 17.97±0.06                                                          | 4.32±0.04                                                           | 3.11±0.04                                                               | 0.036±0.002                         |
| T007956                         | 160.00±1.62                                                      | 118.51±0.85                                                         | 32.37±0.15                                                          | 7.37±0.07                                                           | 6.09±0.08                                                               | 0.045±0.005                         |
| T008094                         | 180.00±1.85                                                      | 22.85±0.16                                                          | 23.90±0.11                                                          | 3.13±0.03                                                           | 4.48±0.06                                                               | 0.056±0.006                         |
| Wiley 29*                       |                                                                  |                                                                     |                                                                     |                                                                     |                                                                         |                                     |
| Innerkip 30*                    | 66.5                                                             | 110.83                                                              |                                                                     |                                                                     |                                                                         | 0.022                               |
| Innerkip 31*                    | 390                                                              | 51.32                                                               |                                                                     |                                                                     |                                                                         | 0.04                                |
| Innerkip 32*                    | 464                                                              | 100.87                                                              |                                                                     |                                                                     |                                                                         | 0.052                               |
| Innerkip 33*                    | 410                                                              | 39.81                                                               |                                                                     |                                                                     |                                                                         | 0.043                               |
| Clearville 34*                  | 430                                                              | 70.49                                                               |                                                                     |                                                                     |                                                                         | 0.059                               |
| Clearville 35*                  | 83                                                               | 166                                                                 |                                                                     |                                                                     |                                                                         | 0.025                               |
| Gobles 36*                      | 90.6                                                             | 151                                                                 |                                                                     |                                                                     |                                                                         | 0.023                               |
| Raleigh 37*                     | 250                                                              | 100                                                                 |                                                                     |                                                                     |                                                                         | 0.027                               |
| Raleigh 38*                     | 173.5                                                            | 433.75                                                              |                                                                     |                                                                     |                                                                         | 0.032                               |
| Arthur 39*                      | 317                                                              | 79.25                                                               |                                                                     |                                                                     |                                                                         | 0.033                               |
| North Gosfield 40*              | 152                                                              | 7600                                                                |                                                                     |                                                                     |                                                                         | 0.032                               |
| North Gosfield 41*              | 379                                                              | 111.47                                                              |                                                                     |                                                                     |                                                                         | 0.048                               |
| <b>Air</b>                      | 0.52                                                             | 16452.9                                                             | 930.26                                                              | 649.8                                                               | 233.94                                                                  | 1                                   |
| <b>Air saturated water +</b>    | 0.004                                                            | 131.85                                                              | 22.16                                                               | 27.64                                                               | 16.59                                                                   | 1                                   |

+Air saturated water is calculated from Henry's constants based on a temperature of 298 K, a salinity of 35‰, and a pressure of 1 atmosphere, and the concentrations are reported in cm<sup>3</sup> STP/cm<sup>3</sup> H<sub>2</sub>O \*Cambrian samples reported by Sherwood Lollar et al. (1994b).

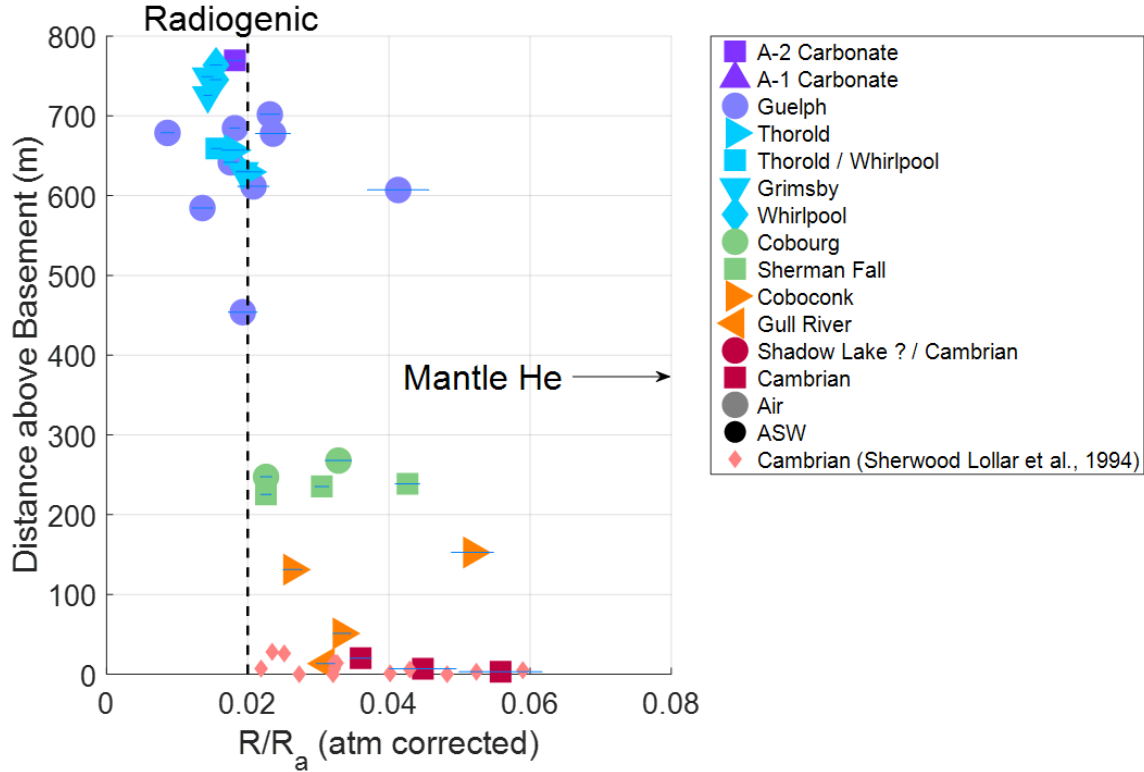
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**Table 5.3:** Ne, Ar, Kr and Xe isotopic ratios.

| Sample name                          | $^{20}\text{Ne}/^{22}\text{Ne}$ | $^{21}\text{Ne}/^{22}\text{Ne}$ | $^{40}\text{Ar}/^{36}\text{Ar}$ | $^{38}\text{Ar}/^{36}\text{Ar}$ | $^{86}\text{Kr}/^{84}\text{Kr}$ | $^{136}\text{Xe}/^{132}\text{Xe}$ |
|--------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------------------------------|
| <b>A-2 Carbonate</b>                 |                                 |                                 |                                 |                                 |                                 |                                   |
| T008636                              | 9.358±0.077                     | 0.0345±0.0004                   | 633±2                           | 0.188±0.001                     | 0.305±0.002                     | 0.330±0.003                       |
| <b>A-1 Carbonate</b>                 |                                 |                                 |                                 |                                 |                                 |                                   |
| T008633                              | 9.781±0.080                     | 0.0288±0.0003                   | 296±2                           | 0.189±0.001                     | 0.305±0.001                     | 0.329±0.003                       |
| T008634                              | 9.661±0.089                     | 0.0287±0.0003                   | 292±1                           | 0.193±0.001                     | 0.290±0.008                     | 0.330±0.002                       |
| <b>Guelph</b>                        |                                 |                                 |                                 |                                 |                                 |                                   |
| T002556                              | 9.547±0.088                     | 0.0432±0.0004                   | 1398±5                          | 0.179±0.002                     | 0.306±0.010                     | 0.331±0.003                       |
| T003899                              | 9.466±0.087                     | 0.0421±0.0004                   | 778±2                           | 0.198±0.001                     | 0.295±0.007                     | 0.330±0.002                       |
| T004918                              | 9.647±0.043                     | 0.0409±0.0004                   | 737±2                           | 0.188±0.001                     | 0.292±0.007                     | 0.332±0.002                       |
| T007415                              | 9.630±0.120                     | 0.0416±0.0004                   | 759±17                          | 0.174±0.007                     | 0.305±0.003                     | 0.330±0.004                       |
| T008468                              | 9.557±0.088                     | 0.0443±0.0005                   | 714±2                           | 0.199±0.001                     | 0.303±0.007                     | 0.330±0.002                       |
| T008657                              | 9.609±0.079                     | 0.0409±0.0004                   | 1026±13                         | 0.176±0.008                     | 0.306±0.003                     | 0.325±0.004                       |
| T009602                              | 9.338±0.077                     | 0.0299±0.0004                   | 793±3                           | 0.152±0.001                     | 0.303±0.001                     | 0.330±0.004                       |
| T010097                              | 9.407±0.087                     | 0.0401±0.0004                   | 1009±3                          | 0.192±0.001                     | 0.297±0.007                     | 0.334±0.002                       |
| T011560                              | 9.498±0.087                     | 0.0418±0.0004                   | 1192±3                          | 0.197±0.001                     | 0.296±0.007                     | 0.332±0.002                       |
| <b>Thorold</b>                       |                                 |                                 |                                 |                                 |                                 |                                   |
| T011554                              | 9.053±0.074                     | 0.0556±0.0006                   | 1124±6                          | 0.190±0.001                     | 0.304±0.001                     | 0.332±0.002                       |
| T011584                              | 8.969±0.074                     | 0.0537±0.0006                   | 863±3                           | 0.180±0.001                     | 0.307±0.001                     | 0.332±0.003                       |
| <b>Thorold / Whirlpool</b>           |                                 |                                 |                                 |                                 |                                 |                                   |
| T011280                              | 9.164±0.075                     | 0.0408±0.0006                   | 1245±5                          | 0.146±0.001                     | 0.304±0.001                     | 0.331±0.004                       |
| <b>Grimsby</b>                       |                                 |                                 |                                 |                                 |                                 |                                   |
| T002374                              | 9.176±0.075                     | 0.0400±0.0006                   | 1189±5                          | 0.158±0.001                     | 0.304±0.001                     | 0.330±0.004                       |
| T003188                              | 9.445±0.117                     | 0.0521±0.0006                   | 908±4                           | 0.155±0.001                     | 0.304±0.001                     | 0.332±0.004                       |
| T012287                              | 9.117±0.075                     | 0.0431±0.0006                   | 1824±12                         | 0.153±0.002                     | 0.305±0.001                     | 0.332±0.004                       |
| <b>Whirlpool</b>                     |                                 |                                 |                                 |                                 |                                 |                                   |
| T008194                              | 9.461±0.077                     | 0.0370±0.0005                   | 1433±6                          | 0.190±0.002                     | 0.306±0.002                     | 0.333±0.003                       |
| T009877                              | 9.078±0.074                     | 0.0438±0.0006                   | 1643±9                          | 0.160±0.002                     | 0.305±0.001                     | 0.331±0.004                       |
| <b>Cobourg</b>                       |                                 |                                 |                                 |                                 |                                 |                                   |
| T007357                              | 9.739±0.079                     | 0.0385±0.0004                   | 1065±4                          | 0.187±0.001                     | 0.304±0.002                     | 0.331±0.003                       |
| T008358                              | 9.429±0.117                     | 0.0497±0.0005                   | 1816±41                         | 0.165±0.015                     | 0.306±0.003                     | 0.333±0.005                       |
| <b>Sherman Fall</b>                  |                                 |                                 |                                 |                                 |                                 |                                   |
| T007793                              | 9.494±0.118                     | 0.0513±0.0005                   | 2106±48                         | 0.163±0.015                     | 0.305±0.003                     | 0.333±0.005                       |
| T007954                              | 9.325±0.076                     | 0.0463±0.0005                   | 1961±9                          | 0.188±0.002                     | 0.305±0.002                     | 0.336±0.003                       |
| T008057                              | 9.366±0.116                     | 0.0495±0.0005                   | 1675±38                         | 0.173±0.008                     | 0.305±0.003                     | 0.334±0.005                       |
| <b>Coboconk</b>                      |                                 |                                 |                                 |                                 |                                 |                                   |
| T0011596                             | 9.130±0.075                     | 0.0311±0.0004                   | 2080±10                         | 0.163±0.002                     | 0.313±0.001                     | 0.353±0.004                       |
| T006907                              | 9.155±0.075                     | 0.0303±0.0004                   | 1394±6                          | 0.165±0.001                     | 0.304±0.000                     | 0.331±0.004                       |
| T008313                              | 9.827±0.080                     | 0.0276±0.0004                   | 779±3                           | 0.146±0.002                     | 0.306±0.001                     | 0.335±0.003                       |
| <b>Gull River</b>                    |                                 |                                 |                                 |                                 |                                 |                                   |
| T008974                              | 9.016±0.074                     | 0.0479±0.0006                   | 2257±11                         | 0.181±0.002                     | 0.307±0.001                     | 0.344±0.004                       |
| <b>Shadow Lake ? / Cambrian</b>      |                                 |                                 |                                 |                                 |                                 |                                   |
| T008532                              | 9.820±0.090                     | 0.0296±0.0003                   | 300±1                           | 0.175±0.002                     | 0.306±0.001                     | 0.331±0.003                       |
| <b>Cambrian</b>                      |                                 |                                 |                                 |                                 |                                 |                                   |
| T007369                              | 9.599±0.079                     | 0.0329±0.0004                   | 1562±7                          | 0.172±0.002                     | 0.306±0.001                     | 0.335±0.003                       |
| T007956                              | 9.512±0.088                     | 0.0333±0.0003                   | 1331±4                          | 0.191±0.001                     | 0.296±0.007                     | 0.350±0.002                       |
| T008094                              | 9.087±0.084                     | 0.0523±0.0005                   | 4596±20                         | 0.157±0.002                     | 0.277±0.011                     | 0.344±0.002                       |
| <b>Air &amp; Air saturated water</b> | 9.8                             | 0.029                           | 296                             | 0.189                           | 0.305                           | 0.329                             |

+Air saturated water is calculated from Henry's constants based on a temperature of 298 K, a salinity of 35‰, and a pressure of 1 atmosphere.

2011; Holland et al., 2013; Warr et al., 2018). The production of  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$  are mainly through nucleogenic reactions with O and F, respectively (Yatsevich and Honda, 1997), and therefore the differences of neon isotopic endmembers ratios are interpreted to reflect the different O/F ratios within effective distance from alpha-emitters, e.g. U and Th (Ballentine and Burnard, 2002). Most samples from the Southwestern Ontario Basin have  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios scattering along the Post Archean Mixing Line (Kennedy et al., 1990; Ballentine and Burnard, 2002). The scattering from the line can be caused by mass fractionation. Alternatively, it



**Figure 5.2:** Air-normalised  $^3\text{He}/^4\text{He}$ , ( $R/R_a$ ) ratio plotted against the distance of the samples above the Precambrian basement. The three air-like samples (A1 carbonate and Shadow Lake/Cambrian samples) are not plotted on the graph.

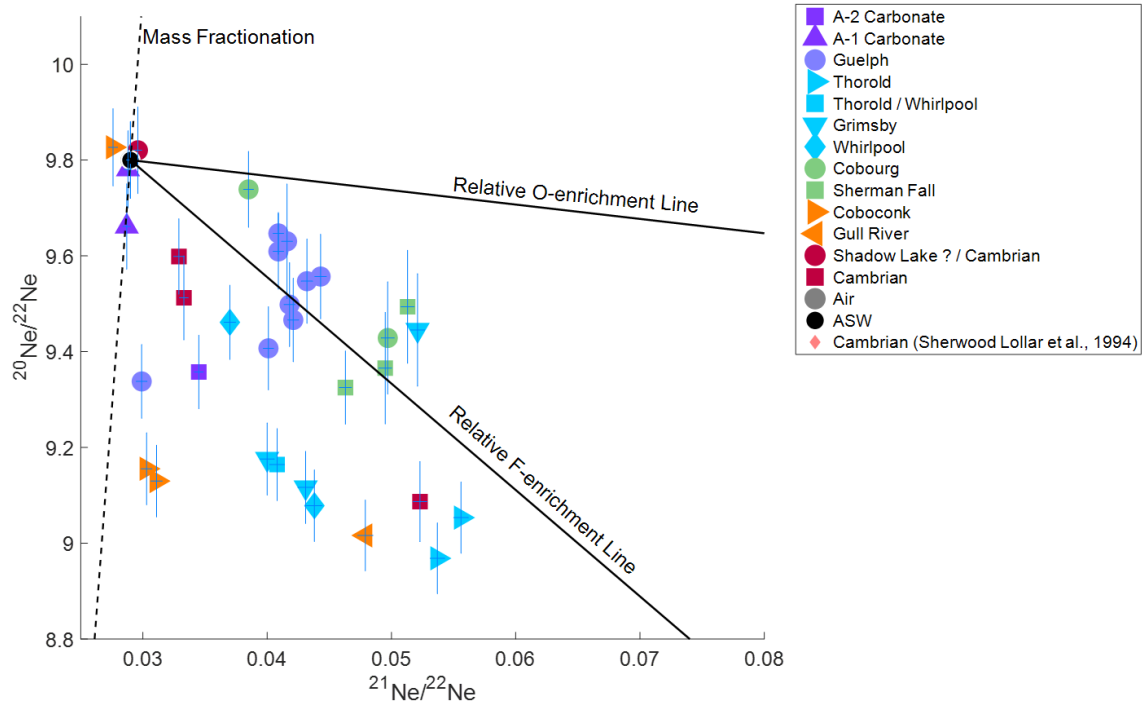
could indicate variance in mineral assemblage in the neon source rocks.

Excess  $^{21}\text{Ne}$  to the atmosphere,  $^{21}\text{Ne}^*$ , account for 2% (Shadow Lake) to 48% (Thorold) of the total  $^{21}\text{Ne}$ .  $^4\text{He}/^{21}\text{Ne}^*$ , ratios range from  $6.86 \times 10^6$  and  $157 \times 10^6$  compare with the theoretical crustal production ratio of  $17.1 \times 10^6$  Ballentine and Burnard, 2002. Silurian Grimsby samples closer to the Appalachian Basin show stronger percentage crustal contributions than Silurian Guelph samples adjacent to the Michigan Basin.

#### 5.5.4 Ar

$^{40}\text{Ar}$  concentrations range from  $1.2 \times 10^{-4} \text{ cm}^3 \text{ STP/cm}^3$  (Sherman Fall) to  $5.7 \times 10^{-4} \text{ cm}^3 \text{ STP/cm}^3$  (Guelph) and  $^{38}\text{Ar}/^{36}\text{Ar}$  ratios vary between 0.146 to 0.199. About half of the samples are within analytical uncertainty of the atmospheric  $^{38}\text{Ar}/^{36}\text{Ar}$  of 0.188, while the others show ratios considerably lower, suggesting non-negligible mass

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**Figure 5.3:**  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  plot. Most samples scatter along the post-Archean mixing line, or ‘the typical radiogenic crustal endmember’ mixing line plotted by Holland et al. (2013). The Post Archean Mixing Line has an endmember  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio of 0.475 (Kennedy et al., 1990). The Archean Neon Mixing Line has a higher endmember  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio of 3.3 (Lippmann-Pipke et al., 2011; Holland et al., 2013; Warr et al., 2018). The production of  $^{21}\text{Ne}$  and  $^{22}\text{Ne}$  are mainly through nucleogenic reactions with O and F, respectively (Yatsevich and Honda, 1997), and therefore the differences of neon isotopic endmembers ratios are interpreted reflecting the different O/F ratios within effective distance from alpha-emitters, e.g. U and Th (Ballentine and Burnard, 2002). Deviations from the lines could be the result of mass fractionation or differences in O/F values in the crust and sediments.

fractionation. No obvious trend can be found correlating with  $^{20}\text{Ne}/^{22}\text{Ne}$ .  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios vary between 633 (A2 Carbonate) and 4596 (Cambrian unit). The proportions of  $^{40}\text{Ar}^*$ , excess  $^{40}\text{Ar}$  to the atmosphere, to total  $^{40}\text{Ar}$ , vary between 53% (A2 Carbonate) and 94% (Cambrian). The  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios demonstrate a general trend towards higher values as the lithological unit gets older and deeper, i.e. closer to the basement.  $^4\text{He}_{\text{crust}}/^{40}\text{Ar}^*$  ratios range between 2.5 and 40.4 and compared to the average crustal production ratio of 5.7 (Ballentine and Burnard, 2002).

### 5.5.5 Kr and Xe

Sample T008974 (Gull River) have the minimum  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  of  $2.5 \times 10^{-9} \text{ cm}^3 \text{ STP/cm}^3$  and  $0.03 \times 10^{-10} \text{ cm}^3 \text{ STP/cm}^3$  respectively. T008468 (Guelph) have the maximum  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  of  $25.3 \times 10^{-9} \text{ cm}^3 \text{ STP/cm}^3$  and  $43.2 \times 10^{-10} \text{ cm}^3 \text{ STP/cm}^3$  respectively.

Most samples have  $^{86}\text{Kr}/^{84}\text{Kr}$  ratios comparable to the atmospheric ratio of 0.305, ranging from 0.303 to 0.307. Two Cambrian samples and four Guelph samples have ratios less than 0.300, and one Coboconk sample has a ratio of 0.313. The variation could be caused by mass-dependent fractionation, but no correlation can be observed compared to  $^{38}\text{Ar}/^{36}\text{Ar}$ . Except for those samples that demonstrate atmospheric  $^{86}\text{Kr}/^{84}\text{Kr}$  within uncertainties, the ratios of five samples are higher than 0.305, indicating a resolvable fissionogenic  $^{86}\text{Kr}$ , account for 0.2% (Cambrian) to 2.5% (Coboconk) of the total  $^{86}\text{Kr}$ .

$^{136}\text{Xe}/^{132}\text{Xe}$  values range from 0.330 (A2 carbonate) to 0.353 (Coboconk), with a majority of samples having ratios higher than the atmospheric value of 0.329), demonstrating a resolvable amount of fissionogenic  $^{136}\text{Xe}$  ( $^{136}\text{Xe}^*$ ), corresponding to 0.03% to 10% of the total  $^{136}\text{Xe}$ . The average  $^4\text{He}_{\text{crust}}/^{136}\text{Xe}^*$ ,  $^{21}\text{Ne}^*/^{136}\text{Xe}^*$  and  $^{40}\text{Ar}^*/^{136}\text{Xe}^*$  is  $(7.4 \pm 5.8) \times 10^8$ ,  $31.0 \pm 33.0$  and  $(7.1 \pm 4.9) \times 10^7$  respectively, comparing to the theoretical upper crust production ratios of  $3.6 \times 10^8$ , 14 and  $6.0 \times 10^7$  (Ballentine and Burnard, 2002), suggesting  $^{136}\text{Xe}$  less efficiently released from source minerals.

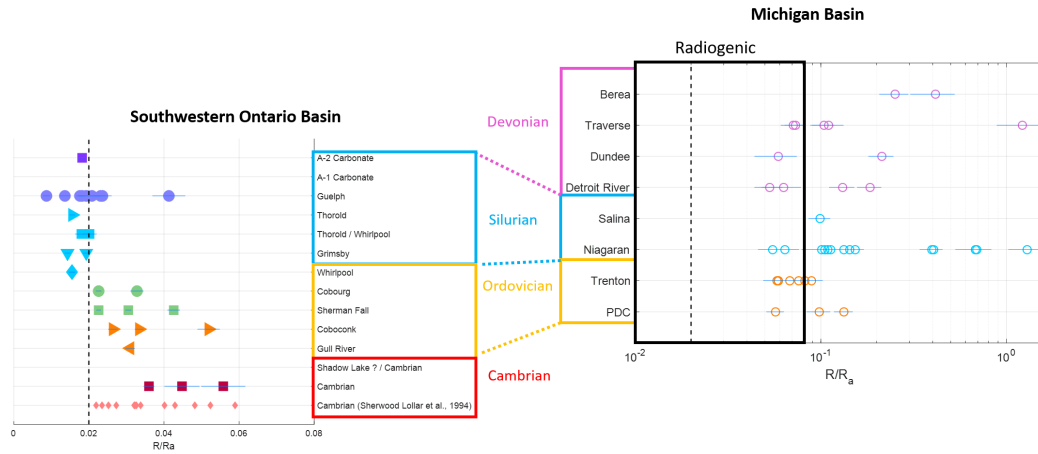
## 5.6 DISCUSSION

### 5.6.1 Distribution of $^3\text{He}/^4\text{He}$

Noble gas analysis has been reported for brine samples collected from eight geological units of Devonian, Silurian and Ordovician ages in the Michigan Basin (Castro et al., 2009; Ma et al., 2009b). The  $^3\text{He}/^4\text{He}$  values of all Michigan Basin samples are higher than the crustal production values of 0.01-0.02  $R_a$  (Figure 5.4), ranging from 0.053



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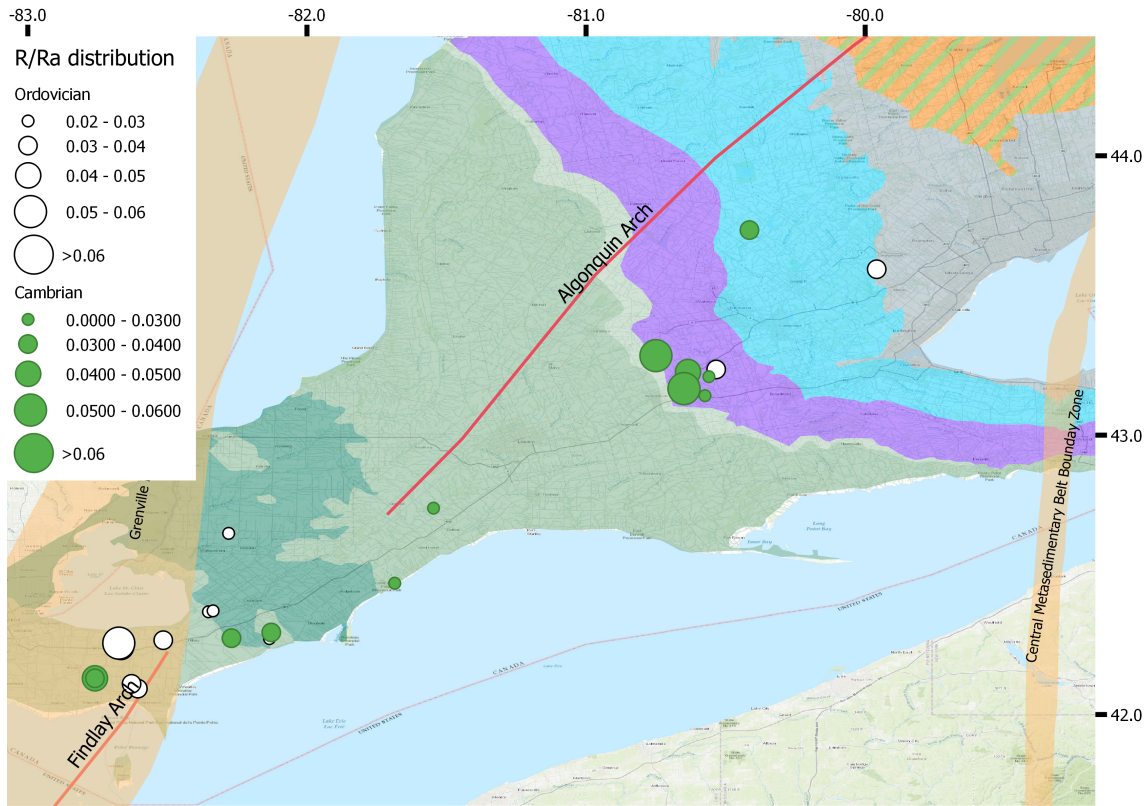


**Figure 5.4:** Comparison of  $R/R_a$  (air-normalised  $^3\text{He}/^4\text{He}$ ) of the Southwestern Ontario Basin and the Michigan Basin. Noble gas data from the Michigan Basin is reported by Castro et al. (2009).  $^3\text{He}/^4\text{He}$  ratios in the two basins are considerably different, indicating a regional scale intermediate to deep water flushing from the Michigan Basin to the Southwestern Ontario Basin during Pleistocene is not likely.

to 1.290  $R_a$ . The values are significantly higher than  $^3\text{He}/^4\text{He}$  values measured from geological units of the same ages in the Southwestern Ontario Basin, suggesting that it is unlikely that the intermediate and deep groundwater systems in the Southwestern Ontario Basin can be attributed to a regional scale flushing such as has been suggested for the Michigan Basin brine during Pleistocene.

Data for Southwestern Ontario for  $^3\text{He}/^4\text{He}$  shows increased values for deeper formations, closer to the basement, with one of the Cambrian samples reaching a value of 0.06  $R_a$ , overlapping with some of the lower ends of  $^3\text{He}/^4\text{He}$  in the Michigan Basin. If mass fractionation causes the variations of  $^3\text{He}/^4\text{He}$  ratios, it is then also expected to affect  $^{38}\text{Ar}/^{36}\text{Ar}$ , producing a negative correlation between  $^3\text{He}/^4\text{He}$  and  $^{38}\text{Ar}/^{36}\text{Ar}$ . However, the elevated  $^3\text{He}/^4\text{He}$  ratios are not observed for samples with low  $^{38}\text{Ar}/^{36}\text{Ar}$ , and therefore, simple mass fractionation can be ruled out as the cause. By plotting the  $^3\text{He}/^4\text{He}$  values of the Cambrian, Ordovician samples on the map, no apparent pattern or trend can be observed with the current data set, suggesting  $^3\text{He}$  is not likely to be supplied from a regional source, such as brine in the Michigan Basin (Figure 5.5).

The main pathway to produce  $^3\text{He}$  in the crust is through neutron capture by  $^6\text{Li}$ . The  $^3\text{He}/^4\text{He}$  production ratios for the Ordovician and Cambrian units were measured



**Figure 5.5:** The distribution of air-normalised  $^3\text{He}/^4\text{He}$  ratios (i.e.  $R/R_a$ ) of the Ordovician and Cambrian samples. No apparent trend or pattern can be seen suggesting  $^3\text{He}$  is not supplied from a point source.

and reported by Clark et al. (2013). The calculated average for Ordovician shale, Ordovician dolomite and Cambrian sandstone are 0.0174, 0.0031, 0.0013 respectively, lower than the observations in this thesis. The basement is considered the most likely cause of the elevated  $^3\text{He}/^4\text{He}$  values seen here, consistent with previous suggestions by Sherwood Lollar et al. (1994b). This indicates that there is likely He flux from the Precambrian basement to the overlying sedimentary units in the Southwestern Ontario Basin.

The  $^3\text{He}/^4\text{He}$  signatures do not support a Pleistocene regional scale deepwater migration between the basins. In the following sections of this chapter, the evolution and transport of noble gases are analysed in the context of static groundwater and a hydrogeologic system controlled by diffusion.

## 5. Quantifying and Modelling Basement He and Ar fluxes into Sedimentary Basins: A Case Study on the Southwestern Ontario Basin

### 5.6.2 Noble Gases in Groundwater

Concentrations of noble gases dissolved in groundwater prior to degassing can be calculated assuming  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  are atmospherically derived and the groundwater recharge conditions (temperature, pressure and salinity) are known. The atmosphere-derived noble gases in the produced gas phase sampled are assumed to be transported by and degassed from groundwater (e.g. Ballentine et al., 2002), although it should be noted that atmosphere-derived noble gases from anthropogenic activity can be a significant additional source in hydrocarbon systems associated with some enhanced hydrocarbon recovery techniques (Barry et al., 2018b).

Degassing of noble gases at phase equilibrium is governed by Henry's law. The degassing relationship between  $^4\text{He}$  and  $^{20}\text{Ne}$  can be estimated from Henry's constants following the equation (Ballentine et al., 2002),

$$\left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_{\text{gas}} = \left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_{\text{groundwater}} \times \frac{\frac{V_g}{V_l} + \frac{1}{K_{\text{Ne}}}}{\frac{V_g}{V_l} + \frac{1}{K_{\text{He}}}}, \quad (5.1)$$

where  $\left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_{\text{gas}}$  is the ratio measured in the gas samples;  $\left(\frac{^4\text{He}}{^{20}\text{Ne}}\right)_{\text{groundwater}}$  is the ratio of groundwater before degassing;  $\frac{V_g}{V_l}$  is the volume ratio between gas and water phases;  $K_{\text{He}}$  and  $K_{\text{Ne}}$  are Henry's constants for He and Ne respectively under degassing conditions. Elemental fractionation between  $^4\text{He}$  and  $^{20}\text{Ne}$  is small compared with, for example,  $^{40}\text{Ar}$  and  $^4\text{He}$ . This is because the solubility of He and Ne in water is similar under the range of pressure, temperature and salinities in the systems studied. The  $\text{CH}_4/^{36}\text{Ar}$  ratios observed provide another important observation. The  $\text{CH}_4/^{36}\text{Ar}$  can be calculated for a  $\text{CH}_4$  saturated air saturated water at the specific reservoir conditions (Elliot et al., 1993; Ballentine et al., 2002), and the ratio in the gas phase can be estimated for the initial gas phase  $\frac{V_g}{V_l} \rightarrow 0$  degassed from the water phase (Figure 5.6). Since all the samples demonstrate  $\text{CH}_4/^{36}\text{Ar}$  considerably higher than that this reference value, excess  $\text{CH}_4$  is required above that which can be supplied by degassing alone and  $\frac{V_g}{V_l}$  can be assumed to be higher than 0. Elemental fraction is the greatest when gas-water ratio approaches 0 but reduces

## 5.6. DISCUSSION

rapidly as gas volume increases. Therefore, the high  $\text{CH}_4/^{36}\text{Ar}$  provides observational evidence to simplify Equation 5.1 to:

$$\left(\frac{{}^4\text{He}}{{}^{20}\text{Ne}}\right)_{\text{gas}} = \left(\frac{{}^4\text{He}}{{}^{20}\text{Ne}}\right)_{\text{groundwater}} . \quad (5.2)$$

Groundwater  ${}^4\text{He}$  concentrations can, therefore, be calculated by rearranging Equation 5.2 to:

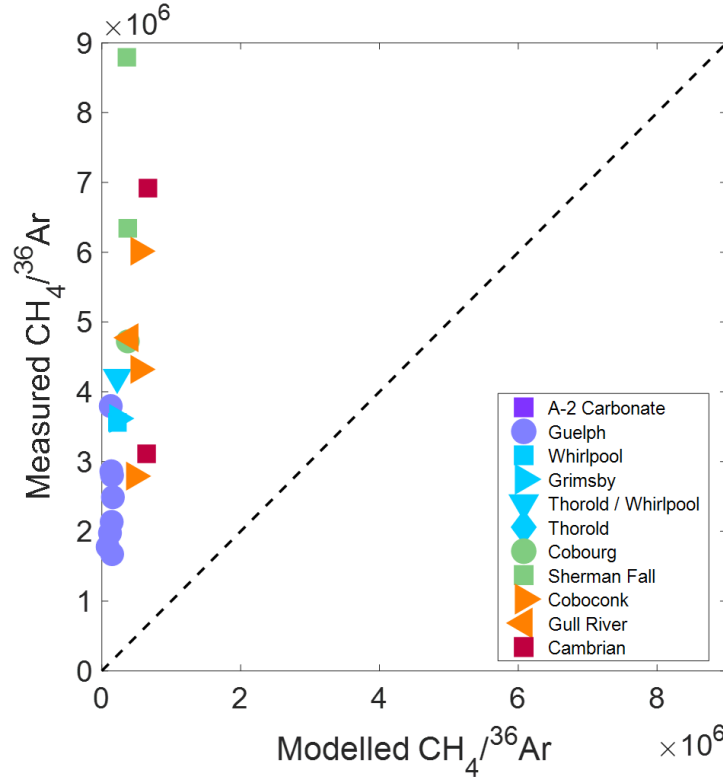
$${}^4\text{He}_{\text{groundwater}} = \left(\frac{{}^4\text{He}}{{}^{20}\text{Ne}}\right)_{\text{gas}} \times {}^{20}\text{Ne}_{\text{asw}} . \quad (5.3)$$

${}^4\text{He}_{\text{groundwater}}$  represents the concentration of  ${}^4\text{He}$  in groundwater with unit  $\text{cm}^3 \text{ STP}/\text{cm}^3 \text{ H}_2\text{O}$  and  ${}^{20}\text{Ne}_{\text{asw}}$  is the concentration of  ${}^{20}\text{Ne}$  in air saturated water. The equation inherently assumed that the groundwater is degassed after the accumulation of He. In closed systems, where gas is constantly in contact and equilibrating with the groundwater system, the time of degassing is not significant. However, in an open system, where gas exsolved is readily lost while He is accumulated in groundwater, more complicated models are required to estimate  ${}^4\text{He}_{\text{groundwater}}$ .

In this study, in situ pore water is considered to be originated from seawater (salinity 35 ‰) at 298 K under one atmospheric pressure ( $1.36 \times 10^{-7} \text{ cm}^3 {}^{20}\text{Ne} \text{ STP}/\text{H}_2\text{O}$ ). The exception to this is the Silurian units, which formed evaporites units due to cut off from open water. Connate water for Silurian strata is, therefore, more likely to have had elevated salinities, which could have contained as little as a third of the noble gases compared to typical seawater, which could have influenced the underlying units where the samples for this study is obtained.  ${}^{20}\text{Ne}$  concentration in groundwater will be further discussed later.

The calculation for  ${}^{40}\text{Ar}_{\text{groundwater}}$  takes into consideration mass fractionation. Assuming negligible production of  ${}^{38}\text{Ar}$  and  ${}^{36}\text{Ar}$  in crustal systems, deviations from

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**Figure 5.6:** Measured gas sample  $CH_4/^{36}Ar$  compared with the modelled  $CH_4/^{36}Ar$  of the initial gas-phase exsolved from the groundwater. The initial gas composition is calculated, assuming  $V_g/V_l$  approaches 0. The groundwater is considered to be saturated in  $CH_4$  where  $CH_4$  solubility is estimated for water at reservoir temperature, pressure and salinity following Duan and Mao (2006) and  $^{36}Ar$  concentration is calculated from 298K seawater recharged at 1 bar pressure.

the atmospheric ratio of 0.188 are assumed to be caused by mass fractionation, and  $^{40}Ar_{groundwater}$  can be calculated with the following equation:

$$^{40}Ar_{groundwater} = \left( \frac{^{38}Ar}{^{36}Ar} \right)_{groundwater} \times \frac{\sqrt{36/38}}{\sqrt{36/40}} \times \frac{\left( \frac{^{40}Ar}{^{36}Ar} \right)_{gas}}{\left( \frac{^{38}Ar}{^{36}Ar} \right)_{gas}} \times ^{36}Ar_{groundwater} . \quad (5.4)$$

Using Equations 5.3 and 5.4, the initial, undegassed  $^4He$  and  $^{40}Ar$  concentrations were derived and presented in Table 5.4.

### 5.6.3 Air Correction

A minor amount of air could be entrapped into the sample either through poor sample handling or as the result of water injection during hydrocarbon production (Chapter

## 5.6. DISCUSSION

**Table 5.4:** Calculated estimated He in groundwater prior to degassing and excess Ne and Ar and their elemental ratios.

| Sample name                | Before Air correction                                                                                 |                                                                                                          |                                           | After Air Correction                                                                                   |                                                                                                           |                                           |
|----------------------------|-------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|-------------------------------------------|--------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|-------------------------------------------|
|                            | $^4\text{He}_{\text{water}} \times 10^{-4}$<br>$\text{cm}^3 \text{ STP/cm}^3$<br>$\text{H}_2\text{O}$ | $^{40}\text{Ar}_{\text{water}} \times 10^{-4}$<br>$\text{cm}^3 \text{ STP/cm}^3$<br>$\text{H}_2\text{O}$ | Closed System<br>He Age (Ma) <sup>+</sup> | $^4\text{He}_{\text{water}} \times 10^{-4}$<br>$\text{cm}^3 \text{ STP/ cm}^3$<br>$\text{H}_2\text{O}$ | $^{40}\text{Ar}_{\text{water}} \times 10^{-4}$<br>$\text{cm}^3 \text{ STP/ cm}^3$<br>$\text{H}_2\text{O}$ | Closed System<br>He Age (Ma) <sup>+</sup> |
| <b>A-2 Carbonate</b>       |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T008636                    | 16.1 ± 1.02                                                                                           | 5.3 ± 0.04                                                                                               | 714 ± 277                                 | 25.9 ± 0.28                                                                                            | 2.9 ± 0.02                                                                                                | 1106 ± 412                                |
| <b>Guelph</b>              |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T002556                    | 43.6 ± 4.67                                                                                           | 14.2 ± 0.13                                                                                              | 902 ± 343                                 | 130.8 ± 1.66                                                                                           | 10.1 ± 0.09                                                                                               | 2330 ± 724                                |
| T003899                    | 30.2 ± 3.23                                                                                           | 7.1 ± 0.04                                                                                               | 639 ± 251                                 | 55.8 ± 0.69                                                                                            | 4.3 ± 0.03                                                                                                | 1130 ± 419                                |
| T004918                    | 83.4 ± 8.96                                                                                           | 7.1 ± 0.05                                                                                               | 1611 ± 562                                | 83.5 ± 1.12                                                                                            | 3.4 ± 0.02                                                                                                | 1613 ± 562                                |
| T007415                    | 65.0 ± 2.83                                                                                           | 7.9 ± 0.37                                                                                               | 1296 ± 471                                | 117.5 ± 1.63                                                                                           | 4.2 ± 0.11                                                                                                | 2141 ± 688                                |
| T008468                    | 20.8 ± 2.22                                                                                           | 6.5 ± 0.04                                                                                               | 446 ± 178                                 | 20.8 ± 0.25                                                                                            | 3.3 ± 0.02                                                                                                | 446 ± 178                                 |
| T008657                    | 63.3 ± 3.89                                                                                           | 10.5 ± 0.51                                                                                              | 1265 ± 462                                | 117.5 ± 1.47                                                                                           | 5.8 ± 0.10                                                                                                | 2142 ± 688                                |
| T009602                    | 24.9 ± 1.43                                                                                           | 9.5 ± 0.08                                                                                               | 531 ± 210                                 | 58.3 ± 0.70                                                                                            | 4.8 ± 0.04                                                                                                | 1175 ± 434                                |
| T010097                    | 75.5 ± 8.06                                                                                           | 9.5 ± 0.07                                                                                               | 1478 ± 525                                | 154.1 ± 1.88                                                                                           | 5.9 ± 0.04                                                                                                | 2636 ± 772                                |
| T011560                    | 15.2 ± 1.62                                                                                           | 11.0 ± 0.07                                                                                              | 330 ± 133                                 | 53.4 ± 0.65                                                                                            | 9.2 ± 0.07                                                                                                | 1086 ± 405                                |
| <b>Thorold</b>             |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T011554                    | 107.1 ± 9.90                                                                                          | 10.3 ± 0.09                                                                                              | 1175 ± 434                                | 107.3 ± 1.26                                                                                           | 5.1 ± 0.04                                                                                                | 1176 ± 434                                |
| T011584                    | 122.3 ± 11.31                                                                                         | 8.4 ± 0.07                                                                                               | 1322 ± 479                                | 122.4 ± 1.42                                                                                           | 3.9 ± 0.02                                                                                                | 1324 ± 480                                |
| <b>Thorold / Whirlpool</b> |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T011280                    | 45.3 ± 2.27                                                                                           | 14.8 ± 0.15                                                                                              | 526 ± 209                                 | 106.4 ± 1.31                                                                                           | 7.6 ± 0.06                                                                                                | 1167 ± 431                                |
| <b>Grimsby</b>             |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T002374                    | 41.3 ± 2.04                                                                                           | 13.1 ± 0.11                                                                                              | 680 ± 266                                 | 77.5 ± 0.95                                                                                            | 6.6 ± 0.05                                                                                                | 1217 ± 448                                |
| T003188                    | 123.7 ± 5.62                                                                                          | 10.2 ± 0.10                                                                                              | 1828 ± 619                                | 365.3 ± 5.08                                                                                           | 6.0 ± 0.05                                                                                                | 3917 ± 837                                |
| T012287                    | 77.4 ± 4.35                                                                                           | 20.8 ± 0.34                                                                                              | 1216 ± 447                                | 371.7 ± 4.52                                                                                           | 17.1 ± 0.17                                                                                               | 3953 ± 835                                |
| <b>Whirlpool</b>           |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T008194                    | 125.1 ± 6.61                                                                                          | 13.5 ± 0.13                                                                                              | 1232 ± 452                                | 128.5 ± 1.43                                                                                           | 6.7 ± 0.05                                                                                                | 1263 ± 461                                |
| T009877                    | 70.5 ± 3.99                                                                                           | 18.4 ± 0.23                                                                                              | 727 ± 282                                 | 153.6 ± 1.79                                                                                           | 10.1 ± 0.09                                                                                               | 1477 ± 525                                |
| <b>Cobourg</b>             |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T007357                    | 30.6 ± 1.17                                                                                           | 9.7 ± 0.07                                                                                               | 83 ± 34                                   | 145.9 ± 1.55                                                                                           | 9.1 ± 0.05                                                                                                | 385 ± 155                                 |
| T008358                    | 109.9 ± 6.57                                                                                          | 18.9 ± 1.83                                                                                              | 292 ± 119                                 | 110.3 ± 1.53                                                                                           | 8.0 ± 0.22                                                                                                | 293 ± 119                                 |
| <b>Sherman Fall</b>        |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T007793                    | 129.4 ± 4.95                                                                                          | 22.1 ± 2.11                                                                                              | 404 ± 165                                 | 165.5 ± 2.30                                                                                           | 10.1 ± 0.27                                                                                               | 514 ± 208                                 |
| T007954                    | 54.6 ± 2.46                                                                                           | 17.8 ± 0.18                                                                                              | 172 ± 71                                  | 54.9 ± 0.60                                                                                            | 8.7 ± 0.05                                                                                                | 173 ± 71                                  |
| T008057                    | 102.6 ± 3.89                                                                                          | 16.6 ± 0.86                                                                                              | 322 ± 132                                 | 155.1 ± 2.15                                                                                           | 8.5 ± 0.23                                                                                                | 483 ± 196                                 |
| <b>Coboconk</b>            |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T0011596                   | 39.0 ± 1.67                                                                                           | 21.7 ± 0.22                                                                                              | 136 ± 56                                  | 258.2 ± 3.13                                                                                           | 24.4 ± 0.21                                                                                               | 847 ± 325                                 |
| T006907                    | 27.2 ± 1.48                                                                                           | 14.3 ± 0.14                                                                                              | 95 ± 39                                   | 113.5 ± 1.36                                                                                           | 11.4 ± 0.09                                                                                               | 387 ± 156                                 |
| T008313 **                 | 4.7 ± 0.28                                                                                            | 9.0 ± 0.10                                                                                               | 17 ± 7                                    | n/a                                                                                                    | n/a                                                                                                       | n/a                                       |
| <b>Gull River</b>          |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T008974                    | 72.1 ± 3.30                                                                                           | 20.5 ± 0.24                                                                                              | 591 ± 233                                 | 129.7 ± 1.41                                                                                           | 11.9 ± 0.08                                                                                               | 1024 ± 385                                |
| <b>Cambrian</b>            |                                                                                                       |                                                                                                          |                                           |                                                                                                        |                                                                                                           |                                           |
| T007369                    | 25.0 ± 1.14                                                                                           | 15.3 ± 0.17                                                                                              | 363 ± 146                                 | 341.7 ± 3.70                                                                                           | 30.5 ± 0.20                                                                                               | 3422 ± 825                                |
| T007956                    | 20.5 ± 2.19                                                                                           | 11.7 ± 0.08                                                                                              | 300 ± 121                                 | 545.7 ± 6.77                                                                                           | 44.9 ± 0.32                                                                                               | 4382 ± 795                                |
| T008094                    | 119.4 ± 12.78                                                                                         | 49.3 ± 0.70                                                                                              | 1553 ± 543                                | 1238.4 ± 15.50                                                                                         | 78.8 ± 0.63                                                                                               | 5825 ± 632                                |
| Willey 29*                 | 9.1                                                                                                   |                                                                                                          | 135 ± 56                                  |                                                                                                        |                                                                                                           |                                           |
| Innerkip 30*               | 115.5                                                                                                 |                                                                                                          | 1508 ± 531                                |                                                                                                        |                                                                                                           |                                           |
| Innerkip 31*               | 69.8                                                                                                  |                                                                                                          | 962 ± 363                                 |                                                                                                        |                                                                                                           |                                           |
| Innerkip 32*               | 156.4                                                                                                 |                                                                                                          | 1947 ± 641                                |                                                                                                        |                                                                                                           |                                           |
| Innerkip 33*               | 92.5                                                                                                  |                                                                                                          | 1241 ± 452                                |                                                                                                        |                                                                                                           |                                           |
| Clearville 34*             | 7.6                                                                                                   |                                                                                                          | 113 ± 47                                  |                                                                                                        |                                                                                                           |                                           |
| Clearville 35*             | 9.1                                                                                                   |                                                                                                          | 135 ± 56                                  |                                                                                                        |                                                                                                           |                                           |
| Gobles 36*                 | 38                                                                                                    |                                                                                                          | 544 ± 215                                 |                                                                                                        |                                                                                                           |                                           |
| Raleigh 37*                | 6.1                                                                                                   |                                                                                                          | 90 ± 37                                   |                                                                                                        |                                                                                                           |                                           |
| Raleigh 38*                | 60.8                                                                                                  |                                                                                                          | 847 ± 324                                 |                                                                                                        |                                                                                                           |                                           |
| Arthur 39*                 | 0.3                                                                                                   |                                                                                                          | 5 ± 2                                     |                                                                                                        |                                                                                                           |                                           |
| North Gosfield 40*         | 51.6                                                                                                  |                                                                                                          | 727 ± 281                                 |                                                                                                        |                                                                                                           |                                           |
| North Gosfield 41*         | 53.2                                                                                                  |                                                                                                          | 748 ± 289                                 |                                                                                                        |                                                                                                           |                                           |

\*Cambrian samples reported by Sherwood Lollar et al. (1994); Not corrected for air component due to the lack of  $^{36}\text{Ar}$  information. The  $^4\text{He}$  concentration for these samples represent the lower limit

<sup>+</sup> The errors of closed system He ages are calculated assuming ±20% uncertainty with porosity and U and Th concentrations

\*\* T008313 is unresolvable with respect to the air component due to the high  $^{20}\text{Ne}/^{36}\text{Ar}$  ratio (Appendix C.1)

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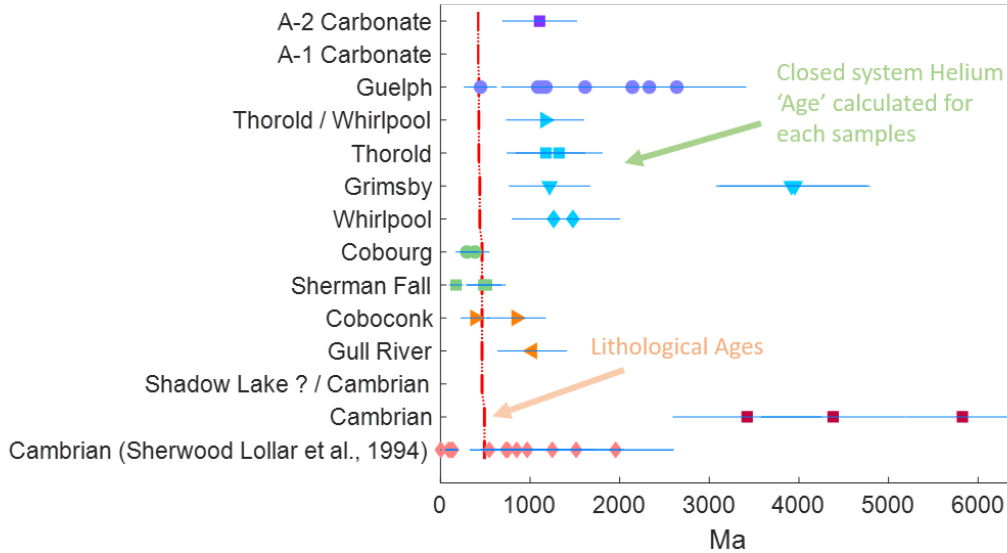
4, Barry et al. (2016)). Subsurface gas could have a considerably lower amount of atmospheric noble gases compared to the atmosphere, e.g.  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$ , depending on the gas-to-water ratio in the subsurface. The addition of an air component could have increased  $^{20}\text{Ne}$  concentration in the gas phase and result in an underestimation of  $^4\text{He}/^{20}\text{Ne}$  for the original pristine sample. However, due to the high concentration of  $^{40}\text{Ar}$  in the atmosphere, air entrapment usually causes a higher degree of  $^{40}\text{Ar}$  increase than that of  $^{36}\text{Ar}$  and results in an overestimation of the  $^{40}\text{Ar}/^{36}\text{Ar}$  in the gas phase. Consequently,  $^4\text{He}$  and  $^{40}\text{Ar}$  concentrations estimated from the air-entrapped  $^4\text{He}/^{20}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios (Equation 5.3 and 5.4) will be underestimated and overestimated, respectively. The amount of air addition can be observed by comparing  $^{20}\text{Ne}$  and  $^{20}\text{Ne}/^{36}\text{Ar}$  of the samples with those expected from subsurface exsolution models (Appendix C.1).  $^4\text{He}$  and  $^{40}\text{Ar}$  concentration after correction are presented in Table 5.4.

### **5.6.4 External Sources of He Evident from a Closed System Reference Model**

The estimated  $^4\text{He}$  concentration in the groundwater is the result of He gain and loss through geological time. In a closed system, taken to be a representative unit volume of rock in which there is neither  $^4\text{He}$  input or loss,  $^4\text{He}_{\text{crust}}$  is sourced entirely from radioactive decay of U and Th in the minerals within each lithological unit. Such production can be calculated with U and Th concentration in the rock matrix (Ballentine and Burnard, 2002). Research on sediment He production and porewater accumulation (e.g. Tolstikhin et al., 2011; Rufer et al., 2018) suggest the release efficiency of  $^4\text{He}$  from the minerals into the water occupying the porosity is close to 100%. The impact of 0 vs 100%  $^4\text{He}$  release efficiency, discussed later, has only a small effect on the derived basement fluxes and does not change the main conclusions drawn from this thesis. The closed system reference ages are the time required to accumulate the  $^4\text{He}$  concentration calculated to be in the porewater associated with 100% He release.

The closed system He reference age for each sample is calculated based on the U and Th concentrations and porosity estimated for the geological units (Appendix C.2) and

### Comparison of Closed System Helium 'Age' to Lithological Age



**Figure 5.7:** Closed system He ages, including samples reported by Sherwood Lollar et al. (1994b). The age refers to the time required for each sample to accumulate the measured amount of radiogenic He exclusively from in situ U, Th decay within the formation. U and Th concentrations are estimated from values reported by Clark et al. (2013). The errors are calculated assuming 20% uncertainty with porosity and U and Th concentrations. The red boxes are the age range of the lithological units, i.e. the theoretical ages for a closed system model. If the calculated He 'age' is older than the lithological one, an external source of He is required. Otherwise, a net He loss should be considered.

are presented in Table 5.6. The reference ages are compared with the lithological age and provide a test for the degree to which a system approaches the closed system reference model, i.e. a higher or lower He age compared to the lithological age indicates an external He source or He loss from the lithological unit respectively (Figure 5.7). Uncertainties of porosities and radioelement concentrations are not reported in the source literature (Sykes et al., 2011). The significance of uncertainties is demonstrated by imposing 20% errors of the parameters and is illustrated in the figure.

Multiple lithological units present wide ranges of the reference He ages obtained from different wells. Except for one Guelph sample with a He age of 446 Ma, most of the Early Silurian and Late Ordovician aged formations of A2 carbonate, Guelph, Thorold, Whirlpool and Grimsby have He ages ranging from 1086 to 3953 Ma after correction, considerably older than the lithological ages. Samples older than the lithological ages are also observed for the Gull River and Cambrian formations. The Cambrian samples



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measured in this study have closed system reference ages between 3422 Ma and 5825 Ma. These ages suggest that a closed system within situ radiogenic production as the sole source of He is insufficient to account for the accumulated He in the groundwater system, indicating an external supply of He. Some other formations have samples showing helium reference ages younger than the lithological ages, indicating net helium loss from the sedimentary units. The samples reported by Sherwood Lollar et al. (1994b) demonstrate helium ages ranging from 5 Ma to 1954 Ma, further suggest that the Cambrian sandstone unit is not a closed system but requires both net helium loss and external helium supply. The inhomogeneity of ages calculated from different wells of the same formation suggests restricted lateral migration of fluids.

