

Geologic Processes that Control Sourcing and Migration of Subsurface Helium



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Abstract

There is an ever-pressing need to find more helium (He) because 1) it is an essential resource for modern life, 2) reserves are dwindling faster than He accumulations are discovered, and 3) new He projects are delayed. The motivation for this work is to provide updated frameworks on the geologic processes and migration mechanisms of He in the mid-continent USA, using noble gas geochemistry, structural geology and geophysics. The Colorado Plateau field area (Four Corners area), USA was chosen to represent a moderate tectonic activity environment, and Yellowstone (and its environs), USA, were chosen to represent a very tectonically active region and to investigate the impact of heat on gas release. In the Four Corners area, utilizing bulk gas and isotopes of hydrocarbons, non-hydrocarbons, and noble gases (n=31), we construct mass balance and noble gas fractionation models that provide evidence for advective fault-controlled systems responsible for basement sourced He accumulations. Regarding Yellowstone, utilizing heat flow data, bulk gas, and isotopes of non-hydrocarbons and noble gases (n=43), we quantify gas origin, fluid flow, and heat influence in a regional context using noble gas heat and fractionation models. We show a poor relationship regarding He and heat flow on a regional scale for Yellowstone, and we propose that localized heat sources are important in releasing He trapped in minerals. Our prediction of fault-controlled He-systems in the Four Corners area is corroborated with high-resolution geophysical data that shows a strong non-random relationship with He-rich occurrences and structural features (faults/intrusions) and historical He-well data (n=94). Based on the distributions of these relationships, we create a regional probabilistic predictive He map to reduce exploration risk. Additional work utilizing soil gas data (n=1974), was used to construct a higher-resolution localized predictive model calibrated with real-world data illustrating areas that are higher-likelihood of containing He-rich gas.

Extended Abstract

From the alpha decay of uranium (U) and thorium (Th), radiogenic ^4He is naturally produced in Earth's crust. Helium (He) has unique thermodynamic properties required for the medical imaging industry, science and engineering, manufacturing, and space exploration, and currently is in increasingly high demand due to its use in many high-tech applications. Despite its great economic value, the mechanisms of helium's sources, migration and retention in sedimentary basins remain poorly understood. The primary motivation for this work is to provide updated frameworks on the geologic processes and migration mechanisms of He-system in the mid-continental region of the USA using noble gas geochemistry, structural geology and geophysics, to ultimately reduce subsurface He exploration risk. Our field areas (Colorado Plateau and Yellowstone) were chosen to represent different levels of tectonic/igneous activity. The Colorado Plateau, USA (Four Corners area) represents an environment that although relatively undeformed has undergone episodes of moderate tectonic activity. Yellowstone and its surrounding environs, USA, represents an environment that is very tectonically active and strongly influenced by the Yellowstone plume.

The Four Corners area on the Colorado Plateau, USA, has had historically economic He-rich gas ($>0.3\%$) often from Paleozoic intervals in its gas fields, but the details of the He-system were unknown. Conducting a regional geologic evaluation, we notice that most of the He-rich historical wells are located near large-scale structural features (i.e., basement faults, and shear zones). Utilizing stainless steel cylinders and copper tubes, natural gas was sampled ($n=31$) from actively producing oil/gas wells from five fields: Ratherford, Tootie Dome, Navajo Springs, Pinta Dome, and Dineh-Bi-Keyah. The gas was analysed to obtain abundance and isotopic data for non-hydrocarbons, hydrocarbons, and noble gas data. He concentrations vary from 0.01% to 7.9%. Breaking the gas data into two major groups, hydrocarbon-rich and He-rich, we construct multiple models to explain noble gas and bulk gas signatures. Firstly, to account for the observed noble gas elemental and isotopic signatures for the hydrocarbon-rich data, we constructed multi-stage gas, water, and oil equilibration models. A closed system oil/water equilibration model and subsequent admixture of air can explain the noble gas signatures of the oil-dominated systems. Concerning the He-rich systems, we noticed a strong consistency with the $^4\text{He}/\text{N}_2$ ratios (also consistent with regional mean values), which indicates that there is no significant fractionation and there is likely a common crustal source of the two gases. This is in contrast to the values observed of $^{20}\text{Ne}/^{36}\text{Ar}$ ratios, which are highly fractionated. The interpretation of this decoupled phenomena, is that there is likely a tectonically controlled migration mechanism (e.g., faults) that are allowing/controlling gas release of He and N_2 from the basement into shallower sediments. This advective driven flux of He and N_2 from depth is interpreted to oversaturate the reservoir, eventually reaching a degassing point to form a He-rich and N_2 -rich gas cap. All the while, $^{20}\text{Ne}/^{36}\text{Ar}$ that is introduced into the system via aquifer recharge, is undergoing extensive fractionation due to episodes of redissolution into the groundwater (migration). Additionally, mass balance models were constructed to determine the impact of different sources of He production, namely external and internal production. We show the volume of rock required to have produced He in the reservoir to be significantly larger than the current volume of the reservoir immediately underneath the field. We determine that internal production (in-reservoir decay of U and Th) is too minor to account for any significant volumes of the He original gas in place. We show that He is likely sourced primarily from the Precambrian granitic basement utilizing volumes beneath the field outline, consistent with the degree of water contact. Given that it is known that deep crustal faults in the Precambrian basement are in close proximity to the He-rich gas fields, this indicates there is strong possibility that faults are serving as primary migration conduits via advective fluid flow (i.e., fracture zones could be facilitating crustal gas mobilization/transport of He).

Now, that we have examined the moderately tectonic active portion of the Colorado Plateau, we transition to a more tectonically active zone in the USA, the Yellowstone caldera and its surrounding environs, to explore the relationship between heat and He. Although the general relationship has been well established in certain geologic environments, there have been few works to date that explore natural systems with implications to He exploration to test the validity of how

igneous processes influence gas release/storage from crustal rocks. By sampling gas from hot springs in and around Yellowstone (n=43), we quantitatively study the relationship between He signatures and thermal aureoles, using bulk gas and noble gas geochemistry combined with heat flow data. More specifically, the study's goal was to assess the validity of the utilization of a distance to heat source He sweet-spot model, by quantifying gas origin and fluid flow in a regional context. Natural gas samples were analysed with a static mass spectrometer for noble gas isotopes, and a dynamic mass spectrometer for bulk gases. After interpreting our data, we constructed heat-noble gas models and observed convective and degassing processes affecting most samples in the hydrothermal system that are being influenced by air saturated water (ASW) dilution and various boiling episodes. Analysing various noble gas solubility fractionation models, we observe that the majority of samples can be explained by an open system gas degassing/stripping scenario for the ASW derived noble gases as well as some influence for radiogenic He and Ar. Additionally, we observe potential evidence for minor contributions of free molecule diffusive fractionation influencing radiogenic Ar and He. We also confirm the relationship between ^4He and groundwater (i.e., groundwater transports dissolved He until it gets degassed) looking at ^{20}Ne isotopes. A geospatial heat-He analysis was completed to test the validity of a He-sweet model and found that there are no significant patterns regarding He%, heat flow, and distance to the Yellowstone caldera, and there is only a narrow range of moderate heat flow values associated with the samples outside of Yellowstone. This seems counterintuitive that there would be no noticeable pattern, but perhaps the heat-He relationship is more localized. Thus, to examine the effects of localized heat patterns, we utilize a 1-D heat diffusion model that computes geothermal temperature gradients and how they change in response to intrusions. Observing the outputs of the model, we see that if intrusions are present they can definitely elevate the temperature of surrounding rocks in the shallow crust to the point where the temperature exceeds the closure temperature of He, thus releasing trapped He into the groundwater, where it can be transported through either diffusion or advection fluid flow. Considering the very active neotectonics of Yellowstone and the surrounding regions and our noble gas fractionation models, we advocate that advection (buoyancy driven vertical migration) is likely more dominant in transporting fluids from depth to the shallower zones in the crust. Therefore, we report that an approach of only using distance from an active volcanic centre is ill-advised to find He sweet-spot zones, and instead exploration strategies should incorporate models focusing on localized heat flow and isotopic geochemistry to constrain degrees of groundwater interaction.

Transitioning back to the Four Corner's area of the Colorado Plateau, we were fortunate to have the chance to work with high-resolution geophysical data to test our predictions in chapter 2 of the importance of fault advective fluid flow influencing He-rich systems. The data sharing was a part of a collaborative effort to work on theoretical models during the COVID-19 lockdown which closed the university and delayed field work (i.e., Yellowstone). An unknown for these Four Corner He-systems was the overall role of structural features in focusing economic amounts of He from deep seated He source rocks to shallow accumulations. Using historical He data from the United States Geological Survey (USGS) (n=94), we test the correlation between economic He wells (>0.3 He %) and structural features utilizing a new high-resolution aeromagnetic survey. An intrusion map, a depth-to-basement map with basement lineaments and faults, and a flattened basement structural high map, were created using Werner deconvolution algorithms. More specifically, the maps were constructed by combining gravity, magnetic, and topography data, with gravity and magnetic depth profiles. Using statistical tests (analysis of variance and generalized linear models) we show that a non-random process is controlling the relationship between He and structural features, namely basement faults and intrusions. We also show that 88% of high-He wells occur <1 km from basement faults; and 85% of high-He wells occur <1 km from intrusions. This is represented with an inverse relationship, as economic He % increases, the distance to the structural features decreases. Strong statistical correlations of basement faults and intrusions to economic He wells suggests that faults/intrusions are facilitating He migration via advective transport. Additionally, the role of gas phase buoyancy and structural trapping is noted, as 88% of all economic He wells are found on a basement high structure; and concerning the remaining wells, over 90% are likely influenced by local domal structures given they are less than 1 km from intrusions. To visualize these relationships, we create probabilistic models for both intrusions and basement faults and subsequently describe the processes facilitating He migration associated with each (i.e., activation of deep basement faults along

zones of weakness, and igneous activity creating increased supplemental shallow fracturing). The probabilistic models, which are based on the distances from economic He wells to the structural feature of interest, illustrate target zones around structural features. Maps are colour coded to indicate a low or high probability of encountering economic He in relation to a structural feature. We then combined the two fault and intrusion probability maps to create a predictive framework to illustrate how a probabilistic approach can be used as a predictive model to improve He exploration success by targeting zones of intersection of basement faults and intrusions within basement structural highs.

Building off the work in chapter 4, we incorporate new soil gas He survey data (n=1974) taken from areas on the Colorado Plateau, Four Corners area, to assess if surface soil surveys can be an effective exploration tool for He when combined with geophysical data. For this work, Akah Nez Field, Beautiful Mountain Field, Porcupine Dome area, Rattlesnake Field, Tom area, Tohache Wash area, and White Rock area, were sampled. We construct structural maps of potential He reservoirs at depth and examine geologic relationships utilizing 2D seismic, well logs, and geophysical potential field data. We observe patterns in the soil gas data in several of the fields (Rattlesnake, Beautiful Mountain, Porcupine Dome, and Tom) as evidence for deep basement faults propagating to the surface/near surface (i.e., there is likely a leaky reservoir seal). In other instances, we observe evidence for fracturing at the crest and flank of reservoir structures likely due to differential compaction (Tohache Wash, Beautiful Mountain, Porcupine Dome, Tom, Akah, and White Rock). Using internal and external production rates and original gas in place calculated volumes, we calculate approximate ages of reservoirs. We subsequently calculate the amount of He that is dissolved in water that has been lost via diffusion only using a 1-D diffusion loss model. We conclude that for the depleted fields (Rattlesnake and Beautiful Mountain), diffusion is likely not a major contributor to He loss, meanwhile for several other fields (Tohache Wash, Akah Nez, and Tom), diffusion appears to play a more dominant role. We advocate that although advection has been a preferred mechanism to charge He accumulations, it is unfavourable in He loss scenarios, because the rate of loss is likely too great compared to the external fluxes of He entering the reservoir and those produced internally in the reservoir. Thus, we propose that diffusion dominated loss systems are most ideal for preserving He for longer periods of time once an accumulation has already formed. Analysing the data, we conclude the Tohache Wash area is the most prospective area given its highest soil gas signatures, likely diffusion dominated leak system, and repeated high He well tests (1969 and 2016). Given we have a much higher resolution of coverage with soil gas grids, we construct an upgraded predictive model calibrated with real-world data for the Tohache area to determine which components are most significant in controlling the He accumulation, and to predict where future He accumulations might be located in adjacent areas. More specifically, we use a novel technique to calibrate a predictive He model utilizing soil gas geochemistry and structural features derived from high-resolution geophysical data using Bayesian regression techniques, which may be translated to other areas outside of the Four Corners Area, USA.

Declaration

I declare that this thesis was composed by myself, that the work contained herein is my own except where explicitly stated otherwise in the text, and that this work has not been submitted for any other degree or professional qualification except as specified.

The work presented in chapter 2, was published in Chemical Geology as Halford, D.T., Karolytè, R., Barry, P.H., Whyte, C.J., Darrah, T.H., Cuzella, J.J., Sonnenberg, S.A., and Ballentine, C.J. High helium reservoirs in the Four Corners area of the Colorado Plateau, USA. Chemical Geology 596, 120790, doi: 10.1016/j.chemgeo.2022.120790 (2022). The project was conceived by DTH, RK, PHB, JJC, SAS, and CJB. DTH managed the project, and prepared the first draft of the manuscript. CJW and THD collected and analysed the samples. Noble gas models and mass balance models were developed by DTH, RK, PHB, and CJB. All authors contributed to the final manuscript.

The work presented in chapters 3-5 is not yet published, but collaborative in nature. The appropriate statement of authorship asserting I made substantial contributions to each manuscript is attached at the end of each work.

Daniel Halford

Acknowledgments

PATER noster, qui es in caelis;

sanctificetur nomen tuum:

Adveniat regnum tuum;

fiat voluntas tua,

sicut in caelo, et in terra.

Panem nostrum cotidianum da nobis hodie:

Et dimitte nobis debita nostra,

sicut et nos dimittimus debitoribus nostris:

et ne nos inducas in tentationem: sed libera nos a malo.

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Selected Abbreviations

ANOVA	Analysis of variance
API	American petroleum institute
ASTER	Advanced Spaceborne Thermal Emission and Reflection Radiometer
Ar	Argon
ASW	Air saturated water
BF	Bayes factor
BLM	Bureau of Land Management
df	Degrees of freedom
GLM	Generalized Linear Model
GOR	Gas-to-oil ratio
GPS	Global positioning system
He	Helium
IDW	Inverse distance weighted
IGRF	International geomagnetic reference field
IUPAC	International Union of Pure and Applied Chemistry
K ^d	Henry's constant dimensionless
Kr	Krypton
LNG	Liquefied natural gas
MAAT	Mean annual air temperature
MORB	Mid-ocean ridge basalts
Ne	Neon
OHIP	Original helium in place
OGIP	Original gas in place
OOIP	Original oil in place
QMS	Quadrupole Mass Spectrometer
R _a	Atmospheric helium isotope ratio
SFT	Split flight tube
SG	Specific gravity
SMU	Southern Methodist University
SRTM	Shuttle Radar Topography Mission
STP	Standard temperature and pressure
RTP	Reduction-to-the-Pole
QMS	Quadrupole mass spectrometer
USGS	United States Geological Survey
VNA	Virtual Network Analysis
VPDB	Vienna Pee Dee belemnite
WHOI	Woods Hole Oceanographic Institution
Xe	Xenon
YSH	Yellowstone hotspot

Selected Units

API	American petroleum institute gravity units
atm	Atmosphere (pressure)
bar	Bar (pressure)
cc/cc or cm ³ /cm ³	Cubic centimetre of gas species (XX) per 1 cubic centimetre of air
cm	Centimetre
C _p	Heat capacity of water
°C	Celsius
°F	Fahrenheit
kft	Thousand feet
km	Kilometre
g	Gram
Ga	One billion years ago
GPa	Gigapascal
°K	Kelvin
Kg	Kilogram
Kpa	Kilopascal
Ma or mya	One million years ago
mbar	Millibar
Mcf or mscf	Thousand standard cubic feet
Mol %	Molar percent
mW	Milli Watt
m	Metre
Pa	Paschal
ppb	Parts per billion
ppm	Parts per million
psi	Pounds per square inch
rcf	Reservoir cubic feet

Length Conversion Table

	cm	meter	km	ft	mile
1 centimeter =	1	10 ⁻²	10 ⁻⁵	3.281 × 10 ⁻²	6.214 × 10 ⁻⁶
1 meter =	100	1	10 ⁻³	3.281	6.214 × 10 ⁻⁴
1 kilometer =	10 ⁵	1000	1	3281	0.6214
1 inch =	2.540	2.540 × 10 ⁻²	2.540 × 10 ⁻³	8.333 × 10 ⁻²	1.578 × 10 ⁻⁵
1 foot =	30.48	0.3048	3.048 × 10 ⁻⁴	1	1.894 × 10 ⁻⁴
1 statute mile =	1.609 × 10 ⁵	1609	1.609	5280	1

Area Conversion Table

	meter ²	cm ²	ft ²	mile ²
1 square meter =	1	10 ⁴	10.76	3.86 × 10 ⁻⁷
1 square cm =	10 ⁻⁴	1	1.076 × 10 ⁻³	3.86 × 10 ⁻¹¹
1 square foot =	9.290 × 10 ⁻²	929.0	1	3.59 × 10 ⁻⁸
1 square inch =	6.452 × 10 ⁻⁴	6.452	6.944 × 10 ⁻³	2.49 × 10 ⁻¹⁰
1 square mile =	2.59 × 10 ⁶	2.59 × 10 ¹⁰	2.788 × 10 ⁷	1

1 square mile = 27,878, 400 ft² = 640 acres; 1 acre = 43,560 ft²; 1 barn = 10⁻²⁸ meter²; 1 hectare = 2.417 acres

Volume Conversion Table

	meter ³	cm ³	liter	ft ³
1 cubic meter =	1	10 ⁶	1000	35.31
1 cubic cm =	10 ⁻⁶	1	1.000 × 10 ⁻³	3.531 × 10 ⁻⁸
1 liter =	1.000 × 10 ⁻³	1000	1	3.531 × 10 ⁻²
1 cubic foot =	2.832 × 10 ⁻²	2.832 × 10 ⁴	28.32	1
1 cubic inch =	1.639 × 10 ⁻⁵	16.39	1.639 × 10 ⁻²	5.787 × 10 ⁻⁴

Temperature Conversion Table

From/To	Celsius	Fahrenheit	Kelvin
Celsius	1	1.8	273.15
Fahrenheit	-17.7778	1	255.92778
Kelvin	-272.15	-459.67	1

Pressure Conversion Table

	atm	dyne/cm ²	Inch of water	Nt/meter ²	lb/in ² (psi)	lb/ft ²
1 atmosphere =	1	1.013 × 10 ⁶	406.8	1.013 × 10 ⁵	14.70	2216
1 dyne per cm ² =	9.869 × 10 ⁻⁷	1	4.015 × 10 ⁻⁴	0.100	1.450 × 10 ⁻⁵	2.089 × 10 ⁻³
1 inch of water at 4°C ^a =	2.458 × 10 ⁻³	2.491	1	249.1	3.613 × 10 ⁻²	5.202
1 newton per meter ² =	9.869 × 10 ⁻⁶	10	4.015 × 10 ⁻³	1	1.450 × 10 ⁻⁴	2.089 × 10 ⁻²
1 pound per in ² =	6.805 × 10 ⁻²	6.895 × 10 ⁴	27.68	6.895 × 10 ³	1	144
1 pound per ft ² =	4.725 × 10 ⁻⁴	478.8	0.1922	47.88	6.944 × 10 ⁻³	1

^a Where the acceleration of gravity has the standard value 9.80665 meter/sec²; 1 pascal = 1 Nt/meter²;

1 bar = 106 dyne/cm²; 1 millibar = 10³ dyne/cm²; 1 torr (mm Hg at 0°C) = 1.93367 × 10⁻² lb/ft²

Chapter 1

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1.1 Introduction

1.1.1 Motivation

Traditionally, helium (He) gas was found accidentally as a secondary by-product of hydrocarbon exploration and not fully utilized due to unfavourable economics (Sears, 2015). Historically, when an exploration well encountered pockets of He gas, the He gas was largely ignored or simply left to vent to the atmosphere because it would not burn, essentially wasting a precious natural resource (Sears, 2015). Often times, He in the gas stream is only a small percentage of the overall gas composition. The main associated gases for He-systems can be CO₂, N₂ or CH₄, or a combination of these gases (Danabalan et al., 2022). Due to an increased utility for He gas, exploration efforts have begun to target He as a primary standalone resource, thus the renewed effort to compile elements of the He system.

The He-system has been studied either directly or indirectly for well over a century in an effort to define a set of parameters (geologic elements and processes) that all act together to aid in the creation and accumulations of economic levels of He gas in subsurface reservoirs (Ballentine and Shewood-Lollar, 2002; Brennan et al., 2016; Broadhead, 2005, 2012; Broadhead and Gillard, 2004; Brown, 2010; Danabalan, 2017; Halford et al., 2022; McDowell et al., 2017; Moor and Esfandiari, 1971; Munnerlyn and Miller, 1963; Olukoga, 2016; Rauzi and Fellows, 2003; Rauzi, 2003; Sears, 2015; Rogers, 1921; Yurkowski, 2016). Based on these previous works, a formal definition of a He system is any “subsurface natural gas system, and it’s associated geological processes and elements that allow the accumulation of economic levels of He (>0.3% for direct and secondary extraction, and >0.04 for LNG operations), in the gas stream beyond the ubiquitous trace amounts found within the Earth’s mantle, atmosphere and crustal sources” (Fig. 1.1) (Halford, 2018; Boreham et al., 2018).

The motivation for this work is to provide updated frameworks concerning the geologic elements and processes (sources and migration mechanisms) of subsurface He in the mid-continent USA, using noble gas geochemistry, structural geology and geophysics. The overall goal with the research of the He system is to mitigate risk when exploring for He as a primary target in the subsurface.

1.1.2 Overview

- Chapter 1 – Consists of general project motivation, He introduction, and comprehensive noble gas geochemistry literature review.
- Chapter 2 – Focuses on using noble gas and bulk gas fractionation modelling and mass balance calculations to quantify the source of He (i.e., the basement), and advective fluid flow migration pathways (i.e., basement faults) of the Four Corners area He-rich gas fields. Work is published in Chemical Geology (Halford et al., 2022).
- Chapter 3 – Using noble gas and bulk gas geochemistry from gas samples collected from hot springs in and around Yellowstone, USA, we explore the relationship between He and heat. We were interested to explore the effect that the Yellowstone hotspot would have on the surrounding crustal rocks and how that impacts gas release or not for He sweet spot modelling.
- Chapter 4 - Using potential field data (gravity/magnetics) combined with geochemical data in the Four Corners area, USA, a geospatial probabilistic model focusing on the relationship between He, basement faults and intrusions was used to create a predictive framework that can be used to mitigate He exploration risk.
- Chapter 5 - We explore structural features relationships with soil gas He surveys, and geophysical data; and also investigate vertical migration mechanisms facilitating He loss from reservoirs in the Four Corners area, USA. We present a novel technique to calibrate an updated predictive He model.
- Chapter 6 – Consists of conclusions from each chapter and future work recommendations.