Previous studies suggested a potential source of He from the underlying crystalline basement but to date, this hypothesis is based on limited data sets and helium data only Sherwood Lollar et al. (1994b). Precambrian  $^4\text{He}$  flux is also observed in a variety of basin system (Torgersen, 2010), including intracratonic basins, e.g. the Great Artesian Basin (Torgersen and Clarke, 1985), the Paris Basin (Castro et al., 1998a) and the Williston Basin (Chapter 4), or extensional basins, e.g. the Pannonian Basin (Oxburgh and O’Nions, 1987; Martel et al., 1989). If basement flux is controlled by crustal radiogenic production, the steady-state flux for continental crust can be calculated from average U and Th concentrations as  $1.47 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (Torgersen and Clarke, 1985). He flux can also be associated with tectonics and volcanisms (Oxburgh and O’Nions, 1987; Martel et al., 1989). If a basement He flux is considered the dominant mechanism of adding extra He into this system, cross-formational diffusive transport is required to explain the high He concentration observed in the shallower Silurian Units.

### **5.6.5 Parameters of 1-D Advection-Diffusion Modelling**

To simulate noble gas vertical profiles in the sedimentary column, a transport model was constructed that takes into consideration both the basement flux and cross-formational diffusive flux. Tailored 1D advection and diffusion models for each well

## 5.6. DISCUSSION

sampled were built. The model is initiated by considering the deepest stratigraphic unit to be deposited instantaneously and for the water-filled porosity of this lithological unit to contain groundwater containing seawater concentrations of radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$ . The model calculates the development of the  $^4\text{He}$  and  $^{40}\text{Ar}$  concentration in the porewater caused by in situ radiogenic ingrowth and a basement flux together with a solution of the diffusive advective transport equation (Equation 5.6.5) to determine the flux to the top surface and resulting concentration gradient. The second lithological unit is considered to be again instantaneously deposited above the first, initially with a porewater containing seawater  $^4\text{He}$  and  $^{40}\text{Ar}$  concentrations. Development of the  $^4\text{He}$  and  $^{40}\text{Ar}$  porewater concentration gradient in the new lithological unit is calculated as before, using in situ radiogenic production but now with the  $^4\text{He}$  and  $^{40}\text{Ar}$  fluxes supplied from the stratigraphic unit at its base. This process is repeated until all stratigraphic units in the basin column have been completed and the porewater  $^4\text{He}$  and  $^{40}\text{Ar}$  concentrations calculated for a simple system. Details within the model include taking into consideration the change in temperature during burial as a function of depth, as this affects the diffusion constants used as the structure evolves, and also a compaction component which changes the pore space with burial (and assumes that any fluid is laterally displaced and therefore does not change the developing concentration gradient).

The transport of the isotopes in the model is governed by the following equation,

$$\phi \frac{\delta C}{\delta t} + q \frac{\delta C}{\delta z} = D_e \frac{\delta^2 C}{\delta z^2} + \phi p, \quad (5.5)$$

where  $\phi$  is the rock porosity,  $C$  is the mass concentration of the solute and  $t$  is the time.  $z$  is the distance from the crystalline basement and  $p$  is the production rate per pore water volume.  $q$  is the average linear velocity, for diffusion-only scenarios,  $q=0$ .  $D_e$  is the effective diffusion coefficient and can be calculated from tortuosity  $\tau$  and diffusion coefficient in water  $D_0$ , following

$$D_e = \tau \times D_0. \quad (5.6)$$

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**Table 5.5:** The units used in the advection-diffusion model, with the harmonic mean of porosity and tortuosity calculated based on information reported by Sykes et al. (2011). Detailed information see Appendix C.2

| Unit                                  | porosity | Tortuosity | U (ppm) | Th (ppm) |
|---------------------------------------|----------|------------|---------|----------|
| Quaternary Drift                      | 0.2      | 0.12       | 1.54    | 2.13     |
| Eroded Unit                           | 0.1      | 0.12       | 3.75    | 11.6     |
| Devonian Shale                        | 0.1      | 0.12       | 3.75    | 11.6     |
| Devonian Dolostone                    | 0.077    | 0.094      | 0.6     | 0.78     |
| Upper Silurian Dolostone              | 0.056    | 0.28       | 0.6     | 0.78     |
| Silina G                              | 0.172    | 0.003      | 0.6     | 0.78     |
| Silina B to Silina F                  | 0.118    | 0.061      | 1.4     | 2.8      |
| Salina B Evaporite                    | 0.089    | 0.001      | 0.6     | 0.78     |
| Silina A2 Carbonate                   | 0.12     | 0.012      | 0.6     | 0.78     |
| Silina A2 Evaporite                   | 0.089    | 0.001      | 0.6     | 0.78     |
| Silina A1 Carbonate                   | 0.02     | 0.011      | 0.6     | 0.78     |
| Silina A1 Evaporite and Silina A0     | 0.012    | 0.003      | 0.6     | 0.78     |
| Guelph - Fossil Hill                  | 0.023    | 0.012      | 0.6     | 0.78     |
| Cabot Head                            | 0.116    | 0.032      | 1.54    | 2.13     |
| Manitoulin                            | 0.028    | 0.006      | 0.6     | 0.78     |
| Upper Ordovician Shale                | 0.061    | 0.01       | 2.8     | 7.74     |
| Middle Ordovician Limestone and Shale | 0.016    | 0.02       | 0.7     | 3        |
| Shadow Lake                           | 0.097    | 0.076      | 1.17    | 1.2      |
| Cambrian Sandstone                    | 0.071    | 0.13       | 1.17    | 1.2      |

The diffusion coefficient of noble gases in water changes with temperature and are modelled for the reservoir conditions after the Ohsumi and Horibe (1984) and Jähne et al. (1987).

The porosity and tortuosity values are summarised from a set of core samples drilled at the location marked in Figure 5.1 (Hobbs et al., 2011; Sykes et al., 2011). Formation isopach thickness for different wells was obtained from the Oil, Gas & Salt Resources Library (<http://www.ogsrlibrary.com/>). For wells not drilled to the Precambrian basement, isopach thickness below the drilling depth is extrapolated from the deep wells nearby (Appendix C.3). Information on detailed lithological logs is limited, and therefore, the 31 geological units are grouped into 19 units and calculated the harmonic mean for the various hydrogeological properties (Appendix C.2 and Table 5.5).

Burial curves reported for the Michigan Basin suggested a potential uniform subsidence rate until 300 Ma and a rapid uplift at 200 Ma (Wang et al., 1994; AECOM and Canada, 2011). Regionally-observed unconformity suggests about 1000 m of the Palaeozoic unit was eroded during the rapid uplift (AECOM and Canada, 2011). To factor in the missing Palaeozoic sections in this model, a 1000 m Palaeozoic sediment is added after the deposition of the currently preserved Devonian units, and then

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removed at 200 Ma. This eroded unit is assumed to share similar hydrogeological properties with the underlying Devonian unit.

The transport of  $^4\text{He}$  and  $^{40}\text{Ar}$  in groundwater is simulated with the models. The upper surface has constant air saturated-water concentrations of  $^4\text{He}$  and  $^{40}\text{Ar}$ . The concentration of  $^{40}\text{Ar}$  is modelled instead of  $^{40}\text{Ar}^*$ , because of the non-negligible proportion of atmospheric  $^{40}\text{Ar}$  in the groundwater system and that fluid transport does not discriminate the sources. Total  $^4\text{He}$  is used instead of crustal He for consistency. However, it is worth noting that atmospheric  $^4\text{He}$  is insignificant in this dataset, as demonstrated by the high  $^4\text{He}/^{20}\text{Ne}$  ratios. The initial concentration of  $^4\text{He}$  and  $^{40}\text{Ar}$  in the porewater is assumed to be the same as 298 K seawater.

As mentioned in the previous section, the release efficiency of  $^4\text{He}$  from the minerals into the water occupying the porosity is close to 100% (e.g. Rufer et al., 2018; Tolstikhin et al., 2011). The release of argon is, however, not as straight-forward. The main pathway to produce  $^{40}\text{Ar}$  is through electron capture by  $^{40}\text{K}$ . The diffusion of radiogenic  $^{40}\text{Ar}$  in the mineral grains to the mineral boundaries depends on time, temperature, grain size and mineral type (Mussett, 1969; Harrison et al., 1985). Assuming a typical thermal gradient of approximately  $20^\circ\text{C}/\text{km}$ , the temperature at the Precambrian and Palaeozoic interface in Southwestern Ontario Basin is less than  $50^\circ\text{C}$  higher than the surface temperature, since the sedimentary sequence is less than 2500 m considering the thickness of the eroded sediments. Such a temperature range is lower than the closure temperatures of Ar for illite, biotite or muscovite (approximate  $250^\circ\text{C}$  and  $350^\circ\text{C}$ ) (Harrison et al., 1985; Harrison et al., 2009; Verdel et al., 2012). Elevated temperatures have been inferred based on heat anomalies discovered from dolomite, altered feldspar,  $\text{CH}_4$  isotopes and clumped isotopes (Sherwood Lollar et al., 1994b; K. Ziegler and Longstaffe, 2000a; Coniglio et al., 2003; Haeri-Ardakani et al., 2013; Giunta et al., 2019). Though the reported range of homogenised temperature is still lower than the closure temperature of Ar, but the time length of such an event is unknown and could have a significant impact. For example, assuming spherical grains  $1\text{ }\mu\text{m}$  (clay size), the exposure of minerals

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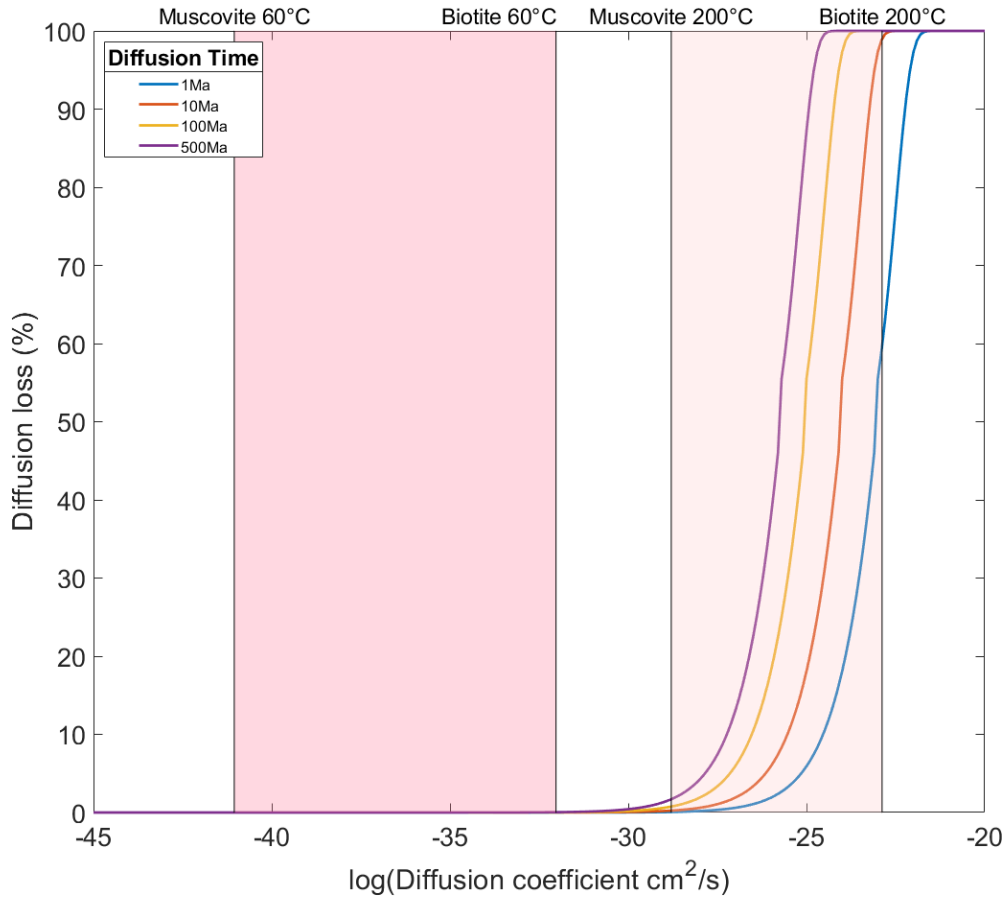
at 200°C for 10 Ma can result in the release of both a tiny fraction of produced Ar from muscovite and an almost complete release from biotite (Figure 5.8). Due to limited information available on the time scale of the recorded heat anomaly and mineral combination of the grains, the additional  $^{40}\text{Ar}$  produced in situ within the sedimentary units is considered minor in the reference model.

In this case, the high  $^{40}\text{Ar}/^{36}\text{Ar}$  for any individual sample indicates an external  $^{40}\text{Ar}$  flux, either being transported horizontally or vertically.  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios demonstrate a general trend to higher values towards the basement, which, similarly to helium concentrations, is consistent with a vertical transport from the basement.

It is also noted that Ne isotopes in the subsurface are dominated by three components (atmosphere, crust and mass fractionation) compared to two for helium, that there is considerable scatter in the data set which makes it hard to draw a conclusion from this comparison.

#### **5.6.6 Diffusive Transport of $^{20}\text{Ne}$**

As mentioned in the previous section, the Silurian evaporite units are deposited with high water salinity, which would reduce  $^{20}\text{Ne}$  concentration in the air saturated water. Since groundwater  $^{20}\text{Ne}$  concentration is an important factor in estimating  $^4\text{He}$  concentration, diffusive transport efficiency of  $^{20}\text{Ne}$  is investigated and demonstrated in Figure 5.9. The initial concentration of the Salina Groups is set as  $4.58 \times 10^{-8} \text{ cm}^3 \text{ STP/cm}^3 \text{ H}_2\text{O}$ , which is the concentration for air saturated water at 298K, 1 atm and 200% salinity, to reflect the high water salinity. The dominant concentration units over geological time progressively overwrite any initial concentration differences. It is, therefore, reasonable to use the typical seawater  $^{20}\text{Ne}$  concentration to estimate  $^4\text{He}_{\text{groundwater}}$ .

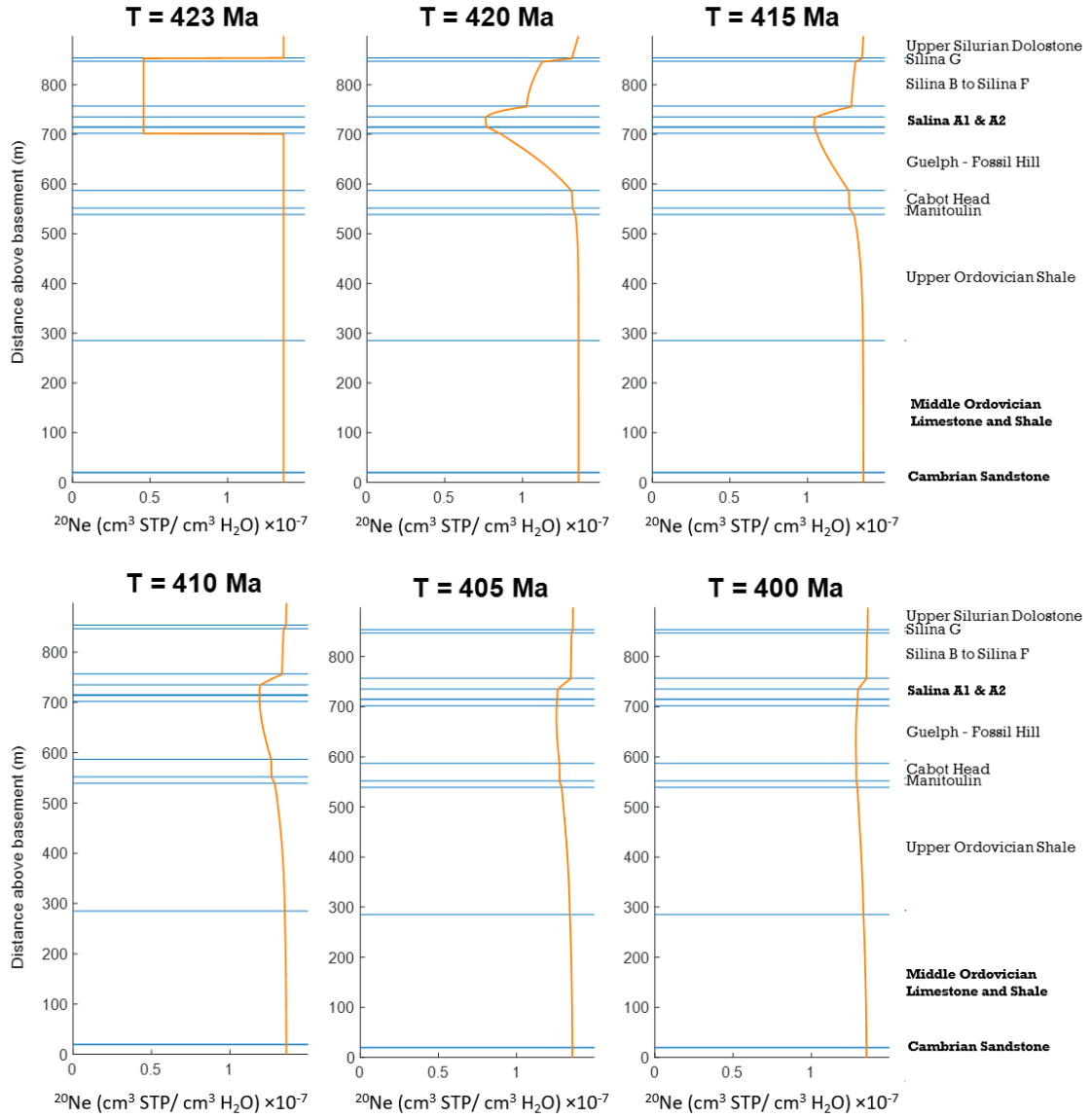


**Figure 5.8:** *Ar loss from the minerals assuming spherical particles. The diffusion coefficients of Muscovite and Biotite at 60°C and 200°C are plotted. Under 60°C no Ar is escaped from the mineral event after 500 Ma. Under 200°C, Biotite can release all its Ar within 10 Ma, but the release from muscovite is negligible.*

### 5.6.7 Basement <sup>4</sup>He and <sup>40</sup>Ar Flux Map

In a diffusion-based model, the concentration gradients of <sup>4</sup>He and <sup>40</sup>Ar are the dominant driving force for the migration of dissolved noble gases. The concentrations of <sup>4</sup>He and <sup>40</sup>Ar at different sites and lithological units are, therefore, the result of the different basement flux. An iterative process was implemented to find the optimum basement <sup>4</sup>He and <sup>40</sup>Ar flux value to fit the observed <sup>4</sup>He and <sup>40</sup>Ar concentrations in groundwater for each well. The iteration starts with a reasonable estimation of the basement flux. If the vertical profiles generated cannot reproduce the groundwater concentrations estimated from the samples within  $\pm 5\%$  error, the basement flux value

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**Figure 5.9:** Diffusive profile of  $^{20}\text{Ne}$ . The initial concentration of the Salina Groups is set as  $4.58 \times 10^{-8} \text{ cm}^3 \text{ STP} / \text{cm}^3 \text{ H}_2\text{O}$ , (air saturated water at 298K, 1 atm and 200‰ salinity) and the other units are set as  $1.37 \times 10^{-7} \text{ cm}^3 \text{ STP} / \text{cm}^3 \text{ H}_2\text{O}$ , (air saturated water at 298K, 1 atm and 35‰ salinity). Over geological time, diffusion of elements is expected to progressively overwrite any initial concentration differences.

## 5.6. DISCUSSION

**Table 5.6:**  $^4\text{He}$  and  $^{40}\text{Ar}$  basement flux after air correction.

| Sample name                | $^4\text{He}$ flux $\times 10^{-6}$ mol/m <sup>2</sup> /yr | $^4\text{He}$ flux $\times 10^{-6}$ mol/m <sup>2</sup> /yr<br>(zero in situ production) | $^{40}\text{Ar} \times 10^{-8}$ flux mol/m <sup>2</sup> /yr |
|----------------------------|------------------------------------------------------------|-----------------------------------------------------------------------------------------|-------------------------------------------------------------|
| <b>A-2 Carbonate</b>       |                                                            |                                                                                         |                                                             |
| T008636                    | 0.36                                                       | 0.4                                                                                     | 0.5                                                         |
| <b>Guelph</b>              |                                                            |                                                                                         |                                                             |
| T002556                    | 0.2                                                        | 0.23                                                                                    | 0.73                                                        |
| T003899                    | 0.1                                                        | 0.13                                                                                    | 0.23                                                        |
| T004918                    | 0.09                                                       | 0.12                                                                                    | 0.09                                                        |
| T007415                    | 0.16                                                       | 0.19                                                                                    | 0.19                                                        |
| T008468                    | 0.01                                                       | 0.04                                                                                    | 0.13                                                        |
| T008657                    | 0.18                                                       | 0.22                                                                                    | 0.38                                                        |
| T009602                    | 0.06                                                       | 0.09                                                                                    | 0.23                                                        |
| T010097                    | 0.24                                                       | 0.27                                                                                    | 0.38                                                        |
| T011560                    | 0.06                                                       | 0.1                                                                                     | 0.65                                                        |
| <b>Thorold</b>             |                                                            |                                                                                         |                                                             |
| T011554                    | 0.21                                                       | 0.25                                                                                    | 0.46                                                        |
| T011584                    | 0.26                                                       | 0.3                                                                                     | 0.34                                                        |
| <b>Thorold / Whirlpool</b> |                                                            |                                                                                         |                                                             |
| T011280                    | 0.2                                                        | 0.24                                                                                    | 0.74                                                        |
| <b>Grimsby</b>             |                                                            |                                                                                         |                                                             |
| T002374                    | 0.11                                                       | 0.15                                                                                    | 0.53                                                        |
| T003188                    | 0.64                                                       | 0.69                                                                                    | 0.5                                                         |
| T012287                    | 1.3                                                        | 1.34                                                                                    | 2.87                                                        |
| <b>Whirlpool</b>           |                                                            |                                                                                         |                                                             |
| T008194                    | 0.46                                                       | 0.51                                                                                    | 1.04                                                        |
| T009877                    | 0.52                                                       | 0.57                                                                                    | 1.61                                                        |
| <b>Cobourg</b>             |                                                            |                                                                                         |                                                             |
| T007357                    | 0.11                                                       | 0.14                                                                                    | 0.32                                                        |
| T008358                    | 0.06                                                       | 0.09                                                                                    | 0.26                                                        |
| <b>Sherman Fall</b>        |                                                            |                                                                                         |                                                             |
| T007793                    | 0.11                                                       | 0.14                                                                                    | 0.32                                                        |
| T007954                    | 0.01                                                       | 0.04                                                                                    | 0.26                                                        |
| T008057                    | 0.08                                                       | 0.11                                                                                    | 0.25                                                        |
| <b>Coboconk</b>            |                                                            |                                                                                         |                                                             |
| T0011596                   | 0.25                                                       | 0.27                                                                                    | 0.99                                                        |
| T006907                    | 0.08                                                       | 0.1                                                                                     | 0.35                                                        |
| T008313                    | <0                                                         | 0                                                                                       | 0.05                                                        |
| <b>Gull River</b>          |                                                            |                                                                                         |                                                             |
| T008974                    | 0.07                                                       | 0.09                                                                                    | 0.32                                                        |
| <b>Cambrian</b>            |                                                            |                                                                                         |                                                             |
| T007369                    | 0.22                                                       | 0.24                                                                                    | 0.87                                                        |
| T007956                    | 0.33                                                       | 0.35                                                                                    | 1.24                                                        |
| T008094                    | 0.77                                                       | 0.79                                                                                    | 2.2                                                         |

The errors of closed system He ages are calculated assuming  $\pm 20\%$  uncertainty with porosity and U and Th concentrations.

Shaded samples are located on the south-east of the Algonquin arch, closer to the Appalachian Basin, and unshaded samples are located on the north-west of the arch, closer to the Michigan Basin.

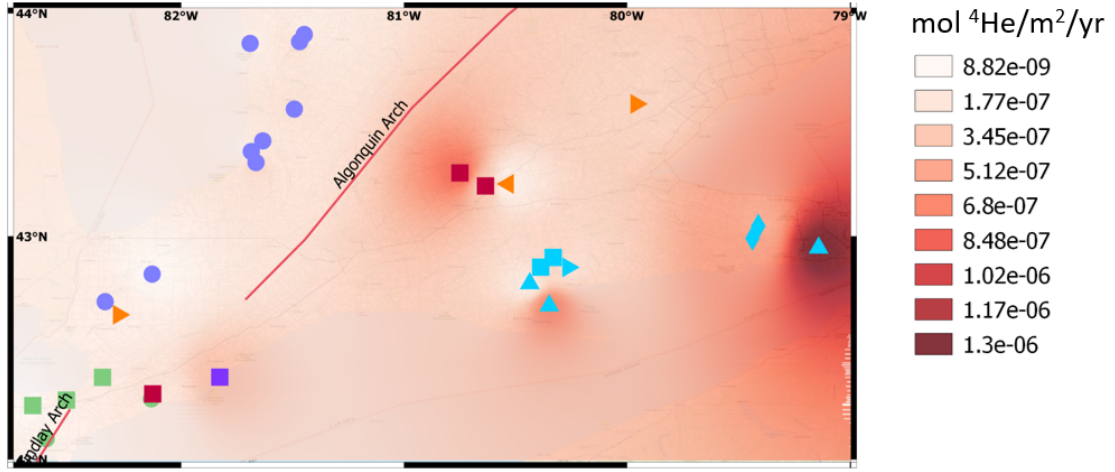
increases or decreases correspondingly. The new vertical profiles are then generated to compare with the observation. The process repeats until the simulated concentration of the reference diffusive model is consistent with the observation within 5% error. The modelled  $^4\text{He}$  and  $^{40}\text{Ar}$  flux are presented in Table 5.6 and interpolated with the Inverse Distance Weighting method to generate  $^4\text{He}$  and  $^{40}\text{Ar}$  basement flux map (Figure 5.10).

The  $^4\text{He}$  flux estimates of this data set range between  $0.01\text{--}1.30 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  with an average of  $0.25 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ . The  $^{40}\text{Ar}$  flux estimates vary between  $0.05\text{--}2.87 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$  with an average of  $0.63 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$ . The basement fluxes estimated can be grouped by their localities with respect to the

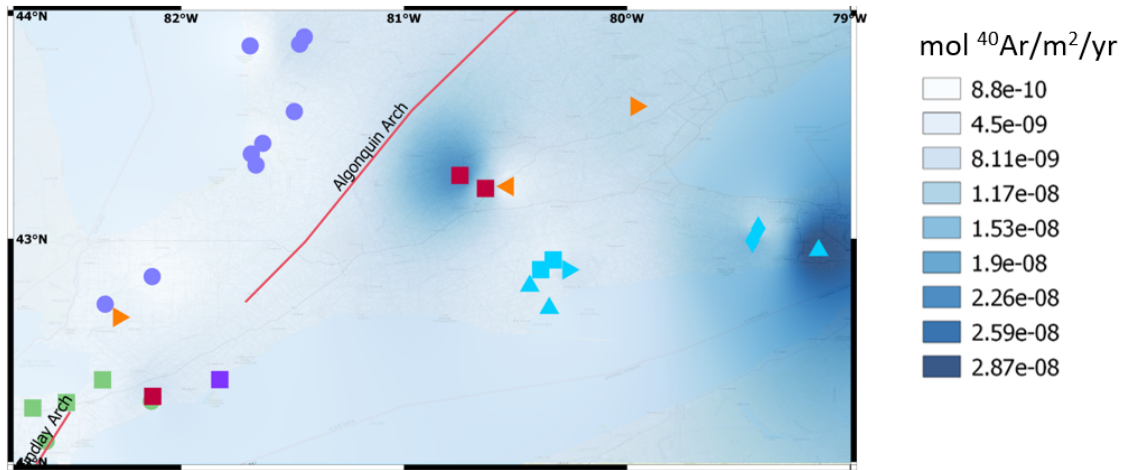


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(a)  $^4\text{He}$  flux map



(b)  $^{40}\text{Ar}$  flux map



**Figure 5.10:** Basement flux map of (a)  $^4\text{He}$  and (b)  $^{40}\text{Ar}$ .

Algonquin Arch, one closer to the Appalachian Basin with average fluxes of  $0.39 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (ranging from  $0.07$  to  $1.30 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ ) and  $0.97 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$  (ranging from  $0.32$  to  $0.32 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$ ), and one closer to the Michigan Basin has average fluxes of  $0.10 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (ranging from  $0.01$  to  $0.24 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ ) and  $0.32 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$  (ranging from  $0.09$  to  $0.73 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$ ). The Appalachian Basin side has fluxes more than three times higher than the other side. The two groups demonstrate statistical differences at a 5% significance level by Student T-test.

## 5.6. DISCUSSION

The low  $^4\text{He}$  flux could be caused by an inefficient He release from the mineral phase. In an extreme scenario where no He is released from the sedimentary units, the basement flux is required to increase by  $0.02\text{--}0.04 \times 10^{-6} \text{ mol/m}^2/\text{yr}$ . The change is insignificant and the general pattern of flux distribution in the basin remains unchanged.

Since existing studies generally suggest a static water body, the flux differences across the basin are most likely caused by the inhomogeneity across crystalline basement: The high basement flux could be associated with higher basement production rates due to higher radioelements concentrations or more efficient noble gas release from minerals and transport through the crystalline basement especially to the southeast of the Algonquin Arch. Radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$  are produced by different parent elements; therefore, the similar flux distribution observed for both elements favours the explanation of noble gas release and transport efficiency.

The high apparent flux could also be the result of horizontal migration of subsurface fluids enriched in radiogenic noble gases, but requires additional studies to provide other lines of evidence.

### 5.6.8 Mantle and Crustal $^4\text{He}$ Flux

Over geological time, terrestrial  $^4\text{He}$  is almost entirely sourced from  $\alpha$ -decay of U and Th (Graham, 2002). Such reactions are accompanied by heat generation, suggesting that the  $^4\text{He}/\text{Heat}$  production ratios are relatively consistent through the crust and mantle.  $^3\text{He}$  is, however, almost entirely primordial, with well-constrained high  $^3\text{He}/^4\text{He}$  ratios from the mantle, distinct from crustal production (Graham, 2002 and reference therein). In a tight crustal environment, where conduction and diffusion are the dominant transport mechanism for heat and He respectively from the mantle and through the crust, heat dissipation is 1000 times greater than the speed of He diffusion, resulting in the decoupling between the two. Therefore, high  $^3\text{He}/^4\text{He}$  ratios are associated with high heat flow, but, as a result of He-heat decoupling and the

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accumulation of crustal  $^4\text{He}$  with time, high heat flow does not necessarily appear with high  $^3\text{He}/^4\text{He}$  ratios (Ballentine and Burnard, 2002).

The Williston Basin is estimated to have a basement flux between  $0.8\text{--}1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (Chapter 4). The  $^4\text{He}$  flux in the Southwestern Ontario Basin is resolvably lower, ranging from this work, between  $0.1\text{--}0.4 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ . The most recent significant tectonic events in the Williston Basin are during the early Proterozoic Trans-Hudson Orogenic Belt, but reactivation of faults during the Palaeozoic and Laramide (Late Cretaceous to Eocene) have been reported (Kent and Christopher, 1994; Gibson, 1995). The Southwestern Ontario Basin has been affected by orogenic events during the Late Ordovician (Taconic) and Carboniferous (Alleghannian) and is currently sitting in a passive tectonic margin and experiencing an extensional stress field (AECOM and Canada, 2011). The higher  $^4\text{He}$  flux in the Williston Basin is accompanied with higher  $^3\text{He}/^4\text{He}$  ( $0.08\text{--}0.36 R_a$ ) for the majority of the samples, substantially higher than the  $^3\text{He}/^4\text{He}$  ( $0.008\text{--}0.06 R_a$ ) observed in the Southwestern Ontario Basin samples.

Modern thermal fluxes ranging from  $58.6$  to  $92 \text{ mW}/\text{m}^2$  were reported on the American side of the Williston Basin (Blackwell, 1969; Combs and Simmons, 1973). Such results were calculated using thermal conductivity, and the values were later questioned by (Gosnold et al., 2012). They used iterative numerical modelling and lowered the estimations to approximately  $44.6\text{--}51.3 \text{ mW}/\text{m}^2$  (Gosnold et al., 2012). More recent drilling and temperature logging in the basin updated the heat flux estimation to  $60 \text{ mW}/\text{m}^2$  in the centre of the basin and approximately  $52 \text{ mW}/\text{m}^2$  closer to the edge of the basin (McDonald et al., 2015). Other deep wells to Precambrian basement indicate that flux ranges between  $50 \text{ mW}/\text{m}^2$  and  $86 \text{ mW}/\text{m}^2$  observed in the deepest Deadwood formation of the Williston Basin in North Dakota (Ricker, 2015). Limited heat flux measurement is published for the Southwestern Ontario Basin. A study by Jessop et al. (1984) reported values approximately  $38$  to  $50 \text{ mW}/\text{m}^2$ . The basement heat flux estimates for the Williston ( $50\text{--}90 \text{ mW}/\text{m}^2$ ) are higher than those for the Southwestern Ontario Basins ( $40\text{--}50 \text{ mW}/\text{m}^2$ ), roughly consistent with the estimated basement  $^4\text{He}$  flux and observed  $^3\text{He}/^4\text{He}$  ratios in the two basins.

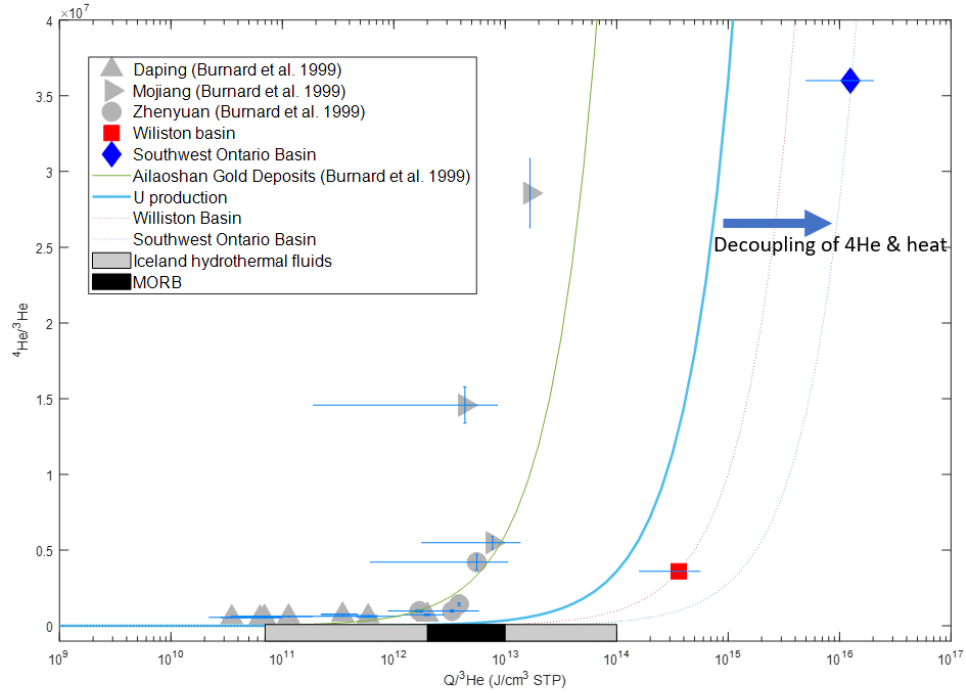
## 5.6. DISCUSSION

Though poorly correlated, the  $^3\text{He}/^4\text{He}$  ratios can be calculated from conductive heat flux following the plot reported by Polyak and Tolstikhin (1985). However, such a relationship is not universal; for example, in permeable systems controlled by advective flow, heat and He are likely transported at similar rates Bach et al., 1999. (Burnard et al., 1999) demonstrated a relationship between He isotopic ratios and heat flux from fluid inclusions collected from a gold deposit hosted on a major Eocene extensional fault. Noble gases there demonstrated a mixing between a mantle-derived magmatic fluid and modern groundwater like fluids. The homogenization temperatures of the coexisting quartz enabled estimation of associated heat flux. The authors observed samples with high and variable  $^3\text{He}/\text{heat}$  (denoted as  $^3\text{He}/Q$ ) ratios ( $\sim 30 \times 10^{-12} \text{ cm}^3 \text{ STP J}^{-1}$ ) and suggested a direct injection of mantle-derived volatiles. The other samples without direct mixing demonstrated  $^3\text{He}/\text{heat}$  ratio of less than  $0.6 \times 10^{-12} \text{ cm}^3 \text{ STP J}^{-1}$ .

Following the correlation reported by Polyak and Tolstikhin (1985), a conductive heat flux of 40, 50 and 60  $\text{mW/m}^2$  correspond to  $^3\text{He}/^4\text{He}$  ratios of 0.01, 0.05 and 0.19  $R_a$  respectively, which are intriguingly close to the observations from the two basins investigated in this thesis. The relationship between  $^3\text{He}/^4\text{He}$  and heat suggests that the two basins both have hydrogeologically tight basement materials, where advection is negligible, and diffusion is the dominant control on noble gas flux.

The heat to He ratios in the Williston and the Southwestern Ontario Basins can be calculated with basement  $^4\text{He}$  flux of  $0.8\text{-}1.6 \times 10^{-6} \text{ mol } ^4\text{He/m}^2/\text{yr}$  and  $0.1\text{-}0.4 \times 10^{-6} \text{ mol } ^4\text{He/m}^2$ , and average  $^3\text{He}/^4\text{He}$  ratios of 0.2  $R_a$  and 0.02  $R_a$ , respectively. The estimated  $Q/^3\text{He}$  in the Williston Basin is  $1.6\text{-}5.6 \times 10^{14} \text{ J/cm}^3 \text{ STP}$  while in the Southwestern Ontario Basin, the values are at least one magnitude higher of  $0.5\text{-}2.0 \times 10^{16} \text{ J/cm}^3 \text{ STP}$ . The heat flux represents the sum of that from the crust and mantle. These values can be compared with heat/He relationship observed at the gold deposit and the theoretical production of U decay, which represent an estimation of a magmatic fluid input and an approximation of the heat and helium production in the crustal environment respectively (Burnard et al., 1999). The differences suggest

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**Figure 5.11:** Figure 5.11. Heat/ $^3\text{He}$  vs  $^4\text{He}/^3\text{He}$ . Daping, Mojiang and Zhenyuan samples are from Ailaoshan gold deposit (Burnard et al., 1999). Data for the Williston Basin and the Southwestern Ontario Basin data are estimated in this study. The high and variable heat/ $^3\text{He}$  ratios of Daping samples are thought to reflect the direct injection of mantle-derived volatiles. Mojiang and Zhenyuan samples demonstrate consistent but higher heat/ $^3\text{He}$ . The green line corresponds to a  $^4\text{He}/\text{heat}$  ratio of  $0.6 \times 10^{-6} \text{ cm}^3 \text{ STP J}^{-1}$ , which was reported to fit the Ailaoshan samples. Both the Williston Basin and the Southwestern Ontario Basin demonstrate dominant radiogenic He isotopic ratios but show lower  $^4\text{He}/\text{heat}$  ratios than the theoretical  $^4\text{He}/\text{heat}$  ratio ( $3.7 \times 10^{-6} \text{ cm}^3 \text{ STP J}^{-1}$ ) during U-series decay (Burnard et al., 1999), suggesting a decoupling of heat and radiogenic He during release and transport in the crystalline basement, due to the faster conductive transport of heat than the diffusive transport of He. Southwestern Ontario Basin has a gradient lower than the Williston Basin in the  $^4\text{He}/^3\text{He}$  VS  $Q/^3\text{He}$  plot, suggesting a stronger decoupling effect.

that heat and helium are transported at different rates which is not consistent with dominantly advective systems.

The decoupling of heat and He here further supports the previous conclusion that the crystalline basement to sedimentary basin transition is diffusion-controlled and absent of advective flow. In stable continental settings, these findings suggest transport of gases through the crystalline basement is dominant by diffusion. Therefore, the observation of higher  $^4\text{He}$  flux,  $^3\text{He}/^4\text{He}$  ratios and less degree of He-heat decoupling

could be an indicator of a more permeable crustal system.

## 5.7 CONCLUSION

Thirty-three natural gas samples were collected from across the Southwestern Ontario Basin from different geological formations. Noble gas isotopic composition and concentrations are analysed and compared to data reported in Michigan Basin deep brines. The dominant crustal helium in the Southwestern Ontario Basin is distinct from the fluids in the Michigan Basin which have resolvable mantle signatures. The  $^3\text{He}/^4\text{He}$  ratios in the Southwestern Ontario Basin do not demonstrate any trend compared to the Michigan Basin data set, suggesting  $^3\text{He}$  is not supplied with a point source. These observations do not support regional scale Pleistocene fluid migration from the Michigan Basin to the Southwestern Ontario Basin.

$^4\text{He}/^{20}\text{Ne}$  and  $^{38}\text{Ar}/^{36}\text{Ar}$  ratios are used to estimate the  $^4\text{He}$  and  $^{40}\text{Ar}$  concentrations in the groundwater associated with the natural gases. The groundwaters demonstrate higher  $^4\text{He}$  concentrations in the groundwater than can be produced by in situ radioactive productions from U and Th in the sedimentary units. This is evidence of an external  $^4\text{He}$  supply, most likely from the crystalline basement. Diffusive transport models of  $^4\text{He}$  and  $^{40}\text{Ar}$  are constructed and the basement fluxes are determined for each well. The best fit basement fluxes are  $0.01\text{--}1.30 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and  $0.05\text{--}2.87 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$ . The basement  $^4\text{He}$  and  $^{40}\text{Ar}$  flux maps show that the Algonquin Arch separates samples with high fluxes (with averages of  $0.39 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and  $0.97 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$ ) observed on the southeast limb of the arch, closer to the Appalachian Basin, from those with lower fluxes (with averages of  $0.10 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and  $0.32 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$ ) on the northwest limb of arch, closer to the Michigan Basin. For a static water body, the differences in fluxes are likely attributed to compositional or permeability differences in the basement rock.

The basement  $^4\text{He}$  flux in the Southwestern Ontario Basin ranges between  $0.1\text{--}0.4 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ , lower than values estimated in the Williston Basin of  $0.8\text{--}1.6$

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$\times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (4) or the theoretical or statistical average crust of  $1.47 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (Torgersen, 2010). The correlation between heat and  $^3\text{He}/^4\text{He}$  and the decoupling between heat and helium observed in the two basins suggest that the crystalline basement has low permeability and transport is controlled by conduction and diffusion, respectively. There could be a positive correlation between  $^4\text{He}$  flux,  $^3\text{He}/^4\text{He}$  and the degree of He-heat decoupling; but quantitative models require further study and would have a significant impact on He exploration projects.





# 6

## Quantifying Gas-Water Ratio and Kr and Xe enrichment by an Error-Weighted, Nonlinear Inversion of Atmospheric Noble Gas Concentrations and Concentration Ratios: A Case Study on the Southwestern Ontario Basin

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## ABSTRACT

Noble gases are chemically inert but can preserve signatures left from physical processes, such as recharging, fluid mixing and degassing. They can also be used as tools in analysing subsurface gas and fluid evolution. Crustal production of  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  is negligible in most basin systems and they can be assumed to be entirely sourced from the atmosphere through groundwater recharge and are therefore useful tools for quantifying subsurface fluid interaction. In some cases, however, an amount of excess Kr and Xe, which has been observed in multiple basin systems complicates the quantification of fluid interaction.

Using the Southwestern Ontario Basin as an example, the numerical solutions of gas-water volume ratios are summarized and derived for different degassing processes described by Barry et al. (2016). Error-weighted, nonlinear inversion matrix models

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are computed to estimate the gas-water ratios and to quantify excess Kr and Xe using  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  concentrations and ratios. Samples from the study area demonstrate different solutions with the concentration and ratio models. Two mechanisms are discussed, air contamination and fluid dilution. While the inversion models give the best fit mathematical solutions, geological, hydrogeological and geochemical context and evidence are always required in order to build a better understanding of the gas-water interaction.

Linear correlation is found between the excess Kr and Xe from gas samples collected in the Southwestern Ontario Basin and other basin systems described here. The modelled Kr and Xe enrichment ( $f_{Xe}$  and  $f_{Kr}$ ) in the Southwestern Ontario Basin have lines of best fit with gradients between 0.200 to 0.230. A global gradient between 0.136 to 0.142 is obtained by applying the inversion model to data reported from multiple basin systems. The gradient is comparable to the theoretical ratios estimated from Kr and Xe adsorption on carbon (charcoal) of  $0.22 \frac{Kr}{Xe}_{ASW}$  and to observations from young ocean sediments of  $0.12 \frac{Kr}{Xe}_{ASW}$ , suggesting the release of adsorbed Kr and Xe from sediments is likely the source of excess Kr and Xe observed in the basin system. A localized higher gradient in the Southwestern Ontario Basin could be due to contributions from Kr and Xe adsorbed on silica sediments ( $0.55 \frac{Kr}{Xe}_{ASW}$ ).

## **6.1 INTRODUCTION**

Noble gases, due to their chemical inertness, are useful tools in identifying and quantifying physical processes in the subsurface. They have been used to investigate and analyse subsurface fluids including crustal degassing (Torgersen and Clarke, 1985; Torgersen, 1989; Torgersen, 2010; Aggarwal et al., 2015), interaction between different fluids (e.g. Ballentine et al., 1991; Pinti and Marty, 1995; Zhou et al., 2005; Gilfillan et al., 2008; Gilfillan et al., 2009; Barry et al., 2016) and groundwater ages (e.g. Zhou and Ballentine, 2006; Lippmann-Pipke et al., 2011; Holland et al., 2013).

## 6.1. INTRODUCTION

Atmospheric noble gases,  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$ , which typically have negligible production in sedimentary and magmatic systems, can be used to estimate the conditions under which water recharged into subsurface (e.g. Ballentine and Hall, 1999; Kipfer et al., 2002) and to quantify the interaction between different fluid phases (e.g. Ballentine et al., 2002; Barry et al., 2016; Barry et al., 2018a; Gilfillan et al., 2008). Air-derived noble gases are introduced into the subsurface through water recharge and can be determined using Henry's law with parameters characterizing the recharging conditions, including the temperature, pressure, and salinity (Ballentine et al., 2002; Kipfer et al., 2002)). A contribution of excess air is also considered in various models, which refers to the full or partial dissolution of air bubbles in water during recharge (Martin Stute, 1989; Martin Stute et al., 1995; Aeschbach-Hertig et al., 2000; Kipfer et al., 2002). Without water mixing or degassing, the concentrations of these isotopes in the groundwater is constant during migration. However, Kr and Xe concentrations in excess of recharge plus excess air values are observed in fluids from multiple basins (e.g. Barry et al., 2016; Györe et al., 2017; Hiyagon and Kennedy, 1992; Torgersen and Kennedy, 1999). There are potentially two different explanations for the enrichment. It could be the result of elemental fractionation caused by diffusional transport and multi-step dissolution of excess air during groundwater recharge at water level (Kipfer et al., 2002). Another theory is the diffusive release of adsorbed Kr and Xe on organic carbon (Torgersen et al., 2004) related to hydrocarbon formation and expulsion (Torgersen and Kennedy, 1999). Excess Kr and Xe are also observed in deep-sea sediments, and a positive correlation between Kr and Xe and silica content was interpreted to be the preferential adsorption on siliceous fossils. Györe et al. (2017) investigated the effect of  $\text{CO}_2$ -enhanced oil recovery (EOR) project in hydrocarbon fields. The air-like injection increases excess Kr and Xe considerably, but the artificial enrichment, which can be an analogue for air addition, has Xe significantly more enriched in Kr comparing to the natural enrichment observed in sedimentary basins.

The challenges involved in quantifying (and therefore accounting for) excess Kr and Xe can potentially add complexity to the analysis and interpretation. Better constraints on the values can help with exploring the enrichment mechanisms. In this

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study, mathematical solutions of gas-water volume ratios are derived and summarized for different degassing processes described by Barry et al. (2016) and computed error-weighted, nonlinear inversion matrix models to estimate the gas-water ratios and excess Kr and Xe.

### **6.2 MATHEMATICAL MODELS FOR WATER DEGASSING**

#### **6.2.1 First Order (FO) Equilibrium System**

Figure 6.1 schematically illustrates the three-endmember reservoir degassing systems. The first order equilibrium model describes the scenario where degassing of groundwater happens in a closed system. In this system a groundwater phase is in contact with a gas phase and noble gases have partitioned into the gas phase at equilibrium under the reservoir temperatures and pressures following Henry's Law as summarised by Barry et al. (2016), Warr et al. (2015), Ballentine and Burnard (2002) among others. In this paper, the dimensionless Henry's constant,  $K_i$ , is used following Ballentine and Hall (1999), and ideal gas behaviour is assumed in all cases, though non-ideality under reservoir conditions is acknowledged and may have a slight effect in these environments (e.g. Ballentine et al., 2002; Warr et al., 2015).

According to Henry's law, the relationship between noble gas concentrations in the gas phase and the water phase is defined by the following equation,

$$C_g^i = K_i C_l^i, \quad (6.1)$$

where  $C_g^i$  and  $C_l^i$  refer to the concentration of  $i$  in the gas and water phase at equilibrium under degassing/reservoir condition respectively, expressed as the amount per volume, e.g.  $\text{cm}^3(\text{RTP})/\text{cm}^3(\text{RTP})$  or  $\text{mol}/\text{cm}^3(\text{RTP})$ . RTP refers to reservoir temperature and pressure. In the first-order equilibrium system with no migration of fluids or external sources or sinks, all noble gases are initially dissolved in the groundwater. The sum total of noble gases in the groundwater prior to degassing is the

## 6.2. MATHEMATICAL MODELS FOR WATER DEGASSING

same as the total amount in the gas and water phase after equilibrium (Figure 6.1), i.e.

$$C_{gw}^i V_{gw} = C_g^i V_g + C_l^i V_l. \quad (6.2)$$

$C_{gw}^i$  refers to the concentrations of isotope  $i$  in groundwater before degassing.  $V_l$  and  $V_g$  are the volume of water and gas at equilibration and  $V_{gw}$  is the volume of groundwater before degassing. In gas-water systems, degassing has little effect on the water phase volume, and therefore,  $V_g = V_{gw}$ . Equation 6.1 can be used to substitute either  $C_g^i$  or  $C_l^i$  in Equation 6.2 to derive equations relating to  $V_g/V_l$  in each phase. The rearranged equations are:

$$C_g^i = \frac{C_{gw}^i}{\frac{1}{K_i} + \frac{V_g}{V_l}}; \quad (6.3)$$

$$C_l^i = \frac{C_{gw}^i}{1 + \frac{V_g}{V_l} K_i}. \quad (6.4)$$

Concentration ratios, i.e. the concentration ratio between two different noble gas elements, can be expressed with the following equations:

$$R_g^i = R_{gw} \frac{\frac{1}{K_{Ar}} + \frac{V_g}{V_l}}{\frac{1}{K_i} + \frac{V_g}{V_l}}; \quad (6.5)$$

$$R_l^i = R_{gw} \frac{1 + \frac{V_g}{V_l} K_{Ar}}{1 + \frac{V_g}{V_l} K_i}. \quad (6.6)$$

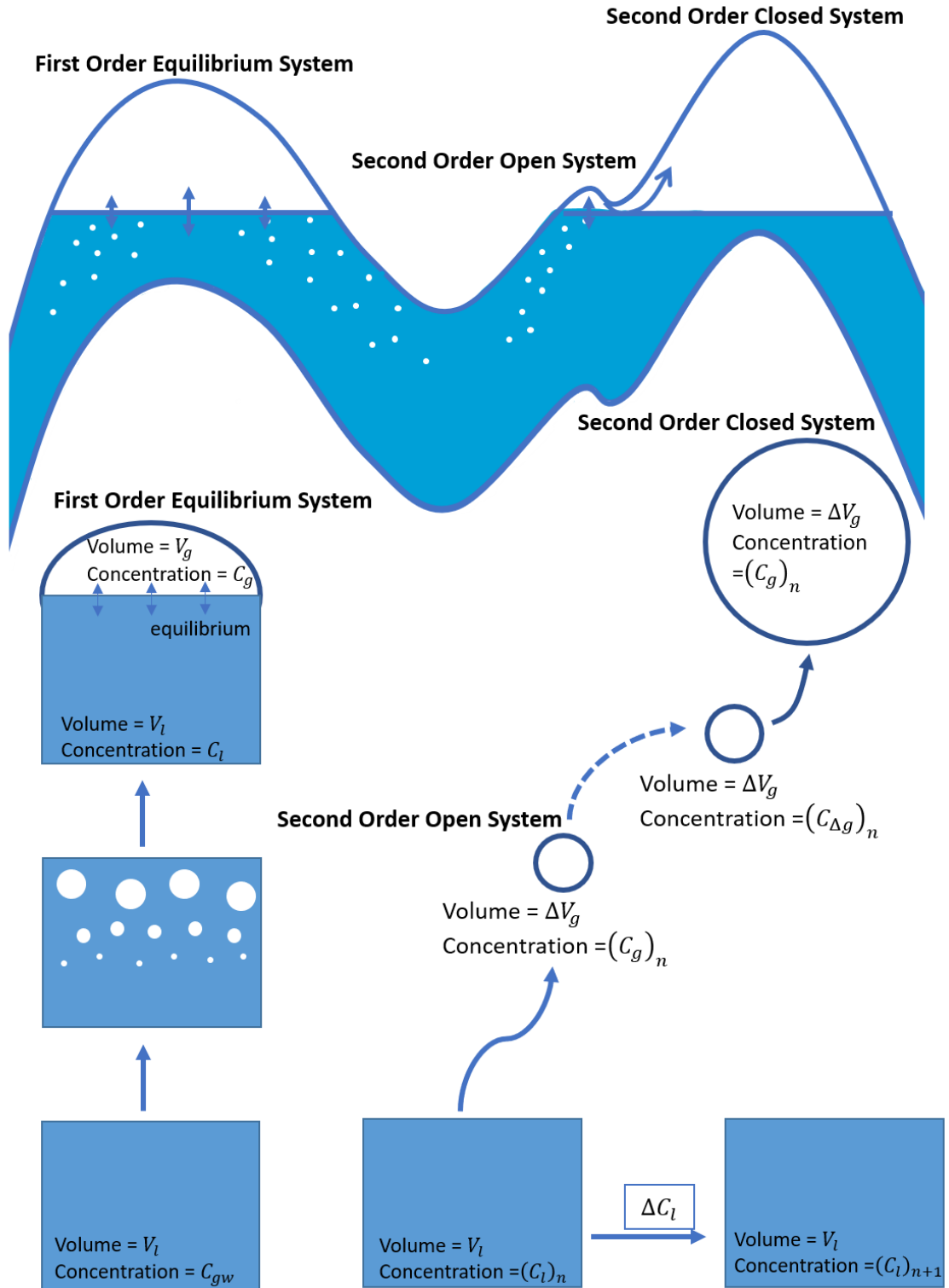
In this specific study,  $R_g^i$  and  $R_l^i$  are the concentration ratios between the specified isotope with respect to  $^{36}\text{Ar}$  in the gas and water phase respectively, i.e.

$$R_g^i = \frac{C_g^i}{C_g^{36\text{Ar}}}, \quad (6.7)$$

and

$$R_l^i = \frac{C_l^i}{C_l^{36\text{Ar}}}. \quad (6.8)$$

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**Figure 6.1:** Schematic illustration of the three-endmember reservoir degassing systems considered here. First-order equilibrium system refers to complete gas-water equilibration in a closed system (Section 6.2.1). Second-order systems describe Rayleigh fractionation gas loss, where gas-phase exsolved migrate away from the gas-water contact. The second-order open system (Section 6.2.2) refers to the latest gas phase formed from a fractionated water, and second-order closed system (Section 6.2.3) is the accumulation (or pocket) of all exsolved gas that has been migrated, termed ‘fill and spill’ by Barry et al. (2016)

## 6.2. MATHEMATICAL MODELS FOR WATER DEGASSING

### 6.2.2 Second-order (SO) Open System

When exsolution takes place in a leaky geological unit, the gas-phase can migrate and decouple from the water phase. This scenario is considered here as the second-order open system. This model assumes an infinitely small volume of gas forms in equilibrium with the water phase, with the gas phase inheriting a noble gas component following Henry's law. The gas then migrates out of the system, thereby removing the associated noble gases. Through this, the noble gas content of the water is progressively removed and fractionated based on elemental solubilities. In this scenario, gas samples collected from such a system represent the composition of the gas exsolving at that time.

To incorporate this into a degassing model,  $\delta V_g$  is used to represent the very small volume of the gas phase formed that migrates out of the system at any time point. The residual noble gas content of the water phase can be determined to calculate the noble gas content in the gas phase to be exsolved. Noble gas components lost from water are equal to those gained in the gas phase for at any time instance and can be expressed with the following equation:

$$-\delta C_l^i V_l = C_g^i \delta V_g, \quad (6.9)$$

where  $\delta C_l^i$  is the concentration change of isotope  $i$  in the liquid phase after one degassing step with a minus sign indicating substance loss. The total gas volume lost  $V_g$  from groundwater is the sum of all gas phases that have been formed and lost. Henry's law, again, governs the partitioning of noble gas isotopes at each degassing step and therefore  $C_g^i$  can be substituted with the  $C_l^i$  (Equation 6.1) and obtain the following equation after rearranging:

$$-\frac{\delta C_l^i}{C_l^i} = K_i \frac{\delta V_g}{V_l}. \quad (6.10)$$

As  $\delta V_g/V_l$  approaches 0,  $\delta C_w^i$  also approaches an infinitely small value, and they can be substituted these with  $d V_g/V_l$  and  $d C_w$  respectively,

$$-\frac{d C_w}{C_w^i} = K_i \frac{d V_g}{V_l}. \quad (6.11)$$



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The equation can then be solved by integration with the initial condition of  $\frac{V_g}{V_l} = 0$ ,  $C_w = C_{gw}$ :

$$C_w^i = C_{gw}^i e^{-K_i \frac{V_g}{V_l}}. \quad (6.12)$$

The concentration of i,  $C_g^i$ , in the gas-phase can also be written as a function of  $\frac{V_g}{V_l}$  (Equation 6.1), the volume ratio of total gas formed to contacted water:

$$C_g^i = K_i C_{gw}^i e^{-K_i \frac{V_g}{V_l}}. \quad (6.13)$$

The concentration ratios in gas and water phases can be calculated with

$$R_l^i = R_{gw}^i e^{(K_{Ar} - K_i) \frac{V_g}{V_l}}; \quad (6.14)$$

$$R_g^i = R_{gw}^i \frac{K_i}{K_{Ar}} e^{(K_{Ar} - K_i) \frac{V_g}{V_l}}. \quad (6.15)$$

### 6.2.3 Second-order (SO) Closed System

If all gas which migrates out of the system as outlined in the previous model is accumulated and trapped in a closed reservoir away from the water-gas contact, (i.e. no re-equilibration with the fractionated water), then the gas pool is described as a second-order closed system. Since the groundwater follows the same exsolution process as the open system, the isotopic concentrations and concentration ratios in the water phase can also be expressed with Equations 6.12 and 6.14. The noble gases accumulated in the gas body equal to the total loss from water, and therefore

$$V_g C_g = (C_{gw} - C_l) V_l. \quad (6.16)$$

By rearranging, the following equations are obtained:

$$C_g^i = C_{gw}^i \frac{1 - e^{-K_i \frac{V_g}{V_l}}}{\frac{V_g}{V_l}}; \quad (6.17)$$

$$R_g^i = R_{gw}^i \frac{1 - e^{-K_i \frac{V_g}{V_l}}}{1 - e^{-K_{Ar} \frac{V_g}{V_l}}}. \quad (6.18)$$

## 6.2. MATHEMATICAL MODELS FOR WATER DEGASSING

**Table 6.1:** Transformation functions for different degassing systems.

| System                         | $U$                                                    | $W$                                                                          |
|--------------------------------|--------------------------------------------------------|------------------------------------------------------------------------------|
| First Order Equilibrium System | $\frac{1}{\frac{1}{K_i} + \frac{V_g}{V_l}}$            | $\frac{1}{\frac{K_{Ar} + \frac{V_g}{V_l}}{\frac{1}{K_i + \frac{V_g}{V_l}}}}$ |
| Second-Order Open System       | $K_i e^{-K_i \frac{V_g}{V_l}}$                         | $K_i e^{(K_{Ar} - K_i) \frac{V_g}{V_l}}$                                     |
| Second-Order Closed System     | $\frac{1 - e^{-K_i \frac{V_g}{V_l}}}{\frac{V_g}{V_l}}$ | $\frac{1 - e^{-K_i \frac{V_g}{V_l}}}{1 - e^{-K_{Ar} \frac{V_g}{V_l}}}$       |

Overall, the three different degassing scenarios can be summarised in the following form

$$C_g^i = C_{gw}^i U; \quad (6.19)$$

$$R_g^i = R_{gw}^i W, \quad (6.20)$$

where  $U$  and  $W$  are the corresponding transforming functions for different models and depends on parameters  $V_g/V_l$  and degassing temperature and groundwater salinity (Table 6.1).

### 6.2.4 Kr and Xe Enrichment

The mathematical expressions derived above can be used to calculate concentrations of  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$ , and concentration ratios of  $^{20}\text{Ne}/^{36}\text{Ar}$ ,  $^{84}\text{Kr}/^{36}\text{Ar}$  and  $^{132}\text{Xe}/^{36}\text{Ar}$  in the gas phase for each of the scenarios listed, if the initial concentrations and ratios in the groundwater are known. To represent the excess amount of Kr and Xe, an excess factor,  $f_i$ , is defined as follows:

$$C_{gw}^i = f_i C_{ASW}^i. \quad (6.21)$$

$f_i$  represents noble gases in excess of air saturated water. This includes both excess air and excess noble gases possibly from sedimentary input. By setting a reference that  $f_{Ne} = 1$  and  $f_{Ar} = 1$ , concentration ratios to  $^{36}\text{Ar}$  can be written as

$$R_{gw}^i = f_i R_{ASW}^i. \quad (6.22)$$

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Therefore, for the three endmember degassing systems, the concentrations of concentration ratios in the gas phase can be expressed in the following format

$$C_g^i = f_i C_{ASW}^i U_i^{model}; \quad (6.23)$$

and,

$$R_g^i = f_i R_{ASW}^i W_i^{model}. \quad (6.24)$$

$f_{Kr}$  can be expressed as a function of  $f_{Xe}$  if correlation is observed between  $F_{Kr}^{ASW}$  and  $F_{Kr}^{ASW}$ , which represent  $\frac{(^{84}Kr/^{36}Ar)_{sample}}{(^{84}Kr/^{36}Ar)_{ASW}}$  and  $\frac{(^{132}Kr/^{36}Ar)_{sample}}{(^{132}Kr/^{36}Ar)_{ASW}}$ , respectively. For example, if a linear relationship is observed in the basin samples, i.e.

$$F_{Kr}^{ASW} = m F_{Kr}^{ASW} + c, \quad (6.25)$$

where m is the gradient and c is the interception of y-axis. The following correlation can be obtained

$$f_{Kr} = m \frac{U_{Xe}^{model}}{U_{Kr}^{model}} f_{Xe} + c \frac{U_{Ar}^{model}}{U_{Kr}^{model}} \quad (6.26)$$

### 6.2.5 Inversion Model

Assuming there are no other complex fluid processes occurring, such as water mixing, the isotopic concentrations and concentration ratios can be expressed with straightforward mathematical models. The parameters include the recharging conditions (temperature, pressure, salinity, excess air), excess noble gases to the groundwater recharge equilibrium concentrations ( $f_i$ ), the degassing condition (temperature, pressure, salinity) and the gas-water ratio ( $V_g/V_l$ ). The second-order open system is used as an example to illustrate the calculation of noble gas content in the subsurface gas phase. Noble gas concentrations can be considered as being a function of a vector m, i.e.:

$$\mathbf{c} = \begin{Bmatrix} [C_g]_{Ne} \\ [C_g]_{Ar} \\ [C_g]_{Kr} \\ [C_g]_{Xe} \end{Bmatrix} = g(\mathbf{m}) = \begin{Bmatrix} f_{Ne} [C_{ASW}]_{Ne} K_{Ne} e^{-K_{Ne} \frac{V_g}{V_l}} \\ f_{Ar} [C_{ASW}]_{Ar} K_{Ar} e^{-K_{Ar} \frac{V_g}{V_l}} \\ f_{Kr} [C_{ASW}]_{Kr} K_{Kr} e^{-K_{Kr} \frac{V_g}{V_l}} \\ f_{Xe} [C_{ASW}]_{Xe} K_{Xe} e^{-K_{Xe} \frac{V_g}{V_l}} \end{Bmatrix}, \quad (6.27)$$

## 6.2. MATHEMATICAL MODELS FOR WATER DEGASSING

where  $m$  is the array contains the unknown parameters,  $\mathbf{c}$  is a  $4 \times 1$  array of noble gas concentrations in the gas body after degassing under reservoir condition.  $C_{ASW}$  is the air-saturated water concentration at recharge point and is a function of recharging condition (Ballentine and Hall, 1999) and  $K_i$  is Henry's constant under degassing conditions and is a function of reservoir temperature and pressure. The four equations limit the degree of freedom and the number of solvable unknowns. Theoretically, the set of equations can solve up to four unknowns. However, to maximise the degree of freedom, the focus is on solving the excess factor  $f$  and gas water ratio  $\frac{V_g}{V_l}$ , i.e.

$$m = \left\{ \begin{array}{c} V_g/V_l \\ f \end{array} \right\}. \quad (6.28)$$

We assume the groundwater is recharged with seawater (0.623 mol NaCl/L, 1 bar) at 298.15K with no excess air, and degassing takes place at reservoir conditions, including temperature, pressure and groundwater salinity. The set of equations is now an overdetermined nonlinear system, and the least square combination of  $f_{Xe}$  and  $V_g/V_l$  can be found. The iterative solving technique that follows was initially outlined by Ballentine and Hall (1999) for modelling noble gases dissolving in groundwater systems. The method and variables of this model are briefly discussed. The iterative calculation requires an initial input of  $m$  (Equation 6.28). With this estimation, an optimum value of  $m$  is approached assuming linearity between two consecutive estimations, where

$$m_{k+1} = m_k + G_k^{-g}(c - g_k) \quad (6.29)$$

and

$$G_k^{-g} = \left\{ G_k^T (cov \mathbf{c})^{-1} G_k \right\}^{-1} G_k^T (cov \mathbf{c})^{-1}, \quad (6.30)$$

where  $cov \mathbf{c}$  is the covariance matrix of the measured data of the sample concentration under reservoir condition  $c$ . The matrix  $G$  is  $4 \times 2$  and is calculated at each iteration step according to:

$$G = [G_{ij}] = \frac{dg_i}{dm_j} \quad (6.31)$$

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where  $i$  and  $j$  represent the row and column of the array or the matrix, respectively. The value of  $cov \mathbf{m}$  can be estimated which allows the error for the fitted model parameters to be estimated

$$cov \mathbf{m} \cong G_k^{-g} cov \mathbf{c} \left( G_k^{-g} \right)^T ; \quad (6.32)$$

where

$$\sigma \left( \frac{V_g}{V_l} \right) = [(cov \mathbf{m})_{1,1}]^{1/2} ; \quad (6.33)$$

$$\sigma_{(f)} = [(cov \mathbf{m})_{2,2}]^{1/2} . \quad (6.34)$$

Assuming the errors of the four measurements are independents, the errors of the estimated concentration can be calculated by:

$$(cov \mathbf{c})^{-1} = diag \left( \frac{1}{\sigma_i^2} \right) ; \quad (6.35)$$

and the  $\chi^2$  of the modelled parameter is

$$\chi^2(m) = \sum \left[ \frac{c_i - g_i}{\sigma_c} \right]^2 . \quad (6.36)$$

The correct model has a mean  $\chi^2$  value close to the degrees of freedom ( $v$ ) and can be used to test the validity of the models.

Elemental models can be calculated with the same technique using the following equations

$$\mathbf{r} = \left\{ \begin{array}{l} [R_g]_{Ne} \\ [R_g]_{Kr} \\ [R_g]_{Xe} \end{array} \right\} = h(m) = \left\{ \begin{array}{l} f_{Ne} R_{ASW} \frac{K_{Ne}}{K_{Ar}} e^{(K_{Ar} - K_{Ne}) \frac{V_g}{V_l}} \\ f_{Kr} R_{ASW} \frac{K_{Kr}}{K_{Ar}} e^{(K_{Ar} - K_{Kr}) \frac{V_g}{V_l}} \\ f_{Xe} R_{ASW} \frac{K_{Xe}}{K_{Ar}} e^{(K_{Ar} - K_{Xe}) \frac{V_g}{V_l}} \end{array} \right\} . \quad (6.37)$$

The ratio model has only three equations and therefore has fewer degrees of freedom. Noticeably, for non-linear equations with potentially multiple inflexion points, the model returns a local solution which depends on the initial parameter estimates. It is therefore vital to have reasonable estimations to start with. A good fit to the model is indicated with low  $\chi^2$  values, and comparable solutions determined for the ratios and the concentrations.

### *6.3. GEOLOGICAL AND HYDROGEOLOGICAL BACKGROUND*

In summary, at each step of an inversion model, the  $\chi^2$  value for a set of input parameters, including the unknown parameters with assigned values is calculated. Better estimations for the unknown parameters are also processed through the matrix equations listed in this section. The iterative model repeats the above step with the new estimates for the parameters, and progressively approaches the combination of parameters that give the minimum  $\chi^2$  value. In this paper, the model is set to stop when  $\chi^2$  values between consecutive steps differ less than 0.00001% or if  $\chi^2$  is smaller than  $10^{-8}$ . The model also stops after 150 steps. If a stable solution is not achieved within 150 steps, it is likely that the answer is not converging to solutions where the minimum  $\chi^2$  value can be found, and the equation is considered not solved.

### **6.3 GEOLOGICAL AND HYDROGEOLOGICAL BACKGROUND**

Gas samples were collected from natural gas wells producing from different geological units in the Southwestern Ontario Basin. Their noble gas measurements and analysis are reported in Chapter 5. The basin preserves less than 1500 m of Palaeozoic sediments resting unconformably on the Algonquin Arch (Sanford et al., 1985), which is a Precambrian topographic high, the Algonquin Arch, that separates the Michigan Basin to the west and the Appalachian Basin to the east. During the Cambrian to Mississippian, the region was located at a tropical latitude (Der Voo, 1988). Periodic transgression and regression of the inland sea and tectonic induced structure uplift formed the currently preserved sedimentary units. These includes the Cambrian sandstone and argillaceous dolostone (Hamblin, 1998) that pinches out on both limbs of the arch, the Middle Ordovician Limestone (Black River and Trenton Groups) (Brookfield and Brett, 1988; Haeri-Ardakani et al., 2013), the Late Ordovician Shale (Queenston, Georgian Bay and Blue Mountain Formations) and Lower Silurian Shale (Manitoulin, Cabot Head Formation), the middle to Late Silurian Evaporites (Salina Group) and the Devonian carbonate (Birchard et al., 2004). The current landscape was shaped during the Pleistocene glaciation.

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In the Southwestern Ontario Basin, groundwater is conceptually divided into two domains defined by their major ion compositions and salinity (Hobbs et al., 2011). The shallow system, less than 200 m below ground surface, has fresh through brackish water and is mainly composed of the Quaternary drift and Devonian sediments (Hobbs et al., 2011; Sykes et al., 2011). The shallow system has been recharged by glacial waters, evident from the stable isotopic compositions of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , but the maximum depth of freshwater penetration is 140 m below ground surface (Weaver et al., 1995; Hobbs et al., 2011).

The intermediate to deep waters in Southwestern Ontario are predominantly brines associated with hydrocarbons. The low topography gradient and the high salinity of deeper waters prevent the penetration of the recharged meteoric and glacial water (Hobbs et al., 2011). The water is thought to be stable over geological time scale and could be diagenetic produced and evolved in situ (Coniglio et al., 2003; Hobbs et al., 2011). Alternatively, water migration could have been driven by ancient tectonic at least 250 Ma ago, evident from geochemical tracers,  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , mineral alteration (Harper et al., 1995; K. Ziegler and Longstaffe, 2000a; K. Ziegler and Longstaffe, 2000b), homogenization temperatures of dolomite and calcite (Haeri-Ardakani et al., 2013).

## **6.4 RESULTS**

Inversion models for all three degassing systems are constructed for each sample collected from the Southwestern Ontario Basin (Chapter 5). For each degassing system, models for both the noble gas isotopic concentrations ( $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$ ) and the concentration ratios ( $^{20}\text{Ne}/^{36}\text{Ar}$ ,  $^{84}\text{Kr}/^{36}\text{Ar}$  and  $^{132}\text{Xe}/^{36}\text{Ar}$ ) are built. The noble gas concentrations at reservoir conditions (Barry et al., 2016) can be converted with the following equation:

$$C_i^{RTP} = C_i^{STP} \frac{273.15 P^R}{T^R} \quad (6.38)$$

where  $P^R$  and  $T^R$  represents reservoir pressure (bar) and temperature (K), respectively.  $RTP$  and  $STP$  refer to reservoir temperature and pressure and standard temperature

#### 6.4. RESULTS

and pressure, respectively. Concentration ratios reported in STP do not need to be converted. Solutions and errors for  $V_g/V_l$  and  $f_{Xe}$  are summarised in Tables 6.2, 6.3 and 6.4.



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**Table 6.2:** Solutions for  $V_g/V_l$  and  $f_{Xe}$  calculated from noble gas concentrations and concentration ratios based on first-order equilibrium model; *NaN means no resolvable solution found.*

| Sample name | Formation     | Concentration Model (first-order equilibrium model) |          |                         |                |                                                    | Ratio Model (first-order equilibrium model) |                   |          |                         |                |                                                    |          |
|-------------|---------------|-----------------------------------------------------|----------|-------------------------|----------------|----------------------------------------------------|---------------------------------------------|-------------------|----------|-------------------------|----------------|----------------------------------------------------|----------|
|             |               | $\frac{V_g}{V_l}$                                   | $f_{Xe}$ | $\frac{V_g}{V_l}$ error | $f_{Xe}$ error | Correlation coefficient $\frac{V_g}{V_l} - f_{Xe}$ | $\chi^2$                                    | $\frac{V_g}{V_l}$ | $f_{Xe}$ | $\frac{V_g}{V_l}$ error | $f_{Xe}$ error | Correlation coefficient $\frac{V_g}{V_l} - f_{Xe}$ | $\chi^2$ |
| T008636     | A-2 Carbonate | 0.1313                                              | 1.373    | 0.00045                 | 0.0162         | 0.309                                              | 1692                                        | 0.019             | 2.48     | 0.00058                 | 0.0338         | -0.51                                              | 21       |
| T002556     | Guelph        | 0.052                                               | 1.143    | 0.00028                 | 0.0157         | 0.425                                              | 2711                                        | 0.0008            | 2.679    | 0.00008                 | 0.0398         | -0.423                                             | 10       |
| T003899     | Guelph        | 0.0761                                              | 1.25     | 0.00034                 | 0.016          | 0.412                                              | 1372                                        | 0.0034            | 2.335    | 0.00018                 | 0.0349         | -0.557                                             | 0.83     |
| T004918     | Guelph        | 0.1333                                              | 2.357    | 0.00063                 | 0.0277         | 0.463                                              | 1140                                        | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 2383     |
| T007415     | Guelph        | 0.0468                                              | 0.955    | 0.00041                 | 0.0162         | 0.577                                              | 336                                         | 0.0037            | 1.996    | 0.00056                 | 0.074          | -0.689                                             | 0.97     |
| T008468     | Guelph        | 0.0975                                              | 9.553    | 0.00046                 | 0.1025         | 0.425                                              | 7743                                        | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 31119    |
| T008657     | Guelph        | 0.0567                                              | 1.053    | 0.00034                 | 0.0156         | 0.493                                              | 805                                         | 0.0037            | 2.405    | 0.00034                 | 0.0587         | -0.64                                              | 0.01     |
| T009602     | Guelph        | 0.0526                                              | 0.949    | 0.00024                 | 0.0132         | 0.378                                              | 2913                                        | 0.0018            | 2.165    | 0.0001                  | 0.0328         | -0.432                                             | 0.76     |
| T010097     | Guelph        | 0.0729                                              | 1.3      | 0.00033                 | 0.0165         | 0.412                                              | 1653                                        | 0.0027            | 2.578    | 0.00015                 | 0.0374         | -0.527                                             | 7.87     |
| T011560     | Guelph        | 0.0359                                              | 1.198    | 0.00018                 | 0.0156         | 0.393                                              | 3349                                        | 0.0004            | 2.657    | 0.00006                 | 0.0362         | -0.381                                             | 0.4      |
| T011554     | Thorold       | 0.097                                               | 1.356    | 0.00046                 | 0.0168         | 0.406                                              | 163                                         | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 61       |
| T011584     | Thorold       | 0.0974                                              | 1.241    | 0.00038                 | 0.0144         | 0.343                                              | 1062                                        | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 1332     |
| T011280     | Thorold*      | 0.0717                                              | 0.796    | 0.00032                 | 0.0109         | 0.355                                              | 2802                                        | 0.0033            | 1.838    | 0.00015                 | 0.028          | -0.438                                             | 23       |
| T002374     | Grimsby       | 0.0842                                              | 1.012    | 0.00037                 | 0.0137         | 0.372                                              | 1746                                        | 0.0053            | 2.081    | 0.00023                 | 0.0325         | -0.51                                              | 8.97     |
| T003188     | Grimsby       | 0.094                                               | 0.822    | 0.00052                 | 0.0113         | 0.436                                              | 1722                                        | 0.0017            | 1.836    | 0.00014                 | 0.0285         | -0.49                                              | 39       |
| T012287     | Grimsby       | 0.2013                                              | 1.188    | 0.00101                 | 0.0164         | 0.455                                              | 5465                                        | 0.0006            | 4.05     | 0.00008                 | 0.0591         | -0.355                                             | 78       |
| T008194     | Whirlpool     | 0.1611                                              | 1.309    | 0.00055                 | 0.0153         | 0.338                                              | 85                                          | 0.0769            | 1.411    | 0.01302                 | 0.0283         | -0.792                                             | 91       |
| T009877     | Whirlpool     | 0.1549                                              | 1.182    | 0.00065                 | 0.0153         | 0.398                                              | 2615                                        | 0.0032            | 2.945    | 0.00015                 | 0.0438         | -0.488                                             | 95       |
| T007357     | Cobourg       | 0.0614                                              | 0.663    | 0.00023                 | 0.0096         | 0.33                                               | 11646                                       | -0.0002           | 1.846    | 0.00005                 | 0.0251         | -0.241                                             | 183      |
| T008358     | Cobourg       | 0.2199                                              | 3.729    | 0.00193                 | 0.0548         | 0.672                                              | 36                                          | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 63       |
| T007793     | Sherman Fall  | 0.2329                                              | 2.428    | 0.00203                 | 0.0387         | 0.672                                              | 50                                          | 0.0198            | 3.86     | 0.00386                 | 0.1705         | -0.83                                              | 0.97     |
| T007954     | Sherman Fall  | 0.1979                                              | 4.179    | 0.00068                 | 0.0409         | 0.375                                              | 1812                                        | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 3205     |
| T008057     | Sherman Fall  | 0.0905                                              | 1.164    | 0.00078                 | 0.0198         | 0.594                                              | 171                                         | 0.0099            | 2.126    | 0.00151                 | 0.0862         | -0.753                                             | 0.63     |
| T0011596    | Coboconk      | 0.0352                                              | 1.901    | 0.00018                 | 0.0235         | 0.354                                              | 6568                                        | -0.0003           | 5.132    | 0.00006                 | 0.0665         | -0.291                                             | 144      |
| T006907     | Coboconk      | 0.0552                                              | 0.825    | 0.00026                 | 0.0117         | 0.364                                              | 6127                                        | 0.0001            | 2.211    | 0.00008                 | 0.0317         | -0.309                                             | 0.06     |
| T008313     | Coboconk      | 0.0228                                              | 0.962    | 0.0001                  | 0.013          | 0.272                                              | 23125                                       | -0.0021           | 2.858    | 0.00002                 | 0.0358         | -0.143                                             | 2.79     |
| T008974     | Gull River    | 0.0855                                              | 0.765    | 0.00031                 | 0.0124         | 0.336                                              | 4208                                        | 0.0089            | 1.6      | 0.00032                 | 0.0263         | -0.415                                             | 673      |
| T007369     | Cambrian      | 0.0488                                              | 0.983    | 0.00019                 | 0.0128         | 0.312                                              | 16489                                       | -0.0017           | 3.151    | 0.00004                 | 0.0395         | -0.2                                               | 63       |
| T007956     | Cambrian      | 0.0233                                              | 1.27     | 0.00014                 | 0.0171         | 0.366                                              | 6029                                        | -0.0017           | 2.81     | 0.00004                 | 0.0377         | -0.229                                             | 56       |
| T008094     | Cambrian      | 0.1407                                              | 3.345    | 0.00076                 | 0.0397         | 0.508                                              | 5947                                        | -0.0011           | 9.694    | 0.00006                 | 0.1146         | -0.298                                             | 0.03     |

\* Thorold / Whirlpool

**Table 6.3:** Solutions for  $V_g/V_l$  and  $f_{Xe}$  calculated from noble gas concentrations and concentration ratios based on second-order open model.

| Sample name | Formation           | Concentration Model (second-order open model) |          |                   |          |                                                    | Ratio Model (second-order open model) |                   |          |                   |          | $\chi^2$ |                                                    |
|-------------|---------------------|-----------------------------------------------|----------|-------------------|----------|----------------------------------------------------|---------------------------------------|-------------------|----------|-------------------|----------|----------|----------------------------------------------------|
|             |                     | $\frac{V_g}{V_l}$                             | $f_{Xe}$ | $\frac{V_g}{V_l}$ | $f_{Xe}$ | Correlation coefficient $\frac{V_g - f_{Xe}}{V_l}$ | $\chi^2$                              | $\frac{V_g}{V_l}$ | $f_{Xe}$ | $\frac{V_g}{V_l}$ | $f_{Xe}$ |          | Correlation coefficient $\frac{V_g - f_{Xe}}{V_l}$ |
| T008636     | A-2 Carbonate       | 0.0355                                        | 0.754    | 0.00007           | 0.0089   | 0.247                                              | 49925                                 | 0.0065            | 2.922    | 0.00007           | 0.0352   | -0.219   | 21                                                 |
| T002556     | Guelph              | 0.0138                                        | 0.648    | 0.00003           | 0.0085   | 0.316                                              | 15805                                 | 0.0007            | 2.696    | 0.00006           | 0.039    | -0.368   | 10                                                 |
| T003899     | Guelph              | 0.0158                                        | 0.601    | 0.00003           | 0.0074   | 0.3                                                | 15724                                 | 0.0019            | 2.462    | 0.00005           | 0.033    | -0.378   | 0.82                                               |
| T004918     | Guelph              | 0.0178                                        | 0.748    | 0.00003           | 0.0087   | 0.317                                              | 10148                                 | 0.006             | 2.545    | 0.00006           | 0.0334   | -0.428   | 1.01                                               |
| T007415     | Guelph              | 0.0112                                        | 0.416    | 0.00004           | 0.0076   | 0.437                                              | 6769                                  | 0.0019            | 2.12     | 0.00016           | 0.065    | -0.479   | 0.97                                               |
| T008468     | Guelph              | 0.013                                         | 2.768    | 0.00002           | 0.0302   | 0.202                                              | 4882                                  | 0.0088            | 5.236    | 0.00005           | 0.0641   | -0.407   | 18                                                 |
| T008657     | Guelph              | 0.0119                                        | 0.375    | 0.00003           | 0.0068   | 0.386                                              | 17402                                 | 0.0019            | 2.559    | 0.00009           | 0.0532   | -0.432   | 0.01                                               |
| T009602     | Guelph              | 0.0135                                        | 0.509    | 0.00003           | 0.007    | 0.294                                              | 25384                                 | 0.0012            | 2.214    | 0.00005           | 0.032    | -0.327   | 0.76                                               |
| T010097     | Guelph              | 0.0156                                        | 0.639    | 0.00003           | 0.0077   | 0.296                                              | 16175                                 | 0.0016            | 2.685    | 0.00005           | 0.0356   | -0.372   | 7.85                                               |
| T011560     | Guelph              | 0.0117                                        | 0.773    | 0.00003           | 0.0097   | 0.287                                              | 14647                                 | 0.0004            | 2.661    | 0.00005           | 0.0359   | -0.358   | 0.4                                                |
| T011554     | Thorold             | 0.0183                                        | 0.523    | 0.00004           | 0.0068   | 0.286                                              | 19395                                 | 0.0056            | 1.912    | 0.00006           | 0.0269   | -0.322   | 39                                                 |
| T011584     | Thorold             | 0.019                                         | 0.514    | 0.00003           | 0.0061   | 0.223                                              | 19475                                 | 0.0064            | 1.574    | 0.00005           | 0.0198   | -0.293   | 126                                                |
| T011280     | Thorold*            | 0.0185                                        | 0.436    | 0.00004           | 0.0058   | 0.276                                              | 29476                                 | 0.002             | 1.918    | 0.00006           | 0.0274   | -0.286   | 23                                                 |
| T002374     | Grimsby             | 0.0192                                        | 0.504    | 0.00004           | 0.0067   | 0.293                                              | 28405                                 | 0.0026            | 2.252    | 0.00006           | 0.0317   | -0.296   | 8.96                                               |
| T003188     | Grimsby             | 0.0205                                        | 0.409    | 0.00004           | 0.0052   | 0.297                                              | 9962                                  | 0.0013            | 1.866    | 0.00008           | 0.0274   | -0.384   | 39                                                 |
| T012287     | Grimsby             | 0.0278                                        | 0.461    | 0.00006           | 0.0057   | 0.388                                              | 29996                                 | 0.0005            | 4.055    | 0.00006           | 0.0586   | -0.329   | 78                                                 |
| T008194     | Whirlpool           | 0.0202                                        | 0.397    | 0.00003           | 0.0048   | 0.276                                              | 51421                                 | 0.0041            | 2.158    | 0.00004           | 0.0275   | -0.274   | 90                                                 |
| T009877     | Whirlpool           | 0.0218                                        | 0.442    | 0.00004           | 0.0054   | 0.34                                               | 37265                                 | 0.0018            | 3.099    | 0.00005           | 0.0424   | -0.316   | 95                                                 |
| T007357     | Cobourg             | 0.0186                                        | 0.414    | 0.00003           | 0.0058   | 0.272                                              | 46161                                 | -0.0002           | 1.848    | 0.00005           | 0.0252   | -0.254   | 183                                                |
| T008358     | Cobourg             | 0.0218                                        | 0.664    | 0.00007           | 0.0116   | 0.517                                              | 7786                                  | 0.0068            | 4.82     | 0.00021           | 0.1341   | -0.494   | 1.61                                               |
| T007793     | Sherman Fall        | 0.0267                                        | 0.63     | 0.00011           | 0.011    | 0.639                                              | 9579                                  | 0.0047            | 4.727    | 0.00022           | 0.1341   | -0.497   | 0.93                                               |
| T007954     | Sherman Fall        | 0.0231                                        | 1.037    | 0.00003           | 0.0112   | 0.246                                              | 39730                                 | 0.0083            | 4.298    | 0.00006           | 0.0482   | -0.322   | 80                                                 |
| T008057     | Sherman Fall        | 0.0183                                        | 0.432    | 0.00007           | 0.0081   | 0.47                                               | 7535                                  | 0.0037            | 2.395    | 0.00022           | 0.0721   | -0.464   | 0.63                                               |
| T0011596    | Coboconk            | 0.014                                         | 1.345    | 0.00004           | 0.0165   | 0.253                                              | 24803                                 | -0.0002           | 5.127    | 0.00007           | 0.067    | -0.317   | 144                                                |
| T006907     | Coboconk            | 0.0178                                        | 0.517    | 0.00004           | 0.0073   | 0.284                                              | 28266                                 | 0.0001            | 2.211    | 0.00007           | 0.0317   | -0.31    | 0.06                                               |
| T008313     | Coboconk            | 0.0109                                        | 0.741    | 0.00003           | 0.0103   | 0.207                                              | 48167                                 | -0.0033           | 2.989    | 0.00005           | 0.0382   | -0.244   | 2.79                                               |
| T008974     | Gull River          | 0.0229                                        | 0.351    | 0.00004           | 0.0068   | 0.303                                              | 49147                                 | 0.004             | 1.752    | 0.00007           | 0.0268   | -0.223   | 672                                                |
| T007369     | Cambrian            | 0.0177                                        | 0.67     | 0.00004           | 0.0086   | 0.242                                              | 50825                                 | -0.0022           | 3.209    | 0.00007           | 0.041    | -0.281   | 63                                                 |
| T007956     | Cambrian            | 0.0119                                        | 1.041    | 0.00004           | 0.0138   | 0.283                                              | 12614                                 | -0.0022           | 2.868    | 0.00008           | 0.0396   | -0.326   | 56                                                 |
| T008094     | Cambrian            | 0.029                                         | 1.656    | 0.00006           | 0.0177   | 0.372                                              | 18320                                 | -0.0013           | 9.766    | 0.00009           | 0.1198   | -0.392   | 0.03                                               |
|             | Thorold / Whirlpool |                                               |          |                   |          |                                                    |                                       |                   |          |                   |          |          |                                                    |

\* Thorold / Whirlpool

6. Quantifying Gas-Water Ratio and Kr and Xe enrichment by an Error-Weighted, Nonlinear Inversion of Atmospheric Noble Gas Concentrations and Concentration Ratios: A Case Study on the Southwestern Ontario Basin

**Table 6.4:** Solutions for  $V_g/V_l$  and  $f_{Xe}$  calculated from noble gas concentrations and concentration ratios based on second-order closed model; NaN means no resolvable solution found.

| Sample name | Formation     | Concentration Model (second-order closed model) |          |                         |                |                                                    | Ratio Model (second-order closed model) |                   |          |                         |                |                                                    |           |
|-------------|---------------|-------------------------------------------------|----------|-------------------------|----------------|----------------------------------------------------|-----------------------------------------|-------------------|----------|-------------------------|----------------|----------------------------------------------------|-----------|
|             |               | $\frac{V_g}{V_l}$                               | $f_{Xe}$ | $\frac{V_g}{V_l}$ error | $f_{Xe}$ error | Correlation coefficient $\frac{V_g}{V_l} - f_{Xe}$ | $\chi^2$                                | $\frac{V_g}{V_l}$ | $f_{Xe}$ | $\frac{V_g}{V_l}$ error | $f_{Xe}$ error | Correlation coefficient $\frac{V_g}{V_l} - f_{Xe}$ | $\chi^2$  |
| T008636     | A-2 Carbonate | 0.1247                                          | 0.966    | 0.00051                 | 0.0126         | 0.396                                              | 5345                                    | 0.0188            | 2.739    | 0.00033                 | 0.0344         | -0.359                                             | 21        |
| T002556     | Guelph        | 0.0439                                          | 0.707    | 0.00031                 | 0.0119         | 0.561                                              | 7510                                    | 0.0015            | 2.691    | 0.00013                 | 0.0392         | -0.383                                             | 10        |
| T003899     | Guelph        | 0.0682                                          | 0.883    | 0.00047                 | 0.0141         | 0.617                                              | 3966                                    | 0.0046            | 2.413    | 0.00017                 | 0.0336         | -0.452                                             | 0.83      |
| T004918     | Guelph        | 0.1596                                          | 2.638    | 0.00126                 | 0.0368         | 0.693                                              | 1911                                    | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 1.00E+105 |
| T007415     | Guelph        | 0.0497                                          | 0.781    | 0.00042                 | 0.0142         | 0.622                                              | 508                                     | 0.0048            | 2.073    | 0.0005                  | 0.0682         | -0.576                                             | 0.97      |
| T008468     | Guelph        | 0.1255                                          | 10.914   | 0.00084                 | 0.1304         | 0.6                                                | 9189                                    | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 1.00E+05  |
| T008657     | Guelph        | 0.0579                                          | 0.837    | 0.00034                 | 0.0134         | 0.546                                              | 1189                                    | 0.0048            | 2.5      | 0.00031                 | 0.055          | -0.524                                             | 0.01      |
| T009602     | Guelph        | 0.0474                                          | 0.63     | 0.00026                 | 0.0103         | 0.476                                              | 6578                                    | 0.0028            | 2.196    | 0.00013                 | 0.0322         | -0.364                                             | 0.76      |
| T010097     | Guelph        | 0.0632                                          | 0.876    | 0.00043                 | 0.0139         | 0.608                                              | 5305                                    | 0.0039            | 2.646    | 0.00015                 | 0.0361         | -0.432                                             | 7.86      |
| T011560     | Guelph        | 0.0308                                          | 0.723    | 0.00023                 | 0.0119         | 0.551                                              | 10867                                   | 0.0007            | 2.66     | 0.00011                 | 0.036          | -0.361                                             | 0.4       |
| T011554     | Thorold       | 0.1034                                          | 1.196    | 0.0006                  | 0.016          | 0.528                                              | 81                                      | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 218       |
| T011584     | Thorold       | 0.1103                                          | 1.177    | 0.00062                 | 0.015          | 0.528                                              | 1055                                    | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 826       |
| T011280     | Thorold*      | 0.0643                                          | 0.532    | 0.00033                 | 0.0083         | 0.44                                               | 6681                                    | 0.0048            | 1.889    | 0.00016                 | 0.0276         | -0.345                                             | 23        |
| T002374     | Grimsby       | 0.0772                                          | 0.714    | 0.00041                 | 0.011          | 0.478                                              | 4174                                    | 0.0066            | 2.186    | 0.00019                 | 0.0319         | -0.389                                             | 8.96      |
| T003188     | Grimsby       | 0.0805                                          | 0.547    | 0.00067                 | 0.0095         | 0.639                                              | 4694                                    | 0.0029            | 1.856    | 0.00019                 | 0.0277         | -0.422                                             | 39        |
| T012287     | Grimsby       | 0.1508                                          | 0.698    | 0.00086                 | 0.0117         | 0.53                                               | 12087                                   | 0.001             | 4.056    | 0.00013                 | 0.0586         | -0.331                                             | 78        |
| T008194     | Whirlpool     | 0.163                                           | 1.193    | 0.00066                 | 0.0146         | 0.422                                              | 119                                     | 0.0204            | 1.69     | 0.00103                 | 0.0361         | -0.819                                             | 91        |
| T009877     | Whirlpool     | 0.1333                                          | 0.857    | 0.00066                 | 0.0124         | 0.481                                              | 5394                                    | 0.0044            | 3.042    | 0.00015                 | 0.0428         | -0.384                                             | 95        |
| T007357     | Cobourg       | 0.0518                                          | 0.358    | 0.00023                 | 0.0068         | 0.41                                               | 24848                                   | -0.0005           | 1.846    | 0.00011                 | 0.0252         | -0.248                                             | 183       |
| T008358     | Cobourg       | 0.2268                                          | 3.497    | 0.00207                 | 0.0546         | 0.716                                              | 27                                      | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 1.00E+22  |
| T007793     | Sherman Fall  | 0.2336                                          | 2.209    | 0.00212                 | 0.0376         | 0.713                                              | 71                                      | 0.0151            | 4.319    | 0.00145                 | 0.1569         | -0.735                                             | 0.95      |
| T007954     | Sherman Fall  | 0.2167                                          | 4.163    | 0.00089                 | 0.0424         | 0.469                                              | 1935                                    | NaN               | NaN      | NaN                     | NaN            | NaN                                                | 2224      |
| T008057     | Sherman Fall  | 0.0943                                          | 0.973    | 0.00081                 | 0.0179         | 0.646                                              | 268                                     | 0.0104            | 2.283    | 0.00094                 | 0.078          | -0.625                                             | 0.63      |
| T0011596    | Coboconk      | 0.0276                                          | 1.087    | 0.00015                 | 0.0159         | 0.326                                              | 23455                                   | -0.0005           | 5.134    | 0.00013                 | 0.0667         | -0.3                                               | 144       |
| T006907     | Coboconk      | 0.0478                                          | 0.487    | 0.00025                 | 0.0084         | 0.419                                              | 14396                                   | 0.0001            | 2.211    | 0.00015                 | 0.0317         | -0.306                                             | 0.06      |
| T008313     | Coboconk      | 0.0155                                          | 0.425    | 0.00007                 | 0.0088         | 0.202                                              | 75589                                   | -0.00057          | 2.948    | 0.00008                 | 0.0373         | -0.21                                              | 2.79      |
| T008974     | Gull River    | 0.0856                                          | 0.532    | 0.00035                 | 0.0101         | 0.408                                              | 6714                                    | 0.0106            | 1.692    | 0.00025                 | 0.0265         | -0.304                                             | 673       |
| T007369     | Cambrian      | 0.0359                                          | 0.465    | 0.00015                 | 0.0081         | 0.302                                              | 50995                                   | -0.004            | 3.192    | 0.00011                 | 0.0405         | -0.251                                             | 63        |
| T007956     | Cambrian      | 0.0186                                          | 0.715    | 0.00017                 | 0.0127         | 0.398                                              | 20950                                   | -0.004            | 2.848    | 0.00013                 | 0.0389         | -0.291                                             | 56        |
| T008094     | Cambrian      | 0.0901                                          | 1.512    | 0.00073                 | 0.0265         | 0.691                                              | 24257                                   | -0.0025           | 9.742    | 0.00015                 | 0.1169         | -0.34                                              | 0.03      |

\* Thorold / Whirlpool

#### 6.4.1 First-order Equilibrium System

Resolvable solutions for  $V_g/V_l$  and  $f_{Xe}$  for concentrations and concentration ratios are presented in Table 6.2. The high  $\chi^2$  values of the concentration model indicate the least  $\chi^2$  solutions cannot reproduce the measured amount of noble gas concentrations in the gas samples. Solutions obtained from the ratio model differ significantly from those of the concentration model but have  $\chi^2$  up to 4 magnitudes lower, indicating better estimations for the unknown  $V_g/V_l$  and  $f_{Xe}$ . The ratio model has six samples showing negative  $V_g/V_l$  and six samples unresolvable.

#### 6.4.2 Second-order Open and Closed Systems

Solutions calculated from the second-order open and closed systems are presented in Table 6.3 & 6.4, respectively. In both degassing systems, resolvable samples have different  $V_g/V_l$  and  $f_{Xe}$  answers for the concentration and ratio models, with higher  $\chi^2$  obtained from the concentration models. The six samples with negative  $V_g/V_l$  values from the first-order ratio model remain negative for the second-order ratio models. The six samples that cannot be solved with first-order ratio models can be resolved considering a second-order open system but remain unresolvable with the second-order closed system.

#### 6.4.3 $\chi^2$ Values

The minimum  $\chi^2$  values obtained from the concentration and ratio models are presented in the Tables 6.2, 6.3 and 6.4. Theoretically, the fit of many randomly sampled data to a valid model will have a mean  $\chi^2$  value equal to the degrees of freedom. However, the uncertainties of the calculated  $\chi^2$  value also need to be taken into account (Andrae et al., 2010). By considering the probability density function of  $\chi^2$  value, The uncertainty assigned to the model validity can be determined. For example, if the test considers a significant level of 5% (i.e. 95% acceptance probability), for data fit to models with one degree of freedom,  $\chi^2$  values greater than 5 or less than 0.001

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should be rejected. In other words, for samples with  $\chi^2$  within the range of critical values, there is 95% chance that modelled mechanism is a reasonable fit to the data. Similarly, for data fit to models with two degrees of freedom, the critical  $\chi^2$  values with 95% acceptance are 0.05 and 7.3. The concentration models has degrees of freedom of two. All the solutions have  $\chi^2$  values greater than 7.3, suggesting such models are not likely fitting the observations. The ratio models with one degree of freedom have much smaller  $\chi^2$  values. This suggests the ratio models are better fit than the concentration models. Some samples demonstrate acceptable  $\chi^2$  with a 95% uncertainty. For any of these models, samples returning  $\chi^2$  values outside the acceptable range suggest that processes not considered in the models are occurring and are not carried forward for the analysis of excess Kr and Xe.

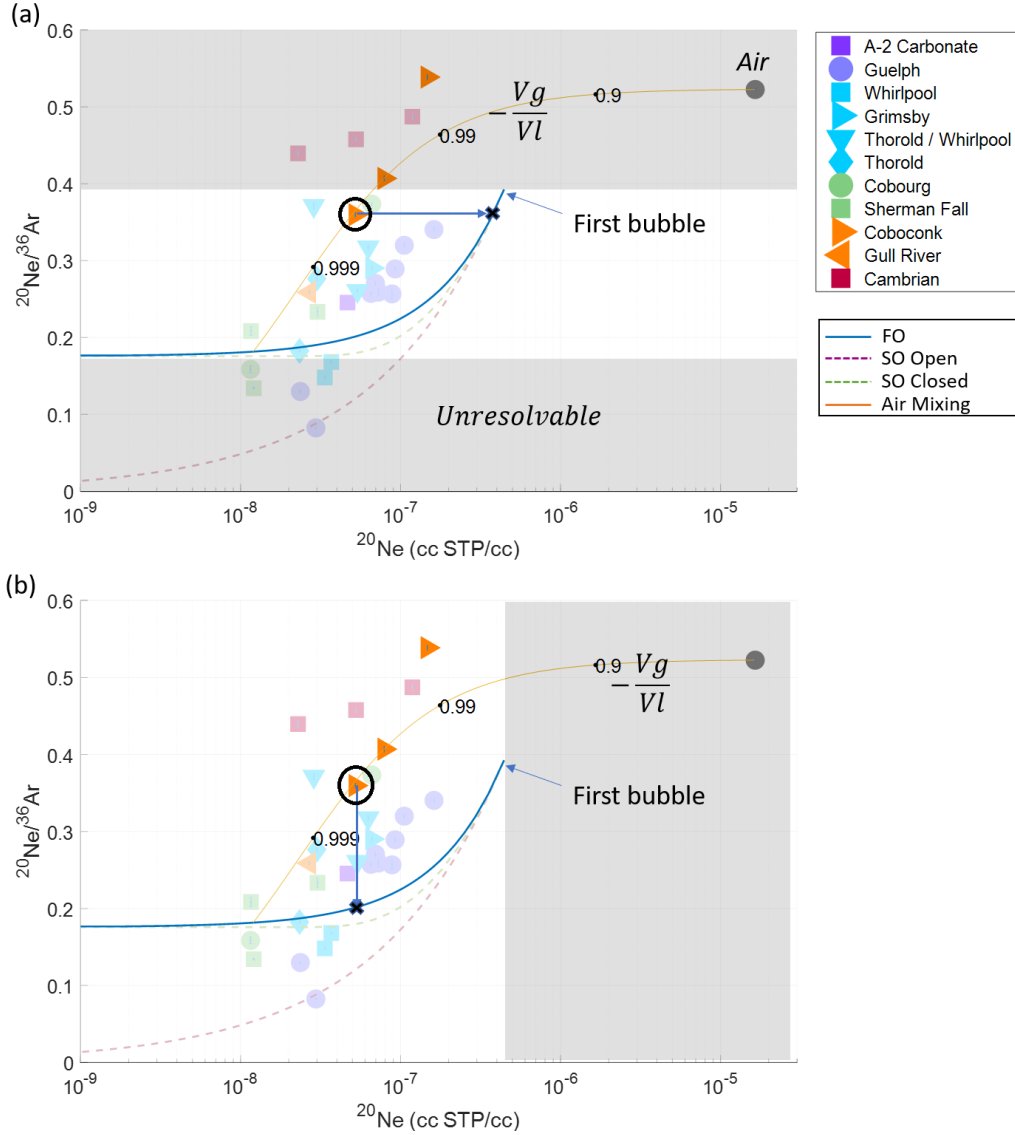
Similar  $\chi^2$  values are observed among the ratio models. This is because for low values of  $V_g/V_l$ , there is very little difference in the trajectory of concentration versus element ratio 6.2, and the miss fit of the data to the models represented by the  $\chi^2$  values is similar for all models.

## **6.5 DISCUSSION**

### **6.5.1 Unresolvable Samples and Negative Solutions of $V_g/V_l$**

There are 6 samples that cannot be resolved with the first-order and second-order closed systems ratio models. These include two Guelph samples, two Grimsby samples and a Cobourg and a Sherman Fall sample (Table 6.2 and 6.4). Figure 6.2 helps illustrate unresolvable  $V_g/V_l$  in the  $^{20}\text{Ne}$  and  $^{20}\text{Ne}/^{36}\text{Ar}$  space. The lines plotted on the figure represent the changes of noble gas concentrations and elemental ratios with an increase in degassing volume. The unresolvable samples are only found for ratio models when the measured ratios are lower than those that can be produced through degassing.

Six other samples demonstrate negative  $V_g/V_l$  solutions with the ratio models of all three systems, indicating a greater extent of elemental fractionation than that can



**Figure 6.2:**  $^{20}\text{Ne}/^{36}\text{Ar}$  and  $^{20}\text{Ne}$  in the gas phase constructed during groundwater degassing for Coboconk formation (1041 m below ground surface) with Coboconk samples highlighted (one of the samples is unresolvable). These plots help visually understand the unresolvable concentration and ratio range. The blue and dashed lines represent mathematically modelled  $^{20}\text{Ne}$  concentrations and  $^{20}\text{Ne}/^{36}\text{Ar}$  ratios in the gas phase in different degassing scenarios from groundwater at reservoir temperature and pressure. The first bubble point illustrates  $^{20}\text{Ne}/^{36}\text{Ar}$  and  $^{20}\text{Ne}$  when degassing volume approaches 0. As gas volume expands,  $^{20}\text{Ne}$  concentration in the gas phase decreases along the degassing lines. Take the circled Coboconk sample as an example. (a) The ratio model tries to find the ratio fit on the degassing model (marked as a black cross). Measurements that sit in shaded area above the first bubble ratio (i.e. maximum fractionation) have negative  $V_g/V_l$ , while samples below the minimum ratios that can be achieved during degassing are unresolvable (e.g. the shaded area below the first-order degassing line). (b) The concentration model tries to find the concentration fit on the degassing model (marked as a black cross). Samples sit to the right of the first bubble concentration have negative  $V_g/V_l$ . Since there is no minimum concentration during a degassing process, all samples can be solved mathematically with the concentration models.

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be generated from the exsolution of air-saturated water at reservoir temperature and pressure, i.e. when  $V_g/V_l$  approaches 0. Theoretically, negative  $V_g/V_l$  solutions can be produced by both the concentration and the ratio models. The unresolvable samples and negative  $V_g/V_l$  solutions are further analysed in the following sections.

**6.5.2 Discrepancies between Solutions of the Concentration and Ratio models**

In all the three degassing scenarios described above,  $V_g/V_l$  solutions demonstrate discrepancies between those produced from the concentration and ratio models. The mismatch occurs when the samples deviate from the degassing line (Figure 6.2). Possible reasons are discussed as follows.

**Air Mixing**

Noble gases concentrations and elemental ratios can be shifted from the degassing line through air contamination, as demonstrated with the air-mixing line in Figure 6.2. The air-mixing process is calculated with  $^{20}\text{Ne}$  and  $^{20}\text{Ne}/^{36}\text{Ar}$ , and its effects have been discussed in Chapter 5. Air contamination factor,  $t$ , can also be solved by integrating with the inversion model using the following equation,

$$C_g^i = (1 - t)f_i C_{ASW}^i U_i^{model} + t C_{air}^i . \quad (6.39)$$

The solutions are presented in Table 6.8, 6.9 and 6.10, and except for T008468 (Guelph), all negative  $V_g/V_l$  are corrected to positive values.