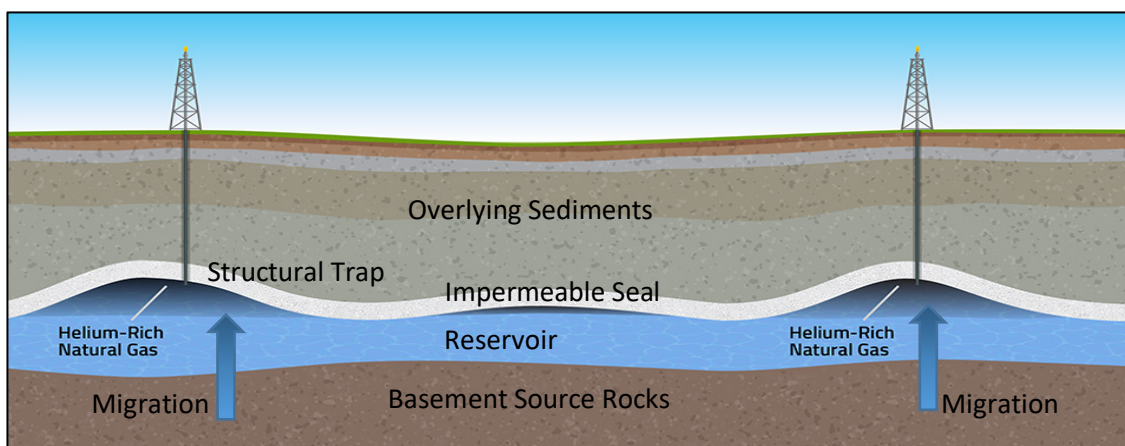


Figure 1.1: Schematic showing the main geologic elements and processes of a helium system (mod. Powell, 2021).

1.1.3 Helium System

The main elements of the He system (source, migration, reservoir, trap, seal) and processes (migration, accumulation) are derived from the petroleum system (Dow, 1974; Demaison, 1984; Meissner et al., 1984; Ulmishek, 1986; Magoon, 1987, 1988, 1989a, 1989b, 1992a, 1992b; Magoon and Dow, 1994a, 1994b; Perrodon, 1992; Magoon, 1995; Magoon and Beaumont, 1999). Despite similarities in the terminology of elements and processes of the two systems, there are striking differences comparing the science behind several aspects of helium and petroleum systems.

He source rocks do not require any organic matter like petroleum source rocks do, instead they require copious amounts of uranium (U) and thorium (Th) (e.g. the minerals in the granitic basement), which will eventually decay and emit α -particles which create He (Ballentine et al., 2002; Oxburgh and O’Nions, 1987; Ozima and Podosek, 2002). Maturation of a He accumulation, is controlled by the production rates of radiogenic He, which are dependent on time and the volume of rock (Ballentine et al., 2002; Oxburgh and O’Nions, 1987; Ozima and Podosek, 2002). Stage one migration out from a source rock mineral is dependent on closure temperature, mineral degradation, and faulting (Ballentine and Burnard, 2002). These variables influence how the α -particle (He nucleus) will be expelled from the host mineral and subsequently dissolve into a groundwater solution as He (once it collects nearby electrons). Stage two migration requires a geologic event (i.e., faulting, igneous activity) to create pathways for advective fluid flow with some amount of diffusion to transport He from the relatively impermeable basement (i.e., source rock) into overlying sediments, essentially acting as a funnelling/concentrating process (Broadhead and Gillard, 2004; Brown, 2010; Cheng, 2020; Danabalan et al., 2022). Stage three migration focuses on lateral migration influenced by groundwater-gas interactions with another migrating carrier gas phase (often CO₂, N₂ or CH₄) influencing the He, as well as by other forces such as stripping (removal of dissolved gases in groundwater into a gas phase) and buoyancy (Ballentine and Lollar, 2002; Danabalan et al., 2022; Mtili et al., 2021). It is important to note that while other gas phases are necessary to exsolve dissolved He into the gas phase and further accumulation of He, the other gas phases must not be too dominant in that they effectively dilute out the He to uneconomic quantities (Brown, 2010). Accumulation in the gas phase (from an original dissolved state) is considered to be controlled by gas

phase partitioning governed by the laws of solubility. The reservoirs, traps, and seals are largely comparable to those of a petroleum system, in that a porous and permeable reservoir beneath a tight caprock or trap (structural, stratigraphic, or both) is ideal. Additionally, overburden lithologies are not as critical for petroleum systems, although some added benefits for He-systems could be the protection of the seal (increased capillary pressure) (Rice, 2022).

1.1.4 Helium's Applications

Despite helium's relative rarity on Earth, a wide range of applications have been developed that capitalize on helium's unique properties such as having the lowest boiling and melting points, high thermal conductivity, high ionization potential, small molecular size, light mass, unreactive nature, and low viscosity (Fig. 1.2). The main sectors that are heavily dependent on He are those related to cryogenics, lifting, electronics, optical fibres, and industrial applications (National Research Council, 2000, 2010). Within the medical community, magnetic resonance imaging (MRI) devices rely on He to keep systems extremely cold and to keep the magnetic current superconductive allowing the current to travel essentially resistance-free. Due to He's light mass, agencies such as the USA Department of Energy and National Aeronautics and Space Administration use He in weather related projects in the form of balloons and dirigible-based blimps (Sears, 2015). Industrial applications range from using He for welding, leak detection due to its unreactive nature, as well as providing controlled atmospheres for the manufacturing industry (Chan, 2013). Some applications in the electronics sector range are semi-conductors due to He's thermal conductivity, as well as fibre optics, computing data centres, and even quantum computing (Boreham et al., 2018). There are additional applications within the emerging market of space exploration also capitalizing on He's unique features to aid in rocket purging and leak detection due to its small molecular size (National Research Council, 2010).

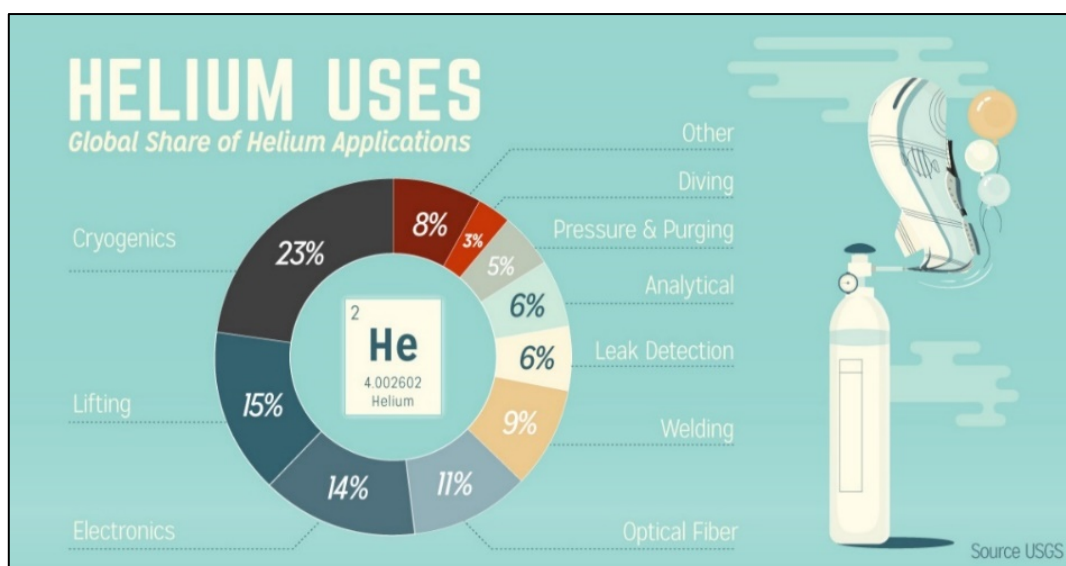


Figure 1.2: Helium’s global share of applications by sector (USGS, 2023; Blaisse, 2023).

1.1.5 Projections of Helium Supply and Demand

One of the most obvious market stressors concerning global and USA based He supply was caused by the 2018 final sale of conservation He (for private non-government users) held in the Cliffside Field, Texas, USA, which is operated by the Bureau of Land Management (BLM). There will likely be an increased stress on the He market (i.e., decreased supply) given that major projects around the world are several years out from fully coming online. Additional factors contributing to a perceived He shortage is 1) the Russian invasion of Ukraine (Linde withdrew from Amur and removed future supply), 2) bypassing of liquefied natural gas (LNG) processes in Algeria and He recovery and instead piping directly to Spain (reduction of feed gas for He plants), 3) depletion of feed gas for an Australian plant in Darwin, and 4) additional planned maintenance in Qatar (Blaisse, 2023). There have been increased efforts in the USA and some parts of Canada to drill for pure He plays, but many of these projects simply need more time to produce a significant gas resource (Edison, 2021). Pure He plays will likely enter into the spotlight more frequently as climate target policies are enacted as >95% of recent He is produced as a by-product of gas or LNG production (Edison, 2021). Additional constraints hampering He gas production levels are the capital, effort, time, and sometimes public opposition that are associated with securing the proper permissions, leases, and property rights. Due to the oligopolistic nature of the He market, if one of the producers were to cease production, there could be devastating ripple effects felt down the supply chain.

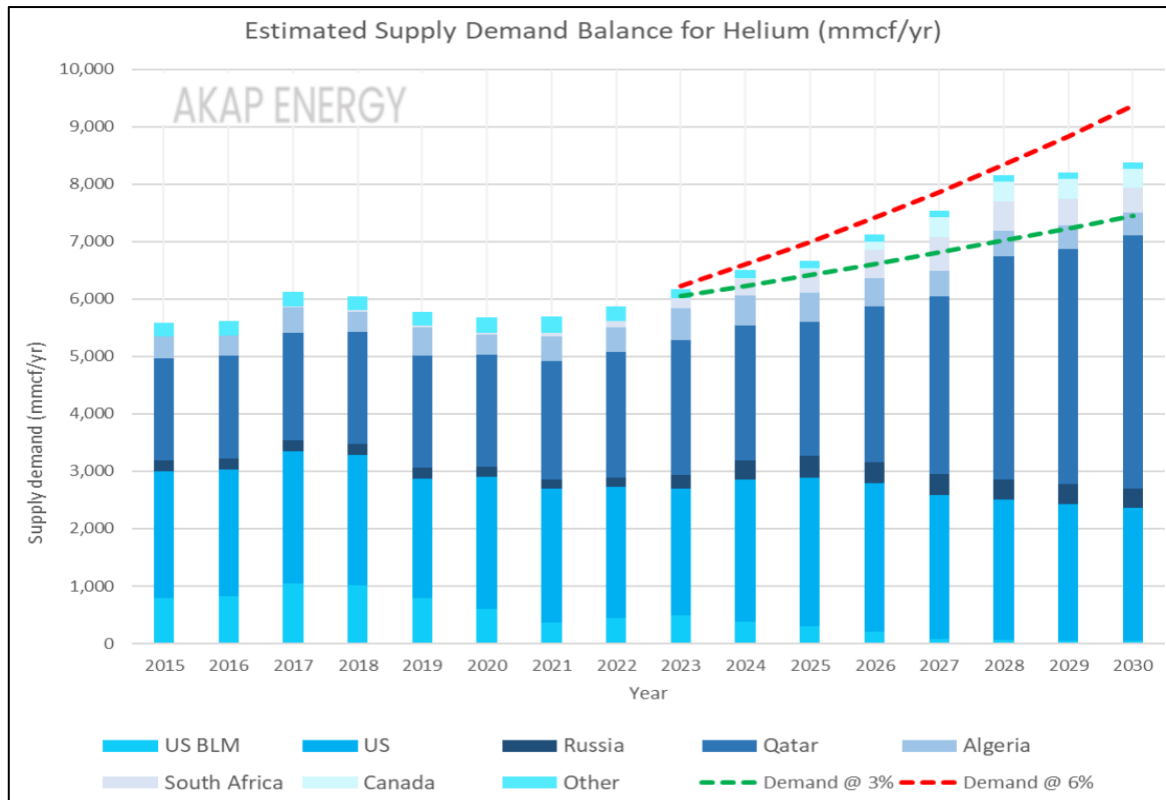


Figure 1.3: Estimated supply and demand balance of helium (AKAP Energy, 2023).

Edison (2019, 2021) states only five major entities in the early 2020's (Bureau of Land Management, LaBarge, Hugoton, Algeria, and Qatar) account for the majority of global upstream He. Since the Bureau of Land Management facility and the giant Hugoton Field are coming to the end of their lives, it is feared that if new ventures do not come online to make up the lost product there could be dire consequences. As such, there have been attempts to replace He in modern applications, but because of helium's unique properties, it is ultimately irreplaceable for the time being. This irreplaceability results in a continued increase in demand for its main markets of science/engineering, MRIs, pressurizing/purging, space related technology, and semiconductors (National Research Council, 2000, 2010; Edison, 2019, 2021).

Historical evidence from 2011-2013 when there was a He shortage and subsequent price spike, which incentivized new supply and drove prices back down to normal levels, shows that demand destruction leads to the remaining demand being more inelastic to price movements (Edison, 2019). Therefore, it is inferred, the He market is expected to act as steady, price inelastic demand growth model. Edison (2019) also states that the current supply constraints ought to further support

pricing and could possibly encourage market increases. Additionally, it was observed that the COVID-19 pandemic accelerated He market balancing due to decreased demand down 10% in 2020 and shortened undersupply in the preceding years (Edison, 2021).

Figure 1.3 illustrates that without increased primary He discoveries, the market will see increased demand and will be hard-pressed to meet the demand at 3% or a more aggressive 6% increase. The potential deficit will likely impact smaller players initially, with ripple effects felt through the market. Edison (2019, 2021) states that in the long run, new projects will yield increased He levels to potentially meet an assumed annual demand growth of 1.5%-4%, but any unforeseen technical, political, or biological (e.g., COVID-19) delays could drastically exacerbate a deficit. It is speculated that a market with virtually no growth could potentially balance the lack of supply, but this seems highly unlikely (Edison, 2019).

1.1.6 Helium's pricing

Because He is not a traded commodity, and the pricing is usually based on long-term and confidential contracts, the exact market pricing for He gas is difficult to accurately ascertain. This often results in opaque pricing because there are only a handful of suppliers and industrial gas buyers (Edison, 2021; AKAP energy, 2023). Given there are no substitutes for He in many cases, most He users are termed price insensitive. Price spikes in the past have resulted from market susceptibility to supply disruption. Another consequence of He shortages and price increases, are losses in global He demand. More specifically, 10% of global demand was estimated to have been lost due to the shortages and price doubling from 2011-2013 (AKAP Energy, 2023). Moreover, considering the volatility of the market, the need for long term contracts (1-7 years) that secure a steady and pre-allocated supply of the resource is very important to many users (AKAP energy, 2023). This translates to the fact that spot prices are not as relevant for producers as they would be for oil/gas. Given the security of cash flows, production and not spot prices is more bankable.

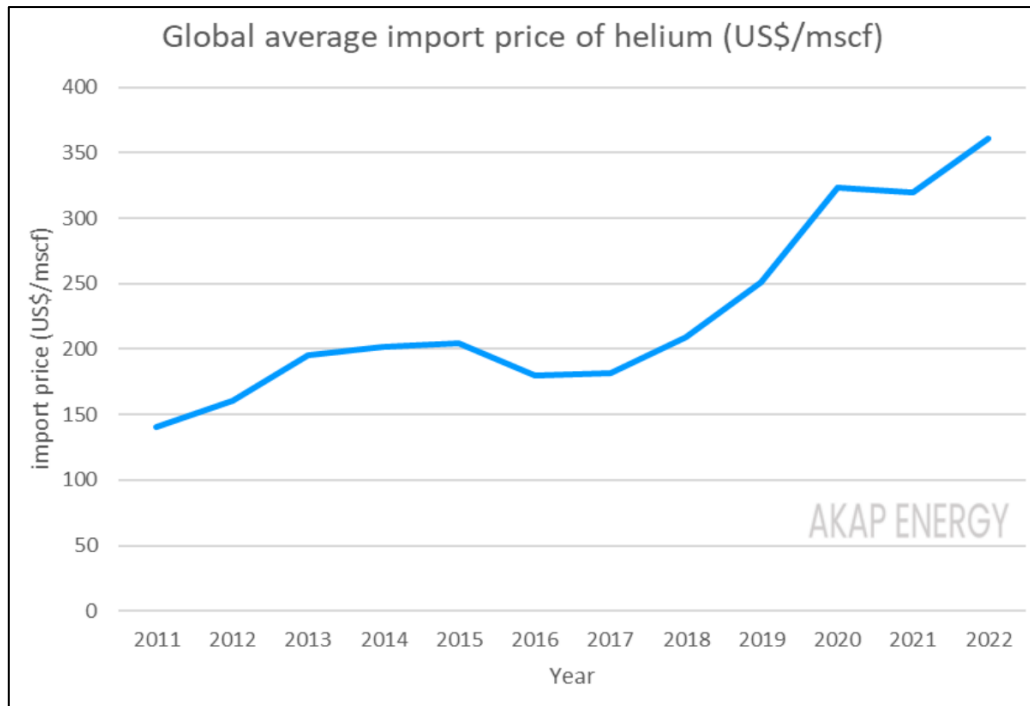


Figure 1.4: Global average import price of high purity He (AKAP Energy, 2023).

Historical data of He prices (shown in \$USD per thousand standard cubic foot or Mcf of gas) from 2000 to present by the USGS show an increasing price trajectory (USGS, 2000-2023). Regarding recent price history, according to the BLM (2023), 2017's fiscal year crude helium's price for government entities was \$86.00/Mcf (in-kind helium) and \$119.00/Mcf for non-government entities (conservation He). These prices are averages at auction, meaning that depending on the bidding and market conditions, the price can fluctuate above the set price. Initial statements from the BLM reported that for the fiscal year 2019 crude He auction (held in August, 2018), the He price jumped up to an average of \$95.00/Mcf for government He and \$279.95/Mcf for private non-government He. This large private price jump was due to aggressive bidding, a desire to increase inventory for future years, and the fact that fiscal year 2019 is the last year that the BLM was selling their federal He supply to private companies until the BLM officially privatizes the remaining He in the Federal Helium Reserve (BLM, 2018; Kornbluth, 2018). For He sold to federal government entities, fiscal year 2021 has seen an increase to \$100.00/Mcf compared to \$86.00/Mcf from fiscal year 2017 (BLM, 2020).

When examining the global average import price of high purity Grade-A He, we observe an increasing trend over the last decade (Fig. 1.4) (AKAP Energy, 2023). Grade-A helium is 99.997%

He or better, while extracted crude helium can range in values of 50-80% He (Blue Star Helium, 2020). Helium's cost and quality have a linear relationship such that high-quality He costs substantially more than crude He. Although exact prices of Grade-A He are not known, it has been estimated they will be substantially higher than crude prices in recent years given the extra costs of processing and other factors. Recent estimates from the USGS puts the price of private industry's Grade-A He at ~\$210.00/Mcf (\$7.57 per cubic meter) plus surcharges in fiscal year 2021 and \$310/Mcf in 2022 plus surcharges (\$11 per cubic meter) (USGS, 2022, 2023). This is much higher than <\$10/Mcf of CH₄ over the same timeline.

1.2 Noble Gas Geochemistry Literature Review

The naturally occurring noble gases are helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radioactive radon (Rn) (Ozima and Podosek, 2002), while oganesson (Og) is a highly reactive and synthetically produced noble gas (Giuliani et al., 2019). While radon and oganesson are technically within group 18 of the periodic table, they are not included in further discussions due to their radioactive nature and extremely short half-life (i.e., no stable isotopes). The noble gases have several unique identifying properties including having: monatomic structure, full valence shell of electrons (i.e., very low chemical reactivity), and very low melting and boiling points. Radioactive decay schemes and primordial (cosmogenic, nucleosynthesis) processes contribute to the overall composition of noble gases on Earth (Porcelli et al., 2002). He (5.24e-6 ccSTP/cc), Ne (1.818e-5 ccSTP/cc), Kr (1.14e-6 ccSTP/cc) and Xe (8.7e-8 ccSTP/cc) and are found in relatively low levels in Earth's atmosphere within the exception of Ar (9.34e-3 ccSTP/cc) (Ozima and Podosek, 2002; Porcelli et al., 2002). Units cc/cc or cm³/cm³ represent a ratio of a cm³ of gas X at standard pressure and temperature over a cm³ of air.

1.2.1 Origins of Noble Gases

1.2.1.1 Helium

³He, which is the rarest form of He found on Earth at 0.00014% (molar abundance) of the total He atmosphere budget, is a primordial isotope generated from nuclear fusion in stars primarily

found in Earth's mantle (Rosman and Taylor, 1998; Porcelli et al., 2002). Despite ^3He presence in greater amounts in stars, it is depleted by several orders of magnitude on Earth due to its high volatility. ^3He is largely considered to have originated on Earth by means of trapping during Earth's planetary accretion (Anderson, 1993). The exact trapping mechanisms are unknown, but there are theories ranging from, implantation of solar wind (Podosek et al., 2000), adsorption to accumulating dust (Marrocchi et al., 2005, 2011), accumulation of interplanetary dust particles in sediments and subsequent recycling into the mantle (Anderson, 1993), gravitational capture from proto-star nebula (Pepin, 2006), and contribution of material from the Late Heavy Bombardment (Holland et al., 2009). Additionally, cosmogenic rays are known to produce ^3He by interacting with the upper few meters of the crust, specifically from thermal neutron capture by lithium in clay-rich areas, $^6\text{Li} (n, \alpha) ^3\text{H} (\beta^-) \rightarrow ^3\text{He}$ (Hiyagon and Kennedy, 1992). Minor amounts of ^3He can be produced by beta decay from tritium (Solomon and Cook, 2000).

^4He , which is the dominant form of He in Earth's atmosphere (>99.99%), is formed through the radioactive decay (α -decay) of ^{232}Th , ^{235}U , and ^{238}U throughout time (1.401e10, 7.038e8, 4.468e9 half-life years, respectively). The α -particle that is emitted is essentially a He nucleus, and once the particle collects electrons from nearby ionized material, ^4He is formed. Given the incompatible nature of ^4He in the mantle, the majority of ^4He is concentrated in the crust. The major lithologies that hold high amounts of U and Th are granitic basement provinces, igneous provinces, and sedimentary units with U-Th rich shales (Brown, 2010; Danabalan, 2017). Recoil and chemical transformation along with diffusion, temperature, mineral alteration and grain size are some of the processes responsible for the transfer of ^4He trapped in minerals in the crust to surrounding fluids (Ballentine and Burnard, 2002; Ballentine et al., 2002, Honda et al., 1982; Warr et al. 2018).