*Table 6.5: Solutions for  $V_g/V_l$  and  $f_{Xe}$  and  $t$  calculated from noble gas concentration ratios based on the first-order equilibrium model.*

| Sample name | Formation     | $\frac{V_g}{V_l}$ | $f_{Xe}$ | $t(\%)$ | $\frac{V_g \text{ error}}{V_l}$ | $f_{Xe \text{ error}}$ | $t \text{ error}(\%)$ | Correlation coefficient $\frac{V_g}{V_l} - f_{Xe}$ | Correlation coefficient $\frac{V_g}{V_l} - t$ | Correlation coefficient $f_{Xe} - t$ | $\chi^2$ |
|-------------|---------------|-------------------|----------|---------|---------------------------------|------------------------|-----------------------|----------------------------------------------------|-----------------------------------------------|--------------------------------------|----------|
| T008636     | A-2 Carbonate | 0.1763            | 1.514    | 0.086   | 0.00238                         | 0.0193                 | 0.001                 | 0.46                                               | 0.216                                         | 0.031                                | 305      |
| T002556     | Guelph        | 0.0845            | 1.439    | 0.321   | 0.00137                         | 0.0208                 | 0.004                 | 0.407                                              | 0.225                                         | -0.037                               | 337      |
| T003899     | Guelph        | 0.1177            | 1.587    | 0.192   | 0.00168                         | 0.0214                 | 0.002                 | 0.453                                              | 0.207                                         | -0.018                               | 4        |
| T004918     | Guelph        | 0.1259            | 1.965    | -0.038  | 0.00155                         | 0.0247                 | 0.001                 | 0.547                                              | 0.124                                         | 0.006                                | 172      |
| T007415     | Guelph        | 0.0744            | 1.23     | 0.223   | 0.00118                         | 0.0189                 | 0.005                 | 0.39                                               | 0.23                                          | -0.072                               | 7        |
| T008468     | Guelph        | 0.0712            | 6.331    | -0.135  | 0.00128                         | 0.0814                 | 0.001                 | 0.639                                              | 0.095                                         | 0.046                                | 2304     |
| T008657     | Guelph        | 0.1009            | 1.58     | 0.21    | 0.00145                         | 0.0223                 | 0.003                 | 0.47                                               | 0.191                                         | -0.024                               | 3        |
| T009602     | Guelph        | 0.0986            | 1.391    | 0.319   | 0.00156                         | 0.0204                 | 0.003                 | 0.413                                              | 0.215                                         | -0.022                               | 23       |
| T010097     | Guelph        | 0.1015            | 1.488    | 0.167   | 0.00143                         | 0.0199                 | 0.003                 | 0.44                                               | 0.202                                         | -0.022                               | 231      |
| T011560     | Guelph        | 0.0713            | 1.698    | 0.608   | 0.00123                         | 0.0243                 | 0.005                 | 0.423                                              | 0.25                                          | -0.031                               | 136      |
| T011554     | Thorold       | 0.0848            | 1.055    | -0.051  | 0.00102                         | 0.0133                 | 0.001                 | 0.394                                              | 0.139                                         | -0.019                               | 178      |
| T011584     | Thorold       | 0.0722            | 0.858    | -0.124  | 0.00078                         | 0.0101                 | 0.001                 | 0.357                                              | 0.134                                         | -0.022                               | 874      |
| T011280     | Thorold*      | 0.11              | 0.947    | 0.176   | 0.00161                         | 0.0138                 | 0.002                 | 0.34                                               | 0.209                                         | -0.046                               | 381      |
| T002374     | Grimsby       | 0.1232            | 1.209    | 0.129   | 0.00176                         | 0.017                  | 0.002                 | 0.401                                              | 0.189                                         | -0.022                               | 163      |
| T003188     | Grimsby       | 0.1201            | 0.829    | 0.122   | 0.00168                         | 0.0119                 | 0.003                 | 0.297                                              | 0.263                                         | -0.106                               | 765      |
| T012287     | Grimsby       | 0.3181            | 1.551    | 0.085   | 0.00475                         | 0.0222                 | 0.001                 | 0.444                                              | 0.199                                         | -0.019                               | 1343     |
| T008194     | Whirlpool     | 0.1464            | 1.037    | -0.02   | 0.00162                         | 0.0129                 | 0.001                 | 0.411                                              | 0.134                                         | 0.002                                | 717      |
| T009877     | Whirlpool     | 0.1937            | 1.257    | 0.051   | 0.00251                         | 0.0169                 | 0.001                 | 0.428                                              | 0.166                                         | -0.01                                | 1168     |
| T007357     | Cobourg       | 0.2984            | 2.081    | 0.36    | 0.00664                         | 0.0346                 | 0.001                 | 0.405                                              | 0.272                                         | -0.028                               | 207      |
| T008358     | Cobourg       | 0.1972            | 2.905    | -0.011  | 0.0029                          | 0.0416                 | 0.001                 | 0.621                                              | 0.092                                         | -0.003                               | 2        |
| T007793     | Sherman Fall  | 0.301             | 2.781    | 0.017   | 0.00448                         | 0.0406                 | 0.001                 | 0.603                                              | 0.122                                         | -0.013                               | 2        |
| T007954     | Sherman Fall  | 0.1224            | 2.268    | -0.058  | 0.00147                         | 0.0271                 | 0                     | 0.581                                              | 0.082                                         | 0.022                                | 1015     |
| T008057     | Sherman Fall  | 0.1312            | 1.426    | 0.062   | 0.00202                         | 0.0217                 | 0.002                 | 0.435                                              | 0.187                                         | -0.057                               | 3        |
| T0011596    | Coboconk      | 0.048             | 1.966    | 0.16    | 0.00084                         | 0.0269                 | 0.002                 | 0.461                                              | 0.154                                         | -0.022                               | 3826     |
| T006907     | Coboconk      | 0.1343            | 1.376    | 0.215   | 0.00237                         | 0.0213                 | 0.001                 | 0.378                                              | 0.209                                         | -0.057                               | 166      |
| T008313     | Coboconk      | 0.1569            | 2.883    | 0.743   | 0.00419                         | 0.0493                 | 0.003                 | 0.417                                              | 0.264                                         | -0.019                               | 1259     |
| T008974     | Gull River    | 0.439             | 3.345    | 0.145   | 0.00838                         | 0.0499                 | 0.001                 | 0.519                                              | 0.188                                         | -0.005                               | 2656     |
| T007369     | Cambrian      | 0.1159            | 1.535    | 0.203   | 0.00202                         | 0.0228                 | 0.001                 | 0.402                                              | 0.181                                         | -0.039                               | 2669     |
| T007956     | Cambrian      | 0.1875            | 4.168    | 0.637   | 0.00546                         | 0.0702                 | 0.003                 | 0.419                                              | 0.275                                         | -0.064                               | 63       |
| T008094     | Cambrian      | 0.4648            | 8.776    | 0.109   | 0.00835                         | 0.1185                 | 0.001                 | 0.647                                              | 0.134                                         | -0.003                               | 160      |

\* Thorold / Whirlpool



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**Table 6.6:** Solutions for  $V_g/V_l$  and  $f_{Xe}$  and  $t$  calculated from noble gas concentration ratios based on the second-order open model.

| Sample name | Formation     | $\frac{V_g}{V_l}$ | $f_{Xe}$ | $t(\%)$ | $\frac{V_g}{V_l}$ | $f_{Xe}$ error | error(%) | Correlation coefficient $\frac{V_g}{V_l} - f_{Xe}$ | Correlation coefficient $\frac{V_g}{V_l} - t$ | Correlation coefficient $f_{Xe} - t$ | $\chi^2$ |
|-------------|---------------|-------------------|----------|---------|-------------------|----------------|----------|----------------------------------------------------|-----------------------------------------------|--------------------------------------|----------|
| T008636     | A-2 Carbonate | 0.0488            | 0.986    | 0.28    | 0.00016           | 0.0126         | 0.001    | 0.378                                              | 0.426                                         | 0.095                                | 80       |
| T002556     | Guelph        | 0.0199            | 0.907    | 0.63    | 0.00012           | 0.015          | 0.005    | 0.551                                              | 0.609                                         | 0.239                                | 78       |
| T003899     | Guelph        | 0.0202            | 0.773    | 0.39    | 0.00007           | 0.0109         | 0.003    | 0.449                                              | 0.621                                         | 0.189                                | 11       |
| T004918     | Guelph        | 0.0199            | 0.87     | 0.13    | 0.00005           | 0.0105         | 0.001    | 0.393                                              | 0.479                                         | 0.128                                | 0.29     |
| T007415     | Guelph        | 0.0174            | 0.703    | 0.51    | 0.00016           | 0.0154         | 0.006    | 0.72                                               | 0.469                                         | 0.227                                | 16       |
| T008468     | Guelph        | 0.0149            | 3.264    | 0.12    | 0.00004           | 0.0359         | 0.002    | 0.339                                              | 0.644                                         | 0.205                                | 36       |
| T008657     | Guelph        | 0.0192            | 0.805    | 0.43    | 0.00014           | 0.0152         | 0.003    | 0.721                                              | 0.406                                         | 0.21                                 | 12       |
| T009602     | Guelph        | 0.0194            | 0.737    | 0.55    | 0.00009           | 0.012          | 0.003    | 0.496                                              | 0.524                                         | 0.169                                | 20       |
| T010097     | Guelph        | 0.0203            | 0.827    | 0.41    | 0.00008           | 0.0116         | 0.003    | 0.461                                              | 0.62                                          | 0.199                                | 54       |
| T011560     | Guelph        | 0.0184            | 1.111    | 0.96    | 0.00012           | 0.018          | 0.007    | 0.548                                              | 0.706                                         | 0.295                                | 35       |
| T011554     | Thorold       | 0.0231            | 0.671    | 0.21    | 0.00008           | 0.0092         | 0.001    | 0.412                                              | 0.428                                         | 0.11                                 | 87       |
| T011584     | Thorold       | 0.0225            | 0.585    | 0.19    | 0.00005           | 0.0074         | 0.001    | 0.281                                              | 0.478                                         | 0.07                                 | 202      |
| T011280     | Thorold*      | 0.0261            | 0.553    | 0.4     | 0.00012           | 0.0091         | 0.002    | 0.429                                              | 0.479                                         | 0.105                                | 121      |
| T002374     | Grimsby       | 0.0257            | 0.657    | 0.32    | 0.0001            | 0.01           | 0.002    | 0.444                                              | 0.462                                         | 0.119                                | 61       |
| T003188     | Grimsby       | 0.0275            | 0.471    | 0.38    | 0.00015           | 0.0081         | 0.004    | 0.428                                              | 0.701                                         | 0.17                                 | 179      |
| T012287     | Grimsby       | 0.037             | 0.656    | 0.17    | 0.00021           | 0.0114         | 0.001    | 0.682                                              | 0.453                                         | 0.229                                | 240      |
| T008194     | Whirlpool     | 0.0239            | 0.486    | 0.14    | 0.00006           | 0.0062         | 0.001    | 0.375                                              | 0.324                                         | 0.069                                | 171      |
| T009877     | Whirlpool     | 0.0269            | 0.567    | 0.18    | 0.00009           | 0.0082         | 0.001    | 0.51                                               | 0.385                                         | 0.124                                | 225      |
| T007357     | Cobourg       | 0.0314            | 0.655    | 0.4     | 0.00018           | 0.0124         | 0.002    | 0.529                                              | 0.573                                         | 0.194                                | 14       |
| T008358     | Cobourg       | 0.0308            | 1.333    | 0.07    | 0.00025           | 0.0272         | 0.001    | 0.829                                              | 0.344                                         | 0.245                                | 6.04     |
| T007793     | Sherman Fall  | 0.0346            | 1.042    | 0.07    | 0.00028           | 0.023          | 0.001    | 0.843                                              | 0.288                                         | 0.187                                | 6.61     |
| T007954     | Sherman Fall  | 0.0288            | 1.48     | 0.07    | 0.00007           | 0.0156         | 0        | 0.412                                              | 0.402                                         | 0.14                                 | 96       |
| T008057     | Sherman Fall  | 0.0272            | 0.76     | 0.18    | 0.00024           | 0.0166         | 0.002    | 0.744                                              | 0.415                                         | 0.214                                | 11       |
| T0011596    | Coboconk      | 0.0307            | 2.678    | 0.48    | 0.0003            | 0.0479         | 0.003    | 0.744                                              | 0.574                                         | 0.369                                | 344      |
| T006907     | Coboconk      | 0.0307            | 0.842    | 0.31    | 0.0002            | 0.0155         | 0.002    | 0.579                                              | 0.556                                         | 0.22                                 | 53       |
| T008313     | Coboconk      | NaN               | NaN      | NaN     | NaN               | NaN            | NaN      | NaN                                                | NaN                                           | NaN                                  | 3315     |
| T008974     | Gull River    | 0.0362            | 0.683    | 0.16    | 0.00015           | 0.0119         | 0.001    | 0.498                                              | 0.429                                         | 0.118                                | 429      |
| T007369     | Cambrian      | 0.04              | 1.596    | 0.32    | 0.00041           | 0.0368         | 0.001    | 0.805                                              | 0.558                                         | 0.388                                | 306      |
| T007956     | Cambrian      | 0.04              | 2.689    | 0.72    | 0.00112           | 0.128          | 0.005    | 0.945                                              | 0.791                                         | 0.706                                | 10       |
| T008094     | Cambrian      | 0.0483            | 3.516    | 0.14    | 0.00055           | 0.0887         | 0.001    | 0.914                                              | 0.69                                          | 0.596                                | 7.63     |

\* Thorold / Whirlpool

**Table 6.7:** Solutions for  $V_g/V_l$  and  $f_{Xe}$  and  $t$  calculated from noble gas concentration ratios based on the second-order closed model; NaN means no resolvable solution found.

| Sample name | Formation     | $\frac{V_g}{V_l}$ | $f_{Xe}$ | $t(\%)$ | $\frac{V_g}{V_l}$ error | $f_{Xe}$ error | error(%) | Correlation coefficient $\frac{V_g}{V_l} - f_{Xe}$ | Correlation coefficient $\frac{V_g}{V_l} - t$ | Correlation coefficient $f_{Xe} - t$ | $\chi^2$ |
|-------------|---------------|-------------------|----------|---------|-------------------------|----------------|----------|----------------------------------------------------|-----------------------------------------------|--------------------------------------|----------|
| T008636     | A-2 Carbonate | 0.2074            | 1.635    | 0.12    | 0.00196                 | 0.0243         | 0.002    | 0.657                                              | 0.876                                         | 0.547                                | 34       |
| T002556     | Guelph        | 0.1096            | 1.812    | 0.42    | 0.00201                 | 0.0412         | 0.008    | 0.816                                              | 0.863                                         | 0.661                                | 45       |
| T003899     | Guelph        | 0.1159            | 1.583    | 0.19    | 0.00137                 | 0.0271         | 0.005    | 0.714                                              | 0.865                                         | 0.573                                | 0.22     |
| T004918     | Guelph        | 0.1096            | 1.715    | -0.07   | 0.00082                 | 0.0235         | 0.002    | 0.627                                              | 0.877                                         | 0.521                                | 16       |
| T007415     | Guelph        | 0.0774            | 1.224    | 0.23    | 0.00199                 | 0.0376         | 0.01     | 0.889                                              | 0.881                                         | 0.745                                | 4.88     |
| T008468     | Guelph        | -0.0036           | 1.252    | -17.73  | 0                       | 0.0087         | 0.014    | -0.08                                              | 0.994                                         | -0.081                               | 5065     |
| T008657     | Guelph        | 0.1013            | 1.578    | 0.21    | 0.00222                 | 0.0435         | 0.006    | 0.893                                              | 0.907                                         | 0.785                                | 1.43     |
| T009602     | Guelph        | 0.1023            | 1.434    | 0.33    | 0.0015                  | 0.029          | 0.005    | 0.755                                              | 0.862                                         | 0.61                                 | 3.32     |
| T010097     | Guelph        | 0.1169            | 1.709    | 0.22    | 0.00148                 | 0.0301         | 0.005    | 0.737                                              | 0.866                                         | 0.596                                | 22       |
| T011560     | Guelph        | 0.0862            | 1.935    | 0.71    | 0.00162                 | 0.0436         | 0.011    | 0.817                                              | 0.88                                          | 0.676                                | 14       |
| T011554     | Thorold       | 0.0963            | 1.113    | -0.02   | 0.00094                 | 0.017          | 0.003    | 0.661                                              | 0.901                                         | 0.569                                | 31       |
| T011584     | Thorold       | 0.0884            | 0.941    | -0.06   | 0.00057                 | 0.0119         | 0.002    | 0.5                                                | 0.879                                         | 0.408                                | 96       |
| T011280     | Thorold*      | 0.1365            | 1.124    | 0.23    | 0.00194                 | 0.0221         | 0.004    | 0.72                                               | 0.863                                         | 0.577                                | 67       |
| T002374     | Grimsby       | 0.1387            | 1.34     | 0.16    | 0.00176                 | 0.0247         | 0.003    | 0.721                                              | 0.868                                         | 0.589                                | 24       |
| T003188     | Grimsby       | 0.1738            | 1.117    | 0.24    | 0.00324                 | 0.0246         | 0.006    | 0.762                                              | 0.884                                         | 0.612                                | 116      |
| T012287     | Grimsby       | 0.5563            | 2.973    | 0.13    | 0.01432                 | 0.0872         | 0.002    | 0.906                                              | 0.863                                         | 0.756                                | 196      |
| T008194     | Whirlpool     | 0.1694            | 1.247    | 0       | 0.00141                 | 0.0178         | 0.001    | 0.634                                              | 0.914                                         | 0.561                                | 88       |
| T009877     | Whirlpool     | 0.2655            | 1.848    | 0.09    | 0.00377                 | 0.0353         | 0.002    | 0.786                                              | 0.878                                         | 0.663                                | 158      |
| T007357     | Cobourg       | 0.2083            | 1.53     | 0.32    | 0.00407                 | 0.0384         | 0.003    | 0.795                                              | 0.86                                          | 0.635                                | 34       |
| T008358     | Cobourg       | 0.1943            | 2.932    | -0.01   | 0.00538                 | 0.0993         | 0.002    | 0.944                                              | 0.963                                         | 0.903                                | 0.51     |
| T007793     | Sherman Fall  | 0.2934            | 2.88     | 0.02    | 0.00896                 | 0.1062         | 0.002    | 0.949                                              | 0.939                                         | 0.88                                 | 0.86     |
| T007954     | Sherman Fall  | 0.1486            | 2.735    | -0.04   | 0.00108                 | 0.0342         | 0.001    | 0.66                                               | 0.942                                         | 0.614                                | 52       |
| T008057     | Sherman Fall  | 0.133             | 1.416    | 0.06    | 0.00344                 | 0.0448         | 0.004    | 0.903                                              | 0.901                                         | 0.784                                | 2.06     |
| T0011596    | Coboconk      | 0.1505            | 4.776    | 0.4     | 0.00442                 | 0.1521         | 0.004    | 0.929                                              | 0.864                                         | 0.783                                | 307      |
| T006907     | Coboconk      | 0.1647            | 1.648    | 0.24    | 0.00342                 | 0.0419         | 0.003    | 0.827                                              | 0.859                                         | 0.667                                | 28       |
| T008313     | Coboconk      | NaN               | NaN      | NaN     | NaN                     | NaN            | NaN      | NaN                                                | NaN                                           | NaN                                  | 131      |
| T008974     | Gull River    | 0.1715            | 1.247    | 0.09    | 0.00219                 | 0.0258         | 0.001    | 0.729                                              | 0.881                                         | 0.602                                | 578      |
| T007369     | Cambrian      | 0.3383            | 4.267    | 0.29    | 0.01315                 | 0.1766         | 0.002    | 0.946                                              | 0.863                                         | 0.796                                | 275      |
| T007956     | Cambrian      | 0.3244            | 7.125    | 0.69    | 0.03409                 | 0.7483         | 0.008    | 0.989                                              | 0.913                                         | 0.891                                | 6.9      |
| T008094     | Cambrian      | 0.7158            | 14.623   | 0.13    | 0.03768                 | 0.7952         | 0.002    | 0.982                                              | 0.888                                         | 0.863                                | 5.19     |

\* Thorold / Whirlpool  
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*6. Quantifying Gas-Water Ratio and Kr and Xe enrichment by an Error-Weighted, Nonlinear Inversion of Atmospheric Noble Gas Concentrations and Concentration Ratios: A Case Study on the Southwestern Ontario Basin*

The contamination factor significantly lowers the  $\chi^2$ , indicating a better fit of the solutions to the measured noble gas contents. Noticeably, the Coboconk sample T008313 cannot be solved by the contamination model due to the higher than atmospheric  $^{20}\text{Ne}/^{36}\text{Ar}$  of the sample. Negative air contaminations are mathematically calculated for some samples regarding the first-order and second-order closed system, but these samples produce positive contamination factors with second-order open systems. However, as demonstrated in Chapter 5, helium concentrations in groundwater after second-order open system correction will be significantly higher than the maximum solubility (C.1). The solutions of  $f_{Xe}$  in a second-order open system are less than one. This indicates the water system is depleted in Kr and Xe, and the enrichment in the gas phase is produced by significant solubility fractionation. These suggest second-order open system air-correction is not likely to be the explanation of the samples with negative contamination factors. Alternatively, the estimated reservoir condition might be inaccurate, but the reconstruction of the degassing models cannot be achieved without accurate field data. It is, therefore, not unreasonable to assume that these samples could be very close to the degassing lines and air-corrections will be insignificant.

## **Fluid Dilution**

An addition of a dilution phase, to the groundwater or the exsolved gas phase, is the second mechanism that can result in the discrepancies between solutions obtained from the concentration and ratio models. The dilution fluids need to be depleted in atmospheric noble gases which could be caused by extensive degassing. The migration of such fluid and the subsequent mixing with the diagenetic water or gas could result in a reduction in noble gas concentrations yet maintaining the same concentration ratios.

We integrate the effects of dilution by adding a dilution factor,  $r$ , to the concentration models:

$$C_g^i = r f_i C_{ASW}^i U_i^{model}, \quad (6.40)$$

## 6.5. DISCUSSION

where  $r = \frac{V_g}{V_g + V_{\text{dilution gas}}}$  and  $V_{\text{dilution gas}}$  is the volume of the dilution gas.  $r$  can also be interpreted as a dilution factor to the groundwater. In this equation,  $f_{Ne}$  and  $f_{Ar}$  are set as 1, and  $f_{Kr}$  and  $f_{Xe}$  are linearly constrained.  $r \times f_i$  is therefore not an unconstrained conglomerate but can be separately determined.

The solutions of the dilution factor,  $r$ , and the corresponding  $V_g/V_l$  and  $f_{Xe}$  are presented in Table 6.8, 6.9 and 6.10. The dilution factor allows a mathematical match between solutions obtained from the concentration and ratio models. There are two requirements for such dilution, 1) geological and hydrogeological evidence of fluid migration; 2) the migrated fluids need to be depleted in atmospheric noble gases.

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**Table 6.8:** Solutions for  $V_g/V_l$ ,  $f_{Xe}$  and  $r$  calculated from noble gas concentration ratios based on first-order equilibrium model; NaN means no resolvable solution found.

| Sample name | Formation     | $\frac{V_g}{V_l}$ | $f_{Xe}$ | $r$   | $\frac{V_g \text{ error}}{V_l}$ | $f_{Xe \text{ error}}$ | $r \text{ error}$ | Correlation coefficient $\frac{V_g}{V_l} - f_{Xe}$ | Correlation coefficient $\frac{V_g}{V_l} - r$ | Correlation coefficient $f_{Xe} - r$ | $\chi^2$ |
|-------------|---------------|-------------------|----------|-------|---------------------------------|------------------------|-------------------|----------------------------------------------------|-----------------------------------------------|--------------------------------------|----------|
| T008636     | A-2 Carbonate | 0.0151            | 2.463    | 0.177 | 0.00043                         | 0.0393                 | 0.003             | -0.691                                             | 0.983                                         | -0.727                               | 13       |
| T002556     | Guelph        | 0.0004            | 2.604    | 0.091 | 0.00007                         | 0.0452                 | 0.0014            | -0.64                                              | 0.951                                         | -0.717                               | 5.44     |
| T003899     | Guelph        | 0.0023            | 2.34     | 0.088 | 0.00013                         | 0.0397                 | 0.0017            | -0.671                                             | 0.976                                         | -0.725                               | 5.38     |
| T004918     | Guelph        | NaN               | NaN      | NaN   | NaN                             | NaN                    | NaN               | NaN                                                | NaN                                           | NaN                                  | NaN      |
| T007415     | Guelph        | 0.0029            | 1.932    | 0.131 | 0.0003                          | 0.0695                 | 0.0061            | -0.886                                             | 0.985                                         | -0.923                               | 0.57     |
| T008468     | Guelph        | NaN               | NaN      | NaN   | NaN                             | NaN                    | NaN               | NaN                                                | NaN                                           | NaN                                  | NaN      |
| T008657     | Guelph        | 0.0025            | 2.442    | 0.1   | 0.0002                          | 0.0704                 | 0.0034            | -0.877                                             | 0.987                                         | -0.907                               | 0.89     |
| T009602     | Guelph        | 0.0011            | 2.156    | 0.095 | 0.00008                         | 0.0382                 | 0.0015            | -0.664                                             | 0.967                                         | -0.72                                | 4.33     |
| T010097     | Guelph        | 0.002             | 2.543    | 0.087 | 0.00011                         | 0.0423                 | 0.0015            | -0.662                                             | 0.971                                         | -0.72                                | 2.91     |
| T011560     | Guelph        | 0                 | 2.608    | 0.121 | 0.00005                         | 0.0403                 | 0.0015            | -0.566                                             | 0.938                                         | -0.655                               | 3.76     |
| T011554     | Thorold       | NaN               | NaN      | NaN   | NaN                             | NaN                    | NaN               | NaN                                                | NaN                                           | NaN                                  | NaN      |
| T011584     | Thorold       | NaN               | NaN      | NaN   | NaN                             | NaN                    | NaN               | NaN                                                | NaN                                           | NaN                                  | NaN      |
| T011280     | Thorold *     | 0.0026            | 1.784    | 0.105 | 0.00012                         | 0.0315                 | 0.0017            | -0.665                                             | 0.968                                         | -0.717                               | 18       |
| T002374     | Grimsby       | 0.0041            | 2.055    | 0.105 | 0.00017                         | 0.0378                 | 0.002             | -0.704                                             | 0.978                                         | -0.749                               | 4.7      |
| T003188     | Grimsby       | 0.0013            | 1.764    | 0.077 | 0.00012                         | 0.0308                 | 0.0013            | -0.624                                             | 0.953                                         | -0.704                               | 35       |
| T012287     | Grimsby       | 0.0003            | 3.79     | 0.028 | 0.00007                         | 0.0676                 | 0.0004            | -0.704                                             | 0.952                                         | -0.768                               | 85       |
| T008194     | Whirlpool     | 0.0399            | 1.426    | 0.258 | 0.00376                         | 0.0323                 | 0.022             | -0.854                                             | 0.999                                         | -0.861                               | 85       |
| T009877     | Whirlpool     | 0.0027            | 2.799    | 0.044 | 0.00012                         | 0.0507                 | 0.0008            | -0.736                                             | 0.977                                         | -0.778                               | 98       |
| T007357     | Cobourg       | -0.0008           | 1.879    | 0.085 | 0.00004                         | 0.0285                 | 0.0008            | -0.524                                             | 0.936                                         | -0.594                               | 231      |
| T008358     | Cobourg       | NaN               | NaN      | NaN   | NaN                             | NaN                    | NaN               | NaN                                                | NaN                                           | NaN                                  | NaN      |
| T007793     | Sherman Fall  | 0.0145            | 3.849    | 0.081 | 0.00203                         | 0.2066                 | 0.0084            | -0.956                                             | 0.997                                         | -0.969                               | 0.21     |
| T007954     | Sherman Fall  | NaN               | NaN      | NaN   | NaN                             | NaN                    | NaN               | NaN                                                | NaN                                           | NaN                                  | NaN      |
| T008057     | Sherman Fall  | 0.0076            | 2.102    | 0.133 | 0.00076                         | 0.0855                 | 0.008             | -0.91                                              | 0.991                                         | -0.938                               | 0.18     |
| T0011596    | Cobocok       | -0.0005           | 4.838    | 0.149 | 0.00006                         | 0.0743                 | 0.0017            | -0.63                                              | 0.935                                         | -0.705                               | 151      |
| T006907     | Cobocok       | -0.0004           | 2.167    | 0.103 | 0.00006                         | 0.0358                 | 0.0012            | -0.611                                             | 0.946                                         | -0.68                                | 1.79     |
| T008313     | Cobocok       | -0.0023           | 2.763    | 0.156 | 0.00002                         | 0.0379                 | 0.001             | -0.468                                             | 0.906                                         | -0.543                               | 9.14     |
| T008974     | Gull River    | 0.0044            | 1.861    | 0.125 | 0.00017                         | 0.0356                 | 0.0019            | -0.676                                             | 0.977                                         | -0.719                               | 801      |
| T007369     | Cambrian      | -0.0019           | 2.996    | 0.097 | 0.00003                         | 0.0423                 | 0.0008            | -0.549                                             | 0.932                                         | -0.615                               | 55       |
| T007956     | Cambrian      | -0.002            | 2.772    | 0.204 | 0.00004                         | 0.0415                 | 0.0018            | -0.471                                             | 0.872                                         | -0.6                                 | 85       |
| T008094     | Cambrian      | -0.0014           | 9.311    | 0.047 | 0.00005                         | 0.1341                 | 0.0005            | -0.608                                             | 0.903                                         | -0.723                               | 4.83     |

\* Thorold / Whirlpool

Table 6.9: Solutions for  $V_g/V_l$ ,  $f_{Xe}$  and  $r$  calculated from noble gas concentration ratios based on second-order open model.

| Sample name | Formation     | $\frac{V_g}{V_l}$ | $f_{Xe}$ | $r$   | $\frac{V_g}{V_l}$ error | $f_{Xe}$ error | $r$ error | Correlation coefficient $\frac{V_g}{V_l} - f_{Xe}$ | Correlation coefficient $\frac{V_g}{V_l} - r$ | Correlation coefficient $f_{Xe} - r$ | $\chi^2$ |
|-------------|---------------|-------------------|----------|-------|-------------------------|----------------|-----------|----------------------------------------------------|-----------------------------------------------|--------------------------------------|----------|
| T008636     | A-2 Carbonate | 0.0066            | 2.895    | 0.148 | 0.00007                 | 0.0393         | 0.0012    | -0.528                                             | 0.924                                         | -0.602                               | 25       |
| T002556     | Guelph        | 0.0007            | 2.662    | 0.103 | 0.00005                 | 0.045          | 0.0014    | -0.617                                             | 0.941                                         | -0.7                                 | 12.25    |
| T003899     | Guelph        | 0.0019            | 2.468    | 0.093 | 0.00005                 | 0.0379         | 0.0012    | -0.574                                             | 0.944                                         | -0.658                               | 0.95     |
| T004918     | Guelph        | 0.006             | 2.551    | 0.132 | 0.00006                 | 0.039          | 0.0018    | -0.597                                             | 0.942                                         | -0.69                                | 1        |
| T007415     | Guelph        | 0.0021            | 2.021    | 0.137 | 0.0001                  | 0.061          | 0.0041    | -0.834                                             | 0.964                                         | -0.895                               | 2        |
| T008468     | Guelph        | 0.0088            | 5.258    | 0.409 | 0.00005                 | 0.0749         | 0.0052    | -0.6                                               | 0.942                                         | -0.68                                | 21       |
| T008657     | Guelph        | 0.0019            | 2.554    | 0.106 | 0.00007                 | 0.0637         | 0.0024    | -0.832                                             | 0.972                                         | -0.878                               | 0.01     |
| T009602     | Guelph        | 0.0012            | 2.222    | 0.106 | 0.00005                 | 0.0375         | 0.0014    | -0.62                                              | 0.95                                          | -0.688                               | 0.91     |
| T010097     | Guelph        | 0.0017            | 2.665    | 0.093 | 0.00005                 | 0.0406         | 0.0011    | -0.575                                             | 0.94                                          | -0.661                               | 9.22     |
| T011560     | Guelph        | 0.0004            | 2.666    | 0.138 | 0.00005                 | 0.0411         | 0.0017    | -0.564                                             | 0.938                                         | -0.652                               | 0.46     |
| T011554     | Thorold       | 0.0057            | 1.859    | 0.165 | 0.00006                 | 0.0305         | 0.0021    | -0.623                                             | 0.936                                         | -0.704                               | 50       |
| T011584     | Thorold       | 0.0064            | 1.539    | 0.188 | 0.00005                 | 0.0213         | 0.0017    | -0.491                                             | 0.922                                         | -0.577                               | 143      |
| T011280     | Thorold*      | 0.0021            | 1.879    | 0.111 | 0.00005                 | 0.0307         | 0.0013    | -0.59                                              | 0.939                                         | -0.661                               | 28       |
| T002374     | Grimsby       | 0.0026            | 2.226    | 0.104 | 0.00005                 | 0.0363         | 0.0012    | -0.599                                             | 0.94                                          | -0.672                               | 10.83    |
| T003188     | Grimsby       | 0.0014            | 1.819    | 0.086 | 0.00007                 | 0.03           | 0.0011    | -0.565                                             | 0.927                                         | -0.665                               | 46       |
| T012287     | Grimsby       | 0.0007            | 3.879    | 0.032 | 0.00006                 | 0.0679         | 0.0005    | -0.69                                              | 0.947                                         | -0.758                               | 111      |
| T008194     | Whirlpool     | 0.0042            | 2.102    | 0.074 | 0.00004                 | 0.0308         | 0.0008    | -0.592                                             | 0.948                                         | -0.651                               | 110      |
| T009877     | Whirlpool     | 0.002             | 2.983    | 0.045 | 0.00005                 | 0.0484         | 0.0006    | -0.654                                             | 0.949                                         | -0.718                               | 125      |
| T007357     | Cobourg       | -0.0005           | 1.935    | 0.096 | 0.00005                 | 0.0298         | 0.001     | -0.546                                             | 0.949                                         | -0.609                               | 199      |
| T008358     | Cobourg       | 0.0071            | 4.563    | 0.099 | 0.00017                 | 0.1666         | 0.0037    | -0.905                                             | 0.974                                         | -0.948                               | 6        |
| T007793     | Sherman Fall  | 0.0049            | 4.523    | 0.059 | 0.00018                 | 0.1634         | 0.0022    | -0.899                                             | 0.974                                         | -0.944                               | 3.13     |
| T007954     | Sherman Fall  | 0.0084            | 4.245    | 0.137 | 0.00006                 | 0.0572         | 0.0015    | -0.644                                             | 0.953                                         | -0.704                               | 101      |
| T008057     | Sherman Fall  | 0.0039            | 2.305    | 0.122 | 0.00015                 | 0.0724         | 0.0037    | -0.844                                             | 0.964                                         | -0.904                               | 1.4      |
| T0011596    | Coboconk      | -0.0001           | 4.963    | 0.168 | 0.00007                 | 0.0772         | 0.0021    | -0.641                                             | 0.943                                         | -0.712                               | 189      |
| T006907     | Coboconk      | 0.0001            | 2.213    | 0.117 | 0.00007                 | 0.0369         | 0.0015    | -0.62                                              | 0.951                                         | -0.685                               | 0.07     |
| T008313     | Coboconk      | -0.0033           | 3.001    | 0.157 | 0.00005                 | 0.0431         | 0.0014    | -0.538                                             | 0.951                                         | -0.594                               | 3.14     |
| T008974     | Gull River    | 0.0033            | 1.994    | 0.131 | 0.00007                 | 0.0353         | 0.0014    | -0.611                                             | 0.954                                         | -0.67                                | 734      |
| T007369     | Cambrian      | -0.0021           | 3.139    | 0.104 | 0.00006                 | 0.0462         | 0.0011    | -0.598                                             | 0.957                                         | -0.651                               | 75       |
| T007956     | Cambrian      | -0.0024           | 2.939    | 0.216 | 0.00008                 | 0.0462         | 0.0025    | -0.547                                             | 0.93                                          | -0.642                               | 64       |
| T008094     | Cambrian      | -0.0013           | 9.768    | 0.052 | 0.00009                 | 0.1478         | 0.0007    | -0.656                                             | 0.934                                         | -0.75                                | 0.04     |

\* Thorold / Whirlpool

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**Table 6.10:** Solutions for  $V_g/V_l$ ,  $f_{Xe}$  and  $r$  calculated from noble gas concentration ratios based on second-order closed model; NaN means no resolvable solution found.

| Sample name | Formation     | $\frac{V_g}{V_l}$ | $f_{Xe}$ | $r$    | $\frac{V_g}{V_l}$ | $f_{Xe}$ | $r$    | $\frac{V_g}{V_l}$ | Correlation coefficient $\frac{V_g}{V_l} - f_{Xe}$ | Correlation coefficient $\frac{V_g}{V_l} - r$ | Correlation coefficient $f_{Xe} - r$ | $\chi^2$ |
|-------------|---------------|-------------------|----------|--------|-------------------|----------|--------|-------------------|----------------------------------------------------|-----------------------------------------------|--------------------------------------|----------|
| T008636     | A-2 Carbonate | 0.019             | 2.726    | 0.167  | 0.00015           | 0.0322   | 0.0008 | 0.0008            | -0.22                                              | 0.775                                         | -0.388                               | 25       |
| T002556     | Guelph        | 0.0015            | 2.674    | 0.102  | 0.00006           | 0.0363   | 0.0007 | 0.0007            | -0.199                                             | 0.703                                         | -0.454                               | 13       |
| T003899     | Guelph        | 0.0046            | 2.415    | 0.098  | 0.00007           | 0.0304   | 0.0005 | 0.0005            | -0.046                                             | 0.628                                         | -0.364                               | 1        |
| T004918     | Guelph        | 2.1818            | 2.712    | 13.466 | 0.0184            | 0.038    | 0.0753 | 0.0753            | 0.522                                              | 0.703                                         | 0.039                                | 2125     |
| T007415     | Guelph        | 0.0052            | 1.993    | 0.143  | 0.00019           | 0.0438   | 0.0029 | 0.0029            | -0.653                                             | 0.918                                         | -0.786                               | 2.24     |
| T008468     | Guelph        | NaN               | NaN      | NaN    | NaN               | NaN      | NaN    | NaN               | NaN                                                | NaN                                           | NaN                                  | 1.00E+04 |
| T008657     | Guelph        | 0.0048            | 2.497    | 0.111  | 0.00013           | 0.044    | 0.0016 | 0.0016            | -0.62                                              | 0.922                                         | -0.732                               | 0.01     |
| T009602     | Guelph        | 0.0028            | 2.201    | 0.108  | 0.00006           | 0.0301   | 0.0007 | 0.0007            | -0.249                                             | 0.776                                         | -0.44                                | 0.94     |
| T010097     | Guelph        | 0.0039            | 2.64     | 0.095  | 0.00007           | 0.033    | 0.0005 | 0.0005            | -0.079                                             | 0.635                                         | -0.383                               | 9.61     |
| T011560     | Guelph        | 0.0007            | 2.662    | 0.138  | 0.00006           | 0.0341   | 0.0007 | 0.0007            | -0.114                                             | 0.63                                          | -0.403                               | 0.48     |
| T011554     | Thorold       | 0.3445            | 1.191    | 3.339  | 0.00323           | 0.0161   | 0.0246 | 0.0246            | 0.331                                              | 0.801                                         | 0.014                                | 100      |
| T011584     | Thorold       | 0.6561            | 1.179    | 5.926  | 0.00461           | 0.0151   | 0.0284 | 0.0284            | 0.39                                               | 0.709                                         | 0.019                                | 1135     |
| T011280     | Thorold*      | 0.0049            | 1.865    | 0.113  | 0.00008           | 0.0255   | 0.0007 | 0.0007            | -0.272                                             | 0.783                                         | -0.444                               | 28       |
| T002374     | Grimsby       | 0.0067            | 2.172    | 0.11   | 0.00009           | 0.0292   | 0.0007 | 0.0007            | -0.244                                             | 0.775                                         | -0.435                               | 11       |
| T003188     | Grimsby       | 0.0029            | 1.836    | 0.085  | 0.00009           | 0.0251   | 0.0005 | 0.0005            | -0.095                                             | 0.599                                         | -0.421                               | 49       |
| T012287     | Grimsby       | 0.0013            | 3.945    | 0.031  | 0.00007           | 0.0547   | 0.0003 | 0.0003            | -0.41                                              | 0.826                                         | -0.569                               | 113      |
| T008194     | Whirlpool     | 0.0207            | 1.678    | 0.128  | 0.00015           | 0.0198   | 0.0007 | 0.0007            | -0.08                                              | 0.825                                         | -0.264                               | 120      |
| T009877     | Whirlpool     | 0.0046            | 2.978    | 0.046  | 0.00007           | 0.0386   | 0.0003 | 0.0003            | -0.328                                             | 0.821                                         | -0.488                               | 128      |
| T007357     | Cobourg       | -0.0007           | 1.897    | 0.098  | 0.00006           | 0.0252   | 0.0005 | 0.0005            | -0.237                                             | 0.775                                         | -0.396                               | 204      |
| T008358     | Cobourg       | 0.53              | 3.531    | 2.346  | 0.0147            | 0.0549   | 0.0617 | 0.0617            | 0.226                                              | 0.954                                         | 0.014                                | 43       |
| T007793     | Sherman Fall  | 0.0158            | 4.219    | 0.071  | 0.00047           | 0.0903   | 0.0017 | 0.0017            | -0.678                                             | 0.938                                         | -0.811                               | 3.93     |
| T007954     | Sherman Fall  | 2.8485            | 4.232    | 13.075 | 0.01905           | 0.0432   | 0.0757 | 0.0757            | 0.235                                              | 0.884                                         | 0.018                                | 2067     |
| T008057     | Sherman Fall  | 0.0109            | 2.215    | 0.136  | 0.00034           | 0.0495   | 0.0029 | 0.0029            | -0.66                                              | 0.926                                         | -0.79                                | 1.63     |
| T0011596    | Cobocok       | -0.0003           | 5.042    | 0.165  | 0.00007           | 0.0637   | 0.0011 | 0.0011            | -0.333                                             | 0.789                                         | -0.505                               | 192      |
| T006907     | Cobocok       | 0.0001            | 2.212    | 0.117  | 0.00008           | 0.0303   | 0.0008 | 0.0008            | -0.295                                             | 0.795                                         | -0.463                               | 0.07     |
| T008313     | Cobocok       | -0.0057           | 2.955    | 0.162  | 0.00005           | 0.0371   | 0.0008 | 0.0008            | -0.262                                             | 0.794                                         | -0.393                               | 3.18     |
| T008974     | Gull River    | 0.0093            | 1.831    | 0.146  | 0.00011           | 0.0274   | 0.0009 | 0.0009            | -0.311                                             | 0.843                                         | -0.45                                | 765      |
| T007369     | Cambrian      | -0.0039           | 3.152    | 0.104  | 0.00006           | 0.039    | 0.0006 | 0.0006            | -0.307                                             | 0.823                                         | -0.435                               | 76       |
| T007956     | Cambrian      | -0.0041           | 2.885    | 0.222  | 0.00008           | 0.0385   | 0.0012 | 0.0012            | -0.151                                             | 0.63                                          | -0.429                               | 66       |
| T008094     | Cambrian      | -0.0025           | 9.743    | 0.052  | 0.00009           | 0.1144   | 0.0003 | 0.0003            | -0.235                                             | 0.688                                         | -0.52                                | 0.04     |

\* Thorold / Whirlpool

## 6.5. DISCUSSION

Al et al. (2015) and Khader and Novakowski (2014) suggested the geochemical and pore pressure profiles could theoretically be attributed to a potential migration of deep Michigan brine migrated laterally towards the Southwestern Ontario Basin during Pleistocene. However, the different  $^3\text{He}/^4\text{He}$  ratios between the Southwestern Ontario Basin and the Michigan Basin suggest that there is unlikely to be a regional-scale water migration during Pleistocene from the Michigan Basin (Chapter 5). Other authors proposed a migration of hydrothermal fluids driven by tectonic events, at least 250 Ma ago (Hobbs et al., 2011; Haeri-Ardakani et al., 2013).

If the migration of the fluid was 250 Ma ago, the dilution is likely to be in the water phase that reduces the concentration of noble gases before degassing processes. This is because gas-water interaction would re-equilibrate the gas-phase-dilution over geological time. A gas-phase dilution is only possible when the degassing is taken place under a second-order closed system, where the gas phase does not contact, and therefore, re-equilibrates with the water phase. The diluting and migrating water that is deprived of atmospheric noble gases suggests significant degassing events before fluid migration, which could be associated with the Palaeozoic hydrothermal event (Ma et al., 2009a). However, since all samples show a considerable amount of dilution, averages around 88%, this raises the question on the feasibility of such a significant amount of fluid replacement across the entire Southwestern Ontario Basin. If the water has been migrated from the Appalachian Basin, severe degassing is required to produce atmospheric noble gas depleted water before its migration. Such an interpretation is, however, speculative at best due to limited data reported to date from the Appalachian Basin.

The dilution mechanism, however, does not explain the negative  $V_g/V_l$ , i.e. the over-fractionation observed in some samples. The negative  $V_g/V_l$  could just as likely be the result of inaccurate estimations of model input parameters, including degassing temperature and groundwater salinity, or the result of water-oil interaction or the redissolution of pre-exsolved gas. With current information, it is hard to distinguish between these different processes.



*6. Quantifying Gas-Water Ratio and Kr and Xe enrichment by an Error-Weighted, Nonlinear Inversion of Atmospheric Noble Gas Concentrations and Concentration Ratios: A Case Study on the Southwestern Ontario Basin*

**6.5.3 Excess Kr and Xe in Basin Systems**

In the Southwestern Ontario basin, the observed fractionation of Kr and Xe in the gas phase (gas reservoirs) comparing to air saturated water,  $F_{Xe}^{ASW}$  and  $F_{Kr}^{ASW}$ , are linearly correlated (Figure 6.3, where  $F_{Xe}^{ASW}$  and  $F_{Kr}^{ASW}$  represent  $F(^{84}Kr/^{36}Ar)_{ASW}$  and  $F(^{132}Xe/^{36}Ar)_{ASW}$ , respectively, in the plot).  $F_i^{ASW}$  is different from  $f_i^{ASW}$ , which refers to the fractionation in the groundwater from air-saturated water prior to degassing. Additional degassing processes are involved in transforming  $f_i^{ASW}$  to  $F_i^{ASW}$ .

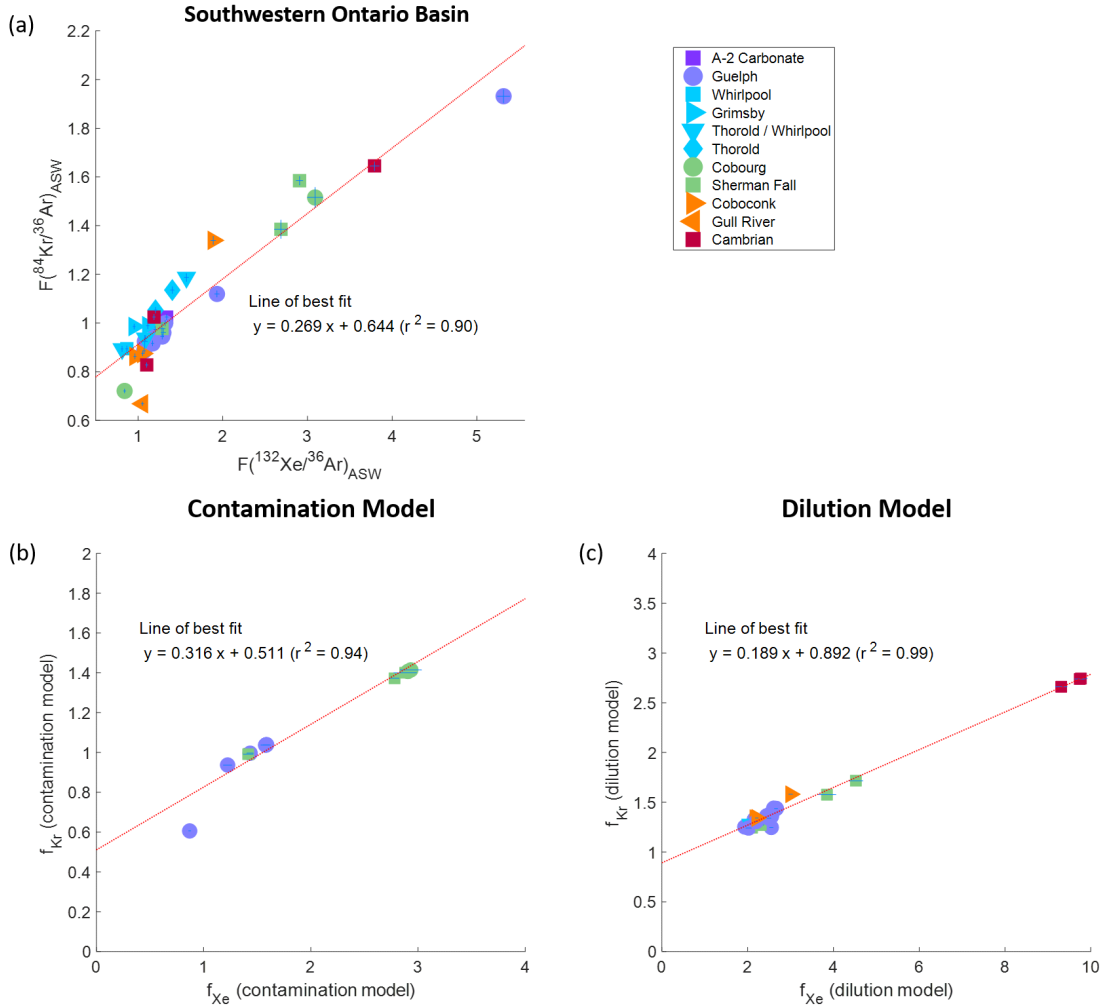
Since in Paleozoic the region is located in warm tropical latitude (Der Voo, 1988) and is periodically covered by seawater, the groundwater can be assumed to be recharged with seawater at temperature 298.15 K, and the following relationship is obtained,

$$F_{Kr}^{ASW} = 0.269F_{Xe}^{ASW} + 0.644 \quad (r^2 = 0.90). \quad (6.41)$$

The comparison of pristine gas with a reservoir that has gone through air-like injection demonstrates a distinct trend of air-mixing compared to the Kr and Xe enrichment observed in the gas field (Györe et al., 2017). Furthermore, seawater-derived groundwater is unlikely to have introduced an excess air component comparing to water recharging through a soil gas-saturated zone. It is, therefore, reasonable to neglect the contribution of excess air in Kr and Xe enrichment.

By considering the samples with acceptable  $\chi^2$  values within 95% uncertainty, solutions of  $f_{Kr}$  and  $f_{Xe}$  are plotted. In an air contamination scenario, the groundwater has  $\frac{f_{Kr}}{f_{Xe}}$  of around 0.316, with  $f_{Kr}$  equals to 0.827 when  $f_{Xe}=1$ . In dilution models, more samples demonstrate acceptable  $\chi^2$  values within 95% uncertainty.  $f_{Kr}$  and  $f_{Xe}$  are linearly correlated with gradients of 0.189 and when  $f_{Xe}=1$ ,  $f_{Kr}$  equals 1.081. Both dilution and contamination models demonstrate gradients less than one suggests the water accumulates Xe faster than Kr, indicating the subsurface source is likely to be more enriched in Xe than Kr. The correlation between  $f_{Kr}$  and  $f_{Xe}$  solutions is controlled by both the preset correlation between  $F_{Kr}$  and  $F_{Xe}$  and the degassing

## 6.5. DISCUSSION



**Figure 6.3:** Fractionation of Kr and Xe in the gas phase and solutions of groundwater enrichment from the air-contamination and dilution models (a)  $F(^{84}\text{Kr}/^{36}\text{Ar})_{\text{ASW}}$  against  $F(^{132}\text{Xe}/^{36}\text{Ar})_{\text{ASW}}$  for gas samples collected from the Southwestern Ontario Basin.  $F(^{84}\text{Kr}/^{36}\text{Ar})_{\text{ASW}}$  against  $F(^{132}\text{Xe}/^{36}\text{Ar})_{\text{ASW}}$  are the fractionation of  $^{84}\text{Kr}/^{36}\text{Ar}$  and  $^{132}\text{Xe}/^{36}\text{Ar}$  ratios measured in the gas sample to the air-saturated water (298.15K 0.623M). The best fit line is plotted in thick dashed line, and the linear equation is shown on the plot. (b) and (c) are  $f(^{84}\text{Kr}/^{36}\text{Ar})$  and  $f(^{132}\text{Xe}/^{36}\text{Ar})$ , excess of Kr and Xe in groundwater, of samples solutions of acceptable  $\chi^2$  values within 95% uncertainty obtained from air-contamination and dilution models respectively. The best fit lines for the models are labelled on the graph.

processes. It can be observed that though the degassing processes have an impact, the gradients of  $f_{\text{Kr}}$  and  $f_{\text{Xe}}$  are still close to the gradient of  $F_{\text{Kr}}$  and  $F_{\text{Xe}}$ .

If there is no air contamination, the concentration ratio model is more reliable due to the uncertainties with pressure estimations and the potential dilution effect. The model is applied to gas samples reported in basin systems around the world to

6. *Quantifying Gas-Water Ratio and Kr and Xe enrichment by an Error-Weighted, Nonlinear Inversion of Atmospheric Noble Gas Concentrations and Concentration Ratios: A Case Study on the Southwestern Ontario Basin*

investigate the Kr and Xe enrichment assuming there is no air contamination with the samples. Kr and Xe data of these gas samples can also fit a linear relationship of  $F_{Kr}^{ASW} = 0.116F_{Xe}^{ASW} + 0.793$  ( $r^2 = 0.90$ ) (Figure 6.4). The degassing process is assumed to take place at reservoir conditions for each locality. The global Kr-Xe enrichment gradients are 0.135 (FO), 0.142 (SO open) and 0.144 (SO closed) (Figure 6.4) and when  $f_{Xe}=1$ ,  $f_{Kr}$  ranges from 1.23 to 1.27. However, noticeably, different solutions of  $f_{Xe}$  and  $f_{Kr}$  are expected if considering the air addition models, as demonstrated by the Southwestern Ontario dataset. Qualitatively, the air-addition models seem to push the solutions towards a higher gradient, suggesting that the gradient between  $f_{Kr}$  and  $f_{Xe}$  obtained without air-addition is likely representing the lower limit. Reliable solutions from the air addition models require good constraints on recharging conditions and reservoir conditions.

Torgersen et al. (2004) explained excess Kr and Xe in basin systems as the result of the diffusive separation of adsorbed noble gases on the sediments, which could be caused by temperature increase during diagenesis or concentration gradient between mineral boundaries and porewater and induced into gas or oil systems through fluid interaction. The adsorption of xenon on charcoal is approximately twenty-five times greater than argon and five times greater than krypton (Dushman and Lafferty, 1962). The different adsorption ability suggests that if being exposed to a certain amount of Kr and Xe, the adsorbed elements on the sediment is approximately 0.22 times that of the ratio initially in the water, i.e. the  $\left(\frac{Kr}{Xe}\right)_{sed} / \left(\frac{Kr}{Xe}\right)_{ASW,298.15,0.623M} = 0.22$ . An arbitrary endmember used in their noble gas releasing model is based on concentrations measured from young ocean sediment. The sediment has  $\left(\frac{Kr}{Xe}\right)_{sed} / \left(\frac{Kr}{Xe}\right)_{air} = 0.0699$ , which gives  $\left(\frac{Kr}{Xe}\right)_{sed} / \left(\frac{Kr}{Xe}\right)_{ASW,298.15,0.623M} \approx 0.12$ . Kr and Xe enrichment is also observed from deep ocean sediments collected by Matsuda and Nagao (1986). Their samples have an average  $\left(\frac{Kr}{Xe}\right)_{sed} / \left(\frac{Kr}{Xe}\right)_{air} = 0.33 \pm 0.025$  ( $n = 7$ ), which gives  $\left(\frac{Kr}{Xe}\right)_{sed} / \left(\frac{Kr}{Xe}\right)_{ASW,298.15,0.623M} \approx 0.55 \pm 0.04$ . They have found the enrichment of heavy noble gases is positively correlated with the silica content in the sediments and argued that siliceous fossils could be the adsorption agents of Kr and Xe.

## 6.5. DISCUSSION

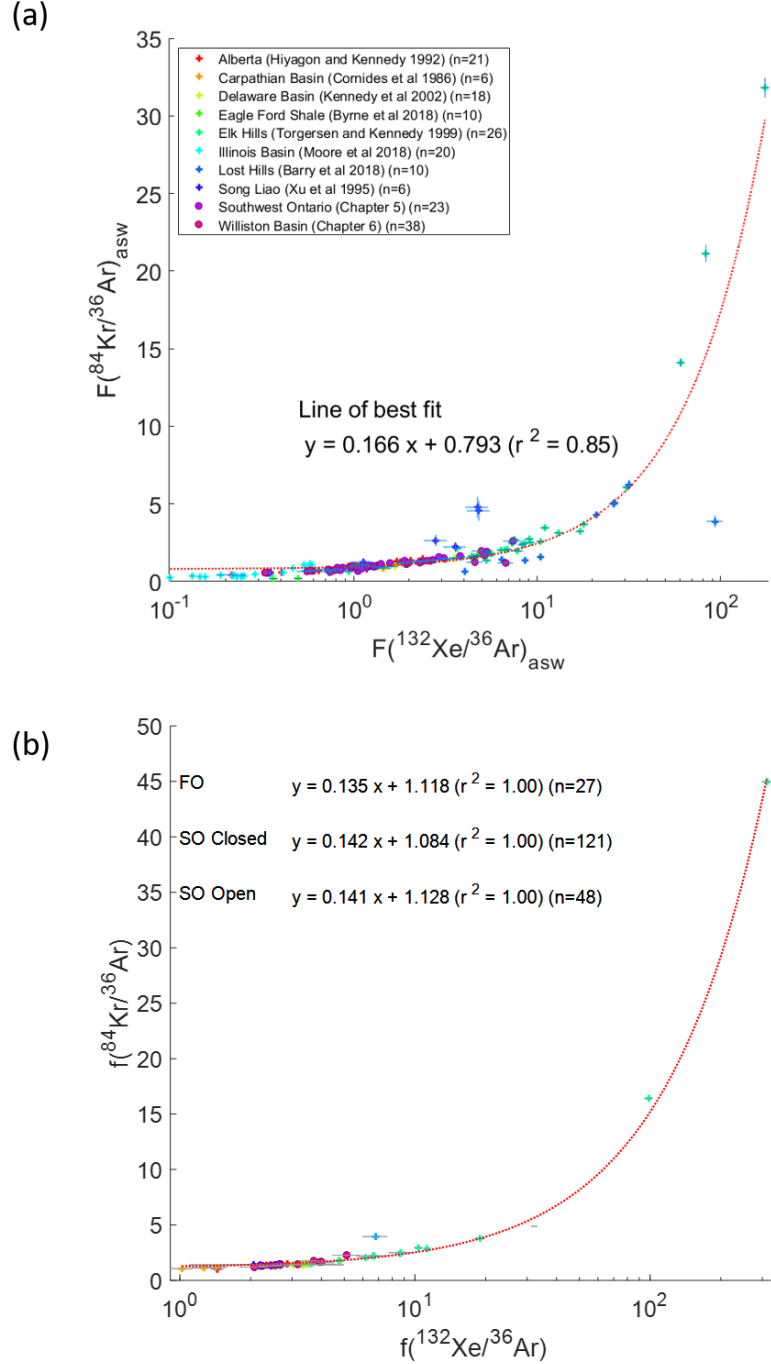
The global gradient between modelled  $f_{Xe}$  and  $f_{Kr}$ , 0.136 to 0.144, is comparable to that of the ocean sediment and lower than theoretical adsorption on charcoal (Torgersen et al., 2004), while locally, the Southwestern Ontario Basin samples are higher, closer to the dry sediment ratios of deep ocean sediments of  $\left(\frac{Kr}{Xe}\right)_{sed} / \left(\frac{Kr}{Xe}\right)_{ASW,298.15,0.623M} \approx 0.55 \pm 0.04$  (Matsuda and Nagao, 1986). This observation suggests Kr and Xe adsorbed on carbon and silica grains is likely the source of the excess elements observed in various basin system. Noble gases are adsorbed before diagenesis but subsequently released in the subsurface, possibly as the result of temperature increase. Kr and Xe surplus are, therefore, linked to the carbon and silica content, the type of organic matter and the releasing condition (e.g. reservoir temperature, noble gas concentration in the surrounding water). When there is no excess Xe, i.e.  $f_{Xe}=1$ ,  $f_{Kr}$  is likely to be higher than one (Figure 6.4), reflecting an earlier release and faster transport of Kr than Xe from the sediments.