1.2.1.2 Neon

The three stable isotopes of neon (^{20}Ne , ^{21}Ne and ^{22}Ne) are the result of primordial (i.e., stellar nucleosynthesis) and nucleogenic production (Li et al., 2022). Given there is no significant production of ^{20}Ne and ^{22}Ne , they are assumed to be essentially primordially sourced with some nucleogenic production (Porcelli and Turekian, 2014). ^{20}Ne and ^{22}Ne have molar abundances of 90.5% and 9.23%

in Earth's atmosphere (Porcelli et al., 2002). One possibility for high ^{20}Ne in the atmosphere is that it was trapped during the planetary accretion of Earth (Clayton, 2007). Small amounts of ^{20}Ne can also be formed by several reactions involving oxygen and sodium ($^{23}\text{Na} (n, \alpha) \rightarrow ^{20}\text{Ne}$; $^{17}\text{O} (\alpha, n) \rightarrow ^{20}\text{Ne}$), and ^{22}Ne can also be formed by several reactions involving fluorine and magnesium ($^{19}\text{F} (\alpha, n) ^{22}\text{Na} (\beta^+) \rightarrow ^{22}\text{Ne}$; $^{19}\text{F} (\alpha, p) \rightarrow ^{22}\text{Ne}$; $^{25}\text{Mg} (n, \alpha) \rightarrow ^{22}\text{Ne}$) (Danabalan, 2017).

^{21}Ne , which has a molar abundance of 0.27% in Earth's atmosphere is mostly produced by nuclear reactions ($^{18}\text{O} (\alpha, n)$, $^{24}\text{Mg} (n, \alpha)$). Nuclear reactions describe a reaction whereas nearby atoms interact with either a neutron or α -particle that were discharged from the decay of U and Th. The (α, n) notation means an 1) α -particle collided with and was absorbed by the reactant, and 2) the reaction produced a neutron (Table 1.1). The production of ^{21}Ne is controlled by magnesium and oxygen concentrations proximal to U and Th. While examining the portions of ^{21}Ne in the crust compared to the mantle, it is observed that magnesium has a more significant role for mantle systems (3.37% - 65.35%) compared to only <0.13% for crustal nucleogenic production (Ballentine and Burnard, 2002; Yatsevich and Honda, 1997). Additionally, cosmogenic production from spallation reactions on Al, Si, Na and Mg can produce ^{21}Ne .

1.2.1.3 Argon

Argon has three stable isotopes (^{36}Ar , ^{38}Ar , and ^{40}Ar). Their molar abundances are ^{36}Ar (0.3364%), ^{38}Ar (0.0632%), and ^{40}Ar (99.60%) in Earth's atmosphere (Porcelli et al., 2002). ^{36}Ar and ^{38}Ar are mostly primordial in origin, while ^{40}Ar is produced from the radioactive decay of ^{40}K via electron capture. There are small amounts of ^{36}Ar that are produced from beta decay $^{35}\text{Cl} (n, \gamma) ^{36}\text{Cl} (\beta^-) \rightarrow ^{36}\text{Ar}$, however this is a relatively minor amount (Danabalan, 2017). Additionally, small amounts of ^{38}Ar , can form in the crust as well from the decay of ^{37}Cl ($^{37}\text{Cl} (n, \gamma) ^{38}\text{Cl} (\beta^-) \rightarrow ^{38}\text{Ar}$) and ^{35}Cl ($^{35}\text{Cl} (\alpha, p) \rightarrow ^{38}\text{Ar}$) (Ballentine and Burnard, 2002). Cosmic spallation of terrestrial surface materials can also form small amounts of ^{38}Ar (Ozima and Podosek, 2002). ^{40}Ar is directly proportional to the amounts of potassium (K) in the crust (~2%) as it is produced from electron capture during the radioactive decay of ^{40}K (Ballentine and Burnard, 2002; Heir, 1965).

Table 1.1: Table showing primary sources and parents/reactions related to the origins for stable isotopes of He, Ne, Ar, Kr, Xe (Ballantine and Burnard, 2002; Boles et al., 2005; Danabalan, 2017; Hiyagon and Kennedy, 1992; Hunt et al., 2012; Ozima and Podosek, 2002; Periodic Table, 2017; Porcelli et al., 2002; Tyne, 2021; USGS, 2004; White, 2013; Yatsevich and Honda, 1997).

Isotope	Primary Source	Parents	Isotope	Primary Source	Parents
³ He	Primordial	² H(p, γ) → ³ He	⁸⁴ Kr	Fissiogenic	²³⁵ U, ²³⁸ U, ²⁴⁴ Pu
⁴ He	Radiogenic	²³⁸ U → ²³⁴ Th + ⁴ He ²³⁵ U → ²³¹ Th + ⁴ He ²³² Th → ²²⁸ Ra + ⁴ He	⁸⁶ Kr	Fissiogenic	²³⁵ U, ²³⁸ U, ²⁴⁴ Pu
²⁰ Ne	Primordial	¹² C + ¹² C → ²⁰ Ne + ⁴ He + γ	¹²⁴ Xe	Primordial	
²¹ Ne	Nucleogenic	¹⁸ O (α, n) → ²¹ Ne ²⁴ Mg (n, α) → ²¹ Ne	¹²⁶ Xe	Primordial	
²² Ne	Primordial		¹²⁸ Xe	Primordial	
³⁶ Ar	Primordial		¹²⁹ Xe	Radiogenic, Fissiogenic	¹²⁹ I → ¹²⁹ Xe + β-
³⁸ Ar	Primordial		¹³⁰ Xe	Primordial	
⁴⁰ Ar	Radiogenic	⁴⁰ K (electron capture) → ⁴⁰ Ar	¹³¹ Xe	Fissiogenic	²³⁵ U, ²³⁸ U, ²⁴⁴ Pu
⁷⁸ Kr	Primordial		¹³² Xe	Fissiogenic	²³⁵ U, ²³⁸ U, ²⁴⁴ Pu
⁸⁰ Kr	Primordial		¹³⁴ Xe	Fissiogenic	²³⁵ U, ²³⁸ U, ²⁴⁴ Pu
⁸² Kr	Primordial		¹³⁶ Xe	Fissiogenic	²³⁵ U, ²³⁸ U, ²⁴⁴ Pu
⁸³ Kr	Fissiogenic	²³⁵ U, ²³⁸ U			

1.2.1.4 Krypton and Xenon

Out of the many isotopes for both Kr and Xe, there are only six stable isotopes for Kr (⁷⁸Kr, ⁸⁰Kr, ⁸²Kr, ⁸³Kr, ⁸⁴Kr, ⁸⁶Kr), and nine stable isotopes for Xe (¹²⁴Xe, ¹²⁶Xe, ¹²⁸Xe, ¹²⁹Xe, ¹³⁰Xe, ¹³¹Xe, ¹³²Xe, ¹³⁴Xe, ¹³⁶Xe). The molar abundances for Kr stable isotopes in Earth's atmosphere of ⁷⁸⁻⁸⁶Kr are: 0.03469%, 2.2571%, 11.523%, 11.477%, 57%, and 17.398%. The molar abundances for Xe stable isotopes in Earth's atmosphere of ¹²⁴⁻¹³⁶Xe are: 0.0951%, 0.0887%, 1.919%, 26.44%, 4.070%, 21.22%, 26.89%, 01.34%, and 8.857% (Porcelli et al., 2002). ⁷⁸Kr, ⁸⁰Kr, ⁸²Kr, ¹²⁴Xe, ¹²⁶Xe, ¹²⁸Xe and ¹³⁰Xe are considered primordial non-radiogenic isotopes (USGS, 2004). ¹²⁹Xe, which is associated with a mantle source, is the daughter product of the extinct ¹²⁹I (Avice et al., 2017; USGS, 2004). Fission of uranium and plutonium is responsible for ⁸⁴Kr, ⁸⁶Kr, ¹³¹Xe, ¹³²Xe, ¹³⁴Xe, and ¹³⁶Xe, while fission of uranium alone can produce ⁸³Kr.

1.2.2 Terrestrial Noble Gases Reservoirs

1.2.2.1 Air Saturated Water

The air saturated water (ASW) reservoir describes an environment where subsurface water holds dissolved atmospheric noble gases as a result of water being in direct contact with the atmosphere (Fig. 1.5). The atmospheric components are largely considered to be primordial in origin

and distinct from solar compositions (Porcelli et al., 2002; Pepin and Porcelli, 2006; Pepin, 2006).

This distinction from solar compositions can be attributed to either gradual or catastrophic loss during Earth's early history (Pepin and Porcelli, 2006; Pepin, 2006). The major ASW noble gases are $^{20,22}\text{Ne}$, $^{36,38}\text{Ar}$, ^{84}Kr , ^{130}Xe , ^{132}Xe (Barry et al., 2016; Danabalan, 2017; Kennedy et al., 2002). The mechanism that allows atmospheric gas to equilibrate with groundwater is where there are aquifer recharge zones for meteoric water to enter underground lithologies, which will transport the water along groundwater flow paths (Prinzhofer, 2013). Another method to introduce atmospheric noble gases into groundwater is from sedimentation (i.e., water which is entrained during deposition) (Ballentine et al., 2001; Battani et al., 2000).

The solubility of each gas in water is controlled by each Henry's Law and is influenced by external parameters such as temperature, salinity, and pressure (Ballentine et al., 2002; Crovetto et al., 1982). Given that the solubilities of each noble gas are slightly different, the end composition of atmospheric air equilibrated with water will be slightly different than the original air composition (Kipfer et al., 2002). However, given that changes to isotopic ratios during equilibrium partitioning of individual noble gases are considered small/negligible (compared to other processes that could affect the ratios), it is assumed they retain air like ratios (Kipfer et al., 2002). The migration of noble gases from groundwater after they have partitioned from air to water is largely controlled by increases in hydrostatic and/or lithostatic pressure more than changes in salinity or temperature (Ballentine et al., 2002; Danabalan, 2017).

Paleo-environmental conditions can be calculated by using the dependency of ASW on salinity, pressure and temperature (Kipfer et al., 2002; Weis and Kyser, 1978; Weis, 1970, 1971). An impediment for this approach is the addition of excess air, which is defined as additional atmospheric air above what Henry's Law predicts (Tyne, 2021). This excess air is likely from the entrapment of air bubbles below the water table that were forced into dissolving into the groundwater due to increased pressure. A variety of theoretical models have been constructed to address this excess air issue such as multi-step partial equilibration models (Kipfer et al., 2002), closed system equilibration models (Aeschbach-Hertig et al., 2000, 2008), partial re-equilibration models (Stute et al., 1995), and unfractionated excess air models (Heaton and Vogel, 1981).

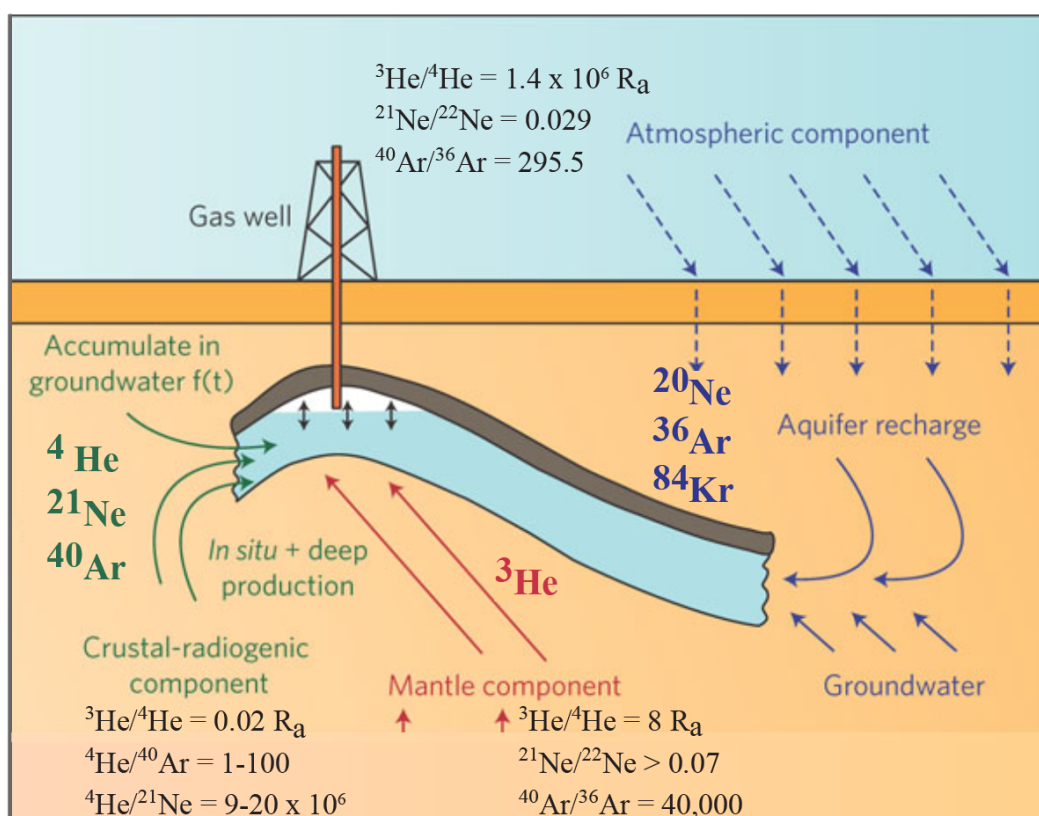


Figure 1.5: Isotopic components interacting with a petroleum system (Ballentine et al., 2002; Byrne et al., 2017; Lollar and Ballentine, 2009; modified from Pinti and Marty, 2000). By understanding the components contributing noble gases into the system, the sources of gases, migration pathways, and mixing of gases can be inferred.

Noble gases can also partition from water to hydrocarbons given they are more soluble in oil compared to water. More specifically, when noble gases encounter hydrocarbons, they can either partition into two (water, oil) or three phases (water, oil, gas). Hydrocarbon gas/water equilibrium ratios can be calculated by using mass balance equations with solubility coefficients (Prinzhofer, 2013). The measurement of different volumes of the different phases involved can be undertaken utilizing the hydrocarbon-water interactions from the atmospheric input signal (Mazor and Bosch, 1987). By studying the oil water interactions, insights can be gathered about relative water flow into a hydrocarbon reservoir (Pinti and Marty, 2000). The oil water contact is useful when studying secondary migration and degradation of hydrocarbons (Dahlberg, 1995; Lafargue and Barker, 1988).

1.2.2.2 Crust

The crustal reservoir of noble gases is largely derived from nucleogenic and/or radiogenic contributions from minerals within the Earth's crust (Prinzhofer, 2013). Nucleogenic nuclides are

generated by terrestrial natural nuclear reactions, and radiogenic nuclides are produced by radioactive decay. Despite the heterogeneity of the Earth's crust, high concentrations of radiogenic isotopes define crustal fluids. In some cases, high concentrations of radiogenic isotopes indicate the systems have experienced isolation for significant portions of geologic time (Holland et al., 2013; War et al., 2018, 2020). Well known examples of radiogenic production is that of ^4He from the α -decay of U and Th, which has a present day production rate of $3.31\text{e-}10\text{ cm}^3(\text{STP})/\text{kg}/\text{yr}$, and ^{40}Ar from the decay of ^{40}K , which has a present day production rate of $6.05\text{e-}11\text{ cm}^3(\text{STP})/\text{kg}/\text{yr}$ (Tyne, 2021). Well known examples of nucleogenic production is that of ^{21}Ne from the nuclear reactions with magnesium and oxygen, which has a present day production rate of $1.51\text{e-}17\text{ cm}^3(\text{STP})/\text{kg}/\text{yr}$ (Tyne, 2021). Some of the most widely used noble gases indicative of a crustal source are ^4He , ^{21}Ne and ^{40}Ar (Fig. 1.5) (Pinti and Marty, 2000).

The amount of parent elements is only one variable in understanding the contribution of crustal derived noble gases into a system. Other variables include: the location of the parent elements/minerals, decay schemes, diffusion constants, subsurface temperatures, and release mechanisms (Pinti and Marty, 2000). The majority of all radiogenic/nucleogenic budget (66%) is within the top ~ 10 km of the crust, 28% at 10-15 km, and 6% below 25 km (Prinzhofer, 2013; Rudnick and Fountain, 1995). Decay schemes are critical in understanding the potential radioactive input into a given system. The physical location is vital to understand the lithological parameters of the formation such as rock type, thickness, porosity, water saturation, and mineralogy. The subsurface temperatures are crucial in that they control the release or entrapment of noble gases in minerals (i.e., closure temperatures). For example, ^{40}Ar is retained until 250-300 $^{\circ}\text{C}$, while ^4He can be extracted/released at much lower temperatures (Danbaban, 2017).

Fully comprehending the processes involved in the production and accumulation of crustal derived noble gases have several important applications to scientists. Looking at the ratios of crustal derived noble gases can provide insight into crustal fluids that are evolving away from recent magmatism (Pinti and Marty, 2000). Thermal maturity and fluid-rock interactions can be determined by knowing the production of decay products (Hunt et al., 2012). Geologic residence times can be calculated for subsurface fluid (essentially fluid chronometers) based off of radiogenic noble gas

isotopes (Prinzhofer, 2013). Transport and release phenomena of large-scale processes can be deduced by examining the $^4\text{He}/^{40}\text{Ar}$ crustal production ratios (Ballentine et al., 1991).

1.2.2.3 Mantle

The mantle is the last major source of noble gases that are found in the subsurface and they are primarily primordial and radiogenic in origin (Ballentine and Holland, 2008; Broadley et al., 2020; Lupton and Craig, 1975; O’Nions and Oxburg, 1988; Oxburg et al., 1986). ^3He is the most useful noble gas in tracing mantle contributions due to its depleted nature (relative to ^4He) in the crustal and atmosphere reservoirs (Fig. 1.5) (Pepin and Porcelli, 2002). Generally, diffusion during geologic timescales with hot mantle temperatures would not generate displacement observed due to the fact the noble gases from the mantle are trapped in minerals (Lupton, 1983). Mantle melting and the generation of magma are usually needed to transport mantle derived volatiles into the shallow subsurface system (Prinzhofer, 2013). More specifically, ^3He can be introduced into the shallow crustal systems via CO_2 transport that is released in areas with igneous activity (i.e., extensional environments, mantle hotspots) or either permeate through the crust (O’Nions and Oxburg, 1988; Pinti and Marty, 2000; Tyne, 2021). ^3He is also very useful for constraining origin and accumulation information about mantle sourced CO_2 to hydrocarbon fields (Pinti and Marty, 2000; Tyne, 2021).

Common isotope ratios of $^3\text{He}/^4\text{He}$ (R) relative to the atmosphere (R_a) are widely used to determine the presence and extent of mantle mixing into a system. Because more ^3He is sourced from the mantle, a higher R/R_a ratio is indicative of more mantle input in comparison to a pure radiogenic endmember of $\sim 0.02 R_a$ (Prinzhofer, 2013). There is variability for R/R_a depending on the environment: $8 \pm 1 R_a$ for mid-ocean ridge basalts (Graham, 2002), $6.1 \pm 2.11 R_a$ for sub-continental lithospheric mantle (Day et al., 2015), and $\sim 50 R_a$ for mantle plumes (Stuart et al., 2003). Higher ratios of $^{40}\text{Ar}/^{36}\text{Ar}$ from 30,000–40,000 are observed for mantle sources (Burnard et al., 1997; Staudacher et al., 1989). Elevated ratios of $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios should be expected with a mantle component (Danabalan, 2017).

1.2.3 Noble Gas Solubility Modelling

1.2.3.1 Henry's Law

To understand how noble gases will behave in subsurface reservoirs, it is essential to study the physical chemistry of noble gases in crustal fluids. Due to the high volatility of noble gases, they have a strong affinity to be in the gaseous phase (Ballentine et al., 2002). However, when there is a mixture of noble gases and liquids, some of the noble gases will dissolve into the liquid to maintain an equilibrium based on Henry's law. Henry's Law essentially states that the mass of a dissolved gas in a solution at equilibrium is proportionally to the partial pressure of the gas in an ideal behaviour environment (Equation 1.1) (Ballentine et al., 2002). In a non-ideal environment, certain gas phase fugacity coefficients and liquid phase activity coefficients are applied (Equation 1.2).

$$\text{Equation 1.1: } p_i = K_i x_i$$

where p is the partial pressure of a gas (i) in equilibrium with a fluid, x is the mole fraction of the gas (i) in solution, and K is the Henry's constant of gas (i).

$$\text{Equation 1.2: } \Phi_i p_i = Y_i K_i x_i$$

where Φ is the gas phase fugacity coefficient and Y is the liquid phase activity coefficient.

$$\text{Equation 1.3: } \gamma = e^{Ck(T)}$$

where C is the concentration of salt in a solution, and $k(T)$ is the Setchenow coefficient

A broad range of gas phase fugacity coefficients have been compiled as a function of depth, temperature and pressure (Ballentine et al., 2002; Dymond and Smith, 1980). In order to calculate the liquid phase activity coefficient, the system's salinity, temperature and relevant Setchenow coefficients are required (Equation 1.3). Setchenow coefficients for noble gases have been empirically derived for a range of NaCl brines (0-5.2 M) between 0-65 °C (Smith and Kennedy, 1983). Each of the noble gases has a relevant Henry's constant that is dependent on temperature and salinity that dictates the relative level of solubility of that gas species. For example, in a liquid water solution at 300 °K, the Henry's constants in order of highest to lowest are He>Ne>Ar>Kr>Xe. This translates to helium being the most insoluble of the group. The ordering of noble gases Henry's constants generally holds true except at higher pressures Ne>He. A broad range of temperatures and subsequent Henry's constants have been described in literature (Ballentine et al., 2002; Crovetto et al., 1982; Smith, 1985; Fernandez-Prini et al., 2003). Henry's constants have also been compiled for heavy oil

(API=25) and light oil (API=34) to describe the dissolution tendencies of noble gases in oil (Kharaka and Specht, 1988)

1.2.3.2 Partitioning

Solubility and noble gas partitioning within fluids in the crust have been investigated thoroughly (Goryunov and Kozlov, 1940; Zartman et al., 1961; Ballentine et al., 1991, 1996; Ballentine et al., 2002; Ballentine and O’Nions, 1994; Battani et al., 2000; Bosch and Mazor, 1988; Hiyagon and Kennedy, 1992; Pinti and Marty, 1995; Torgersen and Kennedy, 1999; Zaikowski and Spangler, 1990). In a situation assuming ideal behaviour, Equation 1.1, can be rewritten to describe the concentrations of a gas (i) in the gas phase in relation to the concentration of a gas (i) in the liquid phase (Equation 1.4).

$$\text{Equation 1.4: } C_g^i = K_i^d C_l^i$$

where C is related to concentration in the gas or liquid phase, and K is the dimensionless form of Henry’s constant.

Following along this line of reasoning and assuming a fixed volume of gas and liquid in liquid-gas systems, the number of moles in the gas phase can be calculated by using the total number of moles present, a liquid to gas volume ratio and the relevant Henry’s constant (Equation 1.5) (Ballentine et al., 2002). This means that for any liquid-gas equilibrium value, the partitioning of gas species between the liquid and gas phases is made possible. For example, the volume of water that a gas phase has equilibrated with can be calculated from one noble gas concentration in the gas phase (Ballentine et al., 2002).

$$\text{Equation 1.5: } i_g = i_T (V_l / V_g K_i^d + 1)^{-1}$$

where i_g is the number of moles in the gas phase, i_T is the total number of moles, V_l / V_g represents the liquid to gas ratio.

Additionally, going a step further taking into account phase partitioning in liquid-liquid systems, similarly the number of moles of a gas (i) in the oil phase can be calculated (Equation 1.6). Comparable to the application mentioned above, the quantification of a system’s oil/water volume ratio can be obtained by using the concentration of one groundwater noble gas concentration in either the oil phase or water phase (Ballentine et al., 2002).

Equation 1.6: $i_{oil} = i_T ((V_{H2O} \rho_{H2O} K_{i-oil}^m / (V_{oil} \rho_{oil} K_{i-H2O}^m) + 1)^{-1}$
where ρ is the water or oil density in g/cm³, and K^m represents Henry's constants by in molality format.

1.2.3.3 Relative Fractionation Models

In the cases where a reasonable estimate of an initial gas concentrations in a fluid are available, one can investigate the change in noble gas ratios (Ballentine et al., 2002). At the most basic theoretical approach, this fractionation (relative partitioning of heavier and lighter isotopes of noble gases between phases) can be quantified in simple closed system models, which can represent instances of a theoretical bubble of gas progressively outgassing from a dissolved state in groundwater or the inverse where a theoretical bubble of gas is progressively ingassing/redissolving back into a groundwater solution (Bosch and Mazar, 1988) (equations 1.7 and 1.8). Similarly, batch closed system fractionation models can be used in oil-water systems, where they quantify oil into water or water into oil equilibrium scenarios (Bosch and Mazar, 1988) (equations 1.9 and 1.10). The high solubility of noble gases in oil can result in significant fractionation between two phases that have come to equilibrium (Ballentine et al., 2002; Torgersen and Kennedy, 1999). For oil-water and gas-water systems, the first drop of oil or bubble of gas that interacts with groundwater (extremely large water to oil or water to gas ratios) represents the initial charging of the reservoir (Ballentine et al., 2002). In more complex scenarios, more closely mirroring geologic environments, an open system style model or Rayleigh open system model is more applicable (Holland and Gilfillan, 2013) (equations 1.11 and 1.12). This type of fractionation represents a simple dynamic model that illustrates the maximum magnitude of noble gas fractionation between two phases that have been equilibrated (Ballentine et al., 2002). It is also assumed that in these subsurface systems, the hydrocarbon phase (in the case of oil-water systems) or the groundwater phase (in terms of gas-water systems), is devoid of any noble gases and only acquires the atmospheric noble gases through equilibrium with ASW. Models for relative fractionation are often based on the physical parameters (i.e., salinity, temperature, depth, etc.) of the systems being studied. The benefit of using this approach is that one can calculate the remaining amount of Ar in the groundwater, which has implications about the hydrogeological dynamics of the subsurface system (Barry et al., 2016; Cheng, 2020; Pinti and

Marty, 2000), the quality of hydrocarbons, and hydrocarbons' secondary migration in the reservoir (Dahlberg, 1995; Lafargue, and Barker, 1988; Leahy and Colwell, 1990). By convention, gas species are normally compared to ^{36}Ar for conventional fractionation models (Ballentine et al., 2002).

$$\text{Equation 1.7: } \left(\frac{i}{\text{Ar}}\right)_g = \left(\frac{i}{\text{Ar}}\right)_{\text{H}_2\text{O}} \left(\frac{V_g}{V_l} + \frac{1}{K_{\text{Ar}}^d}\right) / \left(\frac{V_g}{V_l} + \frac{1}{K_i^d}\right) \text{ closed water to gas outgassing}$$

$$\text{Equation 1.8: } \left(\frac{i}{\text{Ar}}\right)_g = \left(\frac{i}{\text{Ar}}\right)_{\text{H}_2\text{O}} \left(\frac{V_g}{V_l} + \frac{1}{K_{\text{Ar}}^d}\right) / \left(\frac{V_g}{V_l} + \frac{1}{K_i^d}\right) \text{ closed gas to water ingassing}$$

$$\text{Equation 1.9: } \left(\frac{i}{\text{Ar}}\right)_{\text{oil}} = \left(\frac{i}{\text{Ar}}\right)_t \left(\frac{V_{\text{oil}}}{V_{\text{H}_2\text{O}}} + \frac{K_{\text{Ar}}^d}{K_{\text{Ar}}^d}\right) / \left(\frac{V_{\text{oil}}}{V_{\text{water}}} + \frac{K_{i\text{oil}}^d}{K_{i\text{H}_2\text{O}}^d}\right) \text{ closed oil to water}$$

$$\text{Equation 1.10: } \left(\frac{i}{\text{Ar}}\right)_{\text{oil}} = \left(\frac{i}{\text{Ar}}\right)_t \left(\frac{V_{\text{oil}}}{V_{\text{water}}} + \frac{K_{i\text{oil}}^d}{K_{i\text{H}_2\text{O}}^d}\right) / \left(\frac{V_{\text{oil}}}{V_{\text{H}_2\text{O}}} + \frac{K_{\text{Ar}}^d}{K_{\text{Ar}}^d}\right) \text{ closed water to oil}$$

$$\text{Equation 1.11: } \left(\frac{i}{\text{Ar}}\right)_{\text{H}_2\text{O}} = \left(\frac{i}{\text{Ar}}\right)_{\text{initial}} P^{\alpha-1} \text{ open water to gas outgassing}$$

$$\text{Equation 1.12: } \left(\frac{i}{\text{Ar}}\right)_{\text{H}_2\text{O}} = \left(\frac{i}{\text{Ar}}\right)_{\text{initial}} P^{\frac{1}{\alpha}-1} \text{ open gas to water ingassing}$$

$$\alpha = \frac{K_i^{\text{H}_2\text{O}}}{K_{\text{Ar}}^{\text{H}_2\text{O}}} \text{ fractionation factor for water-gas systems}$$

$$\alpha = \frac{K_i^{\text{H}_2\text{O}} K_{\text{Ar}}^{\text{oil}}}{K_i^{\text{oil}} K_{\text{Ar}}^{\text{H}_2\text{O}}} \text{ fractionation factor for water-oil systems}$$

Deviations from the standard predictions of fractionation modelling can result from geologic environments that release excess Kr or Xe. An important process which has the potential to explain the excess isotopic signatures in gas samples, is the adsorption or desorption of noble gases onto solid surfaces (mineral or organic). Preferential adsorption of Kr and Xe on organic-rich shales and kerogens (coal macerals), has been confirmed through several studies in sedimentary basins (Frick and Chang, 1977; Prinzhofer, 2013; Torgersen and Kennedy, 1999; Zhou et al., 2005). Kerogens have been shown to have a higher adsorption rate than shales, which indicates that they could fractionate heavier noble gases from lighter noble gases (Frick and Chang, 1977; Prinzhofer, 2013). Throughout time, as ASW derived heavier noble gases can become adsorbed onto organic rich material in the subsurface, they become enriched beyond the predicted fractionation ratio based on solubility controls alone. Subsequently, if there is a geologic event that liberates the sorbed gas, it is possible to produce the excess Kr and Xe observed in the literature (Gilfillan et al., 2008; 2009).

1.2.4 Noble Gas Release and Transport Mechanisms

1.2.4.1 Diffusion

Diffusion, which is a relatively slow physical process based on movement due to differences in concentration gradients, has the potential to fractionate noble gases (Prinzhofer, 2013). Temperature, tortuosity, pore space fluid and permeability are several factors influencing bulk diffusion. Solubility coefficients in different mediums such as gas, water, and oil, are key to understanding diffusion of noble gases through subsurface systems (Prinzhofer, 2013). Variables that can affect the rate of diffusion are the different mixtures of oil composition, saline conditions and water percentages. Additionally, the lithology is an important variable. For example, systems with high permeability or extensive fracturing, can tend to increase the overall diffusion potential, while the inverse with a decrease in permeability will often lower diffusion's rate. Larger molecules will often travel slower than smaller molecules (Harvey, 1988; Giannesini, 2008; Jahn et al., 1987; Reid et al., 1977). Interestingly, He despite being the smallest noble gas has been reported to be less mobile than neon in a water membrane (Crank, 1975). Diffusion coupled with mineral recrystallization, are processes that allow He to move to pore water from minerals (Brown, 2010). Despite inherent challenges, recent work has been conducted to investigate the potential of diffusion to account for observed He accumulations sitting directly on top of a heavily fractured basement He source rock (Cheng, 2020; Cheng et al., 2021, 2023).

1.2.4.2 Advection

Advection is a relatively fast process where solutes in groundwater are transported by hydraulic pressure gradients usually in fracture/fault systems or permeable aquifers (i.e., major interconnected fractures). Movement of groundwater or carrier fluids in the subsurface can be attributed to chemical changes (hydrocarbon generation or metamorphism) and/or external sources (aquifers or magmatic fluids) (Ballentine and Burnard, 2002; Brown, 2010). An important requirement for effective transport of He via advection is the presence of fluids to enable bulk movement and for temperatures to have exceeded closure temperature of He retentive minerals (i.e., extensional event, volcanic event, orogenic event, or deep burial) (Danabalan et al., 2022). The

proportion of transport caused by advection is reduced as one moves away from the main fracture set because the lengths, apertures, connectivity and frequencies of the micro fractures diminish rapidly (Wogelius et al., 2020). Micro fracture porosity as well as secondary porosity (i.e., mineral dissolution/alteration) can provide environments for solute transport via groundwater (Wogelius et al., 2020). Traditionally, advection has been associated with groundwater flow in tectonically active systems (Craddock et al., 2017; Danabalan et al., 2022; Halford et al., 2022), but recent work into more perceived quiescent basins has seen proxy evidence for advection resulting from fluid flow concerning economic He zones located near deep fault/fracture networks observed on proprietary seismic data.

1.2.4.3 Recoil loss

Recoil loss occurs as the elevated kinetic energies from released α -particles are ejected from host minerals and create damage fission tracks (Ballentine and Burnard, 2002). The ejection of α -particles (i.e., ^4He) can be retained in the host mineral, travel into another adjacent mineral or enter into surrounding pore space or pore water (Ballentine and Burnard, 2002). The distance the α -particles travels will vary based on mineral size (i.e., larger sizes hinder recoil rates), density of minerals and mineral chemistry. If the particle encounters a water filled pore, it will likely be stopped more effectively than if it had encountered an open pore, where the diffusivity will be higher (Hurley, 1950). Rama and Moore (1984) state that He being ejected has a higher likelihood of ending in an adjacent mineral grain if there is low density fluids in the space between grains. High temperatures can anneal or heal fission tracks and reduce the quicker transport of the molecule and the particle will have to resort to the much slower diffusion (Brown, 2010). At 110 °C, annealing can occur in apatite (a common host mineral for U and Th) (Ballentine and Burnard, 2002). The closure temperature range for apatite is roughly 50-100 °C which is the temperature that ^4He would be released (Farley, 2000, 2002; Lippolt et al., 1994; Shuster et al., 2006; Wolf et al., 1996). If the mineral grains are not too large, and the temperatures are not at annealing levels, coupled with a U and Th on grain boundaries and chemical breakdown/dissolution, recoil loss might be an important mechanism for releasing ^4He (Andrews et al., 1989a; Torgersen and Clarke, 1985; Torgersen, 1989).

1.2.4.4 Fracturing

Fracturing can provide migration pathways that allow noble gases to be released from source minerals and rocks (Ballentine and Burnard, 2002). Extensive fracturing can allow gas release even if closure temperatures are not reached because it transforms the subsurface system into an open system rather than a closed system. Granted fractures can be both open or closed depending on the chemistry of the system (i.e., mineral dissolution or precipitation). Work by Honda et al., (1982) shows that the release of noble gases from generation minerals can be controlled by micro fracturing caused by compressional events. The degree to which a system is fractured can allow migration from the host mineral into the surrounding source rock and even out of the source rock into overlying sedimentary packages (Ballentine and Burnard, 2002). Cross formation vertical flow can be studied by quantifying the degree to which fault and fracture networks cross cut lithologic intervals (Kennedy et al., 2002). Without physical hand samples of rock, it is extremely challenging to quantify the exact impact that heterogeneous fractures have on the transport of noble gases.

1.2.4.5 Mineral transformation

In instances of diagenesis, metamorphism mineral dissolution or other alterations, minerals can be transformed and subsequently release noble gases from host minerals as the noble gases are incompatible with the new mineral after transformation. This process requires the availability of pathways for noble gases to break free of the recrystallization location (Ballentine and Burnard, 2002). Although theoretically possible, this process is not likely to account for significant gas loss from the crust (Torgersen et al., 1989). Likewise, Ballentine and Burnard (2002) state that mineral transformation cannot fractionate noble gases like diffusion or recoil loss can.

1.2.5 Applications of Noble Gases

Given that the noble gas contributions/signatures derived from the atmosphere/air saturated water, crust, or mantle are distinct and are well documented, isotopic cross plots and models can be constructed to study the interaction of noble gases from different sources in subsurface crustal fluids, and to quantitatively study the subsurface environment and how it has evolved over time (Barry et al.,

2016, 2018; Ballentine et al., 2002; Byrne et al., 2017; Darrah et al., 2014; Gilfillan et al., 2008, 2009; Hunt et al., 2012; Ozima and Podosek, 2002; Prinzhofer, 2013). Combinations of isotopic ratios such as $^4\text{He}/^{20}\text{Ne}$ allows scientists to resolve and deconvolve different He contributions from the atmosphere compared to crustal sources (Hilton et al., 1996). Another example of resolving components is the calculation of $^{21}\text{Ne}^*$ and $^{40}\text{Ar}^*$, which is ^{21}Ne mainly derived from nucleogenic reactions and ^{40}Ar excess that is mainly derived from radiogenic production, by utilizing isotopic values of air and measured sample ^{40}Ar and ^{36}Ar , and ^{20}Ne , ^{21}Ne and ^{22}Ne (Equations 1.13 and 1.14) (Ballentine et al., 2002; Zhang et al., 2019).

$$\text{Equation 1.13: } ^{21}\text{Ne}^* = ^{21}\text{Ne}_{\text{measured}} - ((^{21}\text{Ne}/^{22}\text{Ne})_{\text{air}} / (^{20}\text{Ne}/^{22}\text{Ne})_{\text{air}}) \times (^{20}\text{Ne}_{\text{measured}})$$

$$\text{Equation 1.14: } ^{40}\text{Ar}^* = ((^{40}\text{Ar}/^{36}\text{Ar})_{\text{measured}} - (^{40}\text{Ar}/^{36}\text{Ar})_{\text{air}}) \times (^{36}\text{Ar}_{\text{measured}})$$

1.2.5.1 Noble Gases in Petroleum Systems

The noble gases combined with hydrocarbon data can be utilized as an important geochemical tool in understanding different components and processes of petroleum systems. Although not heavily utilized in the oil/gas industry (outside of academia), due to high prohibitive costs, the noble gases allow researchers to identify the relationships between different phases (gas, water, oil) and quantify the extent to which they equilibrated within the reservoir via solubility models. Phase relationships may be closed (batch) system, following equilibrium solubility, or open system, following Rayleigh fractionation (Ballentine et al., 2002; Gilfillan et al., 2008; Hiyagon and Kennedy, 1992; Pinti and Marty, 1995; Torgersen and Kennedy, 1999). Deviations from the expected hydrocarbon solubility trends, can indicate additional processes that are influencing the system, some of which could be anthropogenic addition and sample contamination, or dynamic aquifer systems (Barry et al., 2016, 2018).

Insight into the physical behaviour of petroleum systems such as the general scale of the fluid system, mixing between several endmembers, overall hydrogeological regime, and the genetic fingerprinting and sourcing of gas families is made possible with the noble gases because they are non-reactive conservative physical tracers (Byrne et al., 2018, Hunt et al., 2012, Merrill et al., 2014,

Pinti and Marty, 1995; Prinzhofer, 2013; Warr et al., 2018). Atmospheric noble gases allow the calculation of possible mass balance scenarios between oil, water and gas phases (Prinzhofer, 2013). Deviations from known crustal production rates can provide information regarding transportation and release mechanisms (Ballentine et al., 1991). Geologic residence times of fluids in the subsurface can be estimated using radiogenic or nucleogenic noble gases (Prinzhofer, 2013). Understanding the various methods of noble gas transport such as advection, diffusion, phase exchange flow, or adsorption /desorption, can provide scientists clues regarding migration and storage mechanisms (either sorbed or in the free gas phase). Based on the constant and predictable mineral phase dependent production of decay products, thermal maturity and fluid rock interactions can be calculated (Hunt et al., 2012). Concerning exploration for geothermal resources and/or potential CO₂ sources for enhanced oil recovery, mapping mantle derived noble gases can elucidate details concerning mantle-derived heat and mantle sourced CO₂ gas streams (Pinti and Marty, 2000). Noble gases are a promising candidate to address heterogeneity characterization and production monitoring concerns for both conventional and unconventional reservoirs when other techniques such as organic chemistry or geophysics fail to provide accurate predictions (Prinzhofer, 2013).

Not only can noble gas isotopes in conjunction with hydrocarbon geochemical data be utilized in better constraining the nature and origin of hydrocarbons, they are also being utilized in examining long-term impacts (i.e., pollution) of hydrocarbon production and enhanced oil recovery on adjacent groundwater systems (Darrah et al., 2014). Given there can be both anthropogenic hydrocarbon additions and natural hydrocarbon additions (microbial methane, or natural seepage), the noble gases can provide unique insight as to the exact sources of hydrocarbons additions in the groundwater, which have applications in anthropogenic hydrocarbon leak detection (Darrah et al., 2014, 2015; Harkness et al., 2017). Geochemical monitoring via noble gases can also be optimized for carbon capture and storage where noble gases can be used to study the geochemical signature of CO₂ and the efficiency of CO₂ reinjection, storage and potential leakage in subsurface reservoirs (Pinti and Marty, 2000; Karolytè et al., 2019). Additionally, noble gases can provide a basis to understand basin architecture and connectivity, which has implications for subsurface storage of natural gases (Scott et al., 2021).

1.2.5.2 Noble Gases and Helium Systems

Helium systems, a slight variation to the original petroleum system, can be further understood by studying noble gas isotopes combined with hydrocarbon and non-hydrocarbon isotopes (Boreham et al., 2018; Danabalan et al., 2022; Halford, 2018; Flude et al., 2019; Magoon and Dow, 1994a, 1994b, Mtili et al., 2021). Although He has been known since 1868, the exploration and utilization of noble gas geochemistry to spur exploration for He alone has not occurred until recently (Cady and McFarland, 1906). He systems have been documented to have either methane (CH₄), carbon dioxide (CO₂) or nitrogen (N₂) as carrier gases (Boreham et al., 2018; Danabalan et al., 2022; Halford, 2018, Mtili et al., 2021). Similar to petroleum systems, noble gases can be used to investigate sourcing and migration of He in the subsurface (Danabalan et al., 2022).

Previous investigations studying noble gas isotopes sampled from natural gas from oil/gas fields and natural geothermal springs have suggested that the dominant source of He is from the Precambrian basement, but further work on basement lithologic variability is needed to accurately constraint the best source areas (Ballentine and Sherwood-Lollar, 2002; Cheng, 2020; Cheng et al., 2021, 2023; Wang et al., 2022; Wang et al., 2023; Zhang et al., 2020). Utilizing He mass balance models, the relative amounts of radiogenic He produced in situ from sedimentary formations can be compared to the dominant He produced externally from minerals in the deeper basement (Ballentine et al., 2002; Buttitta et al., 2020, Danabalan, 2017; Wang et al., 2022; Wang et al., 2023; Zhang et al., 2020). The mass balance models include calculations of models showing original gas in place, original helium in place, and He production rates (Ballentine et al., 2002). Several authors have advocated for hot shales (U and Th rich) to be the dominant He source in some cases instead of basement lithologies (Brown, 2010; Wang et al., 2023). Theories of significant amounts of He derived from sedimentary ore deposits have also been put forth (Broadhead and Gillard, 2004; Li et al., 2017). Other models advocate that ³He (originally in the mantle) is introduced into subsurface reservoirs via deep extensional fractures and volcanism (Broadhead and Gillard, 2004). ³He derived from the beta decay of tritium (³H) is another helium generative process, but it is not known to produce any substantial He amounts (Broadhead and Gillard, 2004). Another potential avenue to constraint the source of He in He-rich systems, is to understand the origin of the dominant carrier gases (e.g., N₂).

N₂ is most often present when economic accumulations of He are found, but its exact relationship with He is unknown as well as its source, either from organic, meta-sediment, clay, or mantle contributions (Cartigny and Marty, 2013). It is possible to source both N₂ and He from the same area of the crust, and this has been presented as evidence of a strong carrier gas relationship (Giggenbach and Poreda, 1993, Gilfillan et al., 2008, Gold and Held, 1987; Jenden et al., 1988a; Li et al., 2017).

Since generation rates of radiogenic noble gases are well understood, slight abnormalities from known crustal production ratios can reveal transport and release mechanism information (Ballentine et al., 1991). By quantitatively examining the noble gas components of hydrothermal springs and oil/gas wells, subsurface architecture, underlying fluid-rock interactions, multi-component mixing, and thermal release/migration models can be developed (Kennedy et al., 1988; Lowenstern et al., 2014). Migration modelling using traces of noble gases along with N₂, CH₄ and CO₂ has been undertaken by handful of researchers (Giannesini, 2008; Karolyte et al., 2019). Work done in the midcontinent USA, has advocated that lateral migration of groundwater evidenced by noble gas fractionation serves as a likely mechanism to increase He to economic levels in subsurface reservoirs (Ballentine and Sherwood-Lollar, 2002). Under this approach, dissolved He (in preferable very old groundwater and in low porosity environments) is partitioned (exsolves) into the gas phase as it encounters a gas pocket due to Henry's Law (Brown, 2010; Ballentine and Sherwood-Lollar, 2002). Additionally, it is possible for He-rich gas to exsolve independently of a gas pocket due to the groundwater being oversaturated with He or for He to migrate as a free gas directly to traps (Danabalan et al., 2022). Lower pressures of shallow reservoirs, coupled with higher salinity and cooler temperatures (lower thermal gradient) results in more He in the gas phase (Brown, 2010; Moore and Esfandiari, 1971). Research in subsequent gas release associated with igneous/tectonic activities deep within the crust has advocated that advective fluxes through associated faulting are dominant for He fluid flow in some scenarios (Bebout and Carlson, 1986; Boles et al., 2015; Broadhead and Gillard, 2004; Brown, 2010; Salah and Alsharhan, 1998). Diffusion alone as a migration mechanism for releasing radiogenic He from the deeper crust into shallow environments, was discounted and termed insignificant for primary and secondary migration due to slow rate (Ballentine and Burnard, 2002). However, recent theoretical He migration modelling provides insights

into the diffusive flux of He from basement for both primary and secondary migration (Cheng, 2020; Cheng et al., 2021, 2023). Modelling shows that a He-rich gas phase formed by diffusion from the Precambrian basement to overlying sedimentary reservoirs in the Canadian portion of the Williston Basin requires extremely long time periods of geologic stability and cross formational migration of He (Cheng, 2020; Cheng et al., 2021). Lateral distance models with CO₂ as a carrier gas, have been proposed advocating for He sweet spots as one moves outside of volcanic centres in extensional environments (i.e., CO₂ will be removed by CO₂ dissolution or precipitation of carbonate minerals effectively concentrating the He) (Danabalan et al., 2022; Gilfillan et al., 2009; Weinlich et al., 1999). Despite this, charging, accumulation and migration of crustal He is still relatively poorly understood.