Interestingly, Kr and Xe in samples collected from the crystalline basement demonstrate trends distinctive from that in sedimentary basins (Figure 6.5). No universal correlation can be observed from the three sets of data published to date (Lippmann et al., 2003; Heard et al., 2018; Warr et al., 2018). Two studies show data depleted in Kr and Xe and all of them have localized gradients much higher than those observed in sedimentary basins. This implies the basement experienced different rock-fluid and fluid-fluid interaction processes and separate modelling is required.

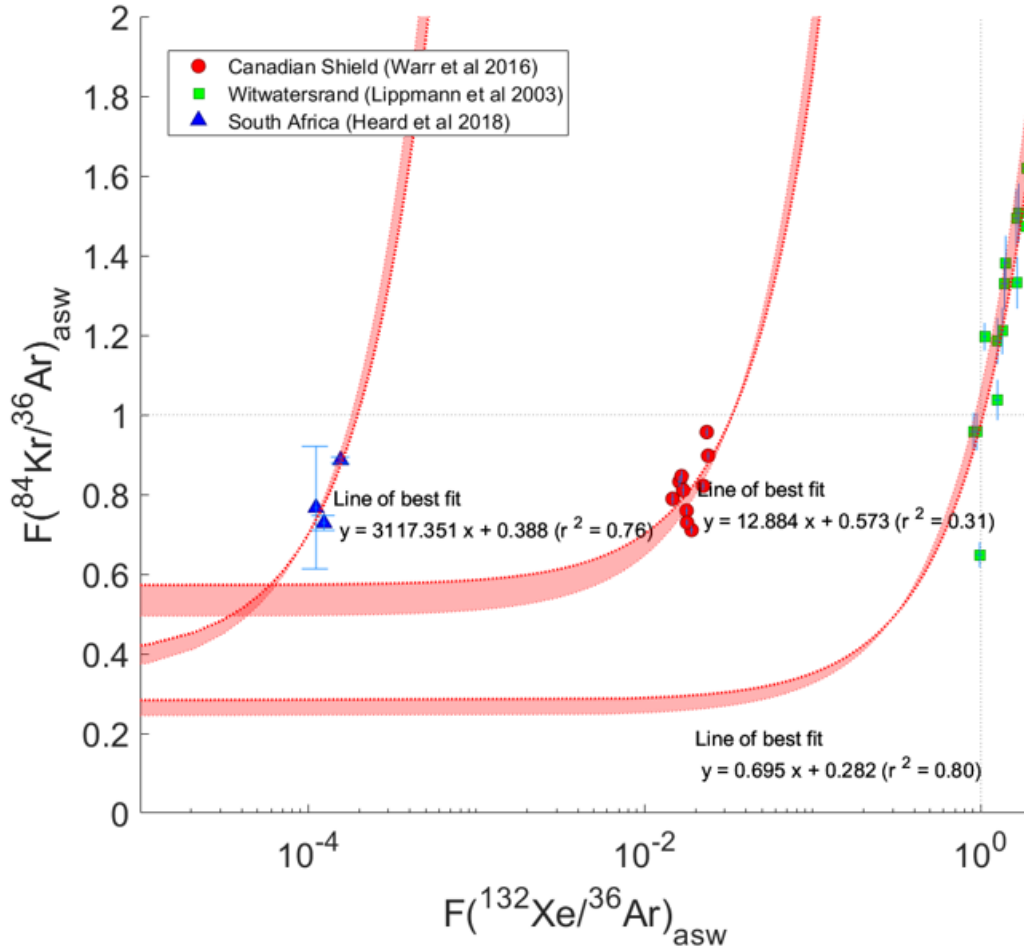
### 6.5.4 Sensitivity Test for Degassing Temperature and Pressure

We explore the effect of degassing conditions, both temperature and salinity, to  $V_g/V_l$  and  $f_{Xe}$  solutions obtained from the inversion models of noble gas ratios. The models are run with lower reservoir temperatures(°C) or the salinities to explore the effect of temperature and salinity estimations on the solutions of  $V_g/V_l$  and  $f_{Xe}$ . A 20% decrease of the parameters is arbitrarily chosen, and for temperatures or salinities, it translates to a considerable amount of flexibility for the parameters. Figure 6.6 compares the solutions for different degassing systems.  $V_g/V_l$  solutions do not vary

6. Quantifying Gas-Water Ratio and Kr and Xe enrichment by an Error-Weighted, Nonlinear Inversion of Atmospheric Noble Gas Concentrations and Concentration Ratios: A Case Study on the Southwestern Ontario Basin



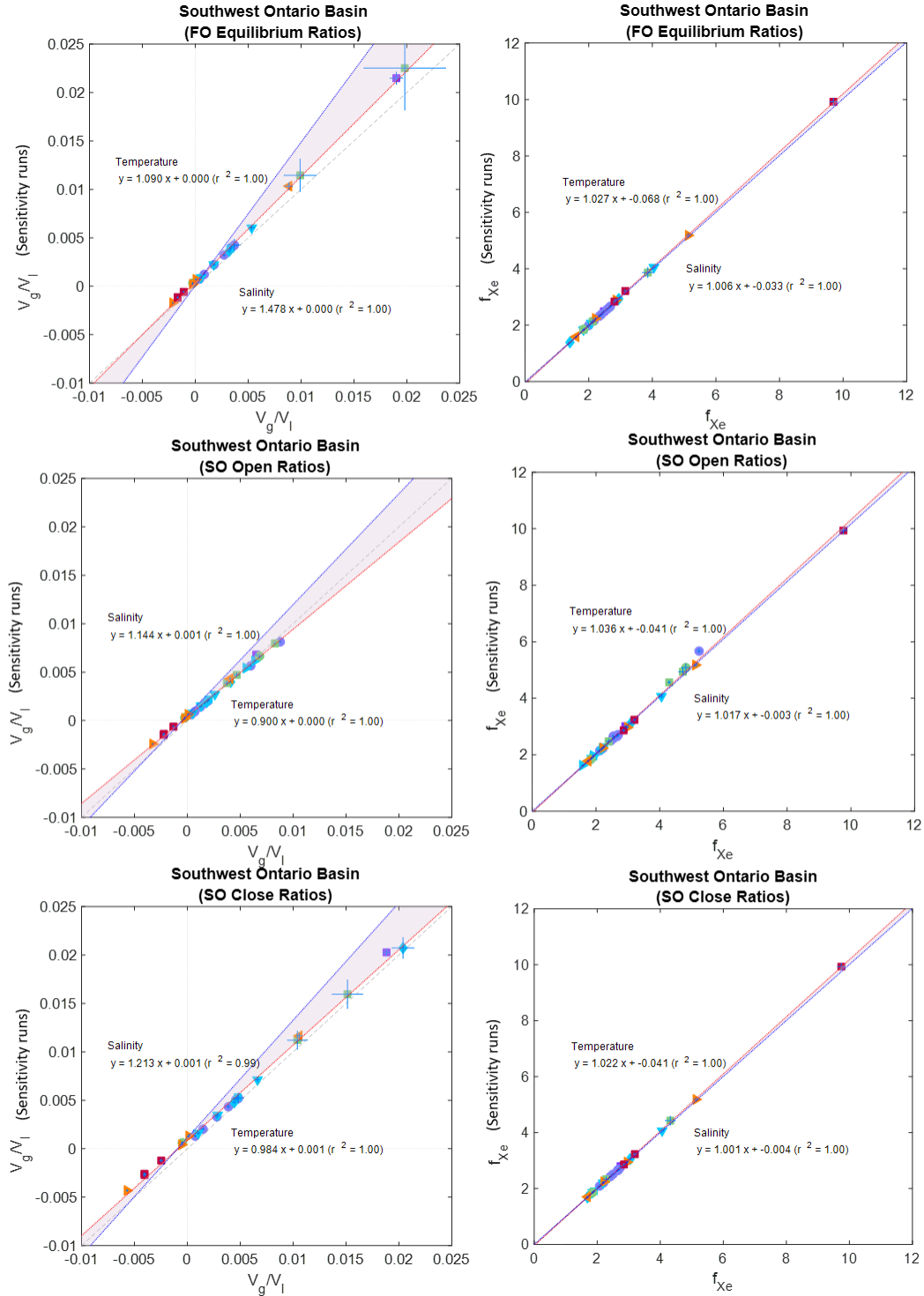
**Figure 6.4:** (a)  $F(^{84}\text{Kr}/^{36}\text{Ar})_{\text{ASW}}$  against  $F(^{132}\text{Xe}/^{36}\text{Ar})_{\text{ASW}}$  for gas samples in basin systems from literature review.  $F(^{84}\text{Kr}/^{36}\text{Ar})_{\text{ASW}}$  and  $F(^{132}\text{Xe}/^{36}\text{Ar})_{\text{ASW}}$  are  $^{84}\text{Kr}/^{36}\text{Ar}$  and  $^{132}\text{Xe}/^{36}\text{Ar}$  ratios in the gas samples normalising to the corresponding ratios in the air-saturated water (298.15K 0.623M). An enrichment of Kr and Xe in the gas phase comparing to the air saturated water is shown by samples from multiple localities. The best fit line is plotted in thick dashed line, and the linear equation is shown on the plot. (b)  $f_{\text{Xe}}$  and  $f_{\text{Kr}}$  solutions calculated from the second-order open model developed in this chapter assuming a seawater recharge at 298.15K.



**Figure 6.5:** Published  $F(^{84}\text{Kr}/^{36}\text{Ar})_{\text{ASW}}$  against  $F(^{132}\text{Xe}/^{36}\text{Ar})_{\text{ASW}}$  data of gas samples derived from brine from the Canadian shield and African basement.  $F(^{84}\text{Kr}/^{36}\text{Ar})_{\text{ASW}}$  against  $F(^{132}\text{Xe}/^{36}\text{Ar})_{\text{ASW}}$  refer to measured brine  $^{84}\text{Kr}/^{36}\text{Ar}$  and  $^{132}\text{Xe}/^{36}\text{Ar}$  ratios normalizing to air-saturated water ratios (298.15K 0.623M).  $F(^{84}\text{Kr}/^{36}\text{Ar})_{\text{ASW}}$  and  $F(^{132}\text{Xe}/^{36}\text{Ar})_{\text{ASW}}$  are the current values in the brine samples and could have been affected by degassing processes. The entire dataset is not linearly correlated, but each locality has a best fit first order line with a gradient far higher than samples from sedimentary basins.

significantly with a 20% change in temperature but are affected by a 20% decrease in salinity.  $V_g/V_l$  solutions with the lower salinity estimations could result in 14% to 50% variations according to the different degassing models. For the types of models as proposed here, it is, therefore, essential to have reliable estimations of salinity for accurate solutions of  $V_g/V_l$ , especially for the first order degassing system.  $f_{\text{Xe}}$  is however not sensitive to changes in temperature or salinity for all degassing scenarios.

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**Figure 6.6:** The comparison between solutions for different degassing systems with a 20% decrease of degassing temperature (red line) or a 20% decrease of salinity (blue line). In each plot, the y-axis is the solutions of sensitivity tests with the changed degassing conditions. The solutions are compared with the original solution on x-axis. The sensitivity for temperature decrease are plotted with sample points, while the sensitivity for salinity decrease is presented with the blue lines. temperature is in unit  $^{\circ}\text{C}$ .  $V_g/V_l$  solutions do not vary significantly with temperature but are affected by salinity (left panel).  $f_{Xe}$  is, however, not sensitive to changes in temperature or salinity for all degassing scenarios (right panel)

## 6.6 CONCLUSIONS

Groundwater degassing is a crucial process involved in the formation of subsurface gas reservoirs, such as natural hydrocarbon gas and helium. The mathematical expressions for three endmember degassing systems, first-order equilibrium, second-order open and closed systems, are derived and summarised. Error-weighted, non-linear inversion models are constructed for atmospheric noble gas concentrations and concentration ratios to solve gas-water ratio,  $V_g/V_l$ , and Kr and Xe enrichment in groundwater before degassing,  $f_{Kr}$  and  $f_{Xe}$ .

The concentration and ratio models are applied to the gas samples collected in the Southwestern Ontario Basin (Chapter 5), but the solutions of  $V_g/V_l$  are significantly different between those obtained from the two types models. The discrepancies of  $V_g/V_l$  solutions can be explained by air contamination or dilution events. Dilution events require diluting fluids depleted in atmospheric noble gases and mechanisms providing driving force for fluid migration. The inversion models produce the best fit mathematical solutions but need to be supported with geological, hydrogeological and geochemical evidence.

A linear correlation is found between the excess Kr and Xe from gas samples collected in the Southwestern Ontario Basin and the nine other basin systems. Solutions of  $f_{Xe}$  and  $f_{Kr}$  for the Southwestern Ontario Basin have lines of best fit with gradients between 0.189 to 0.316. Assuming all samples have negligible air contamination, the global slope ranges from 0.136 to 0.144. These are comparable to the theoretical ratios estimated from Kr and Xe adsorption on carbon (charcoal)  $(0.22 \left(\frac{Kr}{Xe}\right)_{ASW})$  and observations from young ocean sediment  $(0.12 \left(\frac{Kr}{Xe}\right)_{ASW})$  (Torgersen et al., 2004). The localized gradient in the Southwestern Ontario Basin is higher, possibly being contributed by Kr and Xe adsorbed on silica sediments  $(0.55 \left(\frac{Kr}{Xe}\right)_{ASW})$  (Matsuda and Nagao, 1986). The inversion models enable the quantitative estimation of the enrichment/supply of Kr and Xe in the groundwater. The comparison between sediment adsorption and model solutions implies the release of adsorbed Kr and Xe



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from sediments is likely the source of excess Kr and Xe observed in the basin system. Organic carbon and silica content, the types of organic matter, releasing conditions are probably the factors controlling the amount of excess Kr and Xe in the fluids.



# 7

## The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase

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## ABSTRACT

Helium is an important and non-renewable element that faces a supply crisis. Understanding the formation of helium reservoirs and identifying new helium resources has gained growing interest. Current models of helium-rich natural gas occurrence focus on gas stripping of groundwater or uplift-related depressurisation that induces gas exsolution in regions of active tectonism. Here we show that another form of helium-rich gas field formation is viable in quiescent and ancient intracratonic basins. We construct a one-dimensional diffusion-and-exsolution model, in which a basement helium flux is compatible with observed concentration gradients within the Williston Basin, and the  $\text{N}_2/{}^4\text{He}$  basement flux ratio comparable to that observed in helium reservoirs in sedimentary basins. The independently model outputs demonstrate a good match with the sample measurement. The model illustrates that, for the Williston Basin, a nitrogen-helium rich gas phase is predicted to exsolve from the groundwater in sedimentary contact formations directly overlying the crystalline basement. The sedimentary basin architecture, basement helium and nitrogen flux, and the timing and size of gas formed are critical factors that need to be considered in predicting the generation of economically viable helium fields but are likely to occur in similar basin settings.

## *7. The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase*

### **7.1 INTRODUCTION**

Helium is a valuable and non-renewable element widely used in various industries (Pacheco, 2002; Broadhead, 2005; Danabalan, 2017). Its unique properties include low density, fast diffusivity and small elemental size. Its unreactive nature makes it favourable in many commercial applications (Bare et al., 2016). In particular, due to its low boiling point (4.2 K) and specific thermal properties, liquid helium is an irreplaceable cryogenic cooling medium in numerous apparatus, ranging from high energy beam-lines such as the Large Hadron Collider to medical MRI (Magnetic Resonance Imaging) scanners and NMR (Nuclear Magnetic Resonance) spectrometers, from satellite to space vehicles (Pacheco, 2002). Though helium is the second most abundant element in the universe, it is a limited resource on the Earth. Primordial or radiogenic helium that degases into the atmosphere readily escapes to space (Torgersen, 1989; Pepin and Porcelli, 2002). To date, helium cannot be economically extracted from the air, and until recently has solely been found fortuitously as a byproduct of hydrocarbon exploration (Bare et al., 2016; Danabalan, 2017). The sell-off of the US national strategic reserve over the last two decades, limited separation facilities, and geopolitics, all combine to make this element susceptible to supply crisis (e.g. Bare et al., 2016; Ballentine, 2017; Gluyas, 2019). In-kind price of crude helium in the US has increased from \$62.25/Mcf ( $\sim \$2.2/\text{m}^3$ ) in 2009 to \$95/Mcf ( $\sim \$3.4/\text{m}^3$ ) in 2019 (Bureau of Land Management, 2018). The price is more than 25 times higher than the industrial methane natural gas price of \$3.56/Mcf ( $\sim \$0.13/\text{m}^3$ ) reported by the US Energy Information Administration in June 2019.

Helium dissolved in groundwater is unlikely to be economical to produce commercially. A mechanism is required to form a gas phase which allows focusing of the helium into gas reservoirs in geological trapping structures. However, the low concentration of helium in natural fluid systems makes it unlikely to form a free gas phase on its own. This can be achieved through groundwater interaction with existing major gas phases in place within a geological reservoir, the formation of a gas phase on

## 7.1. INTRODUCTION

reaching gas saturation within the groundwater, or an external gas source migrating through the groundwater and ‘gas stripping’ any dissolved helium into the gas phase (e.g. Ballentine and Sherwood Lollar, 2002). Gas fields containing commercial concentrations of helium (0.3% by volume helium if the gas is to be produced for the helium alone) have three primary gas components,  $N_2$ ,  $CO_2$  and  $CH_4$  (Danabalan, 2017). While  $CO_2$  enrichment can be related to magmatic input (e.g. Doe Canyon and St. John’s Dome (Gilfillan et al., 2008)), and  $CH_4$  is mostly linked to hydrocarbon production (e.g. Hugoton-Panhandle (Ballentine and Sherwood Lollar, 2002)),  $N_2$ -rich fields are less well understood.

Nitrogen is always a significant component in helium-rich natural gases, even in  $CO_2$  and  $CH_4$  dominated fields (Ballentine and Sherwood Lollar, 2002 and references therein) but the mechanism that links helium, a radiogenic gas, to nitrogen, expected to be physio-chemically derived from various mineral or organic sources in the subsurface, has not been unambiguously resolved. The relationship between crustal nitrogen and noble gases is explored explicitly by Ballentine and Sherwood Lollar (2002). They found the Hugoton-Panhandle field gases fall on a mixing trajectory requiring two nitrogen sources, only one of which was He-associated. In this case, the mass balance and isotopic composition of the He-associated nitrogen were consistent with a crystalline basement low-grade metamorphic source (Hanschmann, 1981; Kreulen et al., 1982; Bebout and Fogel, 1992; Bebout et al., 1999; Ballentine and Sherwood Lollar, 2002). The non-He-associated nitrogen is likely derived from nitrogen-enriched organic matter in the sedimentary units (Ballentine and Sherwood Lollar, 2002).

$N_2/{}^4He$  ratios measured in gas samples from different localities are also reported. Harley Dome in Utah, USA, has a nitrogen concentration of 84% with  $N_2/{}^4He$  ratio of 12 (Danabalan, 2017). Samples from other US helium-rich gas fields at Bush Dome, Texas Hugoton Field and Red Cave Field mostly have ratios between 13 to 20 (Hugoton/Panhandle fields of West Texas and Kansas), while those from Bradshaw and Panoma fields (Hugoton/Panhandle fields of Kansas), have the ratios  $>40$  (Gold and Held, 1987). Samples collected from the north-south traverse of the field (Ballentine

## 7. The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase

and Sherwood Lollar, 2002) demonstrate ratios ranging from 20 to 50, corresponding to an increasing contribution of non-He-associated nitrogen.  $N_2/{}^4\text{He}$  in the Cambrian unit in the Williston Basin is exceptionally higher, being reported as 89 (Yurkowski and Jensen, 2016), 70 (Chapter 4) and 91 (Danabalan, 2017).

Here, we investigate the formation of helium reservoirs in stable intracratonic sedimentary basins, focusing on the specific scenario in which He-associated  $N_2$  is the primary gas-forming phase and is dominantly derived from the crystalline basement. Other potential sources of  $N_2$  (e.g biogenic  $N_2$ ) are not discounted but its forming mechanism is out of the scope of this study. With the use of numerical models, we explore the role of gas-phase nitrogen in focusing and extracting helium from groundwater and its control on helium distribution in the water in the different stratigraphic units of the basin.

### 7.2 A HELIUM AND NITROGEN DIFFUSION AND EXSOLUTION MODEL

#### 7.2.1 Diffusion

The transport of helium and nitrogen can be numerically simulated with the diffusion and advection equation,

$$\phi \frac{\delta C}{\delta t} + q \frac{\delta C}{\delta z} = D_e \frac{\delta^2 C}{\delta z^2} + p \quad (7.1)$$

where  $\phi$  is the rock porosity,  $C$  is the mass concentration of the solute and  $t$  is time.  $z$  is the distance from the crystalline basement and  $p$  is the production rate per volume of pore water.  $q$  is the average linear velocity. For diffusion only scenarios,  $q=0$ .  $D_e$  is the effective diffusion coefficient and is defined according to Fick's first law,

$$J_d = -D_e \frac{\delta C}{\delta z} \quad (7.2)$$

where  $J_d$  is the diffusive mass flux rate. The helium diffusion coefficient in pure water is a function of temperature (Ohsumi and Horibe, 1984),

$$D_{He}^{water} = 2.309 \times 10^{-2} e^{-1706/T} \quad (7.3)$$

## 7.2. A HELIUM AND NITROGEN DIFFUSION AND EXSOLUTION MODEL

in  $\text{cm}^2/\text{s}$ .  $T$  is the temperature in K. Experiments by Cadogan et al. (2014) demonstrate that the diffusion coefficient of nitrogen is also dominantly controlled by temperature.  $D_{N_2}^{water}$  is approximately linearly proportional to temperature (K). The extrapolated linear correlation is

$$D_{N_2}^{water} = 6.83 \times 10^{-9}T - 1.86 \times 10^{-6} \quad (7.4)$$

in  $\text{cm}^2/\text{s}$ . Equations 7.3 and 7.4 are used to calculate the helium and nitrogen diffusion coefficients at different depths as a function of the applied thermal gradient. The empirically derived diffusion coefficients do not match simple mass fractionation relationship. This is possibly due to the other factors that diffusion coefficients depend on (Bourg and Sposito, 2008), such as molecular mass and size, and the molecular bond between water and the gas molecules. The effective diffusion coefficient for both helium and nitrogen in porous media is estimated following Boving and Grathwohl (2001) 's equation

$$D_e = \phi^{2.2} D_{water} \quad (7.5)$$

where  $\phi$  is the porosity in aquifers and effective porosity in aquitards.

### 7.2.2 Nitrogen Solubility and Gas-Phase formation

The thermodynamic model of nitrogen solubility (Equation 7.6) is determined by Mao and Duan (2006) for  $\text{N}_2\text{-H}_2\text{O-NaCl}$  water systems over a wide of range of temperature (273–400 K), pressure (1-600 bar) and salinity (0-6 mol/kg):

$$\ln \frac{y_i P}{m_i} = \frac{\mu_i^{l(0)}}{RT} - \ln \phi_i + \sum_c 2\lambda_{i,c} m_c + \sum_a 2\lambda_{i,a} m_a + \sum_c \sum_a \epsilon_{i,Na,Cl} m_c m_a. \quad (7.6)$$

$i$  refers to nitrogen in the corresponding system;  $y_i$  is the mole fraction of  $i$  in the gas phase;  $m_i$  is the molality mol/kg of  $i$  in the liquid phase;  $P$  is the total pressure (bar), i.e.  $P_i + P_{H_2O}$  where  $P_{H_2O}$  is the pressure of water vapour;  $\phi_i$  is the fugacity coefficient of  $i$ ;  $\mu_i^{l(0)}$  is chemical potential and  $\lambda_i$  and  $\epsilon_i$  are second-order and third-order



## 7. The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase

interaction parameters respectively.  $a$  and  $c$  refer to anion and cation and  $m_a$  and  $m_c$  indicate the molality of anion and cation, respectively.

By rearranging equation 7.6, the solubility of nitrogen can be calculated from

$$m_i = y_i P \left[ \exp \left( \frac{\mu_i^{l(0)}}{RT} - \ln \phi_i + 2\lambda_{i,Na} m_{NaCl} + \epsilon_{i,Na,Cl} m_{NaCl}^2 \right) \right]^{-1}. \quad (7.7)$$

In the above equation, the mole fraction of nitrogen in the gas phase,  $y_{N_2}$ , can be calculated assuming that water vapour is the only other gas content in the system,

$$y_i = 1 - y_{H_2O} \quad (7.8)$$

All parameters used for calculations are summarised by Mao and Duan (2006).

### 7.2.3 A Combined Diffusion – Gas-Phase Formation Model

In basins where diffusion can be the dominant transport mechanism of substances from the Precambrian basement through the overlain sedimentary units, diffusion-only scenarios can be simulated (Chapter 4 & 5). The diffusion transport model builds each stratigraphic layer as an entire unit overlying pre-existing formations at the start of deposition time. For helium, both in situ radiogenic production from U and Th, and the flux from Precambrian basement are accounted. Nitrogen is assumed to be entirely sourced from the basement with negligible in situ sources. The original helium and nitrogen concentrations in the water column are set to air saturated water values and maintained at this concentration at the top surface of the model representing the groundwater-air contact. Porosity and its changes throughout time, isopach thickness, uranium plus thorium concentration estimations are all summarised in Chapter 4.

The model, considering both helium and nitrogen concentration changes caused by diffusional transport through time and basin development, identifies where nitrogen exceeds saturation. In these lithologies, a nitrogen gas phase is formed, and the impact of gas-phase formation on the dissolved gas system and diffusional regime can, in turn, be investigated. The solubility of nitrogen is controlled by the pressure

### *7.3. GEOLOGICAL SETTING AND MODEL INPUT*

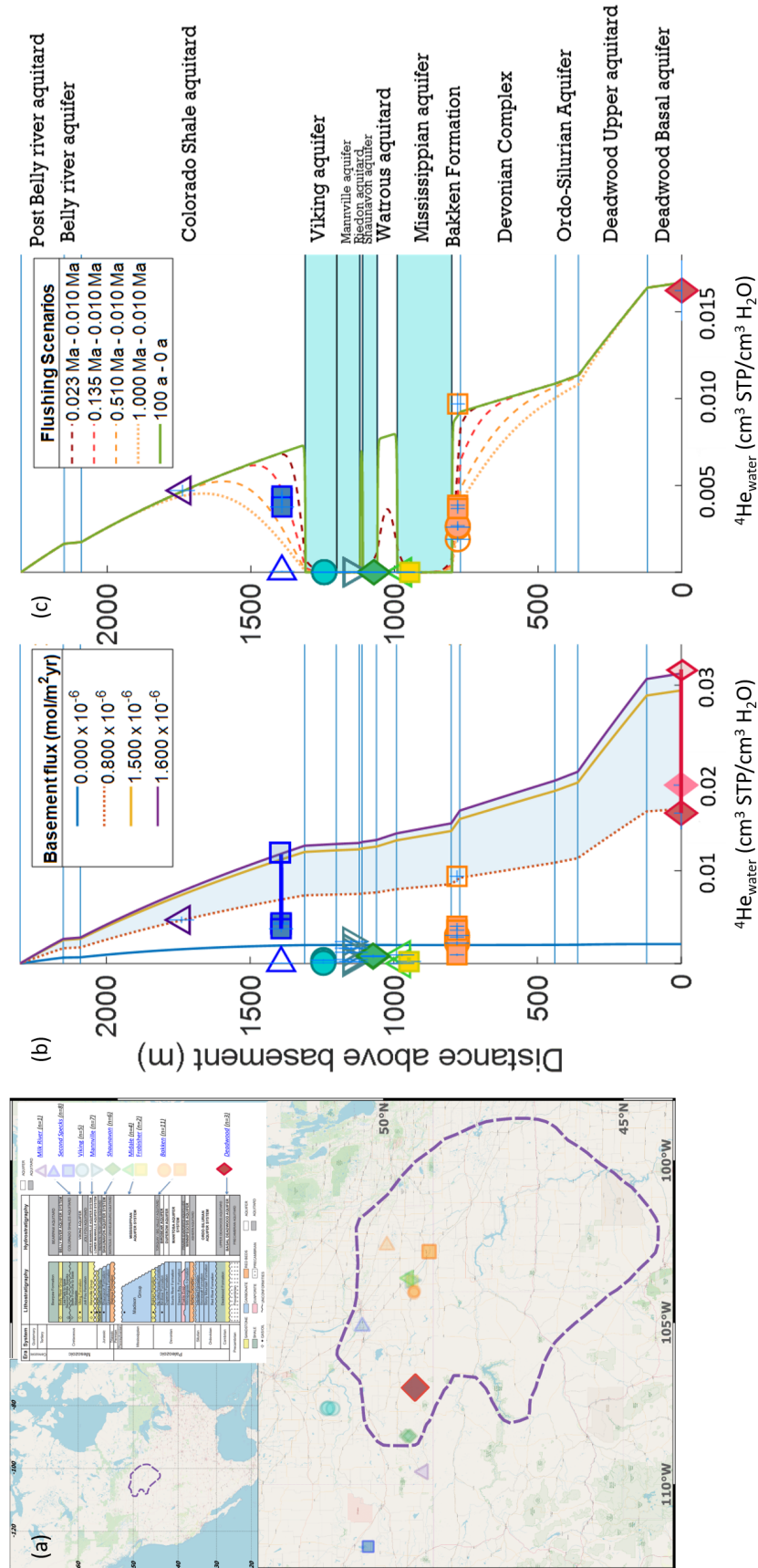
(assumed to be hydrostatic), the temperature of the lithology and the salinity of the pore water (Equation 7.7).

The model is built for the Williston Basin and investigates a range of basement  $^4\text{He}$  flux and  $\text{N}_2/^4\text{He}$  ratios to determine the potential in this basin for gas-phase formation and the controlling processes. By further considering the partitioning of the He and  $\text{N}_2$  between the gas and water phases, the model now has the capability to quantitatively determine the impact of gas-phase formation on the development of the water column helium profile as well as identify any characteristic  $\text{N}_2/^4\text{He}$  ratios of this end member process.

### **7.3 GEOLOGICAL SETTING AND MODEL INPUT**

The Williston Basin is an oval intracratonic basin that straddles the border of the United States and Canada (Figure 7.1). The cause of basin subsidence is thought to be initially related to lithospheric cooling and thinning (Ahern and Mrkvicka, 1984; Ahern and Ditmars, 1985; Crowley et al., 1985; Crowley and Kuhlman, 1988). The succession of marine carbonates and evaporites preserved were caused by cycles of sea-level changes that connected the basin to the proto-Pacific ocean to the west during Cambrian to Jurassic (Bachu and Hitchon, 1996). It later transformed into a clastic, shale-dominated foreland basin responding to basement uplift during Late Jurassic to the pre-Aptian Cretaceous. Foreland folding and thrusting in the late Paleocene to early Eocene led to a significant erosional event which was terminated by regional extension during the Early and Middle Eocene (Price, 1994; Wright et al., 1994). The basin was then glaciated during the Pleistocene to form the current topography.

## 7. The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase



**Figure 7.1:** (a) The outline of the Williston Basin and locations of sampling wells with the Cambrian-located Deadwood well highlighted (the 'International Helium' well reported by Danabalan (2017)). The sampled wells are marked alongside the lithological and hydrogeological stratigraphy Melnik, 2012. (b) Diffusion models for  $^4\text{He}$  indicate the high helium samples in the sedimentary column can be explained with diffusive transport of basement  $^4\text{He}$  between  $0.8\text{--}1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (Chapter 4).  $^4\text{He}_{\text{water}}$  is derived from  $^4\text{He}/^{20}\text{Ne}$  ratios from the natural gas samples, and is subjected to 'air entrapment' and results in a range of values for some samples. The coloured horizontal lines link the corrected concentrations (transparent symbols) with the corresponding uncorrected values. (c) Deviations from the modelled diffusive model are likely the result of horizontal flushing (figure constructed with a basement flux of  $0.8 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ ) (Chapter 4).

### 7.3. GEOLOGICAL SETTING AND MODEL INPUT

Modern basin-scale groundwater flow is dominated by the hydraulic head and recharges at northwest-southeast-trending topographic highs and flows laterally across the basin to discharge along the Manitoba lowlands Paleozoic outcrop belt (Bachu and Hitchon, 1996; Iampen and Rostron, 2000). Both the stratigraphic and hydrostratigraphic columns are presented in Figure 7.1. The brines in the centre of the basin suggest the deep formations have not been disturbed (Grasby et al., 2000), a hypothesis which is supported by the diffusive simulations of  $\delta^{18}\text{O}$  by Hendry et al. (2013),  $\text{Cl}^-$  by Hendry et al. (2013) and the  $^4\text{He}$  diffusive profile Chapter (4). Many of the petroleum systems are self-contained, i.e. no migration or external sources or sinks of hydrocarbon are required (Anna, 2013). Diffusion can nevertheless, play a significant role in the cross-formational transport of gases in tectonically stable sedimentary basins, especially in low permeability units and where the deep regional groundwater system is long-lived (Hendry et al., 2015). Noble gas data and models of the helium distribution observed in the water column within the different lithological units of the Williston Basin also provide multiple lines of evidence that support cross formation diffusive transport as the basin evolves (Chapter 4). The flux estimated to account for the observed helium concentration profile range between  $0.8 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  up to  $1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (Figure 7.1). The values are comparable to the theoretical steady-state flux calculated for the basement from samples collected to the North of the basin. These samples demonstrate an average of  $0.64 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ , ranging from  $(0.29 \sim 1.34) \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  due to variations of U and Th concentrations in the basement samples analysed (Rolandone et al., 2002). The estimated flux range is also similar to the average continental crust of  $1.47 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  (Torgersen and Clarke, 1985; Torgersen et al., 1992).

The model simulation here focuses on observations from a nitrogen-rich natural gas reservoir in the Williston Basin, the Wood Mountain well, which is drilled to the helium-bearing gas pool in the Cambrian sandstone (Deadwood) unit discovered in Saskatchewan in 1960 (Yurkowski and Jensen, 2016). The same reservoir is also sampled and reported in Chapter 4 (Deadwood) and by Danabalan (2017) ('International Helium' well).

## *7. The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase*

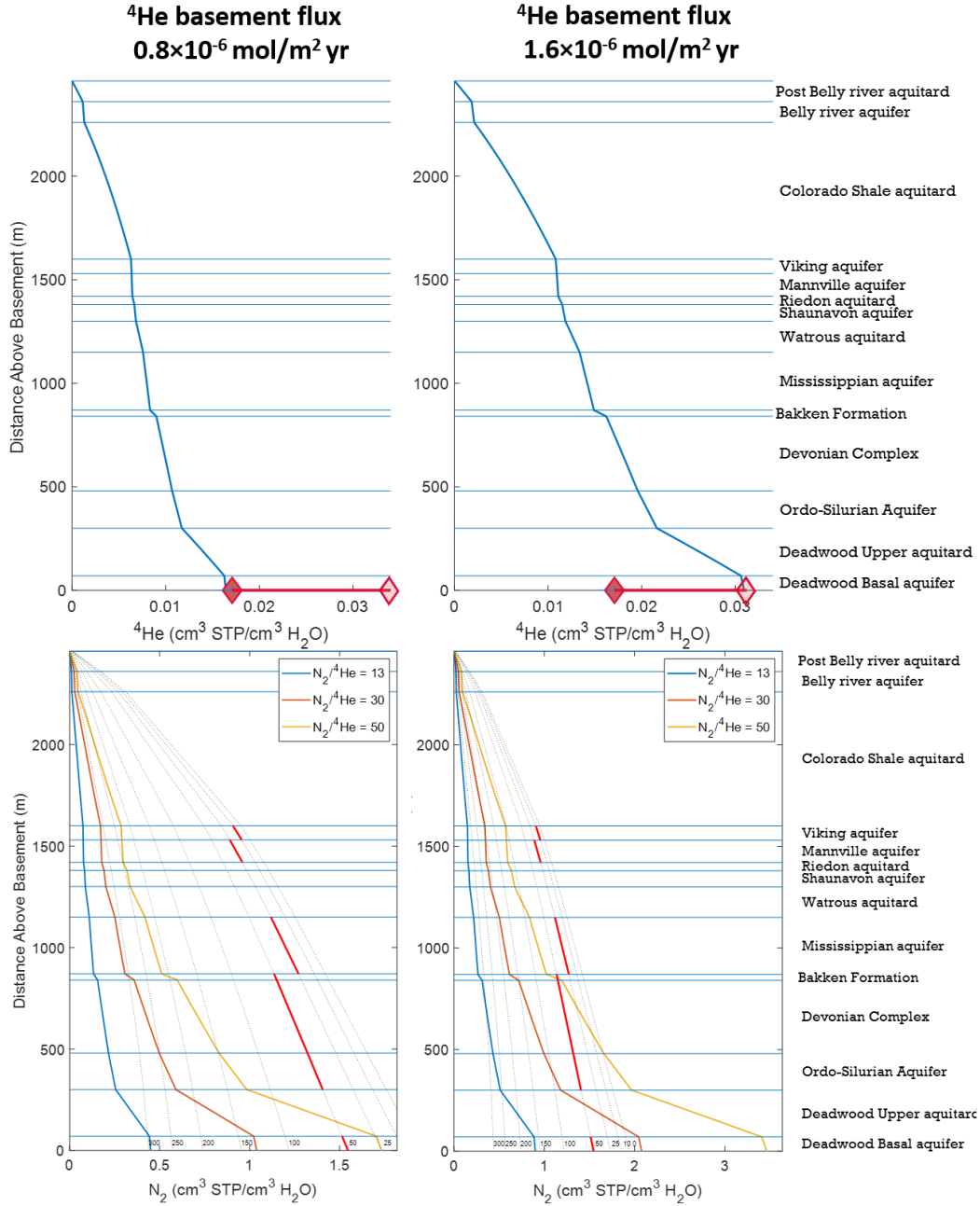
### **7.4 RESULTS AND DISCUSSION**

#### **7.4.1 Nitrogen Diffusive Profiles VS Solubility**

The helium diffusive profiles are constructed for the Deadwood well using a basement helium flux of both  $0.8 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and  $1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ . The values correspond to the lower and upper limit estimated from vertical groundwater  $^4\text{He}$  concentration distribution (Chapter 4). The corresponding diffusive  $\text{N}_2$  distribution is also simulated in parallel with  $\text{N}_2/^4\text{He}$  of 13, 30 and 50 (Figure 7.2).  $\text{N}_2/^4\text{He}$  ratio of 13, reported by Gold and Held (1987), represents an endmember ratio of He-associated  $\text{N}_2$  in Hugoton and Panhandle (Ballentine and Sherwood Lollar, 2002); 30 to 50 marks the range of  $\text{N}_2/^4\text{He}$  ratios observed in many helium-enriched fields (Danabalan, 2017). In addition to the temperature and pressure,  $\text{N}_2$  solubility is also controlled by the salinity of the groundwater; a higher salinity results in lower gas solubility. The salinity of different hydrogeological units is estimated from salinity maps produced by Bachu and Hitchon (1996). The corresponding nitrogen solubility can then be used to predict the formation of the gas phase, which is expected to be formed when the nitrogen level exceeds its solubility under reservoir conditions.

The Deadwood well sits in a low salinity zone with salinity values ranging from 10 to 50 ‰. The simulation results show that under some circumstances nitrogen saturation will be exceeded, and the formation of gas-phase is possible. With a low basement helium flux ( $0.8 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ ), a gas phase will be formed in the groundwater column only when the basement  $\text{N}_2/^4\text{He}$  flux approaches 50. With a higher basement flux ( $1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ ), conditions for the formation of a nitrogen gas phase start be generated in the basal unit with basement  $\text{N}_2/^4\text{He}$  flux ratio between 13 to 30. In the case when the  $\text{N}_2/^4\text{He}$  basement flux ratio approaches 50, units from Cambrian to Devonian Bakken (no included) have their groundwater  $\text{N}_2$  content exceeds the corresponding solubilities, i.e. gas pools are expected to be formed in all these units, including ones higher in the stratigraphic column than the Cambrian Basal aquifer.

## 7.4. RESULTS AND DISCUSSION



**Figure 7.2:** The diffusive concentration profiles of helium (upper panel) with a basement flux of  $0.8 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and  $1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ . For each helium flux value, the diffusive nitrogen profiles modelled are with N<sub>2</sub>/<sup>4</sup>He basement flux ratios of 13, 30 and 50 respectively (lower panels). The horizontal lines are the boundaries of lithological units. The dashed black lines are the solubility of N<sub>2</sub> as a function of different salinity with the salinity values labelled to the right of each line. The solid red lines represent the saturation limit for different formation waters estimated from salinity maps produced by (Bachu and Hitchon, 1996). If the predicted nitrogen concentration for a particular  $^4\text{He}$  flux and basement N<sub>2</sub>/<sup>4</sup>He exceeds solubility (i.e. the coloured concentration line is higher than the solid red line), a nitrogen gas phase is predicted. When He basement flux is  $0.8 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ , gas is predicted to form only in the basal units when N<sub>2</sub>/<sup>4</sup>He is 50. When He basement flux is  $1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ , gas is predicted to develop in the bottom two units when N<sub>2</sub>/<sup>4</sup>He is 25 and in units from Cambrian up to Devonian when N<sub>2</sub>/<sup>4</sup>He is 50.

## *7. The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase*

### **7.4.2 Simulating the Exsolution of Nitrogen: Model Results**

When the concentration of nitrogen in groundwater is predicted by the model to exceed the nitrogen solubility limit, a free gas phase is ‘formed’ within the model. The excess  $N_2$  is calculated and it is further assumed that any free gas formed is quantitatively trapped within the formation which is produced. The extent to which the solubility limit is exceeded will determine the resulting gas-water volume ratio and in turn control the partitioning of the noble gases ( $^4He$  and  $^{20}Ne$ ) into the gas phase. When the basement  $^4He$  flux equals  $0.8 \times 10^{-6}$  mol  $^4He/m^2/yr$ , a gas phase is predicted to form in the Cambrian Deadwood Formation if the basement  $N_2/^4He$  approaches 50 (Figure 7.2). Similarly, when basement flux equals  $1.6 \times 10^{-6}$  mol  $^4He/m^2/yr$ , the  $N_2/^4He$  flux needs to approach 25 for a gas phase to be generated. The model is run to explore a wide parameter space of the basement  $N_2/^4He$  and the most representative scenarios are demonstrated in Figure 7.3 and Table 7.1. Figure 7.3 demonstrates the modelled results for three different scenarios, (a) helium flux of  $0.8 \times 10^{-6}$  mol  $^4He/m^2/yr$  and  $N_2/^4He$  flux ratio of 50; (b) helium flux of  $1.6 \times 10^{-6}$  mol  $^4He/m^2/yr$  and  $N_2/^4He$  flux ratio of 25; and (c) helium flux of  $1.6 \times 10^{-6}$  mol  $^4He/m^2/yr$  and  $N_2/^4He$  flux ratio of 50. The simulated  $N_2/^4He$ ,  $^4He$  concentration and  $^4He/^{20}Ne$  in the gas phase are presented in Table 7.1.

**Table 7.1:** Observed  $N_2/{}^4\text{He}$ ,  ${}^4\text{He}$  and  ${}^4\text{He}/{}^{20}\text{Ne}$  in the Deadwood formation produced gases compared with diffusion-solubility model outputs for different basement flux scenarios.

| Input                                                       |                                        | Output                |                              |                                                                       |                                                      |
|-------------------------------------------------------------|----------------------------------------|-----------------------|------------------------------|-----------------------------------------------------------------------|------------------------------------------------------|
| ${}^4\text{He}$ flux<br>( $10^{-6}$ mol/m <sup>2</sup> /yr) | $N_2/{}^4\text{He}$<br>(Basement Flux) | Vg/Vl                 | $N_2/{}^4\text{He}$<br>(gas) | ${}^4\text{He(gas)}$<br>$10^{-2}$ cm <sup>3</sup> STP/cm <sup>3</sup> | ${}^4\text{He}/{}^{20}\text{Ne}$ (gas)<br>( $10^5$ ) |
| <i>Sample Measurement</i>                                   |                                        |                       |                              |                                                                       |                                                      |
| 0.8*-1.6 <sup>+</sup>                                       | -                                      | -                     | 70-90                        | 1.06-1.36                                                             | 1.2*-2.3 <sup>+</sup>                                |
| <i>Modelling</i>                                            |                                        |                       |                              |                                                                       |                                                      |
| 0.8                                                         | 50                                     | $2.31 \times 10^{-5}$ | 121                          | 0.83                                                                  | 1.23                                                 |
| 1.6                                                         | 25                                     | $2.31 \times 10^{-5}$ | 64                           | 1.56                                                                  | 2.3                                                  |
| 1.6                                                         | 50                                     | 0.041-0.042           | 93-95                        | 1.06-1.08                                                             | 1.7                                                  |

\*apparent helium flux estimated in Chapter 4 before ‘air correction’;

+helium flux after air correction (Chapter 4);

\*\*  $N_2/\text{He}$  reported by Danabalan (2017)

Model results in bold considered best fit to observed gas compositions (see text)



## *7. The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase*

The modelled result can be compared with the Wood Mountain well which contains 96.35% N<sub>2</sub>, 1.08% He and 2.5% other gases (exact composition of the latter unknown) (Yurkowski and Jensen, 2016). The same reservoir is also sampled and reported in Chapter 4 (Deadwood) and by Danabalan (2017) ( ‘International Helium’ well) showing comparable N<sub>2</sub> and Helium content. The Cambrian Deadwood basal unit reported in Chapter 4 and by Danabalan (2017) have N<sub>2</sub>/<sup>4</sup>He ranges from 70 and 90, <sup>4</sup>He concentrations between 1.35% and 1.06% and <sup>4</sup>He/<sup>20</sup>Ne approximately  $1.2 \times 10^5$ .

However, the Cambrian Deadwood sample reported in Chapter 4 demonstrates an air component in the <sup>20</sup>Ne and <sup>20</sup>Ne/<sup>36</sup>Ar space. The gas sample shows a <sup>20</sup>Ne/<sup>36</sup>Ar ratio is slightly higher than that expected from the groundwater exsolution models. The sample demonstrates 0.34% of air addition with a gas-water volume ratio approaches 0, also referred to as the ‘first bubble’ exsolution scenario (Chapter 4). Corresponding air correction does not influence the concentration of helium in the gas phase, but the high <sup>20</sup>Ne concentration in the atmosphere leads to a considerable decrease in <sup>20</sup>Ne in the gas reservoir and thus an increase in <sup>4</sup>He/<sup>20</sup>Ne ratio to  $2.3 \times 10^5$  prior to air mixing (Table 7.1). The corrected <sup>4</sup>He/<sup>20</sup>Ne ratios resulted in the higher <sup>4</sup>He concentration estimated in the groundwater and subsequently increased the apparent He flux from  $0.8 \times 10^{-6}$  mol/m<sup>2</sup>/yr to  $1.6 \times 10^{-6}$  mol/m<sup>2</sup>/yr.

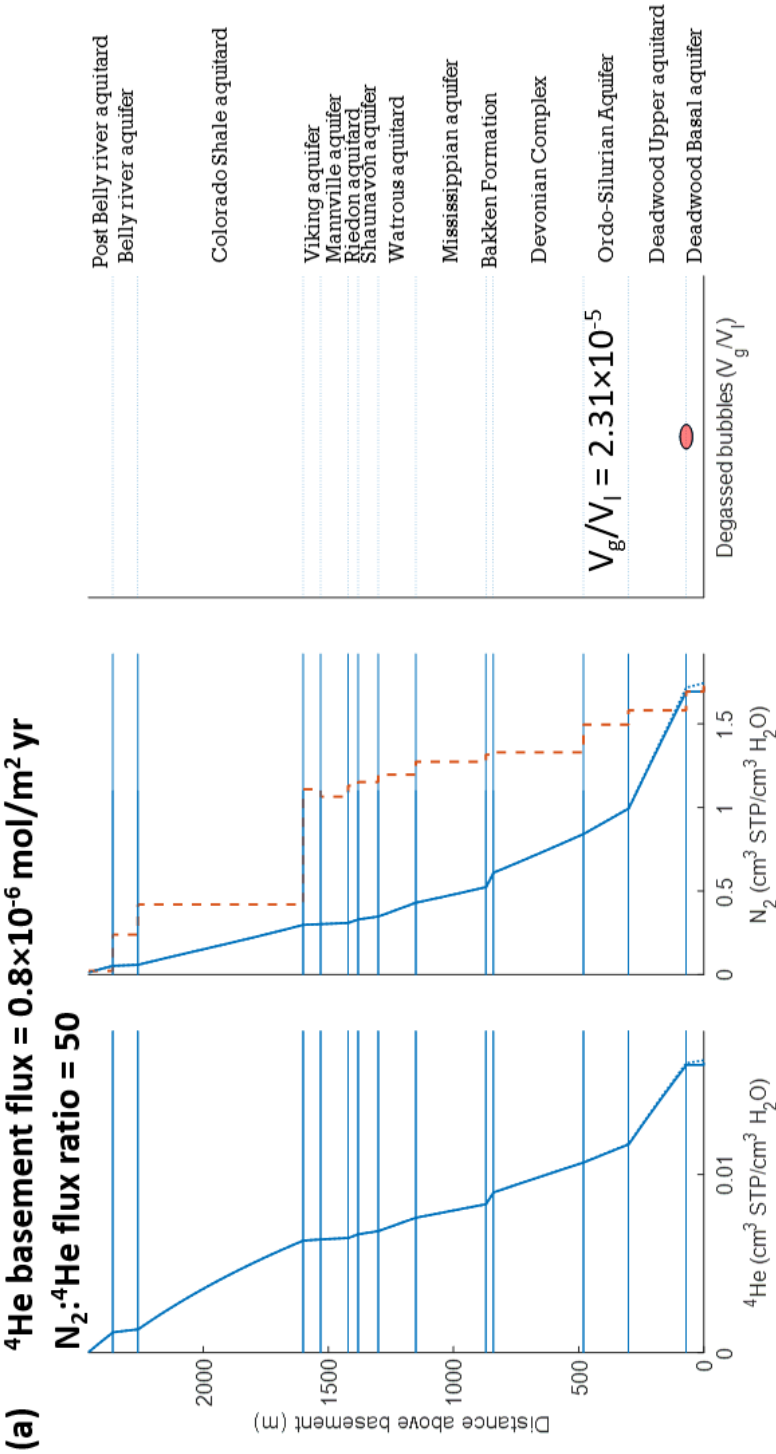
The first model scenario, i.e. a He flux of  $0.8 \times 10^{-6}$  mol <sup>4</sup>He/m<sup>2</sup>/yr and N<sub>2</sub>/<sup>4</sup>He basement flux ratio of 50, generates a tiny gas phase in the Cambrian basal aquifer unit with <sup>4</sup>He/<sup>20</sup>Ne ratios comparable to those observed and reported in Chapter 4 of this thesis. The modelled N<sub>2</sub>/<sup>4</sup>He in the gas phase is higher than measured values, and the simulated helium concentration in the gas phase is lower. With increasing N<sub>2</sub>/<sup>4</sup>He basement ratios, gas formed expands in its volume and the resulted gas pool would see an increase in N<sub>2</sub>/<sup>4</sup>He and a decrease in <sup>4</sup>He concentration.

The second model scenario, a helium basement flux of  $1.6 \times 10^{-6}$  mol <sup>4</sup>He/m<sup>2</sup>/yr and N<sub>2</sub>/<sup>4</sup>He basement flux ratio of 25, also generates a tiny free gas phase in the basal unit. The modelled values of N<sub>2</sub>/<sup>4</sup>He, <sup>4</sup>He concentration and <sup>4</sup>He/<sup>20</sup>Ne in the gas phase are

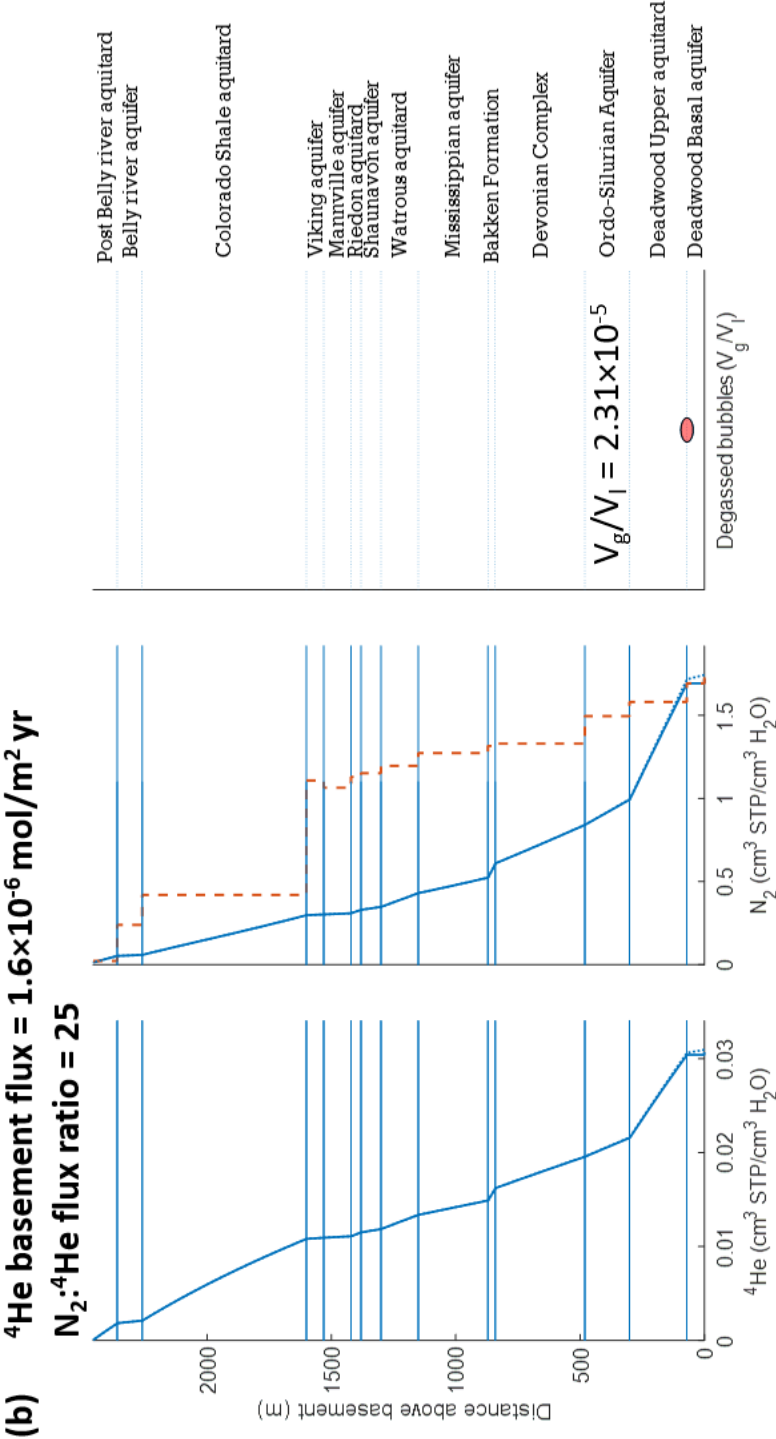
#### 7.4. RESULTS AND DISCUSSION

all comparable to the measured values in the sample after air correction. The gas to water volume ratio is very small, likely indicates an unstable gas bubble at an early stage of gas formation. When  $N_2/{}^4\text{He}$  equals 50, the higher  $N_2/{}^4\text{He}$  flux expands the volume of exsolved gas (Figure 7.3c), which in turn lowers helium concentration and increases  $N_2/{}^4\text{He}$  in the gas phase (Table 7.2). The observed gas content in the samples lies within the ranges of the modelled results of these two scenarios.