Final accumulation of He in a subsurface surface is dependent on a trap or seal. Traps can be either stratigraphic or structural or a combination of both, and seals can range from tight limes, mudstones, tight shales, or anhydrites (Broadhead, and Gillard, 2004; Broadhead, 2012; Downey, 1984; Moore and Esfandiari, 1971). Due to He's small size, a tight seal is often preferred to mitigate the escape of He. Anhydrites are largely considered the best seals due to their lack of connectivity, but their lack of presence does not negate a He accumulation from existing (Allen, 1978; Dunlap, 1969; Masters, 2000; McKenney and Masters, 1968; Rauzi, 2003). Relatively impermeable rocks can be sufficient to slow He to accumulate in economic quantities. Pressure and temperature can also affect the rate of diffusion from a seal. At greater depths (i.e., greater pressures and temperatures), there can be higher diffusive and possibly advective fluxes, which would indicate that a seal at great depths would need to be more effective at mitigating He loss than a seal at shallower depth that experiences less extreme temperatures and pressures (Moore and Esfandiari, 1971).

Chapter 2

High Helium Reservoirs in the Four Corners Area of the Colorado Plateau, USA

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Abstract

Radiogenic ^4He is naturally produced in Earth's crust due to alpha decay of Uranium (U) and Thorium (Th). Helium has unique thermodynamic properties required for the medical imaging industry, aerospace and other fields of high-tech manufacturing, and currently is in increasingly high demand. Despite its economic value, the mechanisms of helium migration and retention in sedimentary basins remain poorly understood.

Oil and gas fields with economic helium ($>0.3\%$) concentrations have been discovered in Palaeozoic intervals in the Colorado Plateau, southwestern USA. Here we report new noble gas isotope and abundance data for gas samples ($n=31$), from actively producing Palaeozoic formations within five fields: Ratherford, Tootie Dome, Navajo Springs, Pinta Dome, and Dineh-Bi-Keyah. Helium concentrations range from 0.01% to 7.9% with varying amounts of liquid and gaseous hydrocarbons, N_2 , and CO_2 . We present multi-stage gas, water, and oil equilibration models to account for the observed noble gas elemental and isotopic signatures. Oil-dominated systems are explained by a closed system oil/water equilibration and subsequent admixture of air. He-rich dry gas samples exhibit uniform $^4\text{He}/\text{N}_2$ ratios consistent with the regional mean values, suggesting a common crustal source and no subsequent fractionation. In contrast, air-derived $^{20}\text{Ne}/^{36}\text{Ar}$ ratios are highly fractionated. These observations are consistent with a tectonically controlled crustal gas release from the basement, groundwater saturation with ^4He and N_2 , and subsequent degassing. Extensive gas-water interaction (i.e., migration) leads to extreme fractionation of $^{20}\text{Ne}/^{36}\text{Ar}$, but does not affect $^4\text{He}/\text{N}_2$ due to water saturation with crustal gases released from the basement.

We show the volume of rock required to have produced helium in the reservoir to be significantly larger than the current reservoir volume immediately beneath the field. Therefore, the reservoir helium concentration cannot be sourced by in-reservoir decay of U and Th and instead requires a process to incorporate exogenous sources of helium in the reservoir without significant dilution from hydrocarbons. For helium-rich fields, excess helium is sourced from the Precambrian granitic basement likely utilizing a large area beneath the field area (i.e., crustal gas mobilization and transport via fracture zones), consistent with the degree of water contact. Deep crustal faults in the Precambrian basement are in close proximity to the high helium fields, indicating that these structures are potentially serving as primary migration conduits via advective fluid flow.

2.1 Introduction

Helium (He) is the second lightest element and the lightest noble gas in the observable universe. It has two stable isotopic forms: ^3He (primordial) and ^4He (radiogenic decay). Although helium is the second most abundant element in the galaxy, it is relatively rare on Earth. Despite helium's rarity on Earth, people have managed to extract it from the ground, typically when it co-occurs with natural gas, and have developed various advanced applications due to its stable electron configuration and low atomic mass (Chan, 2013). Applications of helium include: Magnetic Resonance Imaging (MRIs), spectrometry, chromatography, dirigible/lifting, electronics, semiconductors, science/engineering, fibre optics, diving, welding, and controlled atmospheres (National Research Council, 2010).

Helium reservoirs, which have been traditionally discovered serendipitously as a by-product of hydrocarbon exploration, can be classified by their major gas component: N₂, CH₄, and CO₂-rich. After the Kansas, USA initial discovery, additional helium discoveries have been made across the USA in Texas, Oklahoma, Wyoming, Kansas, New Mexico, Arizona, Utah, Colorado, and Montana (USGS, 2021). Fields within the Four Corners area (New Mexico and Arizona) contain helium up to ~ 10 molar % (Brennan et al., 2016) (Figure 2.1). The economic threshold for a helium-rich field is 0.3% for primary (standalone) and secondary (with other hydrocarbons) production, and 0.04% from the production of liquefied natural gas (National Research Council, 2010; Brennan et al., 2016; Halford, 2018; Anderson, 2018; Boreham et al., 2018). When the terms economic or non-economic helium are used in this study they are referring strictly to the molar percentage of helium found in the gas stream and do not refer to reservoir volume, producibility, feasibility, and/or the economics of various separation strategies (e.g., pressure swing adsorption, nitrogen rejection). Despite helium not being recognized as a valuable primary resource historically (i.e., often vented to the atmosphere because helium is not combustible), currently helium is being considered as a primary exploration target due to favourable economics and increasing global demand.

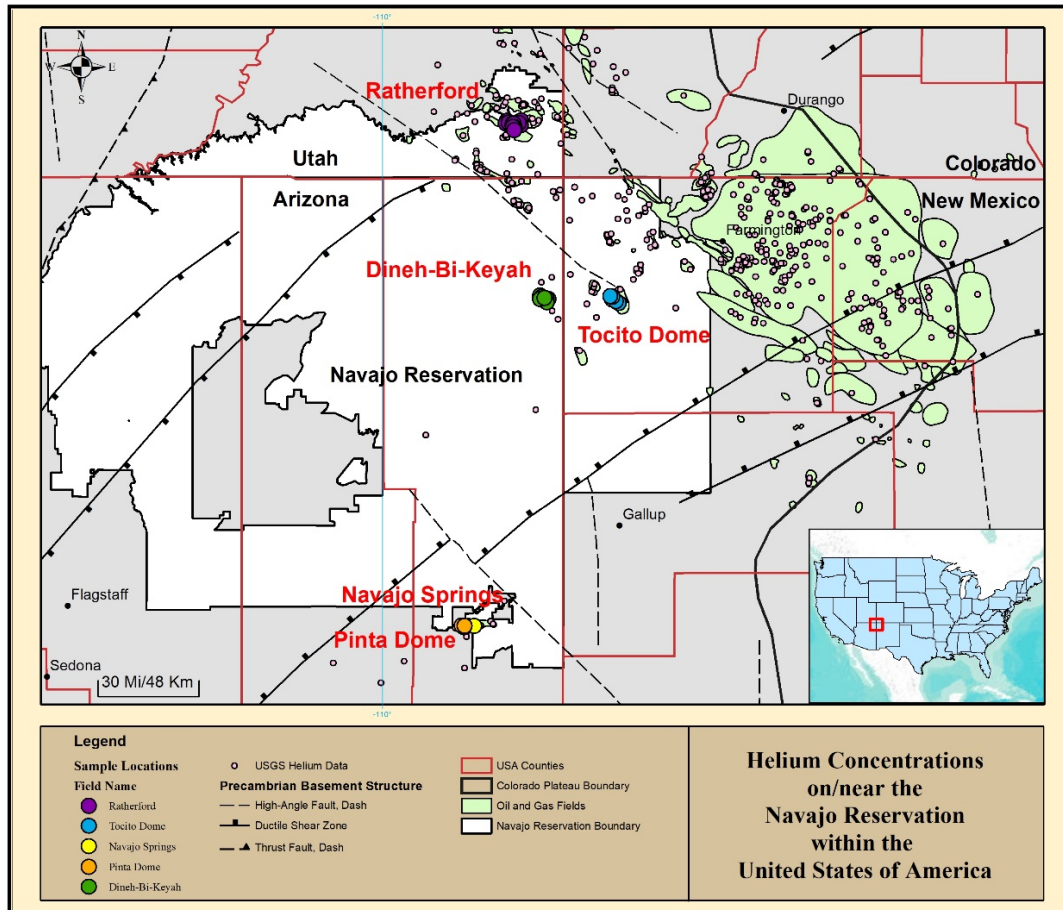


Figure 2.1: Distribution of helium from historical Four Corners area wells along with current sampled locations, which are shown by large coloured circles (USGS helium data - Brennan et al., 2016). Solid fault lines are based on geologic data, while dashed lines are based on geophysical data (Precambrian basement faults - Craddock et al., 2017; Sims et al., 2008).

To aid in the exploration of helium, helium system models, which are a slight variation to the original petroleum system models, are being developed by utilizing elemental compositions and isotopes of noble gases, hydrocarbons, and non-hydrocarbons (Magoon and Dow, 1994a, 1994b; Halford, 2018; Flude et al., 2019). Considering helium as a primary exploration target, there are previously reported critical requirements for the discovery of an economic helium play in the Four Corners area: 1) a portion of shallow crust (basement) to supply helium (source rock), 2) long stable periods to allow helium to accumulate within the impermeable source rocks, 3) faulting/igneous activity/other younger tectonic events, which aided in the advection of helium from the source rock (primary migration) into the overlying sedimentary strata, 4) gas – water interactions with large volumes of pore water (secondary/lateral migration), 5) the presence of a separate migration gas phase to exsolve the helium from solution into a trap, 6) lack of large basin scale charging events of

hydrocarbons, which might dilute the helium in the reservoir (edges of a petroleum system are favourable), 7) the presence of structural, stratigraphic, or combination structural-stratigraphic traps, 8) a seal with very tight and impermeable lithology (evaporites, tight mudstones, tight carbonates, or igneous intrusions), and 9) a period of relative quiescence without large-scale tectonic events to protect the seal and allow additional helium accumulation (Ballentine and Burnard, 2002; Ballentine and Sherwood-Lollar, 2002; Broadhead and Gillard, 2004; Brown, 2010; Danabalan, 2017, Danabalan et al., 2022; Halford, 2018; Zhang et al., 2019) (Table 2.A.1, Figure 2.A.1). This study will investigate several of these factors (1-6) to explain the helium occurrences and lay out a more accurate definition of the helium system in the Four Corners area, which ultimately serves to increase the viability of helium exploration models, lower exploration risk, and spur economic development.

2.2 Geologic Background

2.2.1 Regional Tectonic History of the Colorado Plateau

The Colorado Plateau, which is an elevated crustal block of relatively undeformed strata, straddles Colorado, Utah, New Mexico, and Arizona and is bounded by the Basin and Range province to the northwest, the Rocky Mountains to the northeast, the Rio Grande Rift to the southeast, and the Mogollon Rim to the southwest (Foos, 1999; Gilfillan et al., 2008). The Colorado Plateau is composed of generally flat to slightly dipping sedimentary rocks, which uncomfortably overlie metamorphic and igneous Paleoproterozoic basement rocks (Condie, 1986; Tingey et al., 1991; Re, 2017). The Mazatzal and Yavapai accretionary terranes make up the Paleoproterozoic basement (Karlstrom and Bowring, 1988). There are no structural mountain ranges on the plateau, only volcanic mountains. Volcanism is present around the peripherals of the plateau with minor occurrences within the plateau's boundaries, most likely influencing the low heat flow of the plateau (Gilbert et al., 2007). Although relatively undeformed (possibly due to a thick crust), zones of weakness in basement rocks have localized deformation (i.e., folds and faults, and concomitant fracture systems), which may influence gas migration paths.

The first stage of tectonic uplift commenced during the late Cretaceous (80-50 Ma) was related to Sevier and Laramide contractile deformation (Huntoon, 1974b; Roy, 2005; Roberts et al., 2012). During Late Eocene to Miocene times (35-15 Ma) there was a second phase of uplift (Roberts et al., 2012). It is proposed that Cenozoic uplift was influenced by the flat slab subduction and demise of the Farallon oceanic plate (i.e., Farallon rollback) (Hernández-Urbe & Palin, 2019). This caused the delamination of the mantle lithosphere underneath the plateau, which was replaced by rising asthenosphere (Levander et al., 2011; Hernández-Urbe & Palin, 2019). During the Oligocene, magmas were introduced into the sedimentary sections through deep-seated faults resulting in laccoliths of intermediate composition (Foos, 1999; Fitton et al., 1991; Gilfillan et al., 2008; Roberts et al., 2012; Re, 2017). Around 5 Ma ago, the Colorado Plateau experienced epeirogenic uplift associated with regional extensional tectonism (Baars, 2000; Roy, 2005). According to Foos (1999), this uplift was facilitated by tilting of the plateau to the north and by the reactivation of pre-existing faults.

2.2 Generalized Stratigraphy

The stratigraphy of the Colorado Plateau consists of Proterozoic through Cenozoic aged sediments (Figure A.2) with most sedimentary rocks being deposited in a passive margin (i.e., coastal terrestrial or shallow marine origin) (Stevenson and Wray, 2009; Lillis et al., 2014). On the plateau, episodes of volcanism contributed to the lithologic record from Paleogene - Quaternary. Within the Colorado Plateau's stratigraphic record, Palaeozoic rocks in the Four Corners area produced high He concentrations (Rauzi, 2003; Broadhead and Gillard, 2004; Brown, 2010; Halford, 2018). Palaeozoic rocks with helium potential in the Four Corners region consist of Devonian, Mississippian, Pennsylvanian, and Permian units. The Devonian section includes carbonates (limestones, dolomites), glauconitic sandstones, and black shales. The Mississippian section is predominately limestones. Carbonates (limestones), sandstones, and black shales comprise the Pennsylvanian, whereas the Permian section is mostly sandstones (Fasset, 2010). Oligocene sills within Pennsylvanian strata have produced helium in the Dineh-Ki-Keyah Field in the Four Corners area (McKenny and Masters, 1968; Masters 2000; Rauzi, 2015; Halford, 2018). In this study, gas samples were obtained from the

McCracken Sandstone (Dineh-Bi-Keyah Field), the Barker Creek (Dineh-Bi-Keyah and Tocito Dome fields), a sill intruding the Barker Creek (Dineh-Bi-Keyah Field), the Desert Creek (Ratherford Field), and the Coconino Sandstone (Navajo Springs and Pinta Dome fields).

2.3 Methods

2.3.1 Sample Collection

Natural gas was sampled from existing wellheads on and near the Navajo Nation, from helium producing Palaeozoic formations. Duplicate gas samples were collected in the field from 31 actively producing wells from Utah, New Mexico, and Arizona with stainless-steel cylinders (non-noble gases) and copper tubes (noble gases). The cylinders were evacuated and pre-baked stainless-steel cylinders and thick-walled refrigerator grade copper tubes, which are 40.6 cm (15.98 in) long, and have a 0.95 cm (0.374 in) outside diameter. The cylinders were fitted with vacuum modified Swagelok valves. Copper tubing was connected to the in-line system, allowing for the simultaneous collection of stainless steel and copper tubes. To minimize contamination, once the stainless-steel cylinders and copper tubes were connected in-line to the producing well, they were purged for approximately 10 minutes each (greater than 50 tube volumes of gas) to negate air contamination (Darrah et al., 2015b; Kang et al., 2016). Once the samples were successfully collected, the stainless-steel cylinders were sealed using vacuum in-line modified valves while the copper tubes were sealed with brass refrigeration clamps with a 0.762 mm gap (Darrah et al., 2013; Darrah et al., 2015b; Kang et al., 2016).

2.3.2 Laboratory Analyses

The laboratory analyses were divided into: noble gas (elemental and isotopic abundance), major gas components, stable isotopes of carbon, and stable isotopic values of nitrogen.

For the noble gas analyses a Thermo Fisher Helix Split Flight Tube (SFT) Noble Gas mass spectrometer was utilized at the Ohio State University Noble Gas Laboratory (OSU NGL). Darrah and Poreda (2012) cover the noble gas procedures for the purification and analyses of gas samples. The average precision for noble gas concentrations based on standard reproducibility for noble gas isotope

concentrations are as follows: ^4He (0.69%), ^{22}Ne (1.09%), ^{36}Ar (0.31%), ^{84}Kr (1.51%), and ^{130}Xe (1.58%).

To measure the major gas components (hydrocarbon and non-hydrocarbon compositions), an SRS Quadrupole mass spectrometer and the SRI 8610C Multi-Gas 3+ gas chromatograph with a flame ionization detector and thermal conductivity detector were utilized (Hunt et al., 2012; Darrah and Poreda, 2012; Kang et al., 2016). The standard errors were all less than $\pm 2.97\%$ for major gas concentrations. The average results of the external precision analyses are: CH_4 (1.34%), C_2H_6 (1.57%), C_3H_8 (1.44%), $\text{C}_4\text{H}_{10,i}$ (2.84%), $\text{C}_4\text{H}_{10-n}$ (2.86%), $\text{C}_5\text{H}_{12,i}$ (2.97%), $\text{C}_5\text{H}_{12-n}$ (2.91%), N_2 (0.98%), CO_2 (1.21%), and Ar (0.63%) based on daily replicate measurements during analyses.

Darrah et al. (2013), Jackson et al. (2013), Darrah et al. (2015b), and Harkness et al., (2017), describe the procedures for obtaining stable isotopic values for C in CH_4 . For the hydrocarbon isotopic percentages, firstly a Thermo Finnigan Trace Ultra gas chromatograph was used and secondly a Thermo Fisher Delta V Plus with combustion and dual inlet isotope ratio mass spectrometer was utilized. Detection limits are $0.001 \text{ cm}^3\text{STP}/\text{cm}^3$ for CH_4 . The $\delta^{13}\text{C}-\text{CH}_4$ are calculated versus the Vienna Pee Dee belemnite (VPDB) with a reproducibility for CH_4 ($\pm 0.1\%$). The $\delta^{13}\text{C}-\text{CH}_4$ values are shown in per mil (‰).

The methods of the stable isotopic analyses of nitrogen (N_2) are described in Darrah et al. (2013), Darrah et al. (2015b), Harkness et al. (2017), and Jackson et al. (2013). Using the same methods as described above (Thermo Finnigan Trace Ultra gas chromatographic separation, followed by using the Thermo Fisher Delta V Plus with dual inlet isotope ratio mass spectrometry), the detection limits of nitrogen isotopes are $0.001 \text{ cm}^3\text{STP}/\text{cm}^3$ for $\delta^{15}\text{N}-\text{N}_2$. The $\delta^{15}\text{N}-\text{N}_2$ values (versus air) have a N_2 reproducibility of $\pm 0.3\%$.

Utilizing established atmospheric air standards from Lake Erie, Ohio air, several synthetic natural gas standards from Praxair, which include referenced/cross-validated laboratory standards of N_2 , CO_2 , O_2 , C_1 - C_5 , and the Yellowstone MM standard, average external precisions were determined (Tedesco et al., 2010; Harkness et al., 2017).

2.4 Results

The bulk major gas concentrations (Table 2.1, Figure 2.2) as well as noble gas abundance and isotope ratios (n=31) are presented in Table 2. Observations regarding the fields are: 1) the Ratherford Field is mostly composed of methane, ethane, and propane, with trace amounts of helium. 2) The Tocito Dome Field has marginally economic levels of helium along with substantial methane contributions. Thus, the Ratherford and Tocito Dome are CH₄-rich fields. 3) The Navajo Springs and Pinta Dome samples have minute amounts of methane, are rich in nitrogen, and have the highest helium concentrations observed in this study. 4) The Dineh-Bi-Keyah (DBK) samples are nitrogen-rich, have high helium and variable CO₂ abundances. Thus, Dineh-Bi-Keyah, Pinta Dome, and Navajo Springs fields are classified as He-rich fields.

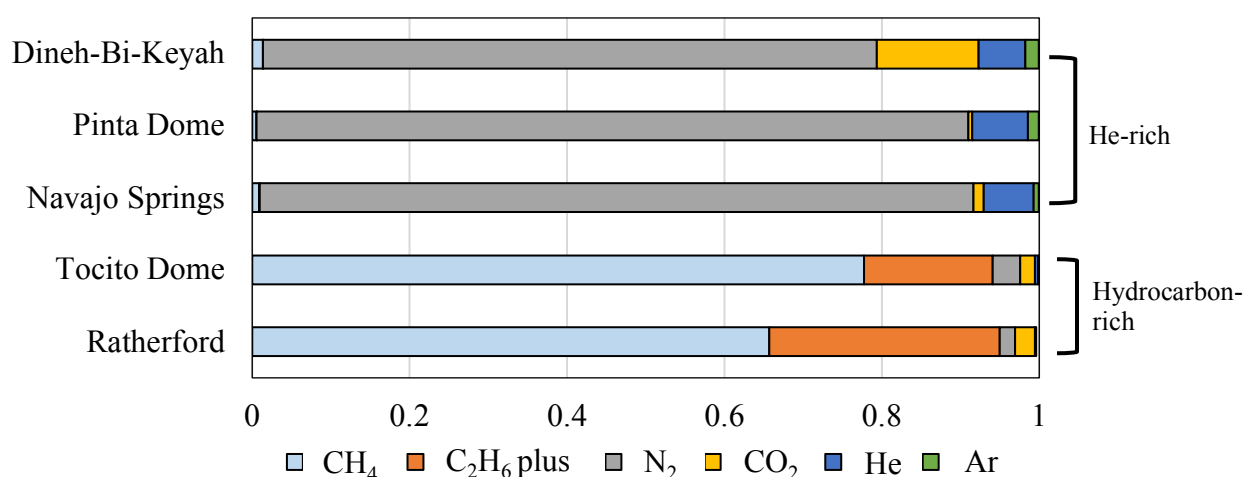


Figure 2.2: Bar chart showing average bulk gas composition (molar fraction) of the sampled wells for the hydrocarbon-rich fields (Ratherford and Tocito Dome) and helium-rich fields (Navajo Springs, Pinta Dome, and Dineh-Bi-Keyah).

2.4.1 Major Volatiles and Stable Isotopes

We establish the hydrocarbon-rich (CH₄-rich) fields as the Ratherford and Tocito Dome fields, and the helium-rich (He-rich) fields as the Navajo Springs, Pinta Dome, and Dineh-Bi-Keyah fields. The data ranges for N₂ (%) are: 0.7-8.0 (CH₄-rich); 76.6-91.3 (He-rich). $\delta^{15}\text{N}$ (N₂) (‰) versus air: -11.7 to -2.5 (CH₄-rich); 3.0 to 7.6 (He-rich). CH₄ (%): 51.8-78.9 (CH₄-rich); 0.02-2.7 (He-rich). $\delta^{13}\text{CH}_4$ (‰ VPDB): -53.6 to -43.0 (CH₄-rich); -36.2 to -30.6 (He-rich). ΣC_2+ (%): 12.8-43.4 (CH₄-rich); 0.00003-0.04 (He-rich).

2.4.2 Noble Gases

Bulk helium for the fields are: 0.01-0.6% (CH₄-rich); 5%-8% (He-rich). ⁴He (μcm³/cm³): 146.0-6,071.3 (CH₄-rich); 50,390.1-79,200.3 (He-rich). The helium isotopic ratios ³He/⁴He, expressed as R/R_a [³He/⁴He R/R_a = (³He/⁴He)_{measured} / (³He/⁴He)_{atmosphere}], for the CH₄-rich fields are strongly radiogenic (0.02-0.09 R_a); while the He-rich fields contain a mantle component (0.05-0.22 R_a) (Andrews, 1985; Ballentine and Burnard, 2002) (Figure 2.3). R_a values are reported relative to the air value R_a = 1.384x10⁻⁶ (air = 1 R_a; Clarke et al., 1976; Sano et al., 1988). The data ranges for ⁴He/²⁰Ne are: 1,654.9-178,172.2 (CH₄-rich); 11,260.7-213,865.4 (He-rich). Since the ⁴He/²⁰Ne ratios are all significantly higher than the ASW value of 0.288 (Kipfer et al., 2002), this indicates that air derived He contributions are negligible.

²⁰Ne (μcm³/cm³) for the fields are: 0.01- 0.2 (CH₄-rich); 0.3-5.7 (He-rich). ²⁰Ne/²²Ne: 9.5-9.8 (CH₄-rich); 9.2-9.7 (He-rich). ²¹Ne/²²Ne: 0.03-0.06 (CH₄-rich); 0.04-0.08 (He-rich). Ratios greater than the air value for ²¹Ne/²²Ne (0.029) are attributed to crustal input (Ballentine and O’Nions, 1992).

The data ranges for ⁴⁰Ar (μcm³/cm³) are: 46.2-1,106.4 (CH₄-rich); 4,230.1-23,204.8 (He-rich). ⁴⁰Ar/³⁶Ar: 355.8-5,177.4 (CH₄-rich); 1,291.9-17,083.2 (He-rich). Compared to the air ⁴⁰Ar/³⁶Ar value of 298.56, the ratios indicate crustal enrichment (Lee et al., 2006).

The data ranges for ⁸⁴Kr (ncm³/cm³) are: 1.3-48.4 (CH₄-rich); 17.4-120.9 (He-rich). ¹³²Xe (ncm³/cm³): 0.04-3.0 (CH₄-rich); 3.3-18.2 (He-rich). Kr (⁸⁶Kr/⁸⁴Kr) and Xe (¹³²Xe/¹³⁰Xe) isotopic ratios are air like (0.3; ⁸⁶Kr/⁸⁴Kr) and (6.6; ¹³²Xe/¹³⁰Xe) (Aregbe et al., 1996; Moreira and Allegre, 1998; Pepin, 2000; Porcelli and Ballentine., 2002; Ballentine and Burnard, 2002; White, 2015).

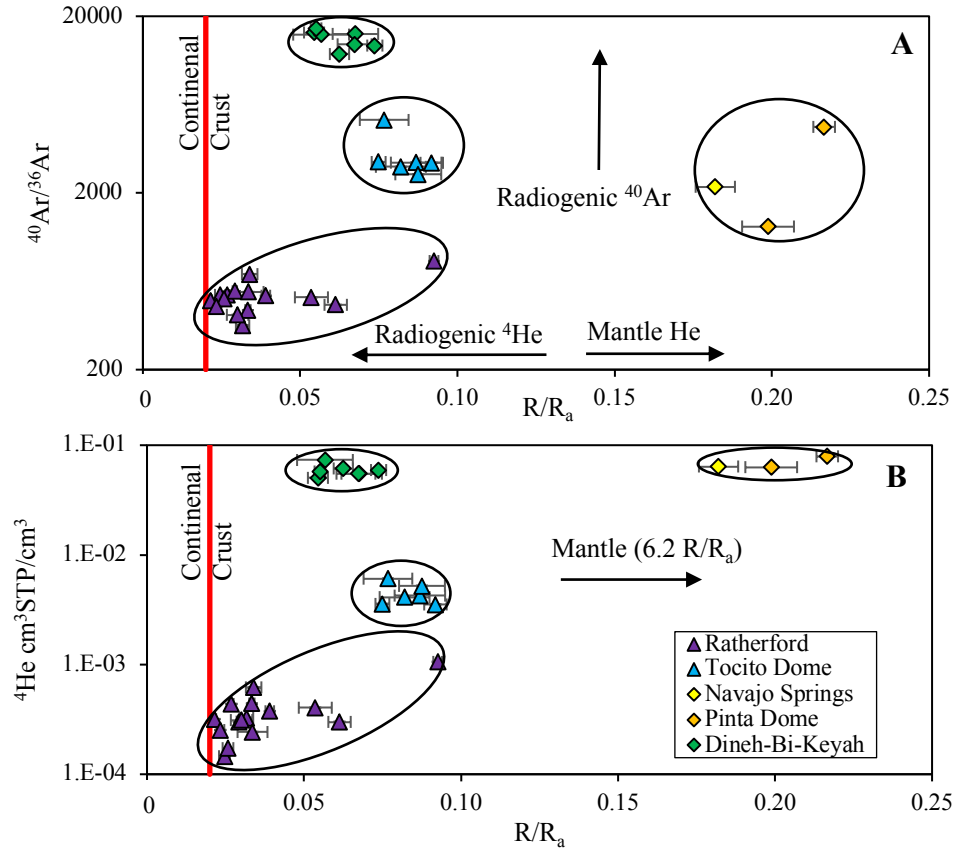


Figure 2.3: Cross plots illustrating four unique groupings of gas families. 3A) R/R_a versus $^{40}\text{Ar}/^{36}\text{Ar}$ and 3B) R/R_a versus ^4He both showing the influence of crustal and mantle components. The red line indicates the crustal R/R_a signature. Continental crust signature is 0.02 (Andrews, 1985; Ballentine and Burnard, 2002; Boreham et al., 2018). Error bars are smaller than symbols for ^4He and $^{40}\text{Ar}/^{36}\text{Ar}$. He-rich fields are represented with diamonds, whereas the hydrocarbon-rich fields are represented with triangles.

Table 2.1: Elemental gas values, R: Ratherford, TD: Tocito Dome, NS: Navajo Springs, PD: Pinta Dome, & DBK: Dineh-Bi-Keyah. Other abbreviations: below detection limit (b.d.l.) and non-applicable (n/a).

ID	CH ₄ cm ³ STP/cm ³	± cm ³ STP/cm ³	C ₂ H ₆ cm ³ STP/cm ³	± cm ³ STP/cm ³	C3 cm ³ STP/cm ³	± cm ³ STP/cm ³	Ci-4 cm ³ STP/cm ³	± cm ³ STP/cm ³	Cn-4 cm ³ STP/cm ³	± cm ³ STP/cm ³
R9-34	0.54	6.86E-03	2.21E-01	3.41E-03	1.25E-01	1.68E-03	1.30E-02	3.80E-04	3.43E-02	1.00E-03
R10-14	0.66	8.29E-03	8.72E-02	2.77E-03	3.05E-02	3.26E-04	2.38E-03	6.61E-05	5.95E-03	1.66E-04
R10-32	0.63	7.97E-03	1.72E-01	3.20E-03	9.30E-02	1.14E-03	9.69E-03	2.93E-04	2.95E-02	8.95E-04
R12-23	0.76	9.59E-03	1.27E-01	1.72E-03	4.99E-02	6.69E-04	4.90E-03	1.27E-04	1.37E-02	3.54E-04
R13-12	0.52	5.31E-03	1.72E-01	3.36E-03	1.16E-01	1.71E-03	1.69E-02	4.70E-04	6.12E-02	1.71E-03
R13-41	0.78	9.83E-03	1.27E-01	2.36E-03	4.18E-02	7.11E-04	3.14E-03	8.43E-05	7.67E-03	2.06E-04
R15-33	0.74	9.38E-03	1.34E-01	2.19E-03	4.97E-02	5.52E-04	4.39E-03	1.37E-04	1.09E-02	3.42E-04
R16-41	0.61	7.74E-03	1.95E-01	2.84E-03	1.06E-01	1.32E-03	7.17E-03	2.14E-04	2.09E-02	6.23E-04
R17-11	0.65	8.17E-03	1.93E-01	3.77E-03	9.51E-02	1.02E-03	8.73E-03	2.17E-04	2.51E-02	6.24E-04
R17-13	0.59	7.37E-03	2.11E-01	3.31E-03	1.08E-01	1.25E-03	1.30E-02	3.63E-04	3.64E-02	1.01E-03
R17-22	0.58	7.31E-03	1.76E-01	2.56E-03	1.12E-01	1.56E-03	1.75E-02	5.49E-04	4.72E-02	1.48E-03
R20-42	0.62	7.83E-03	1.77E-01	3.82E-03	1.07E-01	1.43E-03	1.44E-02	3.87E-04	4.16E-02	1.12E-03
R20-44	0.71	8.96E-03	1.55E-01	2.88E-03	6.35E-02	7.56E-04	5.27E-03	1.57E-04	1.30E-02	3.88E-04
R20-66	0.74	9.39E-03	1.49E-01	2.33E-03	5.91E-02	7.09E-04	4.96E-03	1.18E-04	1.25E-02	2.99E-04
R29-31	0.72	9.02E-03	1.56E-01	1.96E-03	6.13E-02	7.60E-04	5.96E-03	1.96E-04	1.25E-02	4.11E-04
TD N 1	0.78	1.27E-02	9.42E-02	2.46E-03	3.85E-02	4.81E-04	5.98E-03	1.30E-04	1.09E-02	2.38E-04
TD N 11	0.78	8.87E-03	9.83E-02	2.67E-03	4.08E-02	5.96E-04	6.40E-03	1.59E-04	1.12E-02	2.79E-04
TD P 6	0.76	9.64E-03	1.06E-01	1.45E-03	3.74E-02	5.34E-04	7.45E-03	1.78E-04	1.33E-02	3.16E-04
TD U 9	0.79	1.05E-02	1.03E-01	1.70E-03	4.11E-02	5.42E-04	6.08E-03	1.57E-04	1.06E-02	2.74E-04
TD U 12	0.78	1.11E-02	9.51E-02	2.47E-03	3.77E-02	4.75E-04	5.67E-03	1.46E-04	9.50E-03	2.45E-04
NS 31-1	0.01	2.10E-04	1.91E-05	7.94E-07	1.33E-05	7.45E-07	6.91E-06	4.34E-07	1.01E-05	6.37E-07
PD 33-1	0.01	2.92E-04	1.88E-05	9.69E-07	1.85E-05	1.13E-06	9.20E-06	6.70E-07	1.54E-05	1.12E-06
PD 34-1	2.18E-04	5.90E-06	2.96E-07	1.82E-08	b.d.l.	n/a	b.d.l.	n/a	b.d.l.	n/a
DBK B 2	0.02	7.00E-04	1.27E-04	4.00E-06	7.93E-05	3.89E-06	1.63E-05	9.99E-07	2.53E-05	1.55E-06
DBK C 2	0.01	5.34E-04	7.92E-05	4.08E-06	4.53E-05	2.17E-06	8.40E-06	4.81E-07	1.33E-05	7.61E-07
DBK 4	0.01	2.20E-04	6.09E-05	3.42E-06	3.91E-05	1.83E-06	b.d.l.	n/a	b.d.l.	n/a
DBK 15	0.03	1.16E-03	1.98E-04	6.24E-06	1.21E-04	3.75E-06	2.38E-05	1.41E-06	3.83E-05	2.27E-06
DBK 24	0.01	3.65E-04	2.98E-05	1.46E-06	1.96E-05	9.97E-07	b.d.l.	n/a	b.d.l.	n/a
DBK 88 2	2.75E-03	9.41E-05	2.03E-05	1.25E-06	1.24E-05	7.93E-07	b.d.l.	n/a	b.d.l.	n/a
DBK 88 3	0.02	8.32E-04	9.88E-05	4.11E-06	5.20E-05	2.80E-06	1.37E-05	9.23E-07	2.10E-05	1.41E-06
R9-34	0.54	6.86E-03	2.21E-01	3.41E-03	1.25E-01	1.68E-03	1.30E-02	3.80E-04	3.43E-02	1.00E-03

Table 2.1: Continued.

ID	Ci-5 cm ³ STP/cm ³	± cm ³ STP/cm ³	C-5 cm ³ STP/cm ³	± cm ³ STP/cm ³	C-6+ cm ³ STP/cm ³	± cm ³ STP/cm ³	CO ₂ cm ³ STP/cm ³	± cm ³ STP/cm ³	N ₂ cm ³ STP/cm ³	± cm ³ STP/cm ³
R9-34	6.17E-03	1.91E-04	6.28E-03	1.94E-04	5.02E-04	1.61E-05	0.03	3.39E-04	0.01	9.71E-05
R10-14	8.66E-04	2.33E-05	9.31E-04	2.51E-05	2.94E-04	9.41E-06	0.13	2.02E-03	0.08	7.43E-04
R10-32	5.95E-03	1.90E-04	6.44E-03	2.06E-04	8.34E-04	2.67E-05	0.02	3.23E-04	0.02	2.12E-04
R12-23	2.88E-03	8.47E-05	3.34E-03	9.80E-05	1.52E-03	4.85E-05	0.02	2.23E-04	0.02	1.47E-04
R13-12	1.92E-02	6.34E-04	2.82E-02	9.30E-04	2.02E-02	6.45E-04	0.04	5.92E-04	0.01	1.00E-04
R13-41	1.50E-03	4.30E-05	1.75E-03	5.04E-05	7.97E-05	2.55E-06	0.01	1.43E-04	0.02	1.67E-04
R15-33	1.82E-03	5.99E-05	1.89E-03	6.22E-05	7.36E-04	2.36E-05	0.01	1.18E-04	0.04	3.70E-04
R16-41	6.26E-03	2.15E-04	7.60E-03	2.61E-04	2.86E-04	9.16E-06	0.03	3.68E-04	0.01	1.02E-04
R17-11	5.17E-03	1.29E-04	6.94E-03	1.73E-04	5.96E-04	1.91E-05	0.01	5.92E-05	0.01	7.99E-05
R17-13	5.97E-03	2.37E-04	6.91E-03	2.74E-04	2.66E-03	8.51E-05	0.02	3.78E-04	0.01	8.41E-05
R17-22	1.13E-02	3.06E-04	1.16E-02	3.12E-04	7.95E-03	2.54E-04	0.01	1.84E-04	0.02	1.95E-04
R20-42	6.27E-03	1.74E-04	7.83E-03	2.17E-04	5.98E-04	1.91E-05	0.01	8.62E-05	0.01	6.38E-05
R20-44	2.28E-03	8.89E-05	2.65E-03	1.03E-04	1.85E-04	5.92E-06	0.02	2.31E-04	0.02	1.94E-04
R20-66	1.83E-03	5.41E-05	1.93E-03	5.70E-05	5.84E-04	1.87E-05	0.02	2.07E-04	0.01	7.18E-05
R29-31	1.63E-03	5.09E-05	1.63E-03	5.09E-05	b.d.l.	n/a	0.02	1.92E-04	0.01	1.35E-04
TD N 1	2.59E-03	6.48E-05	2.28E-03	5.69E-05	1.11E-03	3.55E-05	0.02	2.11E-04	0.04	3.86E-04
TD N 11	2.88E-03	1.09E-04	2.47E-03	9.36E-05	1.27E-03	4.07E-05	0.02	2.19E-04	0.04	3.03E-04
TD P 6	3.68E-03	1.03E-04	2.85E-03	7.97E-05	2.08E-03	6.65E-05	0.02	2.12E-04	0.05	4.02E-04
TD U 9	3.09E-03	1.08E-04	2.59E-03	9.07E-05	1.52E-03	4.86E-05	0.02	1.86E-04	0.02	2.10E-04
TD U 7	3.49E-03	9.07E-05	3.08E-03	8.00E-05	2.22E-03	7.09E-05	0.02	1.91E-04	0.03	2.51E-04
TD U 12	2.24E-03	7.39E-05	1.87E-03	6.16E-05	9.31E-04	2.98E-05	0.02	2.46E-04	0.04	3.97E-04
NS 31-1	5.57E-06	3.12E-07	5.64E-06	3.16E-07	1.08E-06	3.47E-08	0.01	1.41E-04	0.91	6.29E-03
PD 33-1	1.48E-05	1.03E-06	1.51E-05	1.05E-06	3.03E-06	9.69E-08	0.01	1.10E-04	0.91	4.50E-03
PD 34-1	b.d.l.	n/a	b.d.l.	n/a	b.d.l.	n/a	1.83E-03	3.86E-05	0.9	7.10E-03
DBK B 2	b.d.l.	n/a	b.d.l.	n/a	b.d.l.	n/a	0.13	1.06E-03	0.78	5.02E-03
DBK C 2	b.d.l.	n/a	b.d.l.	n/a	b.d.l.	n/a	0.12	1.07E-03	0.77	4.51E-03
DBK 4	b.d.l.	n/a	b.d.l.	n/a	b.d.l.	n/a	0.14	1.15E-03	0.79	6.00E-03
DBK 15	b.d.l.	n/a	b.d.l.	n/a	b.d.l.	n/a	0.13	1.33E-03	0.77	4.54E-03
DBK 24	b.d.l.	n/a	b.d.l.	n/a	b.d.l.	n/a	0.13	9.25E-04	0.78	7.28E-03
DBK 88 2	b.d.l.	n/a	b.d.l.	n/a	b.d.l.	n/a	0.15	1.85E-03	0.78	3.27E-03
DBK 88 3	b.d.l.	n/a	b.d.l.	n/a	b.d.l.	n/a	0.11	1.04E-03	0.78	3.68E-03

Table 2.2: Isotopic gas values, R: Ratherford, TD: Tocito Dome, NS: Navajo Springs, PD: Pinta Dome, & DBK: Dineh-Bi-Keyah.

ID	$\frac{^3\text{He}}{^4\text{He}}$ R/R _a	± R _a	^4He $\mu\text{cm}^3/\text{cm}^3$	± $\mu\text{cm}^3/\text{cm}^3$	^{20}Ne $\mu\text{cm}^3/\text{cm}^3$	± $\mu\text{cm}^3/\text{cm}^3$	$\frac{^{20}\text{Ne}}{^{22}\text{Ne}}$	±	$\frac{^{21}\text{Ne}}{^{22}\text{Ne}}$	±	$\frac{^{20}\text{Ne}}{^{36}\text{Ar}}$	±	$\frac{^{38}\text{Ar}}{^{36}\text{Ar}}$	±
R9-34	0.02	1.72E-03	145.97	1.27	0.01	1.24E-04	9.77	0.03	0.05	1.69E-04	0.15	1.42E-03	0.2	7.14E-04
R10-14	0.05	5.25E-03	404.22	2.98	0.07	6.95E-04	9.72	0.03	0.03	1.09E-04	0.18	1.80E-03	0.19	7.70E-04
R10-32	0.03	2.47E-03	619.69	4.19	0.07	6.25E-04	9.8	0.03	0.04	1.48E-04	0.21	2.00E-03	0.2	7.69E-04
R12-23	0.03	2.12E-03	326.61	2.34	0.2	1.80E-03	9.77	0.03	0.03	1.12E-04	0.36	3.41E-03	0.2	7.87E-04
R13-12	0.06	3.56E-03	300.07	2.54	0.11	9.88E-04	9.72	0.03	0.03	1.07E-04	0.22	1.89E-03	0.2	1.02E-03
R13-41	0.03	6.84E-04	437.35	2.83	0.08	8.86E-04	9.75	0.02	0.03	1.11E-04	0.19	2.16E-03	0.2	8.13E-04
R15-33	0.09	1.39E-03	1057.62	10.25	0.22	2.74E-03	9.77	0.03	0.03	1.18E-04	0.21	2.88E-03	0.19	7.09E-04
R16-41	0.03	4.76E-03	242.68	1.63	0.04	5.98E-04	9.67	0.03	0.03	1.15E-04	0.13	1.73E-03	0.2	6.99E-04
R17-11	0.02	5.25E-04	317.92	1.9	0.06	5.47E-04	9.76	0.03	0.03	1.11E-04	0.14	1.21E-03	0.2	7.95E-04
R17-13	0.03	1.71E-03	172.95	0.98	0.01	1.50E-04	9.76	0.03	0.03	1.32E-04	0.12	1.37E-03	0.2	7.69E-04
R17-22	0.02	1.24E-03	253	1.71	0.07	6.28E-04	9.76	0.03	0.04	1.49E-04	0.15	1.45E-03	0.2	7.87E-04
R20-42	0.03	6.98E-04	302.04	2.23	0.04	4.36E-04	9.77	0.03	0.03	1.32E-04	0.12	1.30E-03	0.2	5.87E-04
R20-44	0.04	1.37E-03	375.23	3.26	0.05	5.45E-04	9.74	0.03	0.03	1.15E-04	0.13	2.43E-03	0.2	7.51E-04
R20-66	0.03	8.41E-04	441.25	3.69	0.12	1.05E-03	9.76	0.03	0.03	1.11E-04	0.22	1.91E-03	0.19	7.03E-04
R29-31	0.03	3.41E-03	312	1.15	0.13	1.18E-03	9.73	0.02	0.03	1.24E-04	0.23	2.15E-03	0.18	7.35E-04
TD N 1	0.09	7.30E-03	5213.49	45.2	0.05	4.56E-04	9.7	0.03	0.04	1.77E-04	0.13	1.30E-03	0.2	7.45E-04
TD N 11	0.08	7.75E-03	6071.28	16.81	0.03	2.97E-04	9.74	0.03	0.06	2.22E-04	0.18	1.54E-03	0.2	5.86E-04
TD P 6	0.09	3.57E-03	3533.09	13.24	0.12	9.41E-04	9.48	0.02	0.05	1.31E-04	0.32	2.54E-03	0.19	6.89E-04
TD U 7	0.09	8.04E-03	4255.31	20.29	0.1	9.89E-04	9.82	0.03	0.04	1.56E-04	0.37	3.63E-03	0.19	7.14E-04
TD U 9	0.07	2.21E-03	3572.48	12.75	0.1	7.86E-04	9.64	0.03	0.04	1.40E-04	0.37	2.99E-03	0.2	7.23E-04
TD U 12	0.08	7.94E-03	4120.84	24.19	0.03	3.47E-04	9.58	0.02	0.05	1.91E-04	0.1	1.17E-03	0.2	9.71E-04
NS 31-1	0.18	6.25E-03	63983.85	271.73	5.68	5.57E-02	9.34	0.02	0.04	1.49E-04	1.93	2.46E-02	0.19	6.81E-04
PD 33-1	0.2	8.24E-03	63086.58	460.97	3.07	2.73E-02	9.21	0.02	0.04	1.42E-04	0.94	1.16E-02	0.19	6.92E-04
PD 34-1	0.22	3.44E-03	79200.32	778.51	3.18	3.52E-02	9.72	0.02	0.05	1.88E-04	0.65	1.05E-02	0.19	1.02E-03
DBK B 2	0.05	3.19E-03	50390.09	125.32	3.69	3.83E-02	9.38	0.02	0.06	1.97E-04	3.45	3.69E-02	0.19	7.33E-04
DBK C 2	0.06	8.88E-03	73308.2	230.17	2.48	2.65E-02	9.21	0.02	0.08	3.07E-04	1.68	2.27E-02	0.19	8.49E-04
DBK 4	0.07	7.23E-03	55001.97	193.44	1.12	1.13E-02	9.41	0.02	0.08	2.98E-04	2.5	2.65E-02	0.19	6.95E-04
DBK 15	0.07	5.40E-03	54990.64	257.91	2.85	3.56E-02	9.58	0.02	0.07	2.80E-04	1.75	2.29E-02	0.2	7.01E-04
DBK 24	0.06	1.70E-03	57579.14	418.54	1.44	1.52E-02	9.3	0.02	0.08	2.96E-04	1.13	1.43E-02	0.2	7.39E-04
DBK 88 2	0.06	3.07E-03	61397.38	513.09	0.29	2.72E-03	9.3	0.02	0.05	1.84E-04	0.52	5.12E-03	0.19	9.71E-04
DBK 88 3	0.07	2.41E-03	59370.42	205.96	2.81	2.75E-02	9.46	0.02	0.07	2.81E-04	1.68	2.21E-02	0.18	6.73E-04

Table 2.2. Continued.