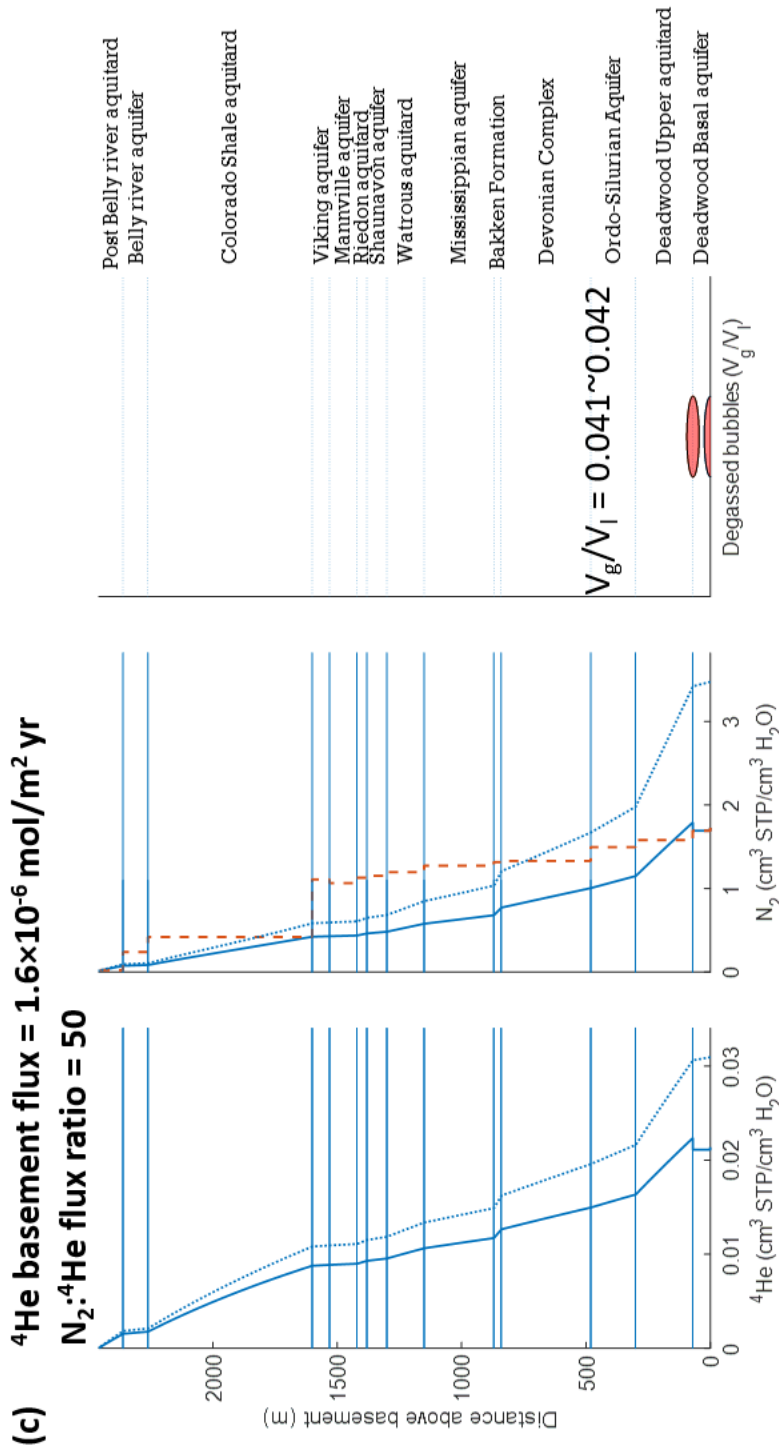
7. The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase



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## 7. The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase



**Figure 7.3:** Diffusion-and-exsolution model for different basement helium and  $\text{N}_2/{}^4\text{He}$  flux scenarios (see text). (a) Helium flux of  $0.8 \times 10^6 \text{ mol } {}^4\text{He}/\text{m}^2/\text{yr}$  and  $\text{N}_2/{}^4\text{He}$  flux ratio of 50; (b) helium flux of  $1.6 \times 10^{-6} \text{ mol } {}^4\text{He}/\text{m}^2/\text{yr}$  and  $\text{N}_2/{}^4\text{He}$  flux ratio of 25; (c) helium flux of  $1.6 \times 10^{-6} \text{ mol } {}^4\text{He}/\text{m}^2/\text{yr}$  and  $\text{N}_2/{}^4\text{He}$  flux ratio of 50. The solid lines represent helium and nitrogen profiles resulting from exsolution. The dotted lines represent the profiles without exsolution which can also be found in Figure 7.2. The ovals show the existence of free gas phase in the Cambrian unit and the numbers are the gas to water volume ratios. The red lines in the  $\text{N}_2$  profiles demonstrate the estimated solubilities for different sedimentary units. The model is simplified by assuming the solubility of  $\text{N}_2$  at the top boundary of a hydrogeological unit is consistent throughout the entire unit.

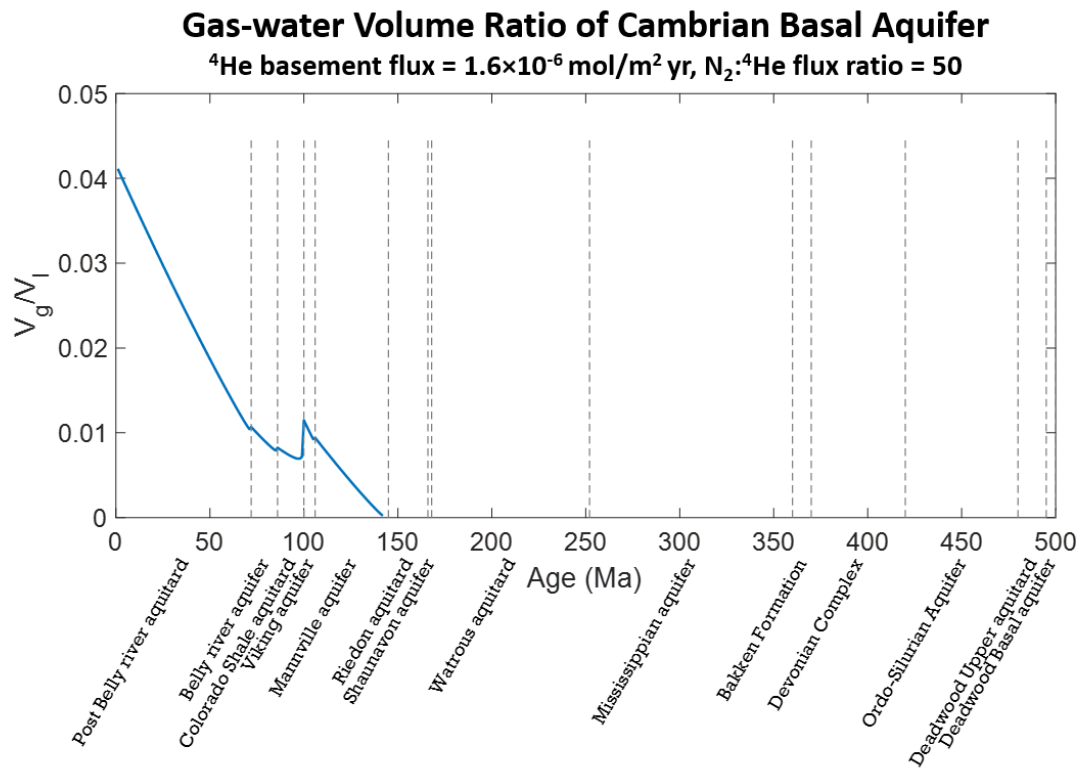
## 7.4. RESULTS AND DISCUSSION

With a basement helium flux of  $1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and basement  $\text{N}_2/^4\text{He}$  ratios between 25-50 respectively, this independent model simulates gas compositions comparable to the sample measurement. The successful reproduction of the measured data in the Deadwood sample suggests that the Deadwood gas field is consistent with both helium and nitrogen sourced from the crystalline basement and that the formation of the gas pool is controlled by nitrogen solubility. This modelled result suggests the importance of helium-associated basement sourced nitrogen in the formation of helium reservoirs in intracratonic, or tectonically stable sedimentary basins. According to the results of this time-stepped models that the gas phase could have been formed some time between 150 Ma ago and present and the gas phase will have gradually expanded to the current size, determined in the model by the gas/water volume ratio parameter  $V_g/V_l$  (Figure 7.4).

### 7.4.3 Effect of Gas-Phase Formation on Solute Diffusion in Water Column

The capacity of the model to include gas-phase formation immediately places a maximum value on nitrogen concentration in the groundwater phase in each lithology – the solubility limit. When the nitrogen solubility limit is reached, further increases in the groundwater nitrogen concentration in the lithology hosting the gas phase ceases. This results in lower concentration gradients and therefore lower rates of nitrogen diffusion compared to diffusion-only models. For helium, the effect of gas-phase formation is more pronounced. This is because helium is approximately five times less soluble in water than nitrogen. The formation of a gas phase, therefore, has a more significant effect on the helium concentration gradient in the water column, which in turn, like nitrogen, controls the rate of helium diffusion. The significance of the gas phase effect is related to the gas-to-water volume ratio. When the gas/water volume ratio formed is small, and in the limit approaches zero (sometimes referred to as the ‘first bubble’), the gas phase has a negligible effect on the water column dissolved gas concentration. This is illustrated in Figures 3(a) and (b), where the  $V_g/V_l$  in the Cambrian Deadwood formation is  $<0.0006$ , and there is

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**Figure 7.4:** The modelled gas-water volume ratio of the Cambrian basal aquifer throughout geological time. The model input parameters are shown for basement  $^4\text{He}$  and  $\text{N}_2$ / $^4\text{He}$  of  $1.6 \times 10^{-6}$  mol  $^4\text{He}$ /m<sup>2</sup>/yr and 50 respectively. The deposition time of different geological units is marked along x-axis. The modelling result corresponding to the listed input indicates that under such scenario, no gas-phase is formed until 150 Ma.

little difference between the  $^4\text{He}$  and  $\text{N}_2$  concentrations predicted by the diffusion-only or diffusion-exsolution model.

In contrast the diffusion-exsolution model results for a He basement flux of  $1.6 \times 10^{-6}$  mol  $^4\text{He}$ /m<sup>2</sup>/yr and  $\text{N}_2$ / $^4\text{He}$  flux ratio of 50 predicts a higher  $V_g/V_l$  ratio ( $>0.004$ ) in the Deadwood formation and a He and  $\text{N}_2$  concentration gradient significantly lower than that predicted by the diffusion-only model (Figure 7.3c). In the diffusion-only model, excess  $\text{N}_2$  is predicted in multiple units. This indicates that if the timing and sequence of exsolution are not considered, nitrogen gas pools would be predicted in both the Cambrian unit and the units higher in the stratigraphic column.

The exsolution model demonstrates the importance of considering gas-phase formation,

## 7.5. CONCLUSION

which acts as an in-lithology sink for both He and N<sub>2</sub> that would have previously been dissolved in the water column. Qualitatively, approaches that consider solely diffusion can thereby risk underestimating the basement helium flux. Nevertheless, gas-phase formation at depth reduces the conditions for gas-phase formation in units higher up in the stratigraphic section. This result is consistent with the nitrogen-dominated helium fields observed in the Williston Basin mostly being close to the basement contact (e.g. International Helium Danabalan, 2017, Chapter 4), Red river formation (Danabalan, 2017)), Swift current (Thompson, 1964), Harley Dome (Danabalan, 2017)).

## 7.5 CONCLUSION

To improve the understanding of the formation of helium reservoirs, models were developed here to evaluate controlling processes on a specific type of helium reservoir, where groundwater is controlled by diffusive transport, and the primary degassing component is helium-associated nitrogen derived from a crystalline basement underlying the sedimentary contact unit.

The differences in diffusion coefficient and solubility of N<sub>2</sub> and He result in a decoupling of the two elements through migration and degassing processes. A time-stepped 1D diffusion-and-exsolution model was developed that incorporates both the vertical migration of N<sub>2</sub> and He separately and the degassing process of nitrogen under reservoir conditions. The modelled results are compared with gas samples collected from a Cambrian well (sample Deadwood in Chapter 4 and sample ‘International Helium’ reported by Danabalan (2017)), which is a nitrogen-enriched helium producing well. With a basement flux of  $1.6 \times 10^{-6}$  mol <sup>4</sup>He/m<sup>2</sup>/yr, consistent with the vertical concentration profile, and a basement flux N<sub>2</sub>/<sup>4</sup>He ratio of 25-50, the gas composition independently derived as model outputs provide a match with the observation. The required basement N<sub>2</sub>/<sup>4</sup>He value is comparable with the N<sub>2</sub>/<sup>4</sup>He that reported in helium gas fields (Danabalan, 2017). This study highlights crustal degassing processes and may help with the prediction of nitrogen-dominated helium pools in intracratonic



## *7. The Formation of Intracratonic Basin Helium Reservoirs in a Basement Sourced Nitrogen Gas Phase*

and tectonic stable sedimentary basins. The model results also demonstrate the formation of a gas-phase restricts the transport of dissolved components further upwards through the stratigraphic section. The model can estimate the timing of free gas generation, which is another vital factor to be considered for helium accumulation and the analysis of potential leaking and migration. This research focuses on basement sourced nitrogen as the major exsolving gas phase but demonstrates the significance of the gas phase in controlling the transport of dissolved gases through the water column. This suggests information on gas formation by other processes, e.g. hydrocarbon generation, is equally important in determining the migration of He and predicting the existence of He reservoirs.



# 8

## Conclusion

## Contents

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### 8.1 SUMMARY

Understanding the dominant mechanism of subsurface fluid migration and the processes controlling crustal degassing is crucial in managing industrial and environmental projects. This thesis focuses on using noble gas concentrations and isotopes as tracer elements in sedimentary basins, quantifying the flux from the Precambrian basement and exploring their migration through the overlying sedimentary units with numerical models. Finite discrete models were constructed to describe the transport of solutes in the groundwater, from first principals using MATLAB<sup>®</sup>, and were compared to measurements made on samples collected from natural systems.

The two sedimentary basins studied are the Williston Basin and the Southwestern Ontario Basin in North America. Twenty-six and thirty-three noble gas samples were collected, respectively, from various localities and different geological formations within the two basins. The samples were analysed with Helix SFT<sup>TM</sup> and Argus VI<sup>TM</sup> mass spectrometers in the noble gas laboratory at the University of Oxford for isotopic concentrations and ratios. In both basins, the initial radiogenic  $^4\text{He}$  concentration in the groundwater were estimated from  $^4\text{He}/^{20}\text{Ne}$  ratios in the gas samples (Ballentine and Burnard, 2002; Ballentine and Sherwood Lollar, 2002). In the Southwestern Ontario Basin,  $^{38}\text{Ar}/^{36}\text{Ar}$  ratios were used to estimate  $^{40}\text{Ar}$  concentrations in the groundwater associated with the natural gases. The estimated groundwater concentrations were then used to compare with those simulated by the numerical transport models with the hypothesised hydrogeological conditions.

## 8. Conclusion

The Williston Basin is an intracratonic basin in North America with Cambrian to Pleistocene multi-layered aquifers and aquitards. Air-normalised  $^3\text{He}/^4\text{He}$  ( $R_a$ ) varies between 0.08  $R_a$  to 0.36  $R_a$ , except for the Bakken Weyburn samples, which are crustally dominated, with a ratio around 0.01  $R_a$ . The higher than crustal endmember (0.02  $R_a$ )  $^3\text{He}/^4\text{He}$  ratios are consistent with a resolvable mantle  $^3\text{He}$  component, which is observed in various units. The neon ratios in the unit overlying the basement (Deadwood Formation) fall on a mixing line between air and a radiogenic production endmember, which is distinct from the modern crust and has been ascribed to an Archean source based on  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  space (Kendrick et al., 2011; Lippmann-Pipke et al., 2011; Holland et al., 2013). The unusual Archean neon signature in the Deadwood Formation suggests there is a noble gas contribution from the underlying Archean rocks. Compared to the calculated in situ radiogenic production,  $^4\text{He}$  depletion in deeper units and excess in shallower units is shown by the  $^4\text{He}$  concentrations in groundwater. The observations stated above are evidence of noble gas cross-formational transport and a deeper input from the crystalline basement.

$^4\text{He}$  flux into the basin is estimated by vertical scale diffusional models, assuming static groundwater and a dominant diffusive transport. Deviation from modelled diffusion profiles is observed for the Viking, Mannville, and Mississippian Formations. This could indicate  $^4\text{He}$  loss due to water disturbance, likely related to anthropogenic water flooding in the oil industry, which is common in these formations of the Williston. The apparent helium flux into the base of the Williston Basin estimated in this work ranges between  $0.8\text{--}1.6 \times 10^{-6}$  mol/m<sup>2</sup>/yr, representing the lower-limit estimations due to the assumptions related. The estimated flux range overlaps with that expected from the steady-state flux calculated from the composition of the Trans-Hudson crust and that reported from other intracratonic basins (Torgersen et al., 1992; Torgersen, 2010). It is also indistinguishable from a steady-state helium flux  $1.47 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  calculated from average U and Th concentrations of continental crust (Torgersen et al., 1992; Torgersen, 2010).

## 8.1. SUMMARY

Southwestern Ontario Basin refers to sedimentary units overlying the Algonquin Arch, a basement high that separates the Michigan Basin to the west and the Appalachian Basin to the east. The dominant crustal helium in the Southwestern Ontario Basin is distinct from the fluids in the Michigan Basin, which have resolvable mantle signatures (Castro et al., 2009; Ma et al., 2009b). No apparent horizontal distribution of  $^3\text{He}/^4\text{He}$  ratios can be observed from the existing dataset (this work and Sherwood Lollar et al., 1994b) in the Southwestern Ontario Basin, implying that  $^3\text{He}$  is not likely to be supplied with a point source. These observations suggest a regional scale Pleistocene fluid migration from the Michigan Basin to the Southwestern Ontario Basin is unlikely. Therefore, basement flux is then analysed with the assumption of a diagenetic and static groundwater system.

The groundwaters in most of the sedimentary units in the Southwestern Ontario Basin demonstrate higher  $^4\text{He}$  concentrations than in situ U and Th radioactive production, indicating an external  $^4\text{He}$  supply, most likely from the crystalline basement. Diffusive transport models of  $^4\text{He}$  and  $^{40}\text{Ar}$  are constructed and the basement fluxes are determined for each well. The samples demonstrate a range of best-fit basement fluxes,  $0.01\text{--}1.30 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and  $0.05\text{--}2.87 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$ . On the southeast limb of the Algonquin arch, closer to the Appalachian Basin, higher basement fluxes are observed (with averages of  $0.39 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and  $0.97 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$ ). On the northwest limb of the Algonquin arch, closer to the Michigan Basin, higher basement fluxes are observed (with averages of  $0.10 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$  and  $0.32 \times 10^{-8}$  mol  $^{40}\text{Ar}/\text{m}^2/\text{yr}$ ). With the assumption of a static water body, the differences in fluxes are likely attributed to compositional or permeability differences in the basement rock.

Processes like groundwater exsolution are crucial in the formation of subsurface gas reservoirs, such as natural gas and helium. Mathematical expressions were derived and summarised for the three endmember degassing systems (Barry et al., 2016): first-order equilibrium, second-order open, and closed systems. Concentrations and concentration ratios of atmospheric noble gas isotopes ( $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$ , and  $^{132}\text{Xe}$ ) were used to construct error-weighted, non-linear inversion models to solve the gas-water ratio,

## 8. Conclusion

and Kr and Xe enrichment in groundwater before gas exsolution. The discrepancies in  $\frac{V_g}{V_l}$  solutions obtained from the concentration and ratio models can be explained by air contamination or ancient dilution events. The mathematical solutions require complementary geological, hydrogeological, and geochemical evidence. The linear correlation between the excess Kr and Xe,  $f_{Xe}$  and  $f_{Kr}$  in the Southwestern Ontario Basin have lines of best fit with gradients between 0.190 to 0.230. The inversion model is also applied to published noble gas data from other basins. Assuming those samples reported have negligible air contamination, the global slope ranges from 0.136 to 0.142. These values are comparable to the theoretical ratios estimated of charcoal ( $0.22 \left(\frac{Kr}{Xe}\right)_{ASW}$ ) and observations of young ocean sediment ( $0.12 \left(\frac{Kr}{Xe}\right)_{ASW}$ ) (Torgersen et al., 2004). The higher gradient in the Southwestern Ontario Basin is possibly caused by Kr and Xe adsorbed on silica sediments ( $0.55 \left(\frac{Kr}{Xe}\right)_{ASW}$ ) (Matsuda and Nagao, 1986). The comparison suggests that the excess Kr and Xe is likely to be released from sediments. Groundwater exsolution is crucial in the formation of helium reservoirs in stable intracratonic sedimentary basins. Numerical models were developed to evaluate controlling processes on a specific type of helium reservoir, where groundwater is controlled by diffusive transport, and the primary degassing component is helium-associated nitrogen derived from a crystalline basement. With a basement helium flux of  $1.6 \times 10^{-6}$  mol  $^4\text{He}/\text{m}^2/\text{yr}$ , which is compatible with observed concentration gradients, and the  $\text{N}_2/\text{He}$  basement flux ratio of 25-50, which is comparable to that observed in helium reservoirs in sedimentary basins Danabalan (2017), the model reproduced similar gas compositions to those observed in the Cambrian helium reservoir in the Williston Basin. The model demonstrates the significance of the existence of a gas-phase, the timing of gas generation, and the residence time of groundwater in controlling the transport of dissolved gases and their concentrations through the water column. Such analysis could help with the prediction of nitrogen-dominated helium pools in intracratonic and tectonically stable sedimentary basins.

## 8.2 OUTLOOK AND FUTURE RESEARCH

This work developed mathematical and numerical models to explore the transport of noble gases in sedimentary basins and estimated apparent fluxes from the Precambrian basement. These simple and fast 1D models can provide first-order analysis with limited information. There are potential in solving more complicated questions, including identifying and timing flushing events, but requires a higher sampling resolution.

These models provide a reference for understanding fluid migration in the basins. Data that remain unexplained would require the incorporation of two-dimensional flow. In the thesis, I focused on exploring the significance of diffusion as the dominant transport mechanism. However, other transporting mechanisms, such as vertical advection, horizontal migration, are not disregarded. This worth further exploration, possibly with the help of 2D or 3D models.

$^4\text{He}$  groundwater dating usually assumes zero flux lost from the basin; however, the diffusion model presented here suggests the  $^4\text{He}$  flux lost is also affected by basin architecture development and hydrogeological events. More research would be required to examine the significance of such effects on  $^4\text{He}$  dating applications.

Compared to the Southwestern Ontario Basin, the Williston Basin has higher heat flux, higher  $^3\text{He}/^4\text{He}$ , and less degree of decoupling between heat and helium. Such correlations could be associated with the permeability of the crystalline basement as well as the local hot sources. If quantitative models can be constructed, the mechanisms controlling the transport in crystalline basement could be better understood and predicted, which could have a significant impact on helium exploration projects.

In this thesis, models were used to investigate the generation of helium reservoirs enriched in basement-sourced nitrogen. The research highlighted the importance of  $\text{N}_2$  gas exsolution during the analysis of solute transport through the sedimentary column in He-associated  $\text{N}_2$  system. Similarly, the impact of other gases formation, e.g. hydrocarbon generation, or  $\text{CO}_2$  from magma degassing, could be significant in



## 8. *Conclusion*

controlling the migration of solutes, and predicting the existence of helium reservoirs and therefore, worth further research. Gas flow buoyancy after gas phase formation is neglected in this study but the significance of the effect would also improve the understanding in subsurface fluid migration.

To further understand a crustal helium reservoir, research should extend into the crystalline basement. Further exploration is required to quantify the release of helium from the minerals, the transport through the crystalline basement, and the resulting flux from the basement to the overlying systems. An additional research question that this work provokes is the different excess Kr and Xe shown in the crystalline basement compared to that observed in sedimentary basins.

Overall, this work demonstrates the enormous potential of noble gases as geochemical tracers to aid the understanding of subsurface fluid transport in sedimentary systems. The quantification of basement noble gas fluxes plays a vital role in understanding the crustal degassing mechanisms of other associated gases. The methods of analysis can be applied in other sedimentary basin systems, as well as the crystalline basement. Other research methods, such as the numerical modelling presented in this work, and expanding into the analysis and modelling of big data sets, can be applied to the noble gas geochemistry analysis in the future, for the studies of various subsurface environments.



# Appendices





# Literature Review and Methodology

## Appendix

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### A.1 SAMPLE COLLECTION

The sampling of noble gases needs to ensure that there is no air contamination. This is done by collecting with internally polished, refrigeration-grade copper tubing through which the gas cannot diffuse (R. Weiss, 1968). The sample tubes are

## *A.1. SAMPLE COLLECTION*

sealed using stainless steel clamps.

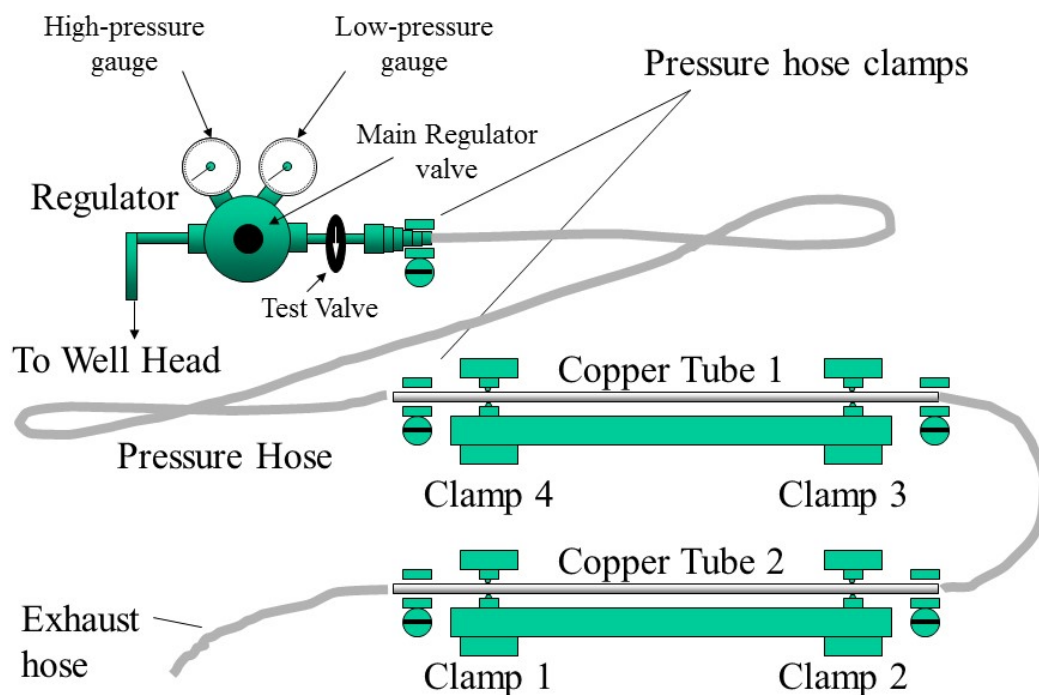
Although there is variability between wells, schematic configurations of noble gas sampling can be found in Figure A.1. If the wellhead pressure is less than the maximum regulator inlet pressure, a gas regulator is fitted to the wellhead in order to step down and regulate the pressure to 1.5 to 2 bar for sampling. An appropriate NPT (National Pipe Thread) adapter is connected the wellhead valve to the high-pressure inlet of the regulator. The connection threads are wrapped with Teflon tape to ensure a good seal. The low-pressure outlet of the gas regulator is connected to the first copper tube using heavy-duty PVC pressure hosing capable of sustaining pressures of at least 2 bar and secured with hose clamps. Duplicate (or more) samples can be taken by attaching sample tubes in series and connecting one after another with the high-pressure hosing. Another piece of the hose is attached to the end of the series of copper tubes as an exhaust port, the outlet of which should be submerged in water to ensure there is no backwards flow of air into the sampling apparatus. A minimum of 10 minutes is required for gas flushing to remove residual air in the system. After flushing, the tubes are clamped in turn starting with the one furthest from the wellhead backwards towards the wellhead.

When a regulator is not available, or the wellhead pressure too high, a T or Y connector is used instead which allows the pressure inside the copper tube to be approximately atmospheric pressure (Figure A.1b). If the wellhead pressure is low, between 1-2 bar, the sampling line can be directly connected to the wellhead.

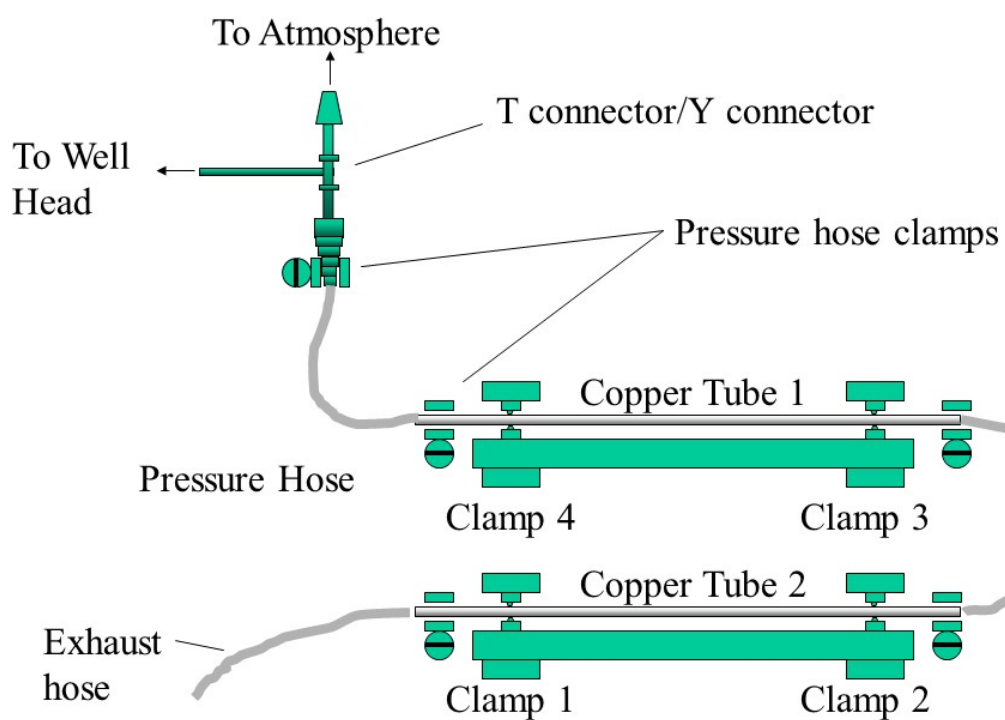
If wells are producing gas-fluid mixtures, the gas phase is extracted and separated from the liquid phase using a custom-designed separation vessel (Figure A.1c). The gas-fluid mixture is directed to a chamber where gases can exsolve from the water and hosing is connected to the top gas-outlet of the chamber to the Cu tubes for sampling.

Samples are packed to prevent the copper tubes from being bent or damaged during transport.

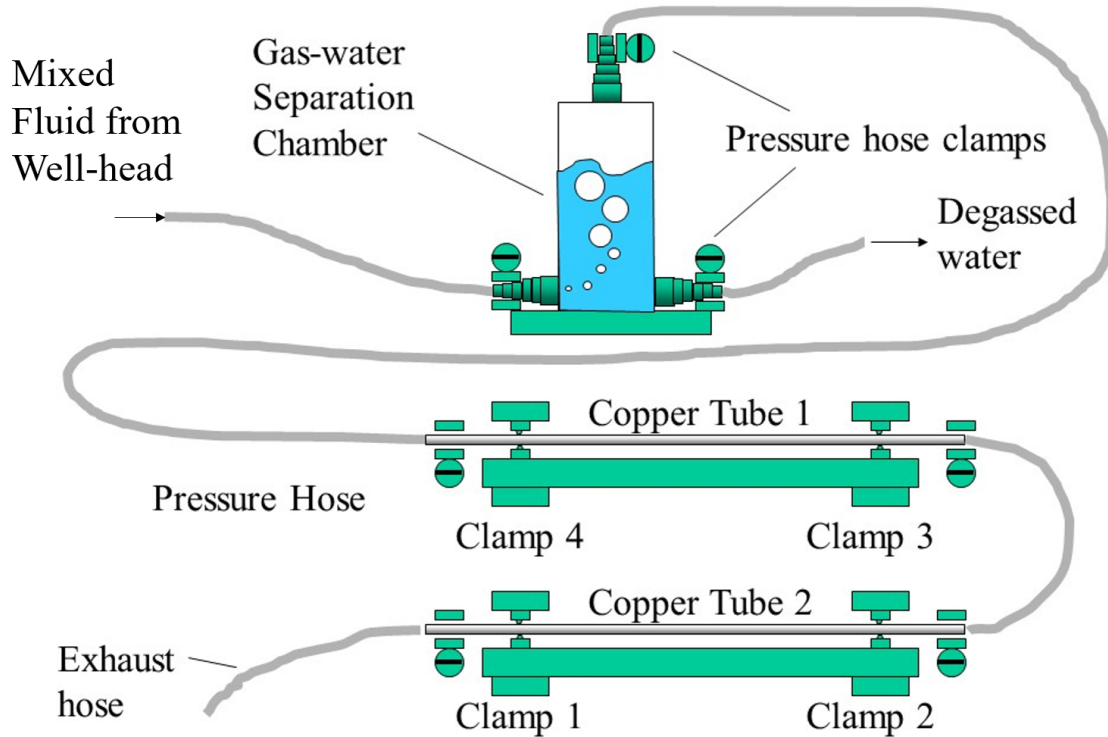
### **Noble Gas Sample Collection System (a)**



### **Noble Gas Sample Collection System (b)**



### Noble Gas Sample Collection System (c)



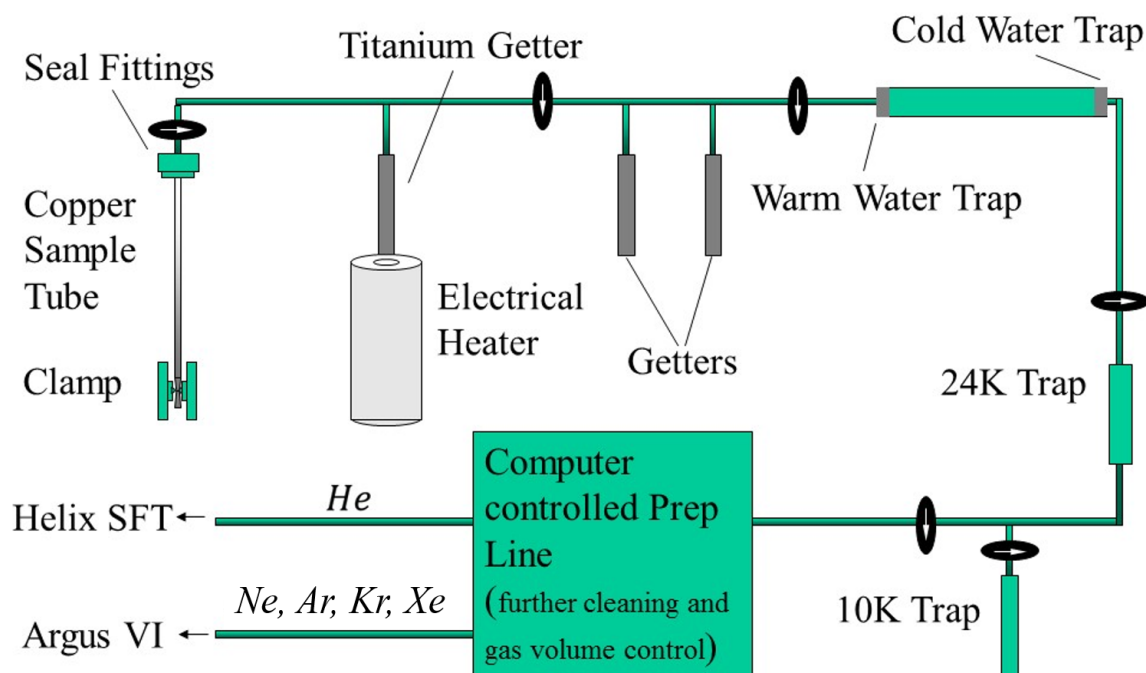
**Figure A.1:** Schematic illustration demonstrating configurations for noble gas sample collection. (a) When a pressure regulator is available, it can be connected to the well-head. The low-pressure outlet is connected to the sampling copper tubes using heavy-duty PVC pressure hosing capable of sustaining pressures of at least 2 bar and secured with hose clamps. The end of the series of copper tubes is attached with another piece of the hose as an exhaust port. (b) When a regulator is not available, it can be replaced with a T or Y connector. (c) When the well produces gas-fluid mixtures a custom-designed separation vessel is connected to extract the gas phases from the fluids and hosing is connected to the top gas-outlet of the chamber for sampling.

## A.2 NOBLE GAS ANALYTICAL EQUIPMENT

The measurement of noble gases includes steps for determining the amount of sample gas to be used for each measurement, purification of noble gases, and cryogenic noble gas separation before allowing samples to enter the specialized mass spectrometers; this configuration is illustrated in Figure A.2, following the configuration described by Barry et al. (2016).



## Noble Gas Sample Pretreatment and Measurement



**Figure A.2:** Simplified diagram of the preparation line for noble gas samples.

### A.2.1 Pressure and Sample Volume

In the Oxford Noble Gas Laboratory, the sample tubes are mounted onto an all-stainless steel Ultra-High Vacuum system, including a rotary vane roughing pump and a diaphragm-backed turbomolecular pump, each fitted with a suitable pressure gauge to measure vacuum in the system while being pumped (i.e., a Pirani thermal conductivity gauge and an inverted magnetron gauge). Air is initially removed from the attachment location using the rough pump (to  $10^{-3}$  mbar, measured with a Pirani gauge), after which pumping is switched to the turbomolecular pump to achieve high vacuum ( $10^{-8}$  mbar, measured with an inverted magnetron gauge).

The amount of noble gases needs to be controlled in order to avoid overloading or damaging the detectors in the mass spectrometer or producing unreliably low signals. The amount of sample gas used for analysis is therefore adjusted by changing the

## *A.2. NOBLE GAS ANALYTICAL EQUIPMENT*

pressure within a known volume by a series of forward expansions and pump-outs, until the desired pressure within the volume is reached. A Baratron<sup>®</sup> capacitance manometer gauge (1000 torr full scale, accuracy  $\pm 0.5\%$  of reading) is connected within the known volume for pressure readings. Samples which are highly depleted or enriched in helium are measured a second time at a different pressure compared to the other noble gases, in order to produce optimal helium abundance and isotope ratio results.

### **A.2.2 Purification**

Hydrocarbons and other reactive gases are removed chemically by exposing the samples to a titanium sponge at 950°C; the rapid drop in pressure during the first minutes of this hot gettering step is evidence of the permanent removal of the most abundant sample gases (e.g., methane, oxygen, nitrogen, and carbon dioxide in various abundance ratios). The Ti is then cooled to room temperature by removing the tube furnace. Cooling the Ti sponge readily removes other gases, including water vapour, methane and hydrogen (Stout and Gibbons, 1955). The remaining gases are then equilibrated with a hot getter (SAES GP-50) and a cold getter (SAES NP-10), set at 250°C and room temperature respectively, which further removes any active gases through chemical reactions.

An aliquot of the sample is then isolated and analysed on a Hiden Analytical HAL-201 (quadrupole mass spectrometer) for a primary indication of gas composition (Warr, 2013). This step ensures the mass spectrometer is not overloaded or contaminated. The quadrupole is isolated from the rest of the line and kept at a pressure of  $10^{-9}$  mbar by a separate ion pump. Moisture content is removed by passing the sample through stainless-steel water traps held at 250K and 180K, respectively (warm water- and cold water-trap respectively in Figure A.2).

### **A.2.3 Noble Gas Separation**

Noble gases are separated based on empirically-derived absorption and release temperatures on two cryogenic traps cooled each by a helium adiabatic expansion module (Compressors are CTI 8200 model and refrigerators are CTI 350 CP). Ar, Kr and Xe are first frozen to a stainless-steel trap at 20K, and He and Ne are trapped in a charcoal trap at 15K. The cryogenic traps are then warmed to release the required noble gas species. These release temperatures are selected based on adsorption and release tests with air-derived noble gases on the Oxford cryogenic cold trap system. He is released between 31K to 34K from the charcoal trap and measured using Helix SFT<sup>TM</sup> mass spectrometer. The residual helium is removed before releasing neon at 90K. Longer pumping times are required for helium-rich samples because inefficient helium removal can raise the neon background values as a result of copious helium atoms and ions hitting the flight tube and releasing embedded noble gas ions. All the heavy gases are released from stainless-steel trap at 200K after neon measurement, and an aliquot of the released gas (mostly Argon) is taken for Ar measurement. The trap is then set to 52K to re-adsorb 99% of Kr and Xe and some Ar, allowing non-adsorbed argon gas to be pumped away. The trap is then warmed up to 70K and cooled back to 52K to liberate and remove more argon from the trap through each temperature cycle. Three cycles are run to ensure that most of the argon is removed. The trap is then set to 300K and the released Kr/Xe gas mixture is inlet into the mass spectrometer for isotope measurements of all stable Kr and Xe isotopes. Ne, Ar, Kr and Xe are measured using Argus VI<sup>TM</sup> mass spectrometer.

The amount of gas entering the mass spectrometer can be further controlled through a series of expansion and splitting steps, which are tailored based on the results reported by Analytical HAL IV (Hidden Quadrupole).

## *A.2. NOBLE GAS ANALYTICAL EQUIPMENT*

### **A.2.4 Mass Spectrometry**

Noble gas mass spectrometers, like all mass spectrometers, consists of an ion source to ionise gas species, a mass filter separating these species according to their mass over charge ratio and collector(s) to read corresponding signals. The mass spectrometers used in this project are a Helix SFT<sup>TM</sup> for the collection of  $^3\text{He}$  and  $^4\text{He}$  and an Argus VI<sup>TM</sup> for the collection of  $^{20}\text{Ne}$ ,  $^{21}\text{Ne}$ ,  $^{22}\text{Ne}$ ,  $^{36}\text{Ar}$ ,  $^{38}\text{Ar}$ ,  $^{40}\text{Ar}$ ,  $^{78}\text{Kr}$ ,  $^{80}\text{Kr}$ ,  $^{82}\text{Kr}$ ,  $^{83}\text{Kr}$ ,  $^{84}\text{Kr}$ ,  $^{86}\text{Kr}$ ,  $^{124}\text{Xe}$ ,  $^{126}\text{Xe}$ ,  $^{128}\text{Xe}$ ,  $^{129}\text{Xe}$ ,  $^{130}\text{Xe}$ ,  $^{131}\text{Xe}$ ,  $^{132}\text{Xe}$ ,  $^{134}\text{Xe}$ ,  $^{136}\text{Xe}$ .

#### **Ion source**

Both mass spectrometers use modified Nier-type electron impact sources. The source contain a filament that creates an electron beam, an ionization chamber where electron bombardment took place, and ion extraction, acceleration, and focus electrodes to transport a well-focused ion beam through the flight tube of the mass spectrometer from the ion source through the magnetic field and into the detector(s) (Burnard et al., 2013). High energy electrons generated by the filament collide with neutral gas atoms or molecules, dislodging one electron to form an ion with one positive charge. Less frequently, more electrons are dislodged, and ions with double or more charge can be formed.

#### **Magnetic sector filter**

The separation of ionised gas beams is achieved with a magnetic sector. The sector was composed of an arc flight tube which was surrounded by a magnetic field. In addition to the mass to charge ratios, the radius of the flight path of the charged particles is also proportional to the ion velocity and inversely proportional to the strength of the magnetic field. By changing the strength of the magnetic field, the isotopes can be directed into the appropriate collectors.

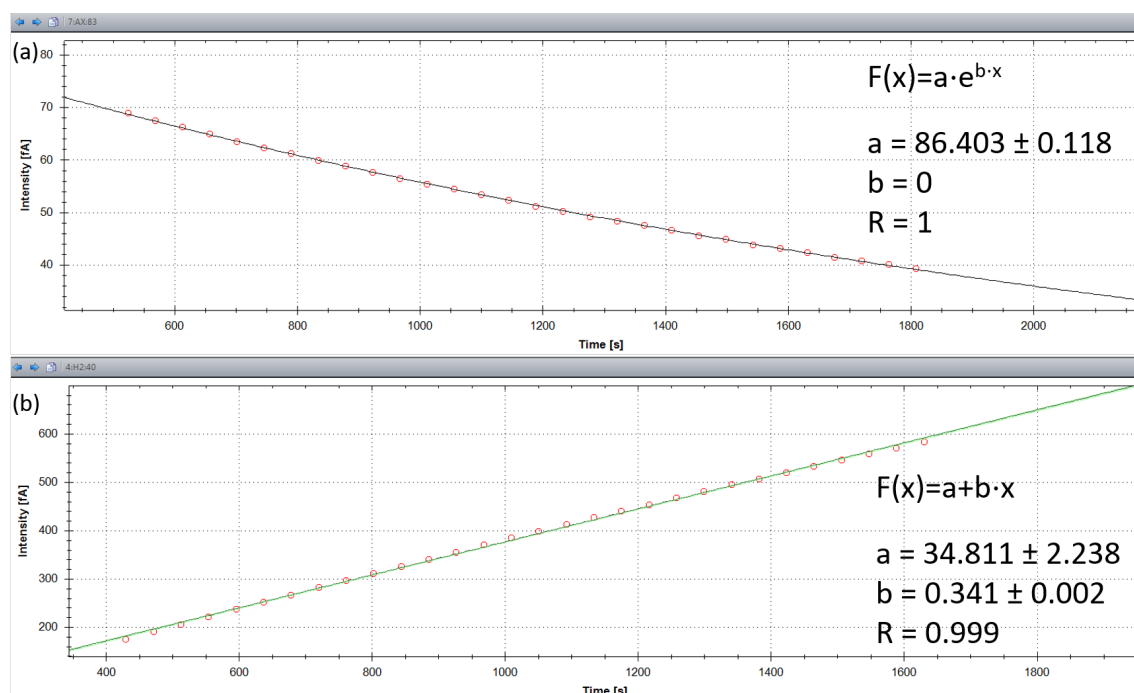
### **A.2.5 Noble Gas Mass Spectrometers**

Most noble gas spectrometers are operated in ‘static’ mode (Burnard et al., 2013). ‘Static’ mode describes the status when pumps are isolated during gas measurements. This method increases sensitivity and enables the measurements for gas species with low abundance. Both Helix SFT<sup>TM</sup> and Argus VI<sup>TM</sup> were operated in ‘static’ mode. Gas consumption by ionisation results in a decreasing signal size over time which is accounted for by extrapolating the signal back to the point in time when the gas is injected into the mass spectrometer, ‘time zero’ (Figure A.3a). For each run, we obtained 100 measurements for helium and 30 for the other gas species in order to extrapolate back to time zero. The settling time and integration time are set to 2000 ms and 4.19 s respectively.

‘Static’ mode also requires a low background in the mass spectrometer to avoid the accumulation of background levels once isolated from the pump (Figure A.3b). The Helix SFT<sup>TM</sup> and Argus VI<sup>TM</sup> mass spectrometers are pumped to a pressure of  $<10^{-9}$  mbar by a Varian VacIon Plus 40 StarCell<sup>TM</sup> and a 20 StarCell<sup>TM</sup> ion pump, respectively. The ultra-high vacuum system is carefully maintained and was only exposed to air during infrequent maintenance procedures, including ion source filament and electron multiplier detector replacements that occur every few years. After any exposure to atmospheric pressure air, the entire mass spectrometer flight tube, ion source, and detector assembly are encased in removable ovens and baked thoroughly at temperatures ranging from 250-350°C for up to 12 hours while being evacuated on turbomolecular or ion pumps.

Helix SFT<sup>TM</sup> and Argus VI<sup>TM</sup> have internal volumes of approximately 1400 cm<sup>3</sup> and 700 cm<sup>3</sup> respectively. The Helix has two collectors, a Faraday cup for <sup>4</sup>He and a secondary electron multiplier (SEM) for <sup>3</sup>He. Collectors fitted to Argus VI<sup>TM</sup> are composed of 5 Faraday cups and a compact discrete dynode (CDD) ion counting multiplier. The detecting cups for both instruments are fixed and Argus VI<sup>TM</sup> has its cups placed to detect the five isotopes of argon (<sup>36</sup>Ar, <sup>37</sup>Ar, <sup>38</sup>Ar, <sup>39</sup>Ar and

## A.2. NOBLE GAS ANALYTICAL EQUIPMENT



**Figure A.3:** Examples demonstrating extrapolation of signals back to time zero. (a) Signal decay was fitted to an exponential function to determine its intensity at the time of sample inlet to the mass spectrometer, (b) while background peaks employed a linear fit to their rate of rising to correct for background signals at the time of samples inlet.

$^{40}\text{Ar}$ ). Magnetic field changes accordingly to measure peaks at different masses for other isotopes. The configuration of isotopes that were measured during each run is summarised in Table A.1.

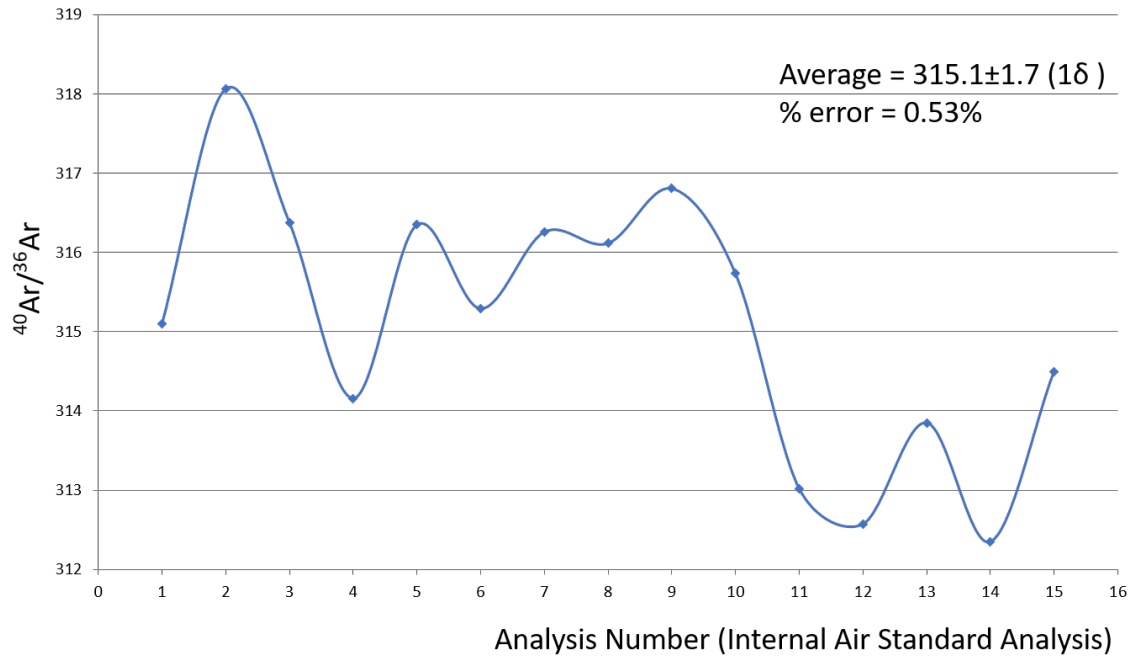
### Machine stability

Internal ‘running’ standards were fully automated protocols that run at least once every night. An aliquot from a separate air tank (air samples collected in the University Parks, Oxford, UK (297 K, 1.01 atm, 95% humidity) was used for each run following standardised and repeated procedure. Signals were monitored and recorded throughout the period of sample measurement. Standard deviations of the internal ‘running’ standards were propagated as systematic errors in calculations to account for internal machine drift. The  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of 15 measurements made during one of the sample-analysis-week are demonstrated in Figure A.3, showing a percentage error of 0.53% ( $1\sigma$ ) during the week. Such an analysis is done frequently to monitor the variations.

## A. Literature Review and Methodology Appendix

**Table A.1:** Configurations of isotopes for each mass spectrometry run. The cups in Argus are H2, H1, AX, L1, L2 and CDD from a small mass to a large mass.

| HELIX SFT <sup>TM</sup>      | Faraday cup | SEM       | Peak centring cup |           |           |            |     |
|------------------------------|-------------|-----------|-------------------|-----------|-----------|------------|-----|
| <i>Helium</i>                | 4           | 3         | Faraday cup       |           |           |            |     |
| <b>Argus VI<sup>TM</sup></b> | <b>H2</b>   | <b>H1</b> | <b>AX</b>         | <b>L1</b> | <b>L2</b> | <b>CDD</b> |     |
| <i>Neon</i>                  | 20          |           | 19.2              |           |           | H2         |     |
|                              |             |           | 22                |           |           | AX         |     |
|                              |             |           | 22.9              |           | 21        | CDD        |     |
|                              | 40          |           | 38                |           | 36        | H2         |     |
|                              |             |           | 44                |           |           | AX         |     |
| <i>Argon</i>                 |             | 40        | 39                | 38        | 37        | 36         | H1  |
|                              |             |           | 41.15             |           |           | 38         | CDD |
| <i>Krypton &amp; Xenon</i>   |             | 136       | 132               | 129       |           |            | AX  |
|                              |             |           | 137               | 134       | 130       |            | L1  |
|                              |             |           | 134.5             | 131       | 130       |            | L1  |
|                              |             |           | 136.3             |           |           | 126        | CDD |
|                              | 86          | 84        | 82                |           |           |            | H1  |
|                              |             |           | 85                |           | 80        | 78         | CDD |
|                              |             |           | 83                |           |           |            | AX  |



**Figure A.4:** An example showing the  $^{40}\text{Ar}/^{36}\text{Ar}$  variations of Internal Air Standard measurements made for one week. 15 measurements were made during the week and demonstrate a percentage error of 0.53% (1σ).

## A.2. NOBLE GAS ANALYTICAL EQUIPMENT

### Procedural blanks and Air standards

Blanks and air standards that followed the same protocol as sample measurements were run once per week. Signals from the blanks represented the background of the space from sample inlet to mass spectrometer and were deducted from sample signals, and air standards were used for sample calibration. The procedure air standards were run with air samples collected in the University Parks, Oxford, UK on 24<sup>th</sup> November, 2014 (297 K, 1.01 atm, 95% humidity). By continually recording the number of aliquots and measured results, it has shown that by the time of sample completion, no significant depletion or fractionation is observed.

Sample concentrations and ratios were calculated with the following equations derived from the ideal gas laws:

$$C = \frac{S_{sample} - S_{blank}}{S_{air} - S_{blank}} \times C_{air} \times \frac{P_{air}}{P_{sample}}, \quad (A.1)$$

where C,S and P represent concentration, signal and pressure respectively and the subscripts “sample”, “blank” and “air” refer to procedure runs for the sample, the blank and the air standard. The pressure refers to the final readings before expanding to the Titanium getter.

### Corrections and error propagation

The Argus IV<sup>TM</sup> does not have enough mass resolution to resolve the interference of  $^{40}\text{Ar}^{++}$  on  $^{20}\text{Ne}^+$  and  $\text{CO}_2^{++}$  on  $^{22}\text{Ne}^+$ . Therefore  $^{40}\text{Ar}^{++}$  and  $\text{CO}_2^{++}$  peaks were monitored during the neon analysis. The contribution of  $^{40}\text{Ar}^{++}$  to mass 20 are corrected followed the method described by Niedermann et al. (1993). The  $\text{CO}_2^{++}$  signal was indistinguishable from the procedural blanks, and therefore no  $\text{CO}_2^{++}$  corrections were applied to  $^{22}\text{Ne}^+$ .

The uncertainty involved in the experimental analysis considered systematic errors from the ‘overnight’ standards, pressure readings and the errors involved in signal



### A. Literature Review and Methodology Appendix

extrapolation to the inlet “time zero”. The errors were propagated with the following propagation laws.