ID	$\frac{40_{Ar}}{36_{Ar}}$	$\pm$	^{84}Kr ncm ³ /cm ³	$\pm$ ncm ³ /cm ³	^{132}Xe ncm ³ /cm ³	$\pm$ ncm ³ /cm ³	$\frac{86_{Kr}}{84_{Kr}}$	$\pm$	$\frac{132_{Xe}}{130_{Xe}}$	$\pm$	$\delta^{15}N$ ‰	$\pm$ Per mil	$\delta^{13}C$ ‰ CH ₄	$\pm$ Per mil
R9-34	529.83	1.59	1.25	0.02	0.12	0	0.31	9.10E-04	6.52	2.11E-02	-8.64	0.18	-51.1	0.09
R10-14	513.11	1.19	18.19	0.28	0.9	0.01	0.31	8.72E-04	6.52	2.18E-02	-11.68	0.19	-53.63	0.08
R10-32	694.54	1.94	10.12	0.13	0.04	0	0.3	7.78E-04	6.49	2.61E-02	-7.17	0.17	-48.98	0.09
R12-23	355.77	0.99	20.16	0.3	0.96	0.01	0.3	1.19E-03	6.53	2.55E-02	-6.85	0.2	-49.74	0.09
R13-12	465.53	1.2	8.01	0.19	0.47	0	0.31	8.12E-04	6.57	2.20E-02	-2.48	0.19	-49.57	0.09
R13-41	528.67	1.65	13.38	0.19	0.54	0.01	0.3	8.39E-04	6.54	2.33E-02	-8.81	0.19	-48.47	0.09
R15-33	823.85	2.17	48.35	0.69	2.8	0.03	0.3	8.53E-04	6.46	1.88E-02	-7.3	0.28	-48.86	0.09
R16-41	550.22	1.48	18.4	0.25	1	0.01	0.3	8.03E-04	6.54	1.90E-02	-6.54	0.29	-48.26	0.09
R17-11	493.22	1.17	20.7	0.27	0.79	0.01	0.3	6.28E-04	6.58	2.24E-02	-3.48	0.2	-49.69	0.09
R17-13	505.54	1.15	2.45	0.03	0.23	0	0.3	7.51E-04	6.38	2.14E-02	-7.09	0.2	-48.76	0.1
R17-22	454.44	1.94	5.95	0.09	0.87	0.01	0.3	8.78E-04	6.56	2.55E-02	-4.6	0.15	-50.21	0.08
R20-42	555.25	1.38	18.19	0.23	1.6	0.02	0.31	7.95E-04	6.49	2.14E-02	-3.68	0.2	-51.67	0.08
R20-44	524.14	1.95	12.18	0.2	0.73	0.01	0.3	7.56E-04	6.55	1.95E-02	-9.28	0.18	-46.24	0.08
R20-66	434.11	0.84	27.73	0.35	1.17	0.02	0.3	9.43E-04	6.52	1.99E-02	-4.92	0.25	-49.12	0.08
R29-31	408.69	1.21	16.66	0.24	0.69	0.01	0.3	8.68E-04	6.54	2.10E-02	-3.54	0.16	-47.05	0.1
TD N 1	2550.44	5.17	12.7	0.17	3.03	0.04	0.31	9.16E-04	6.39	4.18E-02	-6.87	0.18	-45.13	0.09
TD N 11	5177.45	10.61	7.75	0.09	2.01	0.02	0.3	9.23E-04	6.5	1.99E-02	-8.03	0.27	-43	0.08
TD P 6	2962.29	8.76	6.74	0.07	0.68	0.01	0.3	1.04E-03	6.47	1.96E-02	-4.41	0.27	-44.04	0.1
TD U 7	2968.43	7.09	17.11	0.24	0.63	0.01	0.3	8.46E-04	6.5	2.37E-02	-3.16	0.24	-44.74	0.08
TD U 9	2994.02	6.55	3.69	0.04	0.52	0.01	0.3	8.46E-04	6.56	2.53E-02	-4.74	0.27	-45.77	0.08
TD U 12	2811.86	8.32	15.62	0.22	1.67	0.02	0.3	8.43E-04	6.5	2.65E-02	-5.74	0.17	-46.85	0.09
NS 31-1	2167.53	5.67	72.65	0.88	6.64	0.07	0.3	8.09E-04	6.45	2.11E-02	4.65	0.23	-34.71	0.13
PD 33-1	1291.91	3.15	74.39	0.79	5.97	0.06	0.3	1.04E-03	6.56	1.94E-02	5.99	0.27	-33.74	0.12
PD 34-1	4730.65	13.58	120.89	1.51	11.38	0.11	0.3	7.83E-04	6.51	2.60E-02	3.17	0.18	-31.12	0.12
DBK B 2	16191	20.22	23.92	0.35	7.64	0.08	0.3	8.13E-04	6.56	3.11E-02	5.99	0.29	-30.57	0.08
DBK C 2	15747.38	25.65	58.7	0.63	9.32	0.09	0.3	8.33E-04	6.59	2.14E-02	2.97	0.26	-35.94	0.08
DBK 4	15893.38	30.65	17.45	0.29	3.3	0.04	0.3	6.34E-04	6.53	2.61E-02	7.64	0.18	-36.19	0.09
DBK 15	13872.28	34.25	72.35	0.77	18.2	0.23	0.3	8.04E-04	6.44	3.57E-02	4.87	0.22	-33.88	0.1
DBK 24	17083.19	15.87	48.16	0.59	8.78	0.09	0.3	8.11E-04	6.55	3.04E-02	3.02	0.2	-31.74	0.1
DBK 88 2	12217.41	29.55	23.24	0.25	5.72	0.08	0.3	7.48E-04	6.33	5.31E-02	7.23	0.24	-35.77	0.08
DBK 88 3	13652.54	36.84	70.21	0.8	17.74	0.19	0.31	8.32E-04	6.48	3.92E-02	6.87	0.25	-31.79	0.09

2.5 Discussion

2.5.1 Crustal Influence

Noble gases can be utilized to fingerprint natural gases and determine the origin of different gas families (Ballentine et al., 2002; Gilfillan et al., 2008; Gilfillan et al., 2009; Hunt et al., 2012). By utilizing helium isotopes, ^4He concentrations, and $^{40}\text{Ar}/^{36}\text{Ar}$ values, we are able to clearly distinguish four different source families of gases on Figures 2.3A and 2.3B and determine their relative origin and mixing between endmembers. Helium production ratios in the continental crust are $\sim 0.02 \text{ R/R}_a$ (Andrews, 1985; Ballentine and Burnard, 2002; Boreham et al., 2018), compared with an average subcontinental lithospheric mantle value of $6.1 \pm 2.1 \text{ R/R}_a$ (Day et al., 2015).

By plotting He isotopes versus $^{40}\text{Ar}/^{36}\text{Ar}$ (Figure 2.3A) and ^4He concentrations (Figure 2.3B), we observe that Four Corners gases are derived from a continental crust source with a contribution from the mantle. The Navajo Springs and the Pinta Dome samples have the highest He isotope values, indicating a resolvable mantle contribution relative to crustal sources based on the R/R_a ratios. Air corrected Rc/R_a values are equal to R/R_a values, so air contamination is negligible. In Figure 2.3A, increases in radiogenic ^{40}Ar relative to ^{36}Ar in the Dineh-Bi-Keyah samples are observed, possibly associated with a thermal release by a recent igneous activity in the field (Danie 1978; Masters 2000). Enrichment in ^{40}Ar tracks with ^4He suggesting a common crustal source.

2.5.2 Regional Nitrogen and Noble Gas Relationships

When plotting $\text{N}_2/^{36}\text{Ar}$ against $^4\text{He}/^{36}\text{Ar}$, two groups are observed, the helium-rich and hydrocarbon-rich, which show a regional underlying relationship between radiogenic helium, crustal-sourced N_2 , and the groundwater system (Figure 2.4). There is a positive correlation between the helium-rich samples of several different fields, which indicates a regional relationship. Helium-rich fields have a consistent regional $^4\text{He}/\text{N}_2$ ratio of 0.07, while the hydrocarbon-rich Ratherford has a $^4\text{He}/\text{N}_2$ ratio of 0.018. High-He samples clearly have excess ^4He and N_2 beyond air/groundwater mixing, perhaps due to lack of hydrocarbon dilution. In contrast, radiogenic Ratherford samples

exhibit a resolvable portion of air-derived N₂ as well as N₂ from ASW (air-saturated water), suggesting a shallow-sourced water-dominated N₂ component.

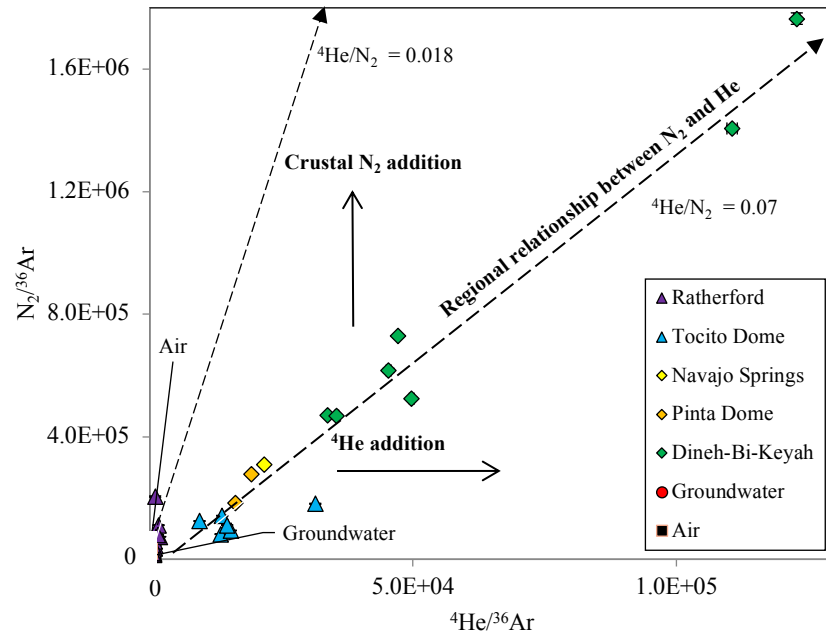


Figure 2.4: $^4\text{He}/^{36}\text{Ar}$ versus $\text{N}_2/^{36}\text{Ar}$ plot, showing two groups – He-rich fields with a regional $^4\text{He}/\text{N}_2$ ratio of 0.07, and a hydrocarbon-rich field (e.g., Ratherford), which has a shallow-sourced N₂ end member and $^4\text{He}/\text{N}_2$ ratio of 0.018. Groundwater and air values are calculated from Kennedy and Truesdell (1995); Marty et al. (1996); Marty et al. (2013).

Nitrogen isotopes combined with helium (Figure 2.5), can be used to delineate N₂ and He sources from organic sedimentary derived nitrogen (i.e., thermal cracking of hydrocarbons/post – mature and mature organics), and crustal nitrogen released from the basement during low temperature metamorphism or from clays (Cartigny and Marty, 2013; Ballentine and Sherwood-Lollar, 2002). In Figure 2.5, air, mantle-derived N₂ and mature organics are negligible in high helium samples, suggesting there must be another source contributing to the N₂ (Halford, 2018). Dominant contributions from the post mature organics, clays and metasediments should be discounted for the hydrocarbon-rich samples.

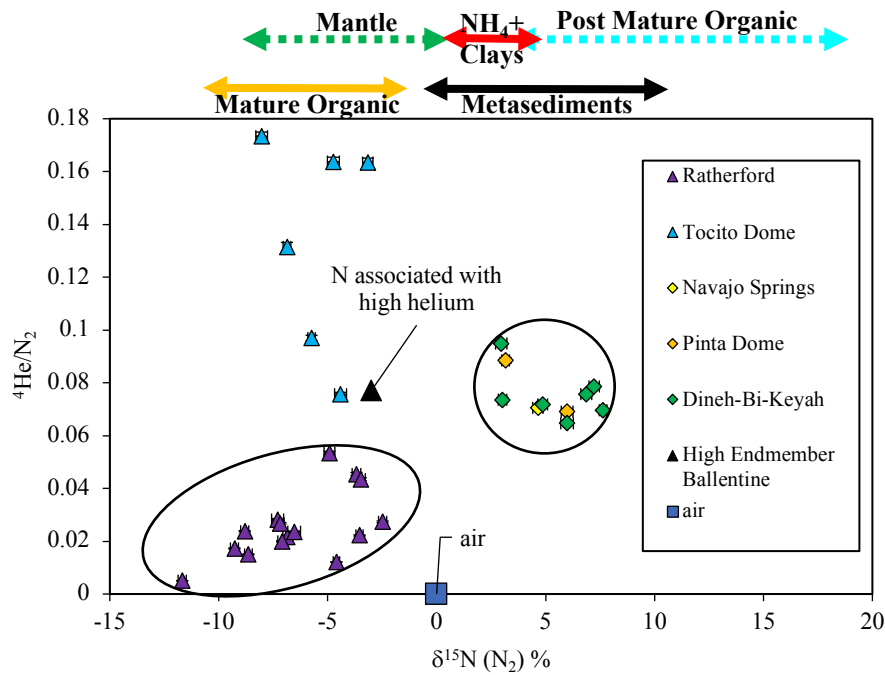


Figure 2.5: Plot of $^4\text{He}/\text{N}_2$ versus $\delta^{15}\text{N}(\text{N}_2) \text{ ‰}$ showing crustal N_2 (metasediments/clays) is the primary source of He-rich associated N_2 . High end-member, which represents the highest $^4\text{He}/\text{N}_2$ sample measured in the Hugoton Panhandle Texas system, is from Ballentine and Sherwood-Lollar (2002); air is from Labidi et al., 2020. $\delta^{15}\text{N}(\text{N}_2)$ ranges are from Cartigny and Marty (2013), Danabalan (2017); and Danabalan et al., (2022). Error bars are smaller than symbols ($^4\text{He}/\text{N}_2$).

2.5.2.1 Hydrocarbon-Rich Fields

The N_2 in Ratherford and Tocito Dome samples are likely from an organic source (Figure 2.5) as a minor component of hydrocarbons (Figure 2.2). However, Ratherford samples are likely receiving a portion of their N_2 from air as the samples plot close to the air end-member in $^{20}\text{Ne}/^{22}\text{Ne}$ vs $^{21}\text{Ne}/^{22}\text{Ne}$ space (Figure 2.6), and near the $\delta^{15}\text{N}(\text{N}_2)$ air value of 0‰ in Figure 2.5. Additionally, we hypothesize that there is a ^4He -poor/ ^{15}N -depleted endmember influencing the Ratherford samples and a ^4He -rich/ ^{15}N -depleted endmember influencing the Tocito Dome samples in Figure 2.5.

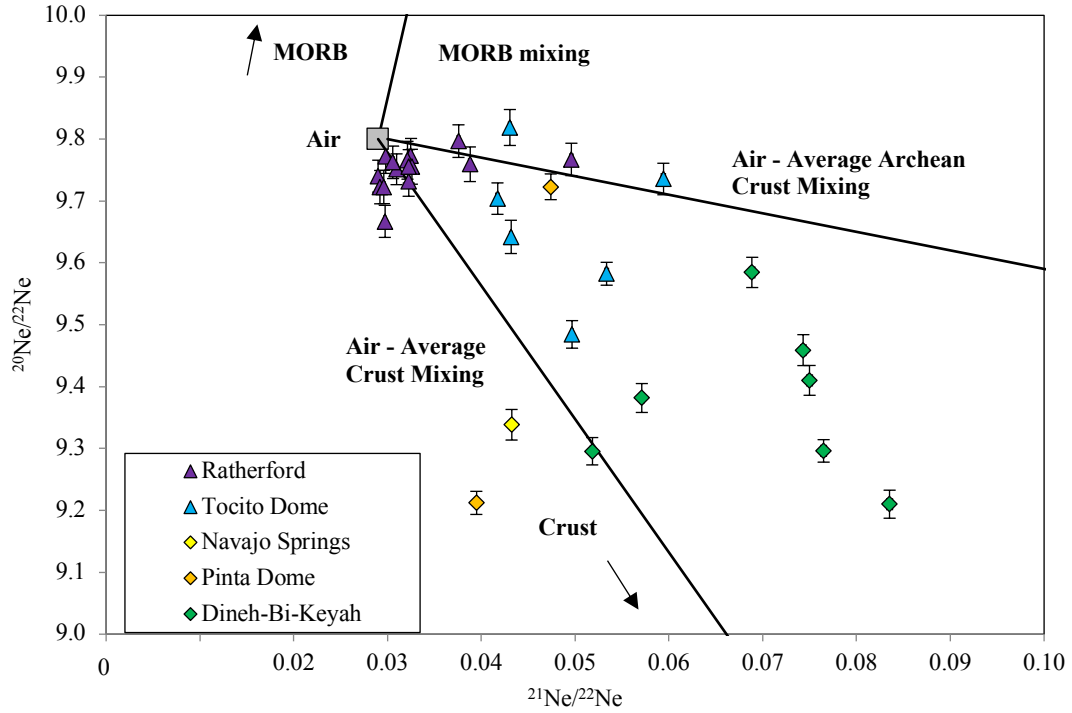


Figure 2.6: Neon plot supporting a strong crustal component mixing with air. Error bars are smaller than printed symbols for $^{21}\text{Ne}/^{22}\text{Ne}$ (Ballentine and O’Nions, 1992; Ballentine and Burnard, 2002; Ballentine and Holland, 2008; Warr et al., 2018; Li et al., 2020).

Ratherford and Tocito Dome samples fall within the overlapping range of mantle (small but discernible mantle component is evident from He isotopes) and mature organics (-7 to -3% $\delta^{15}\text{N}$), suggesting a combination of both mantle and mature organics in N isotope space. The most likely scenario is that the negative nitrogen signature is not mantle dominated given the lack of strong mantle components in helium, neon and argon isotopes, but instead is a signal from sedimentary organic matter in the mature window (Zhu et al., 2000). A mature zone is corroborated by hydrocarbon (gas wetness versus $\delta^{13}\text{C}$ (CH_4)) data (Figure 2.7).

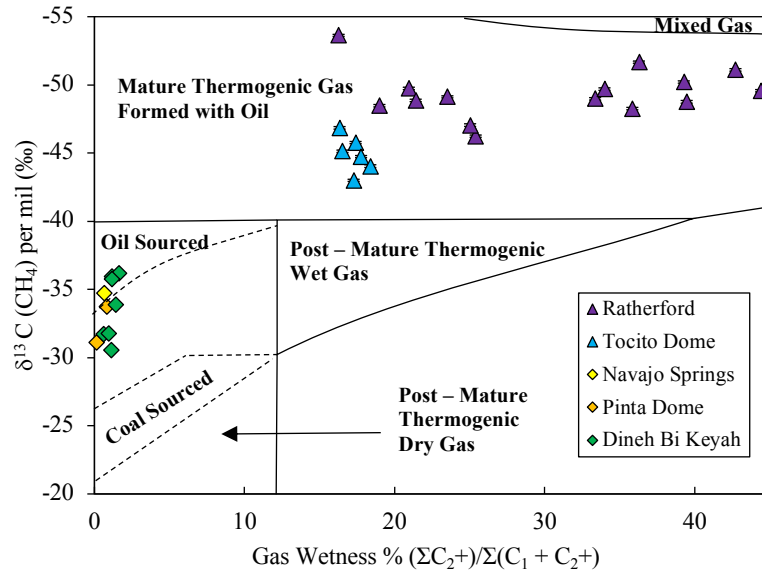


Figure 2.7: $\delta^{13}\text{C}(\text{CH}_4)$ versus gas wetness % ($(\Sigma\text{C}_{2+})/\Sigma(\text{C}_1 + \text{C}_{2+})$) showing data plotted in the approximate ranges of gas composition related to post mature – dry gas, post mature wet gas, mixed gas, and mature gas formed with oil (Schoell, 1983; 1988; Faber et al., 1992; Whiticar, 1994; Ellis, 2014, Travers et al., 2014, Selley and Sonnenberg, 2015). The error bars for gas wetness are smaller than the symbols.

2.5.2.2 Helium-Rich Fields

High helium samples from the Dineh-Bi-Keyah, Pinta Dome, and Navajo Springs fields plot in the areas predicted for denitrification of post – mature organic sediments zone (+4‰ to +18‰), ammonium-rich clays (+1 to +4‰), and low temperature metamorphism of the crust (0‰ to +10‰) (Figure 2.5) (Kreulen et al., 1982; Haendel et al., 1986; Bebout and Fogel, 1992; Bebout et al., 1999; Zhu et al., 2000; Cartigny and Marty, 2013; and Danabalan, 2017). Differentiation of sources is challenging because both metamorphosed rocks (up to greenschist) and modern sediments (+4 to 18‰) are marked by similar $\delta^{15}\text{N}$ ranges (Haendel et al., 1986; Zhu et al. 2000; Boyd, 2001; Cartigny and Marty, 2013; and Danabalan, 2017).