If

$$Q = a + b + \cdots + c$$

then

$$\sigma Q = \sqrt{\sigma a^2 + \sigma b^2 + \cdots + \sigma c^2}, \quad (\text{A.2})$$

where Q is the sum of variables a, b and c, which can be positive or negative, and  $\sigma$  represents the corresponding errors related to the variables. For example, error related to  $(S_{sample} - S_{blank})$  can be calculated as

$$\sigma (S_{sample} - S_{blank}) = \sqrt{(\sigma S_{sample})^2 + (\sigma S_{blank})^2}. \quad (\text{A.3})$$

Alternatively, if multiplication or division is involved, i.e.

$$Q = ab \cdots c$$

then

$$\frac{\sigma Q}{|Q|} = \sqrt{\left(\frac{\sigma a}{a}\right)^2 + \left(\frac{\sigma b}{b}\right)^2 + \cdots + \left(\frac{\sigma c}{c}\right)^2}. \quad (\text{A.4})$$

For example, error related to  $\left(\frac{P_{air}}{P_{sample}}\right)$  can be calculated as

$$\sigma \left(\frac{P_{air}}{P_{sample}}\right) = \left(\frac{P_{air}}{P_{sample}}\right) \times \sqrt{\left(\frac{\sigma P_{air}}{P_{air}}\right)^2 + \left(\frac{\sigma P_{sample}}{P_{sample}}\right)^2}. \quad (\text{A.5})$$



# B

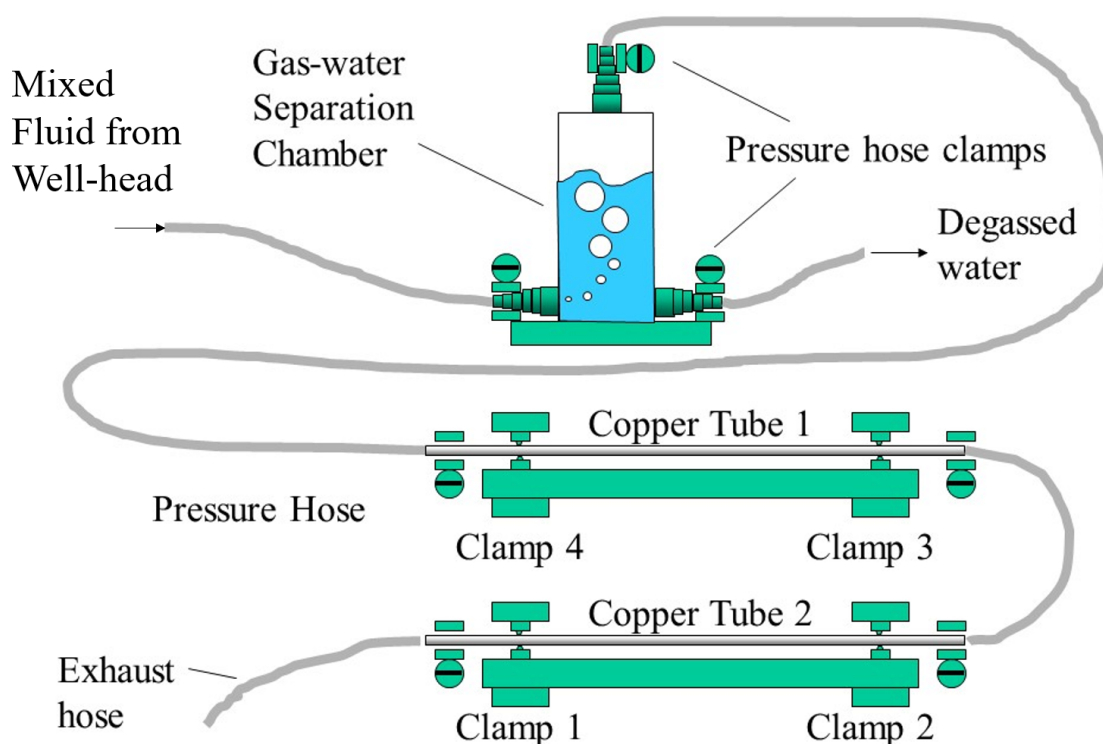
## Williston Basin Appendix

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## B.1. Gas Extraction from a Gas-fluid Mixture



**Figure B.1:** A graphic illustration of the gas-water separation apparatus used for gas extraction from the Mannville gas-water mixtures.

## B.10 Presenting Models onto One Graph . . . . . 257

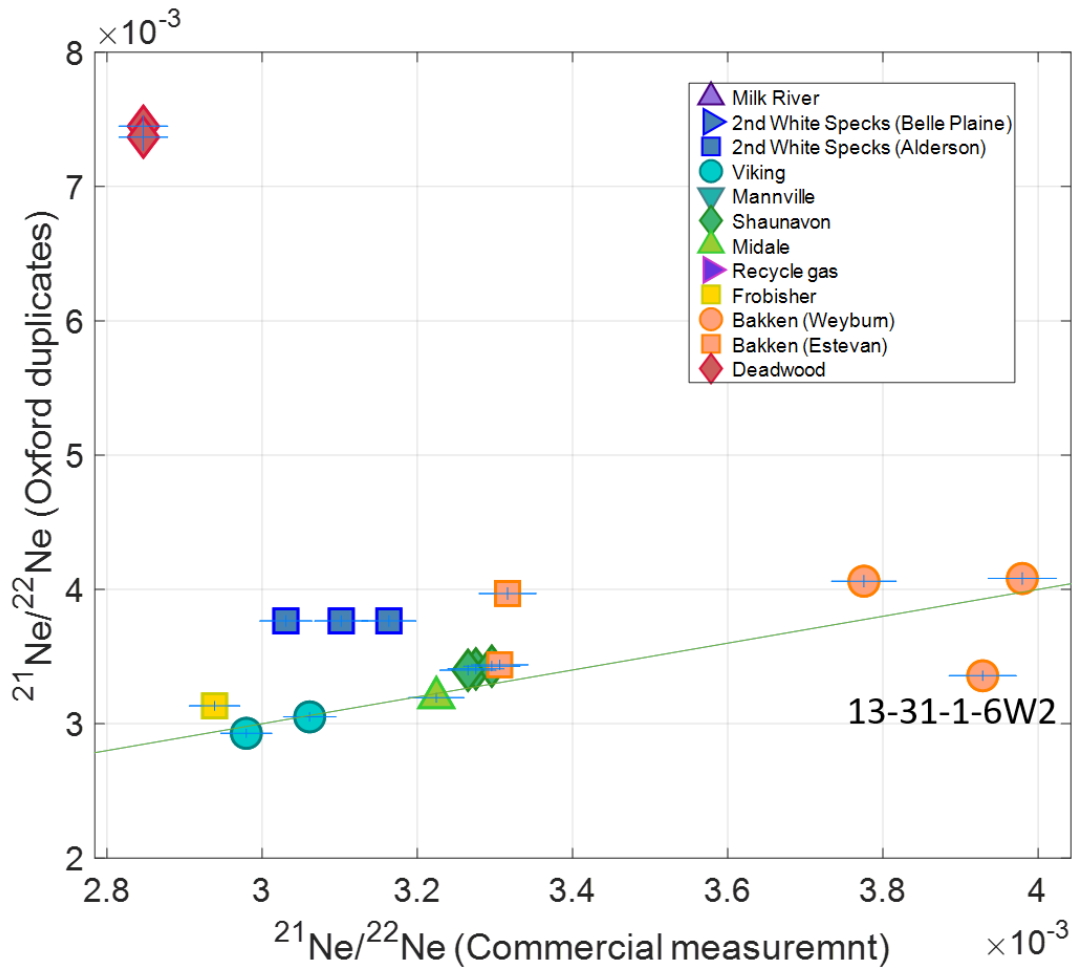
### B.1 Gas Extraction from a Gas-fluid Mixture

Gas sampling for the Mannville formation required a pre-processing step for gas extraction. A custom-designed phase-separation vessel is used (Figure B.1). The gas-fluid mixture from the well head was fed into the base of a portable gas-water separator. The separated gas phase was connected to the copper tube sample vessels from the upper separator port. The copper tubes were flushed with the separated gas to remove any residual air and sealed using clamps which achieve a helium leak-tight cold weld.

## **B.2 Data Selection**

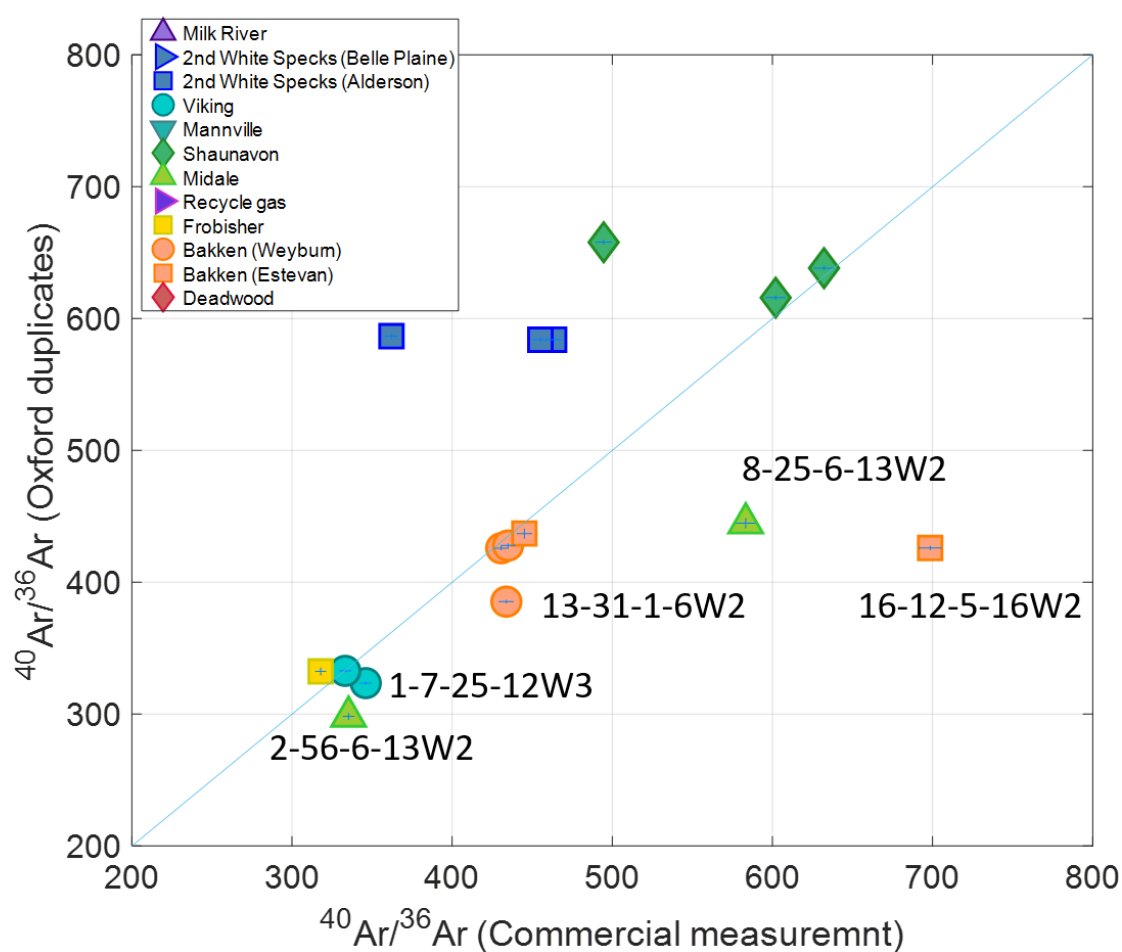
Gas samples collected were originally analysed by a commercial company. The current project re-determined the noble gas abundance and isotopic composition of any remaining duplicates in the noble gas lab at the University of Oxford. Measurements made in the Oxford laboratory gave similar but often higher  $^{21}\text{Ne}/^{22}\text{Ne}$ , apart from sample 13-31-1-6W2 (Figure B.2).  $^{40}\text{Ar}/^{36}\text{Ar}$  values, similarly, were often higher than the commercial analysis (Figure B.3). Therefore, to eliminate potential contamination through sample handling (e.g. collection, storage and measurement), when samples are measured both commercially and internally, samples with both higher  $^{21}\text{Ne}/^{22}\text{Ne}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios are selected, which indicates with the lowest contribution to the sample from the air and, as these are duplicates, a contaminant through sample handling or storage. The Oxford samples that have similar  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios compared to the commercial measurements are also chosen, since these samples demonstrate higher  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios.

Most Oxford measurements have ratios higher than or similar to the commercial ones (Figure B.2 and B.3), and for these samples, Oxford measurements are selected. Due to their higher  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios, commercial samples for the Viking well 1-7-25-12W3, the Midale wells 2-25-6-13W2 and 8-25-6-13W2 and the Bakken wells 13-31-1-6W2 are chosen. Though the commercial sample 16-12-5-16W2 has a higher  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio, it also shows higher  $^{36}\text{Ar}$  and  $^{20}\text{Ne}$  concentrations, which are usually related to air contamination. For these samples only, the Oxford measurement is selected. All measured data are shown in Table B.2. The unshaded sample data are the ones chosen for the analysis in this paper and are presented in Table tab:Willston He Ne Ar. Kr and Xe data are only measured in Oxford; therefore, they are only reported if Oxford duplicate is selected (Table 4.3).



**Figure B.2:** Comparing  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios between duplicates for data selection. Most measurements made in the Oxford laboratory gave similar but often higher  $^{21}\text{Ne}/^{22}\text{Ne}$  value, indicating stronger crustal component.

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**Figure B.3:** Comparing  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios between duplicates for data selection. Most measurements made in the Oxford laboratory gave similar but often higher  $^{40}\text{Ar}/^{36}\text{Ar}$  value, and for these samples, Oxford measurements are selected. Commercial samples for the Viking well 1-7-25-12W3, the Midale wells 2-25-6-13W2 and 8-25-6-13W2 and the Bakken wells 13-31-1-6W2 are chosen. For sample 16-12-5-16W2, Oxford data are selected due to the higher  $^{36}\text{Ar}$  and  $^{20}\text{Ne}$  concentrations, which are usually related to air contamination, even though the commercial duplicate demonstrates higher  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio.

**Table B.1:** Complete sample data, including those measured by the commercial laboratory (sample names start with letter ‘O’), and those measured at the University of Oxford (sample names begin with letter ‘N’). The shaded samples are the ones not been selected.

| Sample name                            | $^4\text{He} \times 10^{-5}$<br>cm <sup>3</sup> STP/cm <sup>3</sup> | $^{20}\text{Ne} \times 10^{-8}$<br>cm <sup>3</sup> STP/cm <sup>3</sup> | $^{40}\text{Ar} \times 10^{-8}$<br>cm <sup>3</sup> STP/cm <sup>3</sup> | R/R <sub>a</sub><br>(air corrected) | $^{20}\text{Ne}/^{22}\text{Ne}$ | $^{21}\text{Ne}/^{22}\text{Ne}$ | $^{40}\text{Ar}/^3/6\text{Ar}$ |
|----------------------------------------|---------------------------------------------------------------------|------------------------------------------------------------------------|------------------------------------------------------------------------|-------------------------------------|---------------------------------|---------------------------------|--------------------------------|
| <b>Milk River</b>                      |                                                                     |                                                                        |                                                                        |                                     |                                 |                                 |                                |
| O14-8-3-27W3                           | 96.2±2.89                                                           | 2.7±0.17                                                               | 214.0±6.42                                                             | 0.15±0.015                          | 9.75±0.044                      | 0.0304±0.00033                  | 388.3±3.88                     |
| <b>2nd White Specks (Belle Plaine)</b> |                                                                     |                                                                        |                                                                        |                                     |                                 |                                 |                                |
| O11-9-17-23W2                          | 14.5±0.43                                                           | 46.6±2.83                                                              | 3570.0±107.10                                                          | 0.08±0.008                          | 9.80±0.044                      | 0.0289±0.00032                  | 319.6±3.20                     |
| <b>2nd White Specks (Alderson)</b>     |                                                                     |                                                                        |                                                                        |                                     |                                 |                                 |                                |
| O8-31-15-14W4                          | 130.0±3.90                                                          | 3.4±0.20                                                               | 419.0±12.57                                                            | 0.11±0.011                          | 9.83±0.044                      | 0.0310±0.00034                  | 362.1±3.62                     |
| N8-31-15-14W4                          | 190.0±2.15                                                          | 8.8±0.80                                                               | 149.0±13.70                                                            | 0.16±0.022                          | 9.71±0.079                      | 0.0369±0.00038                  | 586.6±1.38                     |
| O5-31-15-14W4                          | 160.0±4.80                                                          | 3.9±0.24                                                               | 313.0±9.39                                                             | 0.10±0.010                          | 9.71±0.044                      | 0.0304±0.00033                  | 463.7±4.64                     |
| N5-31-15-14W4                          | 200.0±2.22                                                          | 9.0±0.82                                                               | 153.0±14.00                                                            | 0.16±0.022                          | 9.69±0.079                      | 0.0369±0.00038                  | 584.0±1.44                     |
| O14-31-15-14W4                         | 173.0±5.19                                                          | 9.5±0.58                                                               | 393.0±11.79                                                            | 0.15±0.015                          | 9.79±0.044                      | 0.0297±0.00033                  | 455.1±4.55                     |
| N14-31-15-14W4                         | 170.0±1.90                                                          | 8.9±0.81                                                               | 150.0±13.70                                                            | 0.15±0.020                          | 9.69±0.079                      | 0.0369±0.00038                  | 584.0±1.44                     |
| <b>Viking</b>                          |                                                                     |                                                                        |                                                                        |                                     |                                 |                                 |                                |
| O1-7-25-12W3                           | 26.6±0.80                                                           | 13.2±0.80                                                              | 376.0±11.28                                                            | 0.28±0.028                          | 9.70±0.044                      | 0.0292±0.00032                  | 346.0±3.46                     |
| N1-7-25-12W3                           | 22.5±0.25                                                           | 109.0±9.93                                                             | 789.0±72.10                                                            | 0.30±0.042                          | 9.81±0.080                      | 0.0287±0.00030                  | 323.6±0.67                     |
| O7A-1-32-24-12W3                       | 10.8±0.32                                                           | 6.3±0.38                                                               | 380.0±11.40                                                            | 0.27±0.027                          | 9.80±0.044                      | 0.0300±0.00033                  | 333.2±3.33                     |
| N7A-1-32-24-12W3                       | 10.2±0.12                                                           | 25.4±2.33                                                              | 407.0±37.20                                                            | 0.30±0.042                          | 9.76±0.080                      | 0.0299±0.00031                  | 332.9±0.69                     |
| O16-30-23-12W3                         | 31.9±0.96                                                           | 13.4±0.82                                                              | 411.0±12.33                                                            | 0.27±0.026                          | 9.88±0.044                      | 0.0294±0.00032                  | 367.0±3.67                     |
| <b>Mannville</b>                       |                                                                     |                                                                        |                                                                        |                                     |                                 |                                 |                                |
| O5-16-6-13W2(#6) b                     | 2050.0±61.50                                                        | 207.6±12.59                                                            | 7600.0±228.00                                                          | 0.27±0.026                          | 9.70±0.044                      | 0.0300±0.00033                  | 407.0±4.07                     |
| O5-16-6-13W2(#8) c                     | 2020.0±60.60                                                        | 273.3±16.58                                                            | 7490.0±224.70                                                          | 0.26±0.025                          | 9.59±0.043                      | 0.0298±0.00033                  | 397.1±3.97                     |
| O16-28-5-13W2 d                        | 1610.0±48.30                                                        | 1574.6±95.54                                                           | 9870.0±296.10                                                          | 0.16±0.016                          | 9.72±0.044                      | 0.0292±0.00032                  | 317.8±3.18                     |
| O5-16-6-13W2(#3) e                     | 1610.0±48.30                                                        | 583.9±35.42                                                            | 7860.0±235.80                                                          | 0.19±0.018                          | 9.78±0.044                      | 0.0299±0.00033                  | 381.3±3.81                     |
| O5-16-6-13W2(#6) f                     | 2020.0±60.60                                                        | 198.4±12.04                                                            | 8140.0±244.20                                                          | 0.20±0.019                          | 9.92±0.045                      | 0.0298±0.00033                  | 391.9±3.92                     |
| O5-16-6-13W2(#8) g                     | 2840.0±85.20                                                        | 196.4±11.91                                                            | 7980.0±239.40                                                          | 0.22±0.021                          | 9.77±0.044                      | 0.0297±0.00033                  | 387.8±3.88                     |
| O16-28-5-13W2 h                        | 2020.0±60.60                                                        | 1391.7±84.43                                                           | 14700.0±441.00                                                         | 0.19±0.019                          | 9.87±0.044                      | 0.0286±0.00031                  | 348.3±3.48                     |
| <b>Shanavon</b>                        |                                                                     |                                                                        |                                                                        |                                     |                                 |                                 |                                |
| O15-10-7-19W3                          | 39.3±1.18                                                           | 3.0±0.18                                                               | 232.0±6.96                                                             | 0.20±0.019                          | 9.63±0.043                      | 0.0321±0.00035                  | 494.6±4.95                     |
| N15-10-7-19W3                          | 38.0±0.42                                                           | 6.4±0.58                                                               | 246.0±22.50                                                            | 0.21±0.029                          | 9.73±0.079                      | 0.0334±0.00035                  | 657.9±1.36                     |
| O4C-15-9-6-19W3                        | 45.2±1.36                                                           | 4.0±0.24                                                               | 210.0±6.30                                                             | 0.21±0.020                          | 9.69±0.044                      | 0.0323±0.00036                  | 602.0±6.02                     |
| N4C-15-9-6-19W3                        | 43.3±0.49                                                           | 6.3±0.57                                                               | 210.0±19.20                                                            | 0.20±0.028                          | 9.75±0.080                      | 0.0336±0.00035                  | 615.9±1.28                     |
| O2B-3-28-6-19W3                        | 52.0±1.56                                                           | 3.2±0.19                                                               | 232.0±6.96                                                             | 0.18±0.018                          | 9.64±0.043                      | 0.0320±0.00035                  | 632.2±6.32                     |
| N2B-3-28-6-19W3                        | 54.8±0.61                                                           | 8.0±0.73                                                               | 247.0±22.60                                                            | 0.20±0.028                          | 9.77±0.080                      | 0.0333±0.00034                  | 638.3±1.32                     |
| <b>Midale</b>                          |                                                                     |                                                                        |                                                                        |                                     |                                 |                                 |                                |
| O8-25-6-13W2                           | 2.8±0.09                                                            | 0.5±0.03                                                               | 9.9±0.30                                                               | 0.21±0.021                          | 9.87±0.044                      | 0.0316±0.00035                  | 583.3±5.83                     |
| N8-25-6-13W2                           | 2.4±0.02                                                            | 1.3±0.09                                                               | 16.7±1.15                                                              | 0.22±0.024                          | 9.97±0.081                      | 0.0313±0.00033                  | 444.8±3.51                     |
| O2-25-6-13W2                           | 22.6±0.68                                                           | 229.4±13.92                                                            | 1410.0±42.30                                                           | 0.16±0.016                          | 9.68±0.044                      | 0.0292±0.00032                  | 335.3±3.35                     |
| N2-25-6-13W2                           | 29.8±0.32                                                           | 256.0±17.70                                                            | 1400.0±100.00                                                          | 0.24±0.026                          | 9.78±0.080                      | NaN±NaN                         | 298.3±2.35                     |
| <b>O-Recycled gas</b>                  |                                                                     |                                                                        |                                                                        |                                     |                                 |                                 |                                |
| Probisher                              | 2.7±0.08                                                            | 159.1±9.65                                                             | 36.8±1.10                                                              | 0.16±0.016                          | 9.70±0.044                      | 0.0303±0.00033                  | 394.9±3.95                     |
| O2-32-5-13W2                           | 32.6±0.98                                                           | 167.3±10.15                                                            | 851.0±25.53                                                            | 0.17±0.016                          | 9.96±0.045                      | 0.0288±0.00032                  | 317.9±3.18                     |

Continued on next page



B. Williston Basin Appendix

Table B.1 – Continued from previous page

| Sample name             | $^4\text{He} \times 10^{-5}$<br>$\text{cm}^3 \text{ STP/cm}^3$ | $^{20}\text{Ne} \times 10^{-8}$<br>$\text{cm}^3 \text{ STP/cm}^3$ | $^{40}\text{Ar} \times 10^{-8}$<br>$\text{cm}^3 \text{ STP/cm}^3$ | R/R <sub>a</sub><br>(air corrected) | $^{20}\text{Ne}/^{22}\text{Ne}$ | $^{21}\text{Ne}/^{22}\text{Ne}$ | $^{40}\text{Ar}/^3/6\text{Ar}$ |
|-------------------------|----------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------|---------------------------------|---------------------------------|--------------------------------|
| N2-32-5-13W2            | 30.3±0.34                                                      | 23.0±1.59                                                         | 212.0±14.60                                                       | 0.15±0.017                          | 9.80±0.080                      | 0.0307±0.00032                  | 332.4±2.62                     |
| <b>Bakken (Weyburn)</b> |                                                                |                                                                   |                                                                   |                                     |                                 |                                 |                                |
| O13-31-1-6W2            | 59.1±1.77                                                      | 0.8±0.05                                                          | 75.9±2.28                                                         | 0.01±0.001                          | 9.61±0.043                      | 0.0385±0.00042                  | 433.8±4.34                     |
| N13-31-1-6W2            | 58.4±1.00                                                      | 8.1±0.68                                                          | 116.0±9.67                                                        | 0.01±0.001                          | 9.73±0.079                      | 0.0329±0.00034                  | 385.4±1.04                     |
| O11-31-1-6W2            | 36.0±1.08                                                      | 0.9±0.06                                                          | 60.5±1.81                                                         | 0.01±0.001                          | 9.73±0.044                      | 0.0370±0.00041                  | 430.6±4.31                     |
| N11-31-1-6W2            | 38.2±0.66                                                      | 1.6±0.13                                                          | 72.5±6.03                                                         | 0.01±0.001                          | 9.66±0.079                      | 0.0398±0.00042                  | 425.9±1.15                     |
| O4-6-2-6W2              | 26.1±0.78                                                      | 0.7±0.04                                                          | 47.7±1.43                                                         | 0.01±0.001                          | 9.65±0.043                      | 0.0390±0.00043                  | 434.9±4.35                     |
| N4-6-2-6W2              | 28.8±0.49                                                      | 1.2±0.10                                                          | 61.9±5.15                                                         | 0.01±0.001                          | 9.65±0.079                      | 0.0400±0.00042                  | 427.9±1.15                     |
| <b>Bakken (Estevan)</b> |                                                                |                                                                   |                                                                   |                                     |                                 |                                 |                                |
| O13-24-5-16W2           | 146.0±4.38                                                     | 7.4±0.45                                                          | 156.0±4.68                                                        | 0.16±0.016                          | 9.90±0.045                      | 0.0324±0.00036                  | 445.1±4.45                     |
| N13-24-5-16W2           | 110.0±1.74                                                     | 11.7±0.82                                                         | 123.0±8.60                                                        | 0.17±0.019                          | 9.79±0.080                      | 0.0337±0.00035                  | 437.0±3.45                     |
| O1-21-5-16W2            | 299.0±8.97                                                     | 21.4±1.30                                                         | 814.0±24.42                                                       | 0.28±0.027                          | 9.69±0.044                      | 0.0317±0.00035                  | 304.6±3.05                     |
| O16-12-5-16W2           | 353.0±10.59                                                    | 15.5±0.94                                                         | 8900.0±267.00                                                     | 0.36±0.035                          | 9.86±0.044                      | 0.0325±0.00036                  | 698.5±6.99                     |
| N16-12-5-16W2           | 70.9±1.15                                                      | 3.6±0.33                                                          | 126.0±11.60                                                       | 0.11±0.016                          | 9.67±0.079                      | 0.0389±0.00041                  | 426.0±1.35                     |
| <b>Deadwood</b>         |                                                                |                                                                   |                                                                   |                                     |                                 |                                 |                                |
| O10-3-5-8W3             | 980.0±29.40                                                    | 359.7±21.83                                                       | 4860.0±145.80                                                     | 0.20±0.020                          | 9.91±0.045                      | 0.0279±0.00031                  | 303.4±3.03                     |
| N10-3-5-8W3             | 1390.0±94.00                                                   | 11.6±0.88                                                         | 2300.0±175.00                                                     | 0.15±0.026                          | 9.73±0.079                      | 0.0722±0.00094                  | 7580.0±54.91                   |
| O12-10-5-8W3            | 918.0±27.54                                                    | 288.1±17.48                                                       | 5030.0±150.90                                                     | 0.15±0.015                          | 9.80±0.044                      | 0.0289±0.00032                  | 364.6±3.65                     |

### **B.3 Porosity Estimation**

#### **B.3.1 Deadwood Basal Aquifer and Upper Aquitard**

Curtis (2013) report from rock samples collected from the Cambrian-Ordovician system on the US side of the Williston Basin that porosity varies between 0.02 to 0.21, with a mean of 0.08. The values are comparable to estimations calculated from horizontal permeability (0.073 and 0.09 for Deadwood and Winnipeg, respectively) (Curtis, 2013). The porosity of Deadwood aquifer reported by IHS Accumap (2018) is  $0.13 \pm 0.06$  and is within the uncertainty of the former reported range. The IHS Accumap (2018)'s value of 0.13 is applied for the Deadwood aquifers. A porosity of 0.05 is assigned to the tighter Deadwood aquitard. The effective porosities are considered to be the same as their total porosities for these two units in the model.

#### **B.3.2 Ordovician, Silurian aquifer**

The oldest and youngest formations of the Ordovician and Silurian hydrogeological unit are the Red River and Interlake, respectively. These two dolomitic limestone units both exhibit a range of porosity values MacCary, 1984. An average of 0.09 is recorded by IHS Accumap (2018) and is assigned as the total and effective porosity.

#### **B.3.3 Devonian**

The Devonian units have multiple layers of aquitards and aquifers. The dominant lithology is dolomite and limestone. Three of the units give an average of 0.1 (IHS Accumap, 2018). All the Devonian units (except Bakken) are therefore grouped together and total and effective porosities are assigned as 0.1.

## *B. Williston Basin Appendix*

### **B.3.4 Bakken**

Porosity values measured from the middle member of the Bakken formation vary between 0.01 to 0.16, with an average of 0.05 (Pitman et al., 2001). A higher average of 0.2 is reported by IHS Accumap (2018). Unlike the middle Bakken sandstone unit, the upper and lower Bakken shale units are expected to have low permeability. In the model, all Bakken layers are grouped as a single unit, and the lower porosity average of 0.05 is assigned (both total and effective).

### **B.3.5 Mississippian Aquifer**

These carbonate deposits experience different degrees of dolomitization and are heterogeneous in all dimensions. Lake and Whittaker (2005) report porosities which range from 0.02 to 0.15 for the lower Midale and 0.27 for the upper Midale in Saskatchewan. The Mission Canyon Formation in Glenburn oil field on the southeast edge of the basin has an average porosity of 0.17 (Gerhard, 1985). Three core samples from Montana and Wyoming show an average porosity of 0.08 for the Madison Group (Thayer, 1983). Three units from Mississippian recorded by IHS Accumap (2018) have average values of 0.1. Hendry et al. (2013) modelled  $\delta^{18}\text{O}$  diffusion in these systems using a value of 0.1. The value of 0.1 is used for both the total and effective porosities.

### **B.3.6 Watrous Aquitard**

The total porosity is assigned as 0.13 based on that reported by IHS Accumap (2018), and a value of 0.1 as effective porosity to take into account poor connectivity between pore space when comparing with aquifer units. 0.1 was chosen to match the porosity estimations of Mississippian carbonates.

#### **B.3.7 Shaunavon Aquifer**

A value of 0.15 (IHS Accumap, 2018) is assigned in the model as the total and effective porosities in the model.

#### **B.3.8 Mannville aquifer**

Samples from Southeastern Alberta have an average porosity of 0.208 (n=6) (Kavanagh, 1981). Hendry et al. (2013) reported an average of 0.278 (n=18). These samples give an overall average of 0.26 and agree with the average of 0.25 obtained from a much larger dataset reported by IHS Accumap (2018). 0.25 is therefore used in calculations as the total and effective porosity.

#### **B.3.9 Viking aquifer**

The value 0.23 from IHS Accumap (2018) is used as total and effective porosities.

#### **B.3.10 Colorado group shale**

10 Samples collected from gas wells have porosities ranging from 0.14 to 0.22, with an average of 0.17 (Allen, 2014). Total porosity was reported as 0.33 (n=37) by Hendry et al. (2013). An average of 0.4 recorded by IHS Accumap (2018) is used for total porosity. The pore connectivity for shale units are expected to be ineffective, and therefore, for effective porosity, 0.1 is chosen to take into account the effect of poor pore connectivity in shale layers.

#### **B.3.11 Other systems**

The Rierdon aquitard is assumed to have a similar total porosity as the Shaunavon aquifers, but with effective porosities as 0.1. Belly River is considered to have the same total and effective porosities as the Viking aquifer. For the sediments

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**Table B.2:** Porosity information for different formations (IHS Accumap, 2018).

| Period        | Formation  | No. of samples | Porosity |            |
|---------------|------------|----------------|----------|------------|
| Cretaceous    | Milk River | 1295           | 0.19     | $\pm 0.04$ |
|               | Colorado   | 217            | 0.19     | $\pm 0.06$ |
|               | Mannville  | 15055          | 0.25     | $\pm 0.07$ |
|               | Viking     | 8489           | 0.23     | $\pm 0.05$ |
|               | Shaunavon  | 34264          | 0.15     | $\pm 0.07$ |
|               | Watrous    | 101            | 0.13     | $\pm 0.05$ |
| Mississippian | Midale     | 151754         | 0.14     | $\pm 0.08$ |
|               | Alida Bed  | 44465          | 0.13     | $\pm 0.06$ |
|               | Frobisher  | 112713         | 0.11     | $\pm 0.06$ |
| Devonian      | Bakken     | 19393          | 0.2      | $\pm 0.10$ |
|               | Birdbear   | 6041           | 0.12     | $\pm 0.07$ |
|               | Duperow    | 1192           | 0.11     | $\pm 0.07$ |
|               | Dawson     | 393            | 0.08     | $\pm 0.07$ |
| Ordovician    | Yeoman     | 9040           | 0.09     | $\pm 0.05$ |
|               | Winnipeg   | 8298           | 0.09     | $\pm 0.05$ |
| Cambrian      | Deadwood   | 981            | 0.13     | $\pm 0.06$ |

overlying Belly River, total and effective porosities are assumed to be 0.1, the same as the Colorado Groups.

### B.4 Calculating and Correcting for the Air Component

The proportion of air mixed with the pristine sample is calculated for a first-order equilibrium system and a second-order open system (Barry et al., 2016). For the first order equilibrium systems, the concentration of  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$  (in STP) degassed with a constant gas to water ratio of  $V_g/V_l$  at reservoir temperature  $T$  and pressure  $P$  can be expressed as

$$[^{20}\text{Ne}]_{gas} = [^{20}\text{Ne}]_{ASW} \frac{1}{\frac{1}{K_{Ne}^d} + \frac{V_g}{V_l}} \frac{T}{273.15P} \quad (\text{B.1})$$

where  $K_{Ne}^d$  represents the dimensionless Henry's constant calculated at reservoir temperature and salinity (Ballentine et al., 2002).  $^{20}\text{Ne}$  with subscripts air, ASW, gas and mixture represent the concentration in air, groundwater, exsolved gas and air-gas mixture respectively. Detailed derivation is summarised in Chapter 6.

And the final mixture can be calculated assuming it is composed of  $m$  exsolved

### B.5. Air Entrapment Analysis

gas and (1-m) air, where

$$\left[^{20}\text{Ne}\right]_{mixture} = m \left[^{20}\text{Ne}\right]_{gas} + (1 - m) \left[^{20}\text{Ne}\right]_{air} \quad (\text{B.2})$$

The concentration of  $^{36}\text{Ar}$  can be modelled in a similar way. By assuming the sample is the final mixture of gas, the solutions of  $V_g/V_l$  and  $m$  are obtained using the concentrations of  $^{20}\text{Ne}$  and  $^{36}\text{Ar}$ , i.e.

$$\left[^{20}\text{Ne}\right]_{sample} = m \left[^{20}\text{Ne}\right]_{ASW} \frac{1}{\frac{1}{K_{Ne}^d} + \frac{V_g}{V_l}} \frac{T}{273.15P} + (1 - m) \left[^{20}\text{Ne}\right]_{air} \quad (\text{B.3})$$

and

$$\left[^{36}\text{Ar}\right]_{sample} = m \left[^{36}\text{Ar}\right]_{ASW} \frac{1}{\frac{1}{K_{Ar}^d} + \frac{V_g}{V_l}} \frac{T}{273.15P} + (1 - m) \left[^{36}\text{Ar}\right]_{air} \quad (\text{B.4})$$

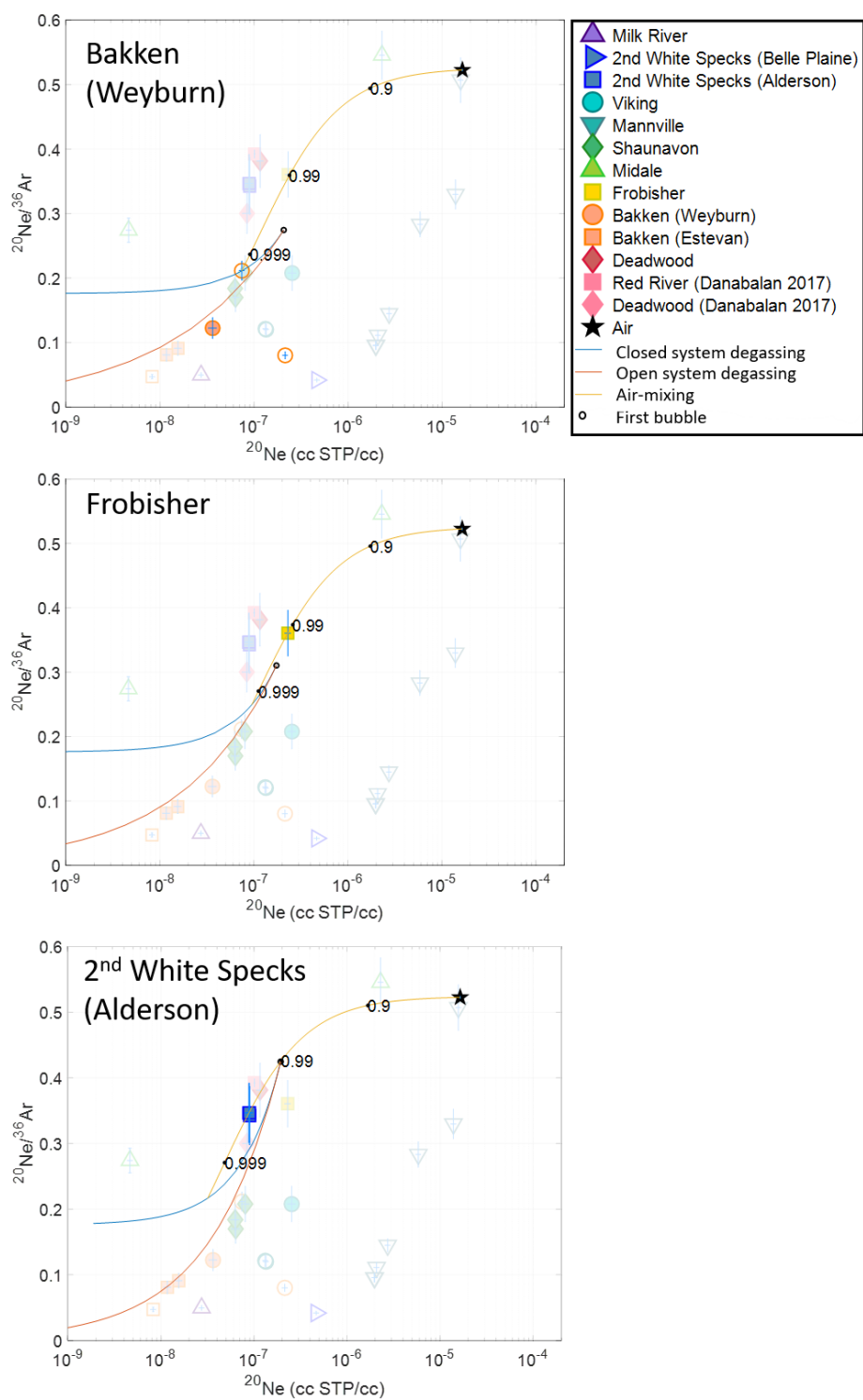
Subscript sample represents the measurement obtained from the samples. With solved  $V_g/V_l$  or  $m$ ,  $\left[^{20}\text{Ne}\right]_{gas}$  can be easily calculated either from air-saturated water or from the measurement of the samples. The correction can be done in a similar way to an open system but with different degassing equations.

### B.5 Air Entrapment Analysis

Degassing models are constructed for hydrogeological units that are not flooded, built with the local pressure, temperature and salinity estimates to derive the mixing trajectories in  $^{20}\text{Ne}/^{36}\text{Ar}$  and  $^{20}\text{Ne}$  space. Figure B.4 demonstrates the degassing models at reservoir conditions for the Bakken (Weyburn), Frobisher, 2nd White Specks (Alderson) samples. Figure B.5 shows the degassing models at reservoir conditions Viking, 2nd White Specks (Belle Plaine) and Milk River samples. Though Mannville formation is heavily flooded, it is plotted in Figure B.5 to illustrate the effect of degassing pressure.

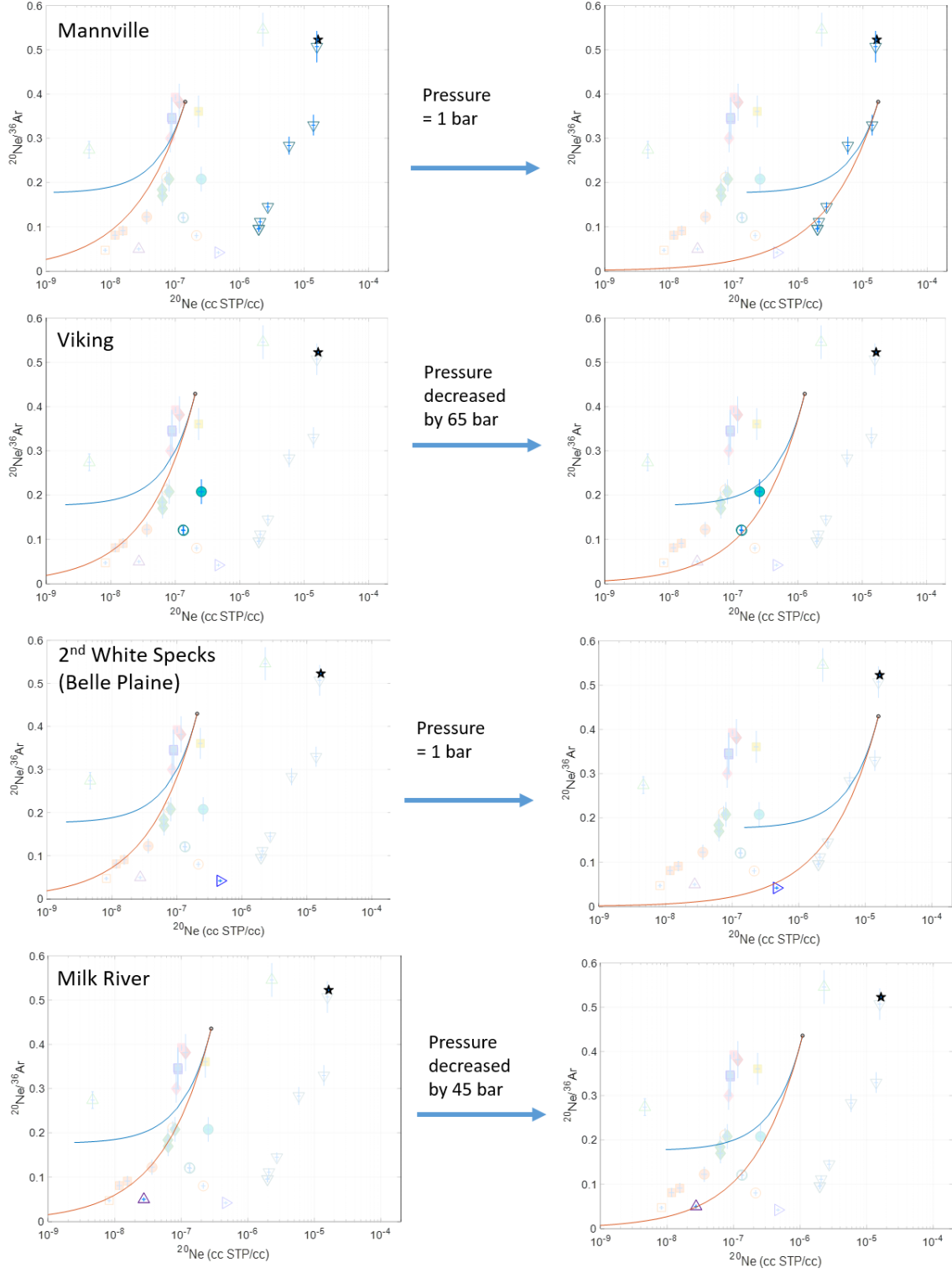
Two of the three Bakken (Weyburn) samples are below the degassing lines, suggesting the estimated degassing condition may be inaccurate. Neither a high temperature

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**Figure B.4:** Modelled  $^{20}\text{Ne}$  and  $^{20}\text{Ne}/^{36}\text{Ar}$  for the close and open degassing system for the Bakken Weyburn, Frobisher and 2nd White Specks (Alderson) reservoir conditions. The numbers on the air-mixing line represent the proportion of exsolved gas in the mixtures. These samples can be corrected to a closed system.

### B.5. Air Entrapment Analysis



**Figure B.5:** Modelled  $^{20}\text{Ne}$  and  $^{20}\text{Ne}/^{36}\text{Ar}$  for the close and open degassing system for the Mannville, Viking, 2nd White Specks (Belle plaine) and Milk River reservoir conditions. The right panel demonstrates the new degassing models with decreases in degassing pressure.



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**Table B.3:** calculated  $V_g/V_l$ ,  $m$  and  $r$  values for closed and open systems.

| Sample                      | Air Mixing    |       |              |       |
|-----------------------------|---------------|-------|--------------|-------|
|                             | Closed system |       | Open System  |       |
|                             | $V_g/V_l$     | $m$   | $V_g/V_l$    | $m$   |
| 2nd White Specks (Alderson) |               |       |              |       |
| 8-31-15-14W4                | 0.05          | 0.997 | 0.037        | 0.995 |
| 5-31-15-14W4                | 0.044         | 0.997 | 0.035        | 0.995 |
| 14-31-15-14W4               | 0.048         | 0.997 | 0.037        | 0.995 |
| Viking                      |               |       |              |       |
| 7A-1-32-24-12W3             |               |       |              |       |
| Shaunavon                   |               |       |              |       |
| 15-10-7-19W3                |               |       |              |       |
| 4C-15-9-6-19W3              |               |       |              |       |
| 2B-3-28-6-19W3              |               |       |              |       |
| Frobisher                   |               |       |              |       |
| 2-32-5-13W2                 |               |       |              |       |
| Bakken (Weyburn)            |               |       |              |       |
| 13-31-1-6W2 Duplicate       | 0.006         | 0.999 | 0.005        | 0.998 |
| 11-31-1-6W2                 |               |       |              |       |
| 4-6-2-6W2                   |               |       |              |       |
| Bakken (Estevan)            |               |       |              |       |
| 16-12-5-16W2                |               |       |              |       |
| Deadwood                    |               |       |              |       |
| 10-3-5-8W3                  | first bubble  | 0.997 | first bubble | 0.997 |

nor a high salinity can explain the outlier data (Figure B.4). The other sample can be explained by the degassing models if pressure is increased by over 90 bar, or temperature by more than 70 K, or salinity by over 50‰.

The Frobisher sample is an observation well for investigating the water/gas injection to the overlying Midale formation. The proportion of air mixing can be resolved. It is not possible to distinguish whether fitting to an original gas composition modelled with either an open or a closed system. Since the sample is close to the first bubble point, air corrections of the two degassing models are not significantly different.

Air component of 2nd White Specks (Alderson) can be resolved from the degassing lines (Figure B.5). The high  $^{21}\text{Ne}^*/^{40}\text{Ar}^*$  values suggest that a closed degassing system is more reasonable.

Viking samples lie below both the degassing lines (Figure B.5) suggesting an inaccurate estimation of degassing conditions. The degassing pressure needs to be reduced by at

*B.6. Closed System He Age Estimated from U and Th reported by Parker and Fleischer (1967)*

least 65 bar to enable the samples to be explained with the degassing models. 2nd White Specks (Belle Plaine) is plotted away from the degassing line but is close to the open system degassing line if the pressure of 1 bar (Figure B.5). Similarly, the Milk River sample may suggest a pressure decrease of 45 bar. Under-pressurization is not unexpected due to oil and gas production.

Mannville formation is a regional disposal layer. Though the formation water is heavily distorted by water flooding, the samples collected follows a degassing line at 1 bar (Figure B.5). This pressure is consistent with the gas stripping process (Rayleigh fractionation) using gas-liquid separation vessel carried out at ground level, confirming the reliability of degassing models providing reasonable temperature, pressure and salinity.

An alternative explanation to explain the mismatch between degassing models and observations is an inaccurate estimation of recharging water. The degassing models are constructed assuming the groundwater is recharged by 298 K seawater at 1 bar pressure. Noble gas content in groundwater is a function of recharging condition. The extreme scenario is to assume groundwater is originally 273 K freshwater. However, in most cases, the freshwater degassing lines are still incapable of explaining the sample data.

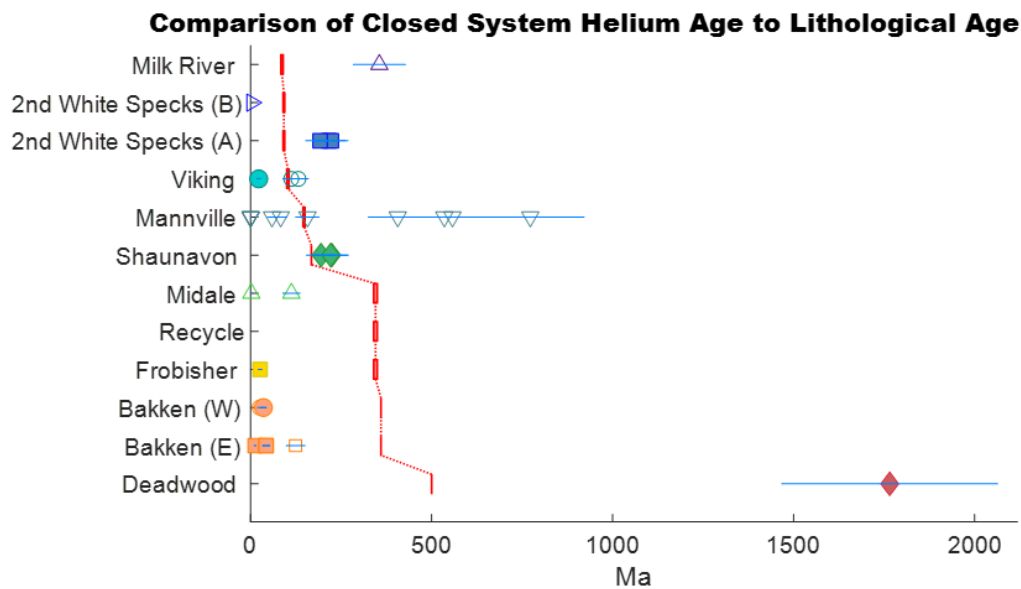
**B.6 Closed System He Age Estimated from U and Th reported by Parker and Fleischer (1967)**

Table B.4 summarised the rock type for each sampled formation and the corresponding U and Th concentration reported by Parker and Fleischer (1967). The concentrations are noticeably lower than the estimations from logs, resulting in older closed system He age for each sample (Figure B.6).

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**Table B.4:** *U and Th concentration reported by Parker and Fleischer (1967).*

| Formation                       | Generalised Rock Type | U (ppm) | Th (ppm) |
|---------------------------------|-----------------------|---------|----------|
| Milk River                      | shale                 | 12      | 3.7      |
| 2nd White Specks (Belle Plaine) | shale                 | 12      | 3.7      |
| 2nd White Specks (Alderson)     | shale                 | 12      | 3.7      |
| Viking                          | sandstone             | 1.7     | 0.45     |
| Mannville                       | sandstone             | 1.7     | 0.45     |
| Shaunavon                       | sandstone             | 1.7     | 0.45     |
| Midale                          | limestone             | 1.7     | 2.2      |
| Recycle                         | limestone             | 1.7     | 2.2      |
| Frobisher                       | limestone             | 1.7     | 2.2      |
| Bakken (Weyburn)                | shale                 | 12      | 3.7      |
| Bakken (Estevan)                | shale                 | 12      | 3.7      |
| Deadwood                        | sandstone             | 1.7     | 0.45     |



**Figure B.6:** *Closed System He Age estimated from U and Th reported by Parker and Fleischer (1967).*

## B.7 Sources of Excess $^3\text{He}$

### B.7.1 Magma Intrusion

The volume of the basin can be approximated to a cone with a radius of 560 km and a height of 5 km. If the magmatic body supplied the northeast quadrant of the Williston Basin, where the samples are located, the mass of rock is approximately  $4.1 \times 10^5 \text{ km}^3$ . With an average of 0.0028 cc  $^4\text{He}/\text{cc H}_2\text{O}$  measured from samples

### *B.7. Sources of Excess $^3\text{He}$*

in this study, a porosity of 0.1 and  $^3\text{He}/^4\text{He}$  ratio of 0.2  $R_a$ , the amount of  $^3\text{He}$  in the basin fluids, today is estimated as  $3.2 \times 10^4 \text{ m}^3 \text{ } ^3\text{He}$  (STP). If the magma source has an average  $^3\text{He}/^4\text{He}$  of 6  $R_a$ , this translates to total magmatic  $^4\text{He}$  of  $3.8 \times 10^9 \text{ m}^3$ . The Mid-Ocean Ridge Basalt contains  $^4\text{He}$  concentration of  $10^{-5} \text{ cm}^3 \text{ STP/g}$  (Graham, 2002), applying a similar degassing flux, the magmatic  $^4\text{He}$  requires a mass of  $3.8 \times 10^{17} \text{ kg}$ , or a volume of  $1.4 \times 10^5 \text{ km}^3$  of the basaltic melt to outgas completely (assuming a rock density of  $2800 \text{ kg/m}^3$ ). Since the magma body is granitic instead of basaltic, volatiles concentrations in the melt are expected to be lower, suggesting a potential greater volume than estimations.

The highest point on the volcanic dome is less than 300 m to the plain (Collier, 1929). The Kelvin-Sunburst Dome occupies an area of roughly  $7810 \text{ km}^2$ , the volume of the dome is estimated as  $2340 \text{ km}^3$ . This suggests that if magma intrusion is the source of excess  $^3\text{He}$ , the laccolith body is at least 60 times greater than the volume of the dome. Magma intrusion is, therefore, unlikely to be the dominant source of excess  $^3\text{He}$ .

#### **B.7.2 Cosmic Rays**

The interaction between cosmic rays and the Earth's atmosphere produces high energy particles. These particles react with earth surface nuclei and produce cosmogenic noble gases. A significant fraction of  $^3\text{He}$  produced will not be preserved and such mechanism is therefore unlikely to be the source of excess  $^3\text{He}$  in a crustal environment (Ballentine and Burnard, 2002).

#### **B.7.3 Interplanetary Dust Particles (IDP)**

Interplanetary dust particles (IDP), fine extraterrestrial materials with diameters between  $1 \mu\text{m}$  -  $1 \text{ mm}$ , are argued to be the primary transport media of extraterrestrial  $^3\text{He}$  (e.g. Farley, 1995. IDP samples collected from the Earth's stratosphere, with varying He concentrations but high  $R/R_a$  ratios ranging between 100 to 293, average at 264 ( $n=20$ ) (Nier and Schlutter, 1990; Nier and Schlutter, 1992). High  $^3\text{He}/^4\text{He}$

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ratios in ocean sediments were reported in different studies (e.g. Merrihue, 1964; Ozima et al., 1984; Amari and Ozima, 1985; Takayanagi and Ozima, 1987; Farley, 1995; Marcantonio et al., 2001). High  $^3\text{He}/^4\text{He}$  ratios are preserved in the deep ocean with slow sedimentation rates. The estimated  $^3\text{He}$  flux supplied by IDP varies geographically (Takayanagi and Ozima, 1987; Farley, 1995; Marcantonio et al., 2001; Winckler and Fischer, 2006; Brook et al., 2009; Chavrit et al., 2016) and may also change in geological time scale (Schmitz et al., 1997; D. Patterson et al., 1998). Little information is available in quantifying the timing and degree of post-depositional  $^3\text{He}$  release and loss. Hajime Hiyagon (1994) suggested He is released through diffusion and that 99% of the gas is released within 100 thousand-years at 100 - 200°C, equivalent to burial depths between 2500 m to 6000 m in a sedimentary basin with a geothermal gradient of 0.03°C/m and a surface temperature of 25°C. Those deep geological formations could have released most of the extraterrestrial  $^3\text{He}$ , since the maximum depth in the Williston Basin is 4900 m (Kent and Christopher, 1994). However, He release of IDPs in shallow units might be incomplete. Other factors such as sedimentation rate, U and Th concentrations in the rock matrix, the age of the unit also affect the  $^3\text{He}/^4\text{He}$  ratios. If IDPs are the primary source of  $^3\text{He}$ , it is hard to for each lithological units to have the right combinations among all the factors and produce  $^3\text{He}/^4\text{He}$  values within a relatively narrow range.

### **B.7.4 Localised High Li Concentrations**

The enrichment of  $^3\text{He}$  could also be the result of localised production enhancement. The dominant production mechanism of  $^3\text{He}$  in the crust is through thermal neutron capture by  $^6\text{Li}$  through  $^6\text{Li}(\text{n},\alpha)^3\text{H}(\beta^-)^3\text{He}$ . The rate of  $^3\text{He}$  production is therefore proportional to the subsurface thermal neutron density, the number of neutrons that reach the thermal energy level and the fraction of neutrons that can be captured by Li.

The proportion of neutrons that reaches the thermal energy level is assumed to be 0.8 (Morrison and Pine, 1955; Ballentine and Burnard, 2002). It can be as high as 1 for rock matrix enriched in light elements (Andrews, 1985; Ballentine and

### B.7. Sources of Excess $^3\text{He}$

Burnard, 2002). The fraction of total neutrons in the matrix that can be captured by Li depends on rock compositions and can be estimated from neutron capture cross-sections and element abundance.

$$F_{Li} = \sigma_{Li} N_{Li} / \sum_i^n \sigma_i N_i \quad (\text{B.5})$$

The fraction of neutrons captured by Li is presented in Chapter 2.

$^3\text{He}$  production can be estimated (Ballentine and Burnard, 2002) following Equation 2.9.

$^3\text{He}/^4\text{He}$  values calculated for different types of rock type vary from 0.001  $R_a$  to 0.01  $R_a$ . Higher ratios are produced from clay and shales, comparable to those estimated for the upper crust (Ballentine and Burnard, 2002).

Theoretically, high  $^3\text{He}/^4\text{He}$  values can be obtained from rock bodies with high lithium concentration. A Li concentration of 35 ppm was proposed for the upper crust (Teng et al., 2004) which could increase the  $R/R_a$  values to 0.0138. High lithium concentration is suggested to be found in magnesium silicates deposited during arid periods in lagoonal facies, within limestones, dolomites and gypsum (Tardy et al., 1972; Hajime Hiyagon, 1994). Under such condition, Li concentration can reach 6150 ppm accompany with a high Mg concentration of 20.4%. If Li and Mg concentrations of limestone and clay and shale are substituted with these high values correspondingly,  $^3\text{He}/^4\text{He}$  of in-situ rock production increased to 0.28  $R_a$  and 0.36  $R_a$ , respectively. If the enrichment of lithium and magnesium is the primary control on the elevated  $^3\text{He}/^4\text{He}$  ratios, this implies an arid lagoonal environment throughout Palaeozoic which does not fit the geological history of the Williston Basin. Furthermore, if basement He flux has a low  $^3\text{He}/^4\text{He}$ , cross-formational He migration would also dilute the localized  $^3\text{He}$  enrichment. Such source can therefore be discounted.

## **B.8 Basin Model**

Porosities of different hydrogeological units at a different time from a well close to the west margin of the Williston Basin is provided (personal communication with Erdem Idiz). The porosity values are reconstruction from a basin model considering only vertical effective stress, i.e. the overburden compression. Porosity factors are calculated, which refer to ratios between porosity values at a particular time and those at present. These factors are used to scale the reported porosity values to estimate the values in the geological histories, summarised in Table B.5.

**Table B.5:** Porosity factor of different hydrogeological units at different time. The porosity factor refers to the ratios between values at a particular time and those at present. It is calculated from reconstructed porosities re-constructed from basin models considering vertical Effective Stress of well close to the west margin of the basin on the US side.

| Hydrogeological Units     | Age (Ma)  |           |           |           |           |           |           |           |           |           |           |          |         |        |  |
|---------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|---------|--------|--|
|                           | 500 - 495 | 495 - 480 | 480 - 420 | 420 - 370 | 370 - 360 | 360 - 252 | 252 - 168 | 168 - 166 | 166 - 145 | 145 - 106 | 106 - 100 | 100 - 86 | 86 - 72 | 72 - 0 |  |
| Deadwood Basal aquifer    | 5.9       | 5.8       | 5.1       | 4.2       | 3.4       | 2.4       | 2         | 2         | 1.9       | 1.5       | 1.3       | 1.2      | 1.1     | 1      |  |
| Deadwood Upper aquitard   | 5.9       | 5.8       | 5.1       | 4.2       | 3.4       | 2.4       | 2         | 2         | 1.9       | 1.5       | 1.3       | 1.2      | 1.1     | 1      |  |
| Ordo-Silurian Aquifer     | -         | -         | -         | 6.8       | 4.9       | 3.2       | 2.5       | 2.4       | 2.3       | 1.7       | 1.4       | 1.3      | 1.2     | 1      |  |
| Devonian Complex          | -         | -         | -         | 6.8       | 4.9       | 3.2       | 2.5       | 2.4       | 2.3       | 1.7       | 1.4       | 1.3      | 1.2     | 1      |  |
| Bakken Formation          | -         | -         | -         | -         | 3.1       | 2.3       | 1.9       | 1.9       | 1.8       | 1.5       | 1.3       | 1.2      | 1.1     | 1      |  |
| Mississippian aquifer     | -         | -         | -         | -         | -         | 2.6       | 2.1       | 2         | 1.9       | 1.6       | 1.3       | 1.2      | 1.2     | 1      |  |
| Watrous aquitard          | -         | -         | -         | -         | -         | 2         | 2         | 1.9       | 1.8       | 1.5       | 1.3       | 1.2      | 1.1     | 1      |  |
| Shanavon aquifer          | -         | -         | -         | -         | -         | -         | 1.9       | 1.8       | 1.7       | 1.4       | 1.2       | 1.2      | 1.1     | 1      |  |
| Riedon aquitard           | -         | -         | -         | -         | -         | -         | 2.4       | 2.2       | 2.1       | 1.6       | 1.3       | 1.3      | 1.2     | 1      |  |
| Mannville aquifer         | -         | -         | -         | -         | -         | -         | -         | -         | 1.8       | 1.5       | 1.3       | 1.2      | 1.1     | 1      |  |
| Viking aquifer            | -         | -         | -         | -         | -         | -         | -         | -         | -         | 1.4       | 1.3       | 1.2      | 1.1     | 1      |  |
| Colorado Shale aquitard   | -         | -         | -         | -         | -         | -         | -         | -         | -         | 1.4       | 1.3       | 1.3      | 1.2     | 1      |  |
| Belly river aquifer       | -         | -         | -         | -         | -         | -         | -         | -         | -         | -         | -         | 1.2      | 1.2     | 1      |  |
| Post Belly river aquitard | -         | -         | -         | -         | -         | -         | -         | -         | -         | -         | -         | -        | -       | 1      |  |



### **B.9 Constructing a Hydrogeological Column Model for Each of the Sample Locations**

Isopach maps of different geological units are published by the Geological Atlas of the West Canadian Sedimentary basin (Mossop and Shetsen, 1994). The thickness of each geological isopach at the sampling locations are extrapolated from the maps using QGIS. The top 30 meters of the Devonian isopach is assumed to be the Bakken formation. The total thickness of sediments is calculated from the elevation map of surface and basement topography.

The distances of samples from the Precambrian are recorded during sampling by the University of Toronto. This information is used to correct the isopach thickness. If the samples collected represent the averages of the formation, the samples can be assumed collected from the centre of the formation. The thickness of isopachs is then proportionally changed to make sure the samples sit in the middle of the geological formations. Exceptions include Milk River, 2nd white specks, Midale and Frobisher samples. Based on the well-logs and cross-section diagrams reported by Geological Atlas of the West Canadian Sedimentary basin (Mossop and Shetsen, 1994), the distance of Milk River, and 2nd White Specks samples to the base of Colorado shale are estimated around  $3/5$  and  $1/8$  the thickness of the entire shale unit, respectively; and the distance of Midale and Frobisher samples to the top of Mississippian aquifer are around 0.06, 0.17 times the thickness of the Mississippian unit, respectively. Details are summarised in Table ??.

# B.9. Constructing a Hydrogeological Column Model for Each of the Sample Locations

| Unit                             | Well  | 2nd White Specks (Belle Plaine) | 2nd White Specks (Alderson) | Viking (1) | Viking (2) | Viking (3) | Mannville | Shaunavon | Midale | Frobisher | Bakken Weyburn (1) | Bakken Weyburn (3) | Bakken Weyburn (3) | Bakken Estevan | Deadwood |
|----------------------------------|-------|---------------------------------|-----------------------------|------------|------------|------------|-----------|-----------|--------|-----------|--------------------|--------------------|--------------------|----------------|----------|
| <i>Deadwood Basal Aquifer</i>    |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 116                              | 0     |                                 | 256.6                       | 72.5       | 72.5       | 75.5       | 0         | 78.5      | 0      | 0         | 86.8               | 81.6               | 98.4               | 121.8          | 73.3     |
| <i>Deadwood Upper Aquitard</i>   |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 239.2                            | 174.7 |                                 | 144.5                       | 245        | 245        | 255        | 113.9     | 200.7     | 96.7   | 98.9      | 430.5              | 404.7              | 487.7              | 361.6          | 227      |
| <i>Ordo-Silurian Aquifer</i>     |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 76.5                             | 281.3 |                                 | 0                           | 161.7      | 161.7      | 168.2      | 372       | 103       | 322    | 324.3     | 225.4              | 211.9              | 255.3              | 178.1          | 180.6    |
| <i>Devonian Complex</i>          |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 334.1                            | 566.8 |                                 | 515.7                       | 631.2      | 631.2      | 656.8      | 511.7     | 315.7     | 445.2  | 439.9     | 286                | 268.8              | 323.9              | 320.4          | 360.9    |
| <i>Bakken Formation</i>          |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 27.6                             | 29.8  |                                 | 28.5                        | 28         | 28         | 29.1       | 27.8      | 24        | 24     | 24        | 29.2               | 29.2               | 30.3               | 29.6           | 30       |
| <i>Mississippian Aquifer</i>     |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 185.4                            | 116.2 |                                 | 207.6                       | 110.6      | 110.6      | 115.1      | 384.9     | 166.9     | 483.7  | 468.3     | 668.6              | 617.7              | 556.4              | 534.5          | 277.3    |
| <i>Watrous Aquitard</i>          |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 69.7                             | 72.4  |                                 | 0                           | 0          | 0          | 0          | 167.3     | 80.2      | 200.9  | 224.2     | 238.2              | 220.1              | 198.3              | 241.2          | 148.8    |
| <i>Shaunavon Aquifer</i>         |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 46.5                             | 75.6  |                                 | 0                           | 1.6        | 1.6        | 1.6        | 81        | 59.6      | 101.9  | 104.8     | 75.9               | 70.1               | 63.1               | 57.2           | 78.9     |
| <i>Riedon Aquitard</i>           |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 12.2                             | 59.8  |                                 | 0                           | 2.6        | 2.6        | 2.7        | 53.7      | 29.6      | 68.4   | 69.4      | 134.4              | 124.1              | 111.8              | 102.6          | 44.7     |
| <i>Mannville Aquifer</i>         |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 81.6                             | 77    |                                 | 138                         | 82.4       | 82.4       | 85.7       | 115.6     | 90.1      | 134.4  | 132.4     | 77.5               | 71.6               | 64.5               | 76.4           | 105.6    |
| <i>Viking Aquifer</i>            |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 111.8                            | 52.7  |                                 | 122.2                       | 47.7       | 47.7       | 46.7       | 84.7      | 107.5     | 87.5   | 88.4      | 0                  | 0                  | 0                  | 0              | 72.4     |
| <i>Colorado Shale Aquitard</i>   |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 784.3                            | 494.3 |                                 | 686.1                       | 586.9      | 586.9      | 545        | 499.3     | 849.5     | 504.1  | 523.3     | 537.1              | 496.1              | 447                | 403.7          | 656.7    |
| <i>Belly river Aquifer</i>       |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 61.8                             | 36.2  |                                 | 247.5                       | 63.7       | 63.7       | 59.1       | 0         | 141.6     | 0      | 0         | 0                  | 0                  | 0                  | 0              | 100.5    |
| <i>Post Belly river Aquitard</i> |       |                                 |                             |            |            |            |           |           |        |           |                    |                    |                    |                |          |
| 154.5                            | 225.9 |                                 | 0                           | 93.5       | 93.5       | 86.9       | 436.9     | 282       | 469.6  | 440.5     | 445.6              | 411.6              | 370.8              | 465.3          | 98.6     |

Viking 1, 2, 3 refer to wells 1-7-25-12W3, 7A-1-32-24-12W3, 16-30-23-12W3 respectively.  
Bakken Weyburn 1, 2, 3 refer to wells 13-24-5-16W2, 1-21-5-16W2 and 16-12-5-16W2 respectively.

## **B.10 Presenting Models onto One Graph**

The simulated value of each sample is obtained from the model built on a hydrogeologic column explicitly constructed for its locality. The ratios between modelled and measured values are calculated. The ratios are then applied to the simulated profile of the Milk River sample (since the Milk River model has all the hydrogeological units) as the reconstructed concentrations. The concentrations are not true values, but rather estimates for a particular well, they demonstrate the goodness of fit between the model approach and observation. Figure 4.9 in the main text is plotted with such an approach.



# C

## Southwestern Ontario Basin Appendix

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### C.1 Air Mixing Component

The  $\frac{^{21}\text{Ne}_{\text{excess}}}{^{40}\text{Ar}_{\text{excess}}}$  versus  $\frac{^{20}\text{Ne}}{^{36}\text{Ar}}$  plot demonstrates the elemental fractionation of samples from the groundwater system (Figure C.1). Samples that have atmospheric and crustal noble gases mixed before fractionation are expected to lie on the line passing through the groundwater  $\frac{^{20}\text{Ne}}{^{36}\text{Ar}}$  ratios and crustal  $\frac{^{21}\text{Ne}_{\text{excess}}}{^{40}\text{Ar}_{\text{excess}}}$  endmember ratios. Samples lie to the right of the line, i.e. more enriched in  $^{20}\text{Ne}$  than  $^{36}\text{Ar}$  can be explained with an addition of air component. Air-mixing signatures are not surprising since several of these wells are abandoned or privately owned, not managed with standardised industrial procedures. We can resolve the amount of air added to the system by restoring data points back to the fractionation line. However, it is worth noticing that

### C.1. Air Mixing Component

the production and releasing of crustal noble gases depend on various parameters and local production ratios of  $^{21}\text{Ne}/^{40}\text{Ar}$  are expected to deviate from the global average of  $3.3 \times 10^{-7}$ ). Furthermore, the recharging condition controls the initial amount of atmospheric noble gases and uncertainties relate to these parameters also affect the accuracy of the fractionation model.

The corrected  $^{20}\text{Ne}/^{36}\text{Ar}$  ratios can be calculated as

$$\left[ \frac{^{20}\text{Ne}}{^{36}\text{Ar}} \right]_c = \left[ \frac{^{20}\text{Ne}}{^{36}\text{Ar}} \right]_{\text{groundwater}} \times \frac{\left[ \frac{^{21}\text{Ne}_{\text{excess}}}{^{40}\text{Ar}_{\text{excess}}} \right]_m}{\left[ \frac{^{21}\text{Ne}_{\text{excess}}}{^{40}\text{Ar}_{\text{excess}}} \right]_{\text{groundwater}}}, \quad (\text{C.1})$$

where subscripts c, m and groundwater represent air-corrected ratios, measured ratios and ratios in the groundwater before fractionation.

The proportion of the original exsolved gas, m, and the proportion of additional air, (1-m), can be solved with the following equations

$$\left[ \frac{^{20}\text{Ne}}{^{36}\text{Ar}} \right]_c = \frac{^{20}\text{Ne}_m - (1-m)^{20}\text{Ne}_{\text{air}}}{^{36}\text{Ar}_m - (1-m)^{36}\text{Ar}_{\text{air}}}. \quad (\text{C.2})$$

We assume that the groundwater is recharged with 298.15K seawater and the local crustal noble gas production is similar to the values estimated for the average crust (Ballentine and Burnard, 2002). The calculated values and the corrected helium concentration in the water are demonstrated in Table C.1.

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Table C.1: The proportion of air in each scenario and the calculated  $^4\text{He}$  and  $^{40}\text{Ar}$  concentrations in groundwater correspondingly.

| Sample name          | Percentage of air    |                     | $^4\text{He}_{\text{water}} \times 10^{-4}$<br>$\text{cm}^3 \text{ STP}/\text{cm}^3 \text{ H}_2\text{O}$ |                 |                  |                         | $^{40}\text{Ar}_{\text{water}} \times 10^{-4}$<br>$\text{cm}^3 \text{ STP}/\text{cm}^3 \text{ H}_2\text{O}$ |                 |                |                         |
|----------------------|----------------------|---------------------|----------------------------------------------------------------------------------------------------------|-----------------|------------------|-------------------------|-------------------------------------------------------------------------------------------------------------|-----------------|----------------|-------------------------|
|                      | $P_{\text{close}}\%$ | $P_{\text{open}}\%$ | $P_{\text{frac}}\%$                                                                                      | close corrected | open corrected   | fractionation corrected | Solubility                                                                                                  | close corrected | open corrected | fractionation corrected |
| <b>A-2 Carbonate</b> |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| <b>Guelph</b>        |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| T008636              | 0.11                 | 0.28                | 0.24                                                                                                     | 25.9±0.28       | 2086.8±22.82     | 111.8±1.22              | 33.1                                                                                                        | 2.9±0.02        | 3.8±0.02       | 3.5±0.02                |
| T002556              | 0.43                 | 0.63                | 0.59                                                                                                     | 130.8±1.66      | 2633.3±33.50     | 533.1±6.78              | 322.5                                                                                                       | 10.1±0.09       | 14.4±0.13      | 13.2±0.12               |
| T003899              | 0.18                 | 0.39                | 0.3                                                                                                      | 55.8±0.69       | 984.5±12.12      | 120.5±1.48              | 136                                                                                                         | 4.3±0.03        | 5.7±0.04       | 5.0±0.03                |
| T004918              | N/A                  | 0.13                | 0.1                                                                                                      | 83.5±1.12       | 930.5±12.43      | 259.3±3.46              | 137.1                                                                                                       | 3.4±0.02        | 4.1±0.03       | 3.9±0.03                |
| T007415              | 0.24                 | 0.52                | 0.4                                                                                                      | 117.5±1.63      | 1691.6±23.45     | 263.6±3.65              | 401.2                                                                                                       | 4.2±0.11        | 5.5±0.15       | 4.8±0.13                |
| T008468              | N/A                  | 0.12                | 0.09                                                                                                     | 20.8±0.25       | 57.7±0.71        | 42.5±0.52               | 42.5                                                                                                        | 3.3±0.02        | 3.6±0.02       | 3.5±0.02                |
| T008657              | 0.2                  | 0.43                | 0.38                                                                                                     | 117.5±1.47      | 2182.3±27.31     | 471.8±5.90              | 323.2                                                                                                       | 5.8±0.10        | 8.0±0.14       | 7.4±0.13                |
| T009602              | 0.32                 | 0.55                | 0.55                                                                                                     | 58.3±0.70       | 1008.6±12.12     | 2042.7±24.56            | 160.3                                                                                                       | 4.8±0.04        | 6.5±0.05       | 6.5±0.05                |
| T010097              | 0.22                 | 0.41                | 0.37                                                                                                     | 154.1±1.88      | 3077.4±37.57     | 602.3±7.35              | 366.8                                                                                                       | 5.9±0.04        | 8.2±0.06       | 7.5±0.05                |
| T011560              | 0.7                  | 0.97                | 0.9                                                                                                      | 53.4±0.65       | 842.1±10.20      | 181.4±2.20              | 173                                                                                                         | 9.2±0.07        | 13.1±0.09      | 11.8±0.08               |
| <b>Thorold</b>       |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| T011554              | N/A                  | 0.21                | 0.14                                                                                                     | 107.3±1.26      | 2140.3±25.11     | 270.5±3.17              | 300.9                                                                                                       | 5.1±0.04        | 6.7±0.06       | 6.0±0.05                |
| T011584              | N/A                  | 0.19                | 0.08                                                                                                     | 122.4±1.42      | 1865.9±21.64     | 205.2±2.38              | 314.1                                                                                                       | 3.9±0.02        | 4.8±0.03       | 4.2±0.02                |
| <b>Thorold*</b>      |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| T011280              | 0.23                 | 0.4                 | 0.37                                                                                                     | 106.4±1.31      | 3903.9±48.22     | 485.5±6.00              | 229.1                                                                                                       | 7.6±0.06        | 10.8±0.09      | 9.9±0.08                |
| <b>Grimsby</b>       |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| T002374              | 0.15                 | 0.32                | 0.29                                                                                                     | 77.5±0.95       | 2588.6±31.74     | 402.4±4.93              | 167.3                                                                                                       | 6.6±0.05        | 9.3±0.08       | 8.6±0.07                |
| T003188              | 0.25                 | 0.38                | 0.26                                                                                                     | 365.3±5.08      | 16661.6±231.74   | 377.6±5.25              | 584.5                                                                                                       | 6.0±0.05        | 8.3±0.07       | 6.0±0.05                |
| T012287              | 0.14                 | 0.17                | 0.17                                                                                                     | 371.7±4.52      | 94554.1±1150.49  | 1717.5±20.90            | 170.4                                                                                                       | 17.1±0.17       | 25.2±0.25      | 22.8±0.23               |
| <b>Whirlpool</b>     |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| T008194              | N/A                  | 0.14                | 0.13                                                                                                     | 128.5±1.43      | 5384.0±59.83     | 1797.4±19.97            | 214.8                                                                                                       | 6.7±0.05        | 9.4±0.06       | 9.2±0.06                |
| T009877              | 0.1                  | 0.18                | 0.17                                                                                                     | 153.6±1.79      | 10793.9±125.58   | 813.1±9.46              | 154.9                                                                                                       | 10.1±0.09       | 14.5±0.12      | 13.4±0.11               |
| <b>Cobourg</b>       |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| T007357              | 0.32                 | 0.4                 | 0.19                                                                                                     | 145.9±1.55      | 4800.1±51.16     | 57.5±0.61               | 347                                                                                                         | 9.1±0.05        | 13.0±0.08      | 6.4±0.04                |
| T008358              | N/A                  | 0.07                | 0.01                                                                                                     | 110.3±1.53      | 3425.7±47.66     | 125.9±1.75              | 220.1                                                                                                       | 8.0±0.22        | 10.8±0.29      | 8.3±0.22                |
| <b>Sherman Fall</b>  |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| T007793              | 0.02                 | 0.07                | 0.02                                                                                                     | 165.5±2.30      | 8926.7±124.07    | 177.6±2.47              | 258.9                                                                                                       | 10.1±0.27       | 14.5±0.39      | 10.3±0.28               |
| T007954              | N/A                  | 0.07                | 0.03                                                                                                     | 54.9±0.60       | 925.9±10.08      | 86.1±0.94               | 114.4                                                                                                       | 8.7±0.05        | 11.0±0.07      | 9.4±0.06                |
| T008057              | 0.06                 | 0.18                | N/A                                                                                                      | 155.1±2.15      | 3684.5±50.97     | 102.9±1.42              | 536.5                                                                                                       | 8.5±0.23        | 12.1±0.32      | 7.4±0.20                |
| <b>Cobocork</b>      |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| T0011596             | 0.41                 | 0.48                | 0.47                                                                                                     | 258.2±3.13      | 11084.6±134.45   | 2036.3±24.70            | 921.9                                                                                                       | 24.4±0.21       | 36.2±0.30      | 34.5±0.29               |
| T006907              | 0.24                 | 0.31                | 0.31                                                                                                     | 113.5±1.36      | 3081.5±36.81     | 1012.7±12.10            | 412.8                                                                                                       | 11.4±0.09       | 16.4±0.13      | 15.9±0.13               |
| T008313              | N/A                  | N/A                 | N/A                                                                                                      | 4.7±0.05        |                  | 4.7±0.05                | 202.8                                                                                                       | 3.4±0.02        | 3.4±0.02       | 3.4±0.02                |
| <b>Gull River</b>    |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| T008974              | 0.07                 | 0.16                | 0.08                                                                                                     | 129.7±1.41      | 3799.0±41.28     | 141.7±1.54              | 605.2                                                                                                       | 11.9±0.08       | 17.4±0.12      | 12.3±0.08               |
| <b>Cambrian</b>      |                      |                     |                                                                                                          |                 |                  |                         |                                                                                                             |                 |                |                         |
| T007369              | 0.3                  | 0.32                | 0.31                                                                                                     | 341.7±3.70      | 25031.7±271.14   | 820.5±8.89              | 632.1                                                                                                       | 30.5±0.20       | 45.1±0.29      | 37.7±0.25               |
| T007956              | 0.69                 | 0.72                | 0.7                                                                                                      | 545.7±6.77      | 44360.3±550.34   | 821.1±10.19             | 1184.5                                                                                                      | 44.9±0.32       | 67.1±0.48      | 50.6±0.36               |
| T008094              | 0.13                 | 0.14                | 0.13                                                                                                     | 1238.4±15.50    | 234751.0±2937.88 | 1374.6±17.20            | 1332.7                                                                                                      | 78.8±0.63       | 118.2±0.94     | 81.5±0.65               |

\* Thorold/Whirlpool

### C.1. Air Mixing Component

Air mixing signature is observed in Figure C.1, and the proportion of mixed air and the gas-to-water ratio can be resolved considering a first-order equilibrium degassing system or a Rayleigh fractionation system (Chapter 5). The calculated results are listed in Table 5.4. Since helium concentration is unlikely to change significantly with respect to a small amount of air mixing, the maximum solubility of helium that can be dissolved at reservoir temperature and pressure equilibrating with the sampled gas phase can be calculated with Henry's constant and is presented in Table C.1. The partial pressure used in calculating the solubility is the product of  $^4\text{He}$  concentration in the gas phase and the reservoir pressure.

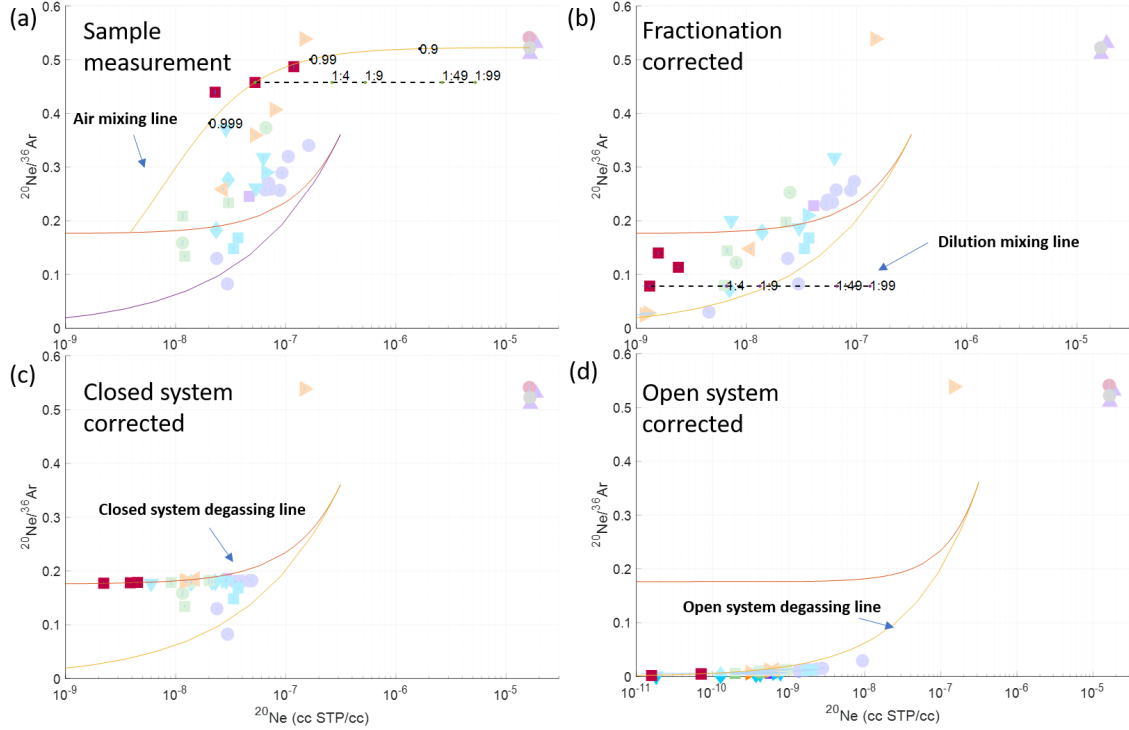
The result suggests the open system is not appropriate since the corrected helium concentration is higher than the maximum solubility. The closed system corrected noble gases have variable  $\frac{^{21}\text{Ne}_{\text{excess}}}{^{40}\text{Ar}_{\text{excess}}}$ ; however, apart from a Guelph sample, a Grimsby sample and the Coboconk samples, most have their ratios ranges between 0.4 to 2.2 times that of the average crust. The extremely low and high  $\frac{^{21}\text{Ne}_{\text{excess}}}{^{40}\text{Ar}_{\text{excess}}}$  samples also demonstrate considerable mass fractionation on the neon plot (Figure C.2), which significantly affects the estimated values of  $^{21}\text{Ne}_{\text{excess}}$ . The  $\frac{^{21}\text{Ne}_{\text{excess}}}{^{40}\text{Ar}_{\text{excess}}}$  anomalies would disappear if restoring neon to a production line by considering mass fractionation.

The atmospheric noble gas concentrations and ratios corrected by fractionation plot do not restore the elements to the degassing lines (Figure C.1), suggesting an additional dilution process or an over-pressured reservoir. Crustal fractionation correction is also sensitive to the estimations of the initial crustal and atmospheric noble gases in the water. With limited information about the well conditions and the relatively tight range of  $\frac{^{21}\text{Ne}_{\text{excess}}}{^{40}\text{Ar}_{\text{excess}}}$ , we correct the concentration referencing to a closed system degassing process.

Noticeably, Coboconk sample (T008313) is unresolvable due to the higher  $^{20}\text{Ne}/^{36}\text{Ar}$  ratio than the air value and is therefore excluded in the analysis in the chapter.



### C. Southwestern Ontario Basin Appendix

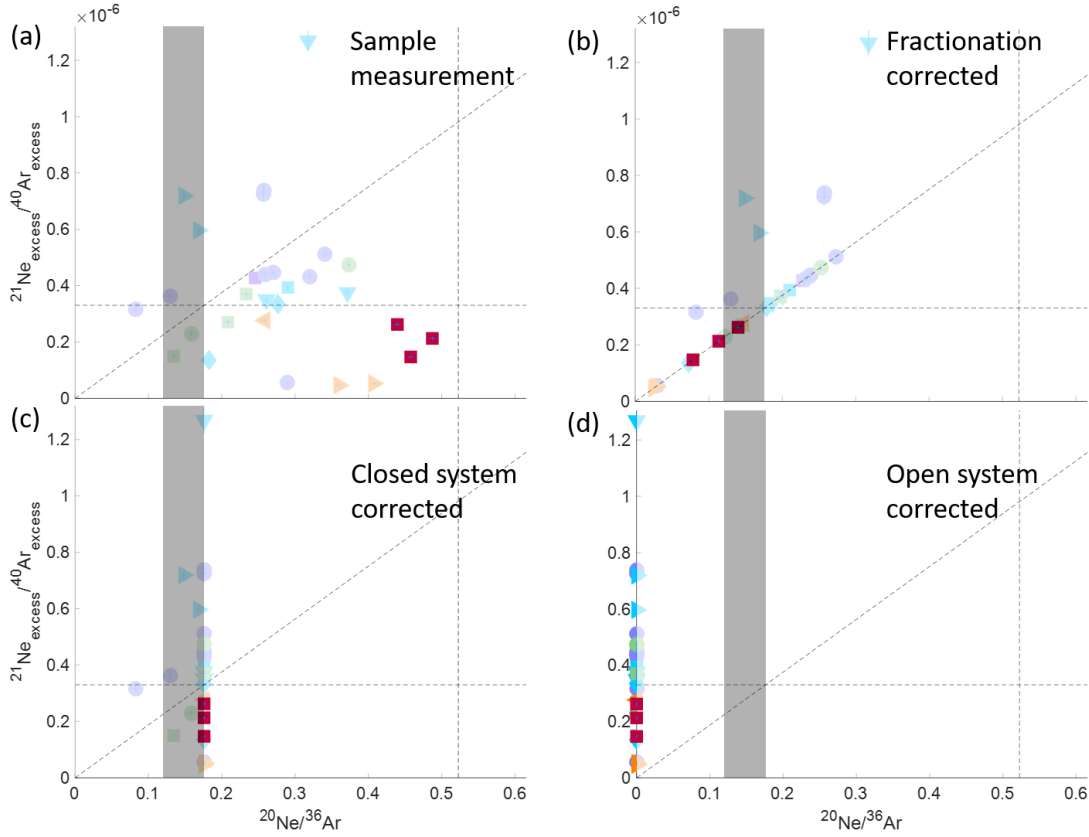


**Figure C.1:** Modelled  $^{20}\text{Ne}$  and  $^{20}\text{Ne}/^{36}\text{Ar}$  for the close and open degassing system for the Deadwood formation, with Deadwood samples highlighted. The arrows on the plot demonstrate shifting of the degassing models with respect to changes in temperature and pressure, as well as the addition of diluting gas. The air mixing line demonstrates the impact of air mixing. The numbers on the mixing line represent the proportion of exsolved gas in the mixtures. The horizontal line extending from the sample point to the right indicate the original concentration corresponding to different mixing ratios. (a) before correction (b) after correction for an elemental fractionation (c) after correction for a closed system (d) after correction for an open system.

### C.2 U, Th, Porosity and Tortuosity

In this study, we grouped the geological formations to 18 units according to hydro-geological and geological properties in Southwestern Ontario (Table C.2) reported by AECOM and Itasca Canada (2011) and Sykes et al. (2011).

U and Th are obtained from Ordovician Gull River, Blue Mountain, Collingwood samples reported by Clark et al. (2013). We assume dolomite units have the similar U and Th concentrations as Gull River, Shale units are similar to Blue Mountain, Shale and carbonate are similar to Collingwood, Glacial till/drift is similar to Collingwood. The corresponding arithmetic mean of U and Th is calculated for the grouped units.



**Figure C.2:**  $^{21}\text{Ne}^*/^{40}\text{Ar}^*$  plotted against  $^{20}\text{Ne}/^{36}\text{Ar}$  with the Cambrian samples highlighted. The horizontal dashed lines represent  $^{21}\text{Ne}^*/^{40}\text{Ar}^*$  of average crustal production (Ballentine and Burnard, 2002). The shaded area represents the range of  $^{20}\text{Ne}/^{36}\text{Ar}$  values for air saturated water recharged by 273K freshwater to 298K seawater. The vertical dashed line represents the air  $^{20}\text{Ne}/^{36}\text{Ar}$  ratio. The dashed slope represents the fractionation expected for groundwater that was recharged by 298K seawater and kept the average crustal  $^{21}\text{Ne}^*/^{40}\text{Ar}^*$  ratio. (a) before correction (b) after correction for an elemental fractionation (c) after correction for a closed system (d) after correction for an open system.

For example, the arithmetic mean of U concentration,  $\bar{U}$ , of formation F1, F2 and F3 of thickness  $z_1$ ,  $z_2$  and  $z_3$  can be calculated following

$$\bar{U} = \frac{F1 \times z_1 + F2 \times z_2 + F3 \times z_3}{z_1 + z_2 + z_3}. \quad (\text{C.3})$$

Porosity and tortuosity for the geological formations are reported by Sykes et al. (2011)). The harmonic mean is calculated for grouped units since such means best characterise ratios among variable units. For example, the harmonic mean of porosity  $\bar{\phi}$ , of formation  $\phi_1$ ,  $\phi_2$  and  $\phi_3$  of thickness  $z_1$ ,  $z_2$  and  $z_3$  can be calculated as following

$$\bar{\phi} = \left( \frac{\frac{1}{\phi_1} + \frac{1}{\phi_2} + \frac{1}{\phi_3}}{z_1 + z_2 + z_3} \right)^{-1}. \quad (\text{C.4})$$

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**Table C.2:** Hydrogeological parameters. \* data from AECOM and Itasca Canada (2011) \*\*data from Sykes et al. (2011) \*\*\* data from Clark et al. (2013). The porosity,  $\phi$ , and tortuosity,  $\tau$ , of the grouped units are harmonic means of the corresponding parameters of the formations and U and Th concentrations are arithmetic means.

| Period     | Formation                 | Lithology *               | z*<br>(m) | $\phi$ ** | $\tau$ ** | U***<br>(ppm) | Th***<br>(ppm) | Grouped Units                     | $\phi$<br>(Har-<br>monic<br>mean) | $\tau$<br>(Har-<br>monic<br>mean) | U<br>(ppm) | Th<br>(ppm) |
|------------|---------------------------|---------------------------|-----------|-----------|-----------|---------------|----------------|-----------------------------------|-----------------------------------|-----------------------------------|------------|-------------|
| Quaternary | Drift                     |                           | -         | 0.2       | 0.4       | 1.54          | 2.13           | Quaternary Drift                  | 0.2                               | 0.4                               | 1.54       | 2.13        |
| Devonian   | Kettle Point              |                           | -         | 0.1       | 0.12      | 3.75          | 11.6           | Devonian Shale                    | 0.1                               | 0.12                              | 3.75       | 11.6        |
|            | Hamilton Group            |                           | -         | 0.1       | 0.12      | 3.75          | 11.6           |                                   |                                   |                                   |            |             |
|            | Dundee                    |                           | -         | 0.1       | 0.12      | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Lucas                     | Dolostone                 | 10.4      | 0.077     | 0.094     | 0.6           | 0.78           | Devonian Dolostone                | 0.077                             | 0.094                             | 0.6        | 0.78        |
|            | Amherstburg (top 20 m)    | Dolostone                 | 19.6      | 0.077     | 0.094     | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Amherstburg (lower 25 m)  | Dolostone                 | 25        | 0.077     | 0.094     | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Bois Blanc                | Dolostone                 | 49        | 0.077     | 0.094     | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
| Silurian   | Bass Islands (upper 20 m) | Dolostone                 | 20        | 0.056     | 0.28      | 0.6           | 0.78           | Upper Silurian Dolostone          | 0.056                             | 0.28                              | 0.6        | 0.78        |
|            | Bass Islands (lower 25 m) | Dolostone                 | 25.3      | 0.056     | 0.28      | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Salina G                  | Dolostone and anhydrite   | 9.3       | 0.172     | 0.003     | 0.6           | 0.78           | Silina G                          | 0.172                             | 0.003                             | 0.6        | 0.78        |
|            | Salina F                  | Shale and anhydrite       | 44.4      | 0.1       | 0.049     | 1.54          | 2.13           | Silina B to Silina F              | 0.118                             | 0.061                             | 1.41       | 2.821       |
|            | Salina E                  | Dolostone and anhydrite   | 20        | 0.1       | 0.057     | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Salina D                  | Dolostone and anhydrite   | 1.6       | 0.089     | 0.064     | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Salina C                  | Shale                     | 15.7      | 0.205     | 0.065     | 3.75          | 11.6           |                                   |                                   |                                   |            |             |
|            | Salina B                  | Dolostone                 | 30.9      | 0.145     | 0.1       | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Salina B evaporite        | Dolostone and anhydrite   | 1.9       | 0.089     | 0.001     | 0.6           | 0.78           | Salina B Evaporite                | 0.089                             | 0.001                             | 0.6        | 0.78        |
|            | Salina A2 carbonate       | Dolostone                 | 26.6      | 0.12      | 0.012     | 0.6           | 0.78           | Silina A2 Carbonate               | 0.12                              | 0.012                             | 0.6        | 0.78        |
|            | Salina A2 evaporite       | Dolostone and anhydrite   | 5.8       | 0.089     | 0.001     | 0.6           | 0.78           | Silina A2 Evaporite               | 0.089                             | 0.001                             | 0.6        | 0.78        |
|            | Salina A1 Upper carbonate | Dolostone                 | 3         | 0.07      | 0.084     | 0.6           | 0.78           | Silina A1 Carbonate               | 0.02                              | 0.011                             | 0.6        | 0.78        |
|            | Salina A1 carbonate       | Dolostone                 | 38.5      | 0.019     | 0.011     | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Salina A1 evaporite       | Dolostone and anhydrite   | 3.5       | 0.007     | 0.0052    | 0.6           | 0.78           | Silina A1 Evaporite and Silina A0 | 0.012                             | 0.003                             | 0.6        | 0.78        |
|            | Salina A0                 | Dolostone                 | 4         | 0.032     | 0.0011    | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Guelph                    | Sucrosic, Vuggy Dolostone | 4.1       | 0.057     | 0.068     | 0.6           | 0.78           | Guelph - Fossil Hill              | 0.023                             | 0.012                             | 0.6        | 0.78        |
|            | Goat Island               | Dolostone                 | 18.8      | 0.02      | 0.009     | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Gasport                   | Dolomitic Limestone       | 6.85      | 0.02      | 0.009     | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Lions Head                | Dolostone                 | 4.45      | 0.031     | 0.24      | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Fossil Hill               | Dolostone                 | 2.3       | 0.031     | 0.62      | 0.6           | 0.78           |                                   |                                   |                                   |            |             |
|            | Cabot Head                | Shale and carbonate       | 23.8      | 0.116     | 0.032     | 1.54          | 2.13           | Cabot Head                        | 0.116                             | 0.032                             | 1.54       | 2.13        |

Continued on next page

C.2. U, Th, Porosity and Tortuosity

Table C.2 – Continued from previous page

| Period     | Formation     | Lithology *                                   | z*<br>(m) | $\phi$ ** | $\tau$ ** | U***<br>(ppm) | Th***<br>(ppm) | Grouped Units                         | $\phi$<br>(Har-<br>monic<br>mean) | $\tau$<br>(Har-<br>monic<br>mean) | U<br>(ppm) | Th<br>(ppm) |
|------------|---------------|-----------------------------------------------|-----------|-----------|-----------|---------------|----------------|---------------------------------------|-----------------------------------|-----------------------------------|------------|-------------|
| Ordovician | Manitoulin    | Dolostone                                     | 12.9      | 0.028     | 0.0064    | 0.6           | 0.78           | Manitoulin                            | 0.028                             | 0.006                             | 0.6        | 0.78        |
|            | Queenston     | Shale                                         | 70.3      | 0.073     | 0.016     | 2.15          | 8.94           | Upper Ordovician Shale                | 0.061                             | 0.01                              | 2.849      | 7.734       |
|            | Georgian Bay  | Shale                                         | 90.9      | 0.071     | 0.0073    | 3.08          | 10.71          |                                       |                                   |                                   |            |             |
|            | Blue Mountain | Shale                                         | 42.7      | 0.078     | 0.013     | 3.75          | 11.6           |                                       |                                   |                                   |            |             |
|            | Collingwood   | Shale with interbedded limestone              | 7.9       | 0.012     | 0.049     | 1.54          | 2.13           |                                       |                                   |                                   |            |             |
|            | Cobourg       | Limestone                                     | 28.6      | 0.015     | 0.03      | 1.175         | 2.18           | Middle Ordovician Limestone and Shale | 0.017                             | 0.02                              | 0.731      | 3.089       |
|            | Sherman Fall  | Limestone and interbedded shale               | 28        | 0.016     | 0.017     | 0.475         | 4.49           |                                       |                                   |                                   |            |             |
|            | Kirkfield     | Limestone and interbedded shale               | 45.9      | 0.021     | 0.024     | 0.61          | 2.8            |                                       |                                   |                                   |            |             |
|            | Coboconk      | Limestone                                     | 23        | 0.009     | 0.036     | 0.6           | 0.78           |                                       |                                   |                                   |            |             |
|            | Gull River    | Limestone                                     | 53.6      | 0.022     | 0.014     | 0.6           | 0.78           |                                       |                                   |                                   |            |             |
|            | Shadow Lake   | Interbedded mudstone, siltstone and sandstone | 5.2       | 0.097     | 0.076     | 1.17          | 1.2            | Shadow Lake                           | 0.097                             | 0.076                             | 1.17       | 1.2         |
| Cambrian   | Cambrian      | Sandstone                                     | 16.9      | 0.071     | 0.13      | 1.17          | 1.2            | Cambrian Sandstone                    | 0.071                             | 0.13                              | 1.17       | 1.2         |

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### **C.3 Constructing a Hydrogeological Column for Each of the Sample Locations**

Formation isopach thickness for different wells was obtained from Oil, Gas & Salt Resources Library (<http://www.ogsrlibrary.com/>). Wells drilled to Precambrian basement include T008532, T008094, T007956, T008045, T008974, T006907, T007369, T007357. For wells not drilled to the Precambrian basement, isopach thickness is extrapolated from the deep wells nearby. The thickness of the sedimentary units changes proportionally to make sure the samples sit in the middle of the formation being collected. Extrapolated isopach thickness used for modelling is presented in Table ??.

### C.3. Constructing a Hydrogeological Column for Each of the Sample Locations

Table C.3: Extrapolated isopach thickness used for modelling, unit in m.

| Sample                                | T011560 | T002556 | T004918 | T007415 | T008657 | T009602 | T010097 | T008468 | T003899 | T006907  |
|---------------------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|----------|
| Formation                             | Guelph  | Guelph  | Guelph  | Guelph  | Guelph  | Guelph  | Guelph  | Guelph  | Guelph  | Coboconk |
| Quaternary Drift                      | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 34      | 29      | 28       |
| Erosion                               | 1000    | 1000    | 1000    | 1000    | 1000    | 1000    | 1000    | 1000    | 1000    | 1000     |
| Devonian Shale                        | 0       | 0       | 0       | 0       | 0       | 0       | 0       | 210     | 181     | 174      |
| Devonian Dolostone                    | 117     | 121     | 149     | 137     | 114     | 142     | 138     | 157     | 135     | 130      |
| Upper Silurian Dolostone              | 51      | 53      | 65      | 60      | 50      | 62      | 60      | 52      | 45      | 43       |
| Silina G                              | 10      | 11      | 13      | 12      | 10      | 13      | 12      | 7       | 6       | 6        |
| Silina B to Silina F                  | 127     | 131     | 162     | 148     | 123     | 154     | 149     | 158     | 136     | 131      |
| Salina B Evaporite                    | 2       | 2       | 3       | 3       | 2       | 3       | 3       | 0       | 0       | 0        |
| Salina A2 Carbonate                   | 30      | 31      | 38      | 35      | 29      | 36      | 35      | 42      | 36      | 35       |
| Silina A2 Evaporite                   | 7       | 7       | 8       | 8       | 6       | 8       | 8       | 24      | 21      | 20       |
| Silina A1 Carbonate and A1 Evaporite  | 47      | 48      | 60      | 55      | 45      | 57      | 55      | 46      | 40      | 38       |
| Silina A0                             | 8       | 9       | 11      | 10      | 8       | 10      | 10      | 0       | 0       | 0        |
| Guelph - Fossil Hill                  | 46      | 46      | 34      | 51      | 53      | 48      | 51      | 53      | 46      | 44       |
| Cabot Head                            | 30      | 30      | 22      | 34      | 34      | 31      | 33      | 45      | 38      | 37       |
| Manitoulin                            | 16      | 16      | 12      | 18      | 19      | 17      | 18      | 14      | 12      | 12       |
| Upper Ordovician Shale                | 264     | 266     | 198     | 298     | 306     | 280     | 294     | 244     | 210     | 202      |
| Middle Ordovician Limestone and Shale | 224     | 225     | 167     | 252     | 259     | 236     | 249     | 319     | 275     | 264      |
| Shadow Lake                           | 6       | 7       | 5       | 7       | 8       | 7       | 7       | 4       | 3       | 3        |
| Cambrian Sandstone                    | 21      | 21      | 16      | 24      | 24      | 22      | 23      | 0       | 0       | 0        |

| Sample                                | T008636       | T008358 | T007357 | T007793      | T007954      | T007369  | T011280             | T011554 | T011584 |
|---------------------------------------|---------------|---------|---------|--------------|--------------|----------|---------------------|---------|---------|
| Formation                             | A-2 Carbonate | Cobourg | Cobourg | Sherman Fall | Sherman Fall | Cambrian | Thorold / Whirlpool | Thorold | Thorold |
| Quaternary Drift                      | 59            | 5       | 43      | 39           | 5            | 54       | 71                  | 76      | 67      |
| Erosion                               | 1000          | 1000    | 1000    | 1000         | 1000         | 1000     | 1000                | 1000    | 1000    |
| Devonian Shale                        | 74            | 57      | 107     | 89           | 62           | 68       | 0                   | 0       | 0       |
| Devonian Dolostone                    | 132           | 115     | 126     | 96           | 125          | 121      | 0                   | 0       | 0       |
| Upper Silurian Dolostone              | 88            | 39      | 77      | 46           | 43           | 81       | 0                   | 0       | 0       |
| Silina G                              | 9             | 7       | 6       | 7            | 7            | 8        | 0                   | 0       | 0       |
| Silina B to Silina F                  | 123           | 67      | 93      | 90           | 73           | 113      | 83                  | 89      | 79      |
| Salina B Evaporite                    | 0             | 41      | 15      | 22           | 44           | 0        | 0                   | 0       | 0       |
| Silina A2 Carbonate                   | 20            | 19      | 21      | 20           | 21           | 18       | 14                  | 15      | 14      |
| Silina A2 Evaporite                   | 6             | 4       | 2       | 1            | 4            | 6        | 0                   | 0       | 0       |
| Silina A1 Carbonate and A1 Evaporite  | 29            | 5       | 17      | 13           | 5            | 27       | 0                   | 0       | 0       |
| Silina A0                             | 0             | 0       | 0       | 0            | 0            | 0        | 0                   | 0       | 0       |
| Guelph - Fossil Hill                  | 87            | 137     | 101     | 115          | 149          | 80       | 129                 | 123     | 118     |
| Cabot Head                            | 37            | 37      | 36      | 35           | 41           | 34       | 14                  | 13      | 14      |
| Manitoulin                            | 14            | 10      | 14      | 13           | 11           | 13       | 14                  | 13      | 14      |
| Upper Ordovician Shale                | 278           | 229     | 257     | 255          | 249          | 257      | 395                 | 378     | 394     |
| Middle Ordovician Limestone and Shale | 289           | 236     | 256     | 266          | 257          | 267      | 231                 | 221     | 230     |
| Shadow Lake                           | 0             | 0       | 1       | 1            | 0            | 0        | 0                   | 0       | 0       |
| Cambrian Sandstone                    | 19            | 34      | 30      | 18           | 37           | 18       | 5                   | 5       | 5       |

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| Sample                                | T002374    | T003188    | T012287    | T009877    | T008194    | T0011596   | T008974    | T007956    | T008094    |
|---------------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Formation                             | Grimsby    | Grimsby    | Grimsby    | Whirlpool  | Whirlpool  | Coboconk   | Gull River | Cambrian   | Cambrian   |
| Quaternary Drift                      | 86<br>1000 | 91<br>1000 | 43<br>1000 | 36<br>1000 | 33<br>1000 | 42<br>1000 | 66<br>1000 | 78<br>1000 | 36<br>1000 |
| Erosion                               | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          |
| Devonian Shale                        | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          |
| Devonian Dolostone                    | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          |
| Upper Silurian Dolostone              | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          |
| Silina G                              | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          |
| Silina B to Silina F                  | 101        | 106        | 51         | 42         | 39         | 50         | 20         | 45         | 85         |
| Salina B Evaporite                    | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          |
| Silina A2 Carbonate                   | 17         | 18         | 9          | 7          | 7          | 9          | 24         | 11         | 18         |
| Silina A2 Evaporite                   | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          |
| Silina A1 Carbonate and A1 Evaporite  | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 12         | 9          |
| Silina A0                             | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          | 0          |
| Guelph - Fossil Hill                  | 156        | 165        | 78         | 65         | 60         | 77         | 112        | 138        | 134        |
| Cabot Head                            | 13         | 15         | 16         | 8          | 7          | 9          | 16         | 16         | 11         |
| Manitoulin                            | 13         | 15         | 16         | 8          | 7          | 9          | 8          | 8          | 14         |
| Upper Ordovician Shale                | 378        | 435        | 449        | 478        | 466        | 268        | 373        | 360        | 340        |
| Middle Ordovician Limestone and Shale | 221        | 254        | 263        | 279        | 273        | 139        | 216        | 221        | 226        |
| Shadow Lake                           | 0          | 0          | 0          | 0          | 0          | 0          | 3          | 0          | 0          |
| Cambrian Sandstone                    | 5          | 6          | 6          | 6          | 6          | 3          | 0          | 7          | 7          |

\*Cambrian samples reported by Sherwood Lollar et al. (1994)

| Sample                                | S29 * | S34 * | S35 * | S41 * | S37 * | S38 * | S40 * | S30 * | S31 * | S32 * | S33 * | S36 * | S39 * |
|---------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Quaternary Drift                      | 66    | 51    | 54    | 54    | 38    | 54    | 5     | 54    | 59    | 59    | 59    | 59    | 0     |
| Erosion                               | 1000  | 1000  | 1000  | 1000  | 1000  | 1000  | 1000  | 1000  | 1000  | 1000  | 1000  | 1000  | 1000  |
| Devonian Shale                        | 45    | 100   | 68    | 68    | 89    | 68    | 59    | 0     | 0     | 0     | 0     | 0     | 0     |
| Devonian Dolostone                    | 126   | 120   | 121   | 121   | 95    | 121   | 119   | 0     | 0     | 0     | 0     | 0     | 0     |
| Upper Silurian Dolostone              | 0     | 75    | 81    | 81    | 46    | 81    | 41    | 0     | 0     | 0     | 0     | 0     | 0     |
| Silina G                              | 36    | 7     | 8     | 8     | 7     | 8     | 7     | 1000  | 0     | 0     | 0     | 0     | 0     |
| Silina B to Silina F                  | 62    | 69    | 113   | 113   | 90    | 113   | 69    | 391   | 69    | 69    | 69    | 69    | 0     |
| Salina B Evaporite                    | 28    | 33    | 0     | 0     | 22    | 0     | 42    | 0     | 0     | 0     | 0     | 0     | 0     |
| Silina A2 Carbonate                   | 0     | 0     | 18    | 18    | 20    | 18    | 19    | 18    | 12    | 12    | 12    | 12    | 0     |
| Silina A2 Evaporite                   | 29    | 25    | 6     | 6     | 1     | 6     | 4     | 6     | 0     | 0     | 0     | 0     | 0     |
| Silina A1 Carbonate and A1 Evaporite  | 17    | 11    | 27    | 27    | 12    | 27    | 5     | 27    | 0     | 0     | 0     | 0     | 0     |
| Silina A0                             | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
| Guelph - Fossil Hill                  | 90    | 95    | 80    | 80    | 115   | 80    | 141   | 127   | 107   | 107   | 107   | 107   | 118   |
| Cabot Head                            | 24    | 36    | 34    | 34    | 35    | 34    | 38    | 257   | 13    | 13    | 13    | 13    | 15    |
| Manitoulin                            | 10    | 10    | 13    | 13    | 13    | 13    | 11    | 0     | 13    | 13    | 13    | 13    | 9     |
| Upper Ordovician Shale                | 302   | 303   | 257   | 257   | 254   | 257   | 235   | 267   | 373   | 373   | 373   | 373   | 335   |
| Middle Ordovician Limestone and Shale | 258   | 265   | 267   | 267   | 265   | 267   | 243   | 18    | 218   | 218   | 218   | 218   | 189   |
| Shadow Lake                           | 1     | 2     | 0     | 0     | 1     | 0     | 0     | 0     | 0     | 0     | 0     | 0     | 0     |
| Cambrian Sandstone                    | 9     | 30    | 18    | 18    | 18    | 18    | 35    | 0     | 5     | 5     | 5     | 5     | 7     |





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