In the case of the Dineh-Bi-Keyah Field, organic N_2 may be partially related to hydrocarbon maturity as the samples plot in the post – mature gas window of carbon isotopes (Figure 2.7). Although the Dineh-Bi-Keyah samples fall in the organic range, we neglect this process as a dominant mechanism due to the minute amounts of hydrocarbons measured in the samples ($\sim 1\% \text{CH}_4$) (Figure 2.2). Furthermore, the influence of nitrogen derived from denitrification of post-mature organic matter

is assumed to be insignificant for the Navajo Springs and Pinta Dome samples due to the lack of substantial hydrocarbon production and average 0.5% CH₄ in the gas stream.

The influence of ammonium (NH₄⁺) ions held in clays can be significant if the correct geologic conditions are present, which are extreme temperature regimes (>500°C) and/or fluid rock chemical interactions with highly saline brines (Williams et al., 1995; Mingram et al., 2005; Danabalan, 2017). Since there are documented intrusions in the Dineh-Bi-Keyah Field, the ammonium release scenario should be considered along with contributions from low temperature metamorphism of crustal basement rocks. Given the lack of igneous activity with Navajo Springs and Pinta Domes sampling areas, it is likely that the source of nitrogen is from low temperature metamorphism ($\delta^{15}\text{N}$ (N₂) 0 to +10‰) of the crustal basement rocks, such as nitrogen fixed in K feldspar and biotite in the shallow crystalline basement rocks. Furthermore, given the strong co-occurrence of ⁴He-N₂ in Figure 2.4, and the observation that ⁴He is mostly crustal sourced, it is reasonable to assume the N₂ must also be derived from a crustal source, a crystalline basement or metasedimentary endmember (Ballentine and Sherwood-Lollar, 2002; Jenden et al., 1988b).

Pursuing the plausibility of metasediment contribution from the underlying basement, median distance from sampled reservoirs to the basement top (for fields with helium >0.3%) was determined to be ~300 meters, corroborating the basement as a highly plausible source based on proximal location. The presence of large basement faults and shear zones in the areas near high He/N₂ accumulations (Figure 2.1) indicate that primary migration of the He/N₂ could be initiated with the release of the gas dissolved in solution from the source rocks via deep faulting, igneous intrusions, or other mechanisms (possibly from regional tectonic uplift and subsequent depressurization), which increase the permeability of the granitic host body (Sorenson, 2005; Sims et al., 2008; Torgersen, 2010; Danabalan et al., 2022). With deep faults acting as migration conduits, the basement sourced helium and nitrogen are subject to advection vertically (i.e., primary migration) through the overlying sedimentary packages followed by updip secondary lateral migration.

2.5.3 Groundwater Derived Noble Gases (^{20}Ne , ^{36}Ar)

Atmosphere (air) derived noble gases (i.e., ^{20}Ne , ^{36}Ar , ^{84}Kr , and ^{130}Xe) are dissolved in groundwater according to their solubility coefficients. This process introduces noble gases in the form of air saturated water (ASW), into the subsurface through aquifer recharge. If groundwater comes into contact with a hydrocarbon phase, the noble gases will partition into oil or gas (Barry et al., 2016, 2017, 2018). These noble gases can be harnessed as geochemical tracers and used as a gauge to measure the degree of reservoir and groundwater interaction (Ballentine and O’Nions, 1994; Pinti and Marty, 2000; Ozima and Podosek, 2002; Gilfillan et al., 2008; Zhou et al., 2012; Prinzhofer, 2013; and Byrne et al. 2017).

Moderate positive correlations are observed between ^{20}Ne and ^4He (Figure 2.A.3). This agrees with the findings of previously published work by Ballentine and Sherwood-Lollar (2002), Danabalan (2017) and Danabalan et al. (2022), which showed an inherent relationship of positive correlations between ^4He and ^{20}Ne , (i.e., mixing before the groundwater essentially degassed the noble gases into the subsurface reservoirs). Moderate-weak positive correlations also exist between ^{36}Ar and ^4He (ASW and radiogenically derived isotopic components), which suggests mixing prior to degassing for the He-rich samples (Danabalan, 2017, Danabalan et al., 2022; Figure 2.A.3). The first order observation is that the highest ^4He is observed where there is the highest ^{36}Ar , indicating that the same process could be influencing both, presumably gas migration via groundwater or we may be observing decoupled systems.

2.5.4 Fractionation Processes

Hydrocarbon and crustal gases acquire their initial atmospheric noble gas signatures through interaction with groundwater. Because each noble gas has a different solubility, the degree that ASW noble gases have interacted with groundwater can be quantified based on their respective fractionation ratios. Since the noble gases are geochemically inert, any fractionation can be interpreted to be the result of physical processes such as phase partitioning and migration (Ballentine et al., 2002).

Furthermore, if a migrating gas phase encounters a groundwater with gases dissolved in solution, dissolved ASW gases can be effectively exsolved from the solution back into the gas phase

(Brown, 2010). This might occur when gas dissolved in pore water begins to move laterally within the reservoir. Exsolution might also be plausible given a change in pressure in the absence of a migrating carrier gas (Ballentine et al, 2002; Danabalan et al., 2022).

2.5.4.1 Oil-Water System

To understand noble gas fractionation of hydrocarbon-rich systems, we present a two-stage equilibrium fractionation and air mixing model, which shows the hydrocarbon-rich samples of the Ratherford and Tocito Dome plotting between ASW and air endmembers (Figure 2.8 A&B) (Barry et al., 2016). A prior assumption is that oil is noble gas free before equilibrating with water (Ballentine et al., 2002). For stage 1, oil and water are assumed to equilibrate within a closed system (Equations 2.A.1 and 2.A.2). The oil equilibration with water curve (Figure 2.8A&B) shows the predicted evolution of the oil phase at different oil/water ratios (Barry et al., 2018). The predicted evolution of the oil phase at different oil/water ratios (from infinitesimally small to large) is presented for two temperatures of 325 °K and 345 °K corresponding to averages for the Ratherford and Tocito Dome fields (Rutledge, 2010; Ballentine et al, 2002). The binary mixing lines (purple – Ratherford; blue – Tocito Dome) represents stage 2, binary mixing with an atmospheric component, showing ~1% air (Ratherford) and 0.5% air (Tocito Dome) admixture into the subsurface system (Equation 2.A.3), which is likely the result of secondary recovery waterfloods (Freeman, 1978; Spencer, 1978). However, the model does not only apply to reservoirs impacted by waterflooding.

Ratherford and Tocito Dome field parameters are shown in Tables 2.A.2, 2.A.3, 2.A.4, and 2.A.5 in the appendix. Measured noble gas concentrations in $\text{cm}^3\text{STP}/\text{cm}^3$ (in the gas phase) are converted into the oil phase in $\text{mol kg}/\text{mol}$ using Equation 2.A.2 (Barry et al., 2018). $\text{GOR}_{\text{metric}}$ (gas to oil ratios) are incorporated from production reports and minimal values are chosen to represent pristine reservoir conditions (Barry et al., 2018).

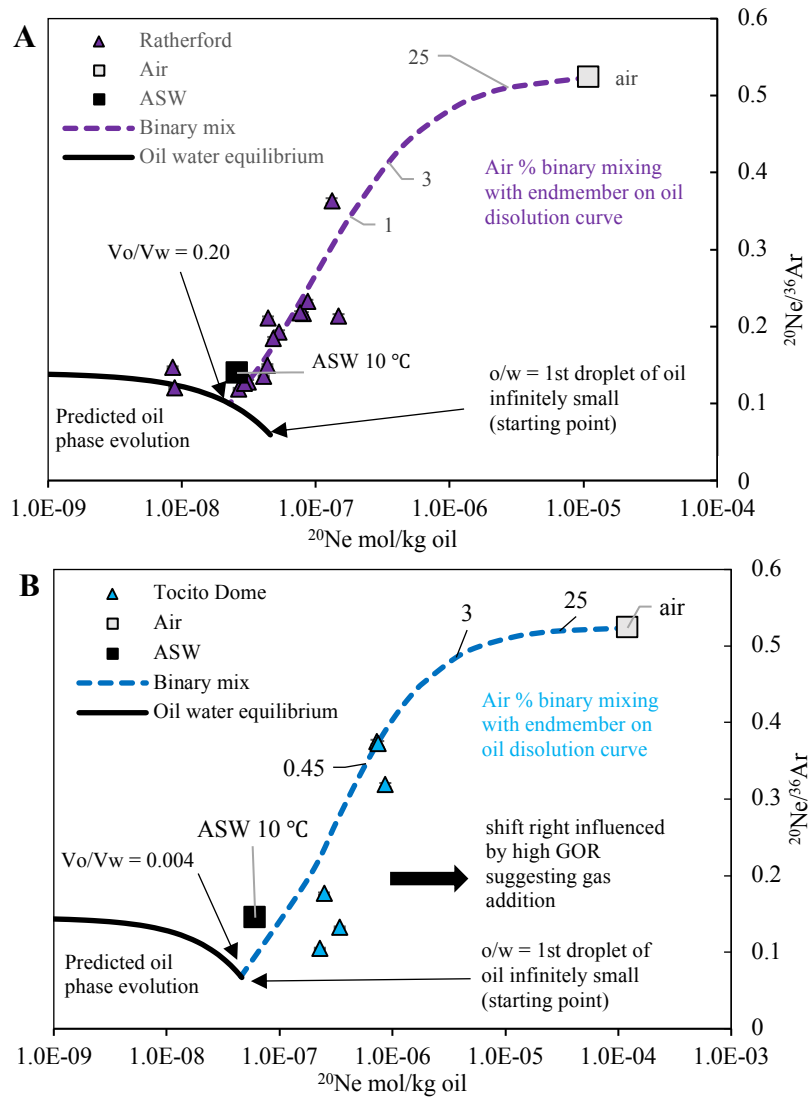


Figure 2.8: $^{20}Ne/^{36}Ar$ fractionation as the result of batch closed system fractionation (oil equilibration with water) and binary mixing between air in Ratherford (A) and Tocito Dome (B) fields. Dashed lines show mixing with air, percent of air in the mixture is annotated.

In Figure 2.8 A&B, we observe $^{20}Ne/^{36}Ar$ and ^{20}Ne values above the oil-water equilibration line for Ratherford and Tocito Dome samples. We postulate that this signal is air derived. The retention of a gas phase (either from degassing from production or secondary charging/mixing episodes) is the opposite scenario to what was observed in Barry et al. (2018). The gas addition/retention narrative conforms agreeably with gas cap calculations for Ratherford and the Tocito Dome, which indicate there is no initial gas cap using virgin GORs (i.e., minimum GOR), and any significant gas volumes produced since initial drilling have resulted from the decrease in reservoir pressure (Barry et al., 2018) (Table 2.A.8). The lowest (virgin) GOR value was chosen as a best estimate due to a lack of initial production (IP) values. Additionally, an average GOR that is measured

at the wellhead was not utilized as it will not necessarily be the most characteristic sample of initial GOR conditions, and will change over time with production fluctuations (Barry et al., 2018).

By utilizing the natural gas isotope data to inform our field simulations, we model these two fields as a two-component water-oil system mixing with air. The two-phase oil fractionation model presents binary mixing curves with end points chosen on the oil water equilibration line to incorporate the largest number of data points. The model assumes oil moves through water to acquire the noble gas signature in stage one. Stage two assumes that equilibration of oil and dissolved noble gases occur with air (Figure 2.9). It is also important to note that for these oil systems, hydrocarbons do not seem to contribute positively to considerable high helium accumulations and are therefore potentially diluting the helium content of the system.

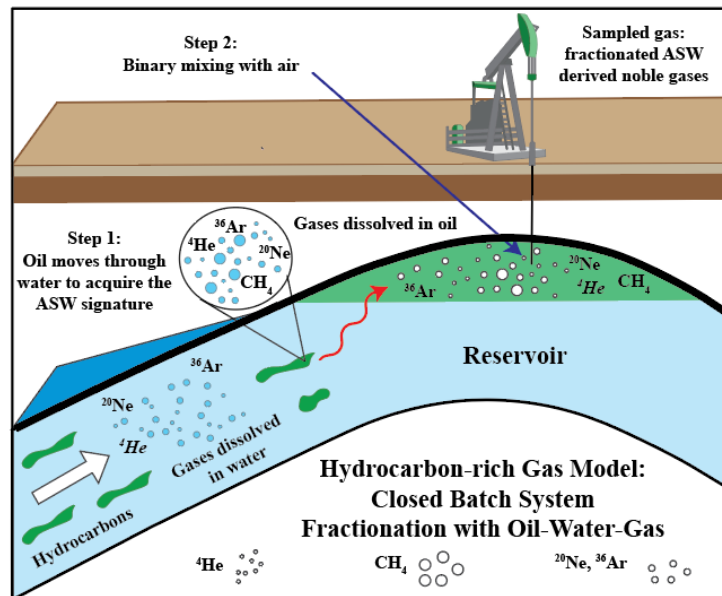


Figure 2.9: Schematic illustrating the conceptual two-stage equilibration model (closed batch system fractionation) devoid of an initial gas cap that explains the Ratherford and Tocito Dome hydrocarbon-rich samples by a two-step approach where 1) oil moves through water to acquire the ASW signatures and 2) binary mixing with air occurs.

2.5.4.2 Gas-Water System

The He-rich samples of Navajo Springs, Pinta Dome, and Dineh-Bi-Keyah fields display $^{20}\text{Ne}/^{36}\text{Ar}$ ratios between 0.5 and 3.5, ranging to significantly above the value of air (0.52) and the maximum values possible through simple closed or open system equilibration with water (Barry et al., 2016). High values of $^{20}\text{Ne}/^{36}\text{Ar}$ have been previously reported to result from gas dissolution in water

in an open system (Gilfillan et al., 2008; Darrah et al., 2014) due to the lower solubility of ^{20}Ne relative to ^{36}Ar . We assume that atmospheric noble gases were fully exsolved from water by a migrating N_2 phase, resulting in a gas phase with a $^{20}\text{Ne}/^{36}\text{Ar}$ ratio equal to that of ASW.

Subsequently, the gas phase is redissolved into the noble gas free water in an open system, following Equation 2.1 (Ballentine et al., 2002). Noble gas concentrations are therefore controlled by their solubility and the solubility of the carrier gas phase (N_2).

In a simple system, where the gas phase re-equilibrates with a column of water that is controlled by N_2 dissolution, we would expect the measured $^{20}\text{Ne}/^{36}\text{Ar}$ and $^4\text{He}/\text{N}_2$ ratios to plot on the open system Rayleigh curves with N_2 as a carrier gas (Equation 2.A.15) (Ballentine et al., 2002; Barry et al., 2016) (Figure 2.10A). The Rayleigh curves were modelled using N_2 solubility values from the IUPAC solubility data series vol. 10 – Battino et al. (1982) and Gevantman (1992). The liquid phase activity coefficient is derived from Table 6 in Valderrama et al. (2016). The gas phase fugacity coefficient is derived by calculating the fugacity of N_2 divided by the pressure ($\phi = f/p$); the complete fugacity equation is listed in the appendix (Equation 2.A.4) (Atkins and De Paula, 2006). Our data plot significantly above and below the modelled N_2 dissolution lines, indicating that the $^{20}\text{Ne}/^{36}\text{Ar}$ and $^4\text{He}/\text{N}_2$ are decoupled, the latter being unaffected by high degrees of re-dissolution into shallow groundwater systems.

$$\text{Equation 2.1: } \left(\frac{[i]}{[\text{N}_2]} \right) = \left(\frac{[i]}{[\text{N}_2]} \right)_o P^{\left(\frac{1}{\alpha} - 1 \right)}$$

where $i = ^4\text{He}, ^{20}\text{Ne}, \text{ and } ^{36}\text{Ar}$, α is the fractionation coefficient $= (\gamma_i/\phi_i \times K_i^{\text{groundwater}})/(\gamma_{\text{N}_2}/\phi_{\text{N}_2} \times K_{\text{N}_2}^{\text{groundwater}})$, where K = Henry's constant Gpa, γ_i/ϕ_i = (liquid phase activity coefficient)/(gas phase fugacity coefficient), $([i]/[\text{N}_2])_o$ = original ratio, and p = the fraction of N_2 remaining in the water phase.

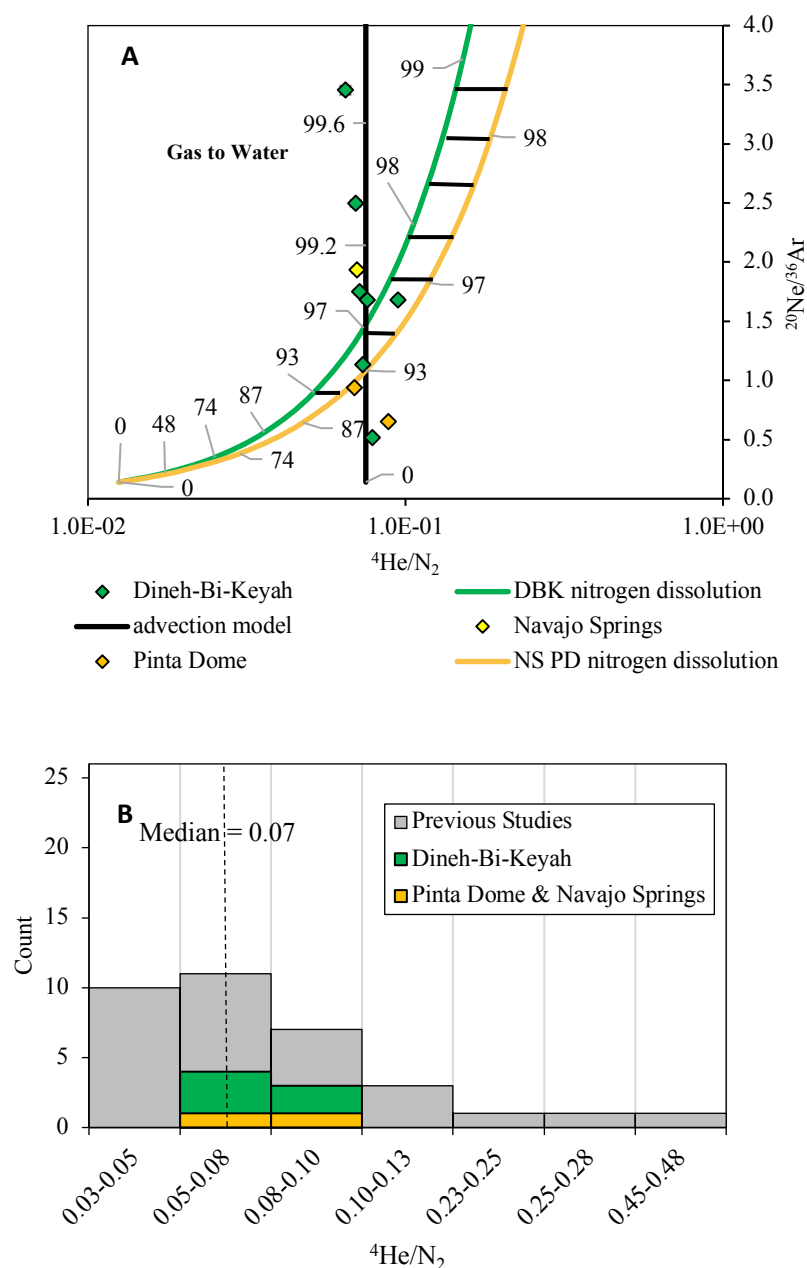


Figure 2.10 A&B: A) He-rich model showing 1) the green and gold curves represent Rayleigh open system fractionation models with N_2 as the primary carrier gas, which is dissolving back into a groundwater solution. The gold curve is modelled with the Pinta Dome and Navajo Springs parameters (Tables 2.A.2, 2.A.3, and 2.A.6); the green curve is modelled with Dineh-Bi-Keyah parameters (Tables 2.A.2, 2.A.3, and 2.A.7). Horizontal black lines between the gold and green curves indicate a potential range of the best fit data. Starting $^4\text{He}/\text{N}_2$ values were chosen to yield a best fit, and the starting $^{20}\text{Ne}/^{36}\text{Ar}$ value is 0.14 (ASW). 2) A black line representing an advection based model based on a constant $^4\text{He}/\text{N}_2$ ratio determined a best fit (0.075) and supported by the median value in Figure 2.4B of 0.07, and a Rayleigh open system fractionation model in the $^{20}\text{Ne}/^{36}\text{Ar}$ space. B) Histogram of He-rich samples and previous data (Craddock et al., 2017; Gilfillan et al., 2008).

$$\text{Equation 2.2: } \left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]} \right)_g = \left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]} \right)_{\text{og}} p^{\left(\frac{1}{\alpha} - 1 \right)}$$

where α is the fractionation coefficient = $(\gamma_{^{20}\text{Ne}}/\phi_{^{20}\text{Ne}} \times K_{^{20}\text{Ne}}^{\text{groundwater}})/(\gamma_{^{36}\text{Ar}}/\phi_{^{36}\text{Ar}} \times K_{^{36}\text{Ar}}^{\text{groundwater}})$, $([^{20}\text{Ne}]/[^{36}\text{Ar}])_{\text{og}}$ = original groundwater phase ratio, and p = the fraction of Ar remaining in the water phase.

Despite the large fractionation in the $^{20}\text{Ne}/^{36}\text{Ar}$, the $^4\text{He}/\text{N}_2$ in He-rich samples are nearly constant (Figure 2.10A). The observed $^4\text{He}/\text{N}_2$ are consistent with median values observed in previous studies on the Colorado Plateau (Figure 2.10B), indicating that the measured $^4\text{He}/\text{N}_2$ likely reflects an unfractionated production ratio likely influenced by an advection-based basement flux (Zhou and Ballentine, 2006). The re-dissolution process (Equation 2.2 – Ballentine et al., 2002) therefore seems to only affect the atmospheric noble gases and not the N_2 and He contents of the gas phase (solid black line, Figure 2.10A).

Figure 2.11 presents a four-stage box model, which incorporates a decoupled dynamic gas phase migration of ^4He and N_2 from the basement (primarily through advection processes) along with a secondary lateral ^{20}Ne and ^{36}Ar migration controlled by groundwater and gas movement. The presence of local high angle basement faults and basement shear zones in the vicinity of high helium fields (Figure 2.1) supports the hypothesis of faults acting as migration conduits (i.e., linking the basement source rock to the reservoir) and transporting ^4He and N_2 via advective fluid flow. The observed $^4\text{He}/\text{N}_2$ ratios likely reflect production ratios in the basement prior to mobilization (Karolyt  et al., 2021).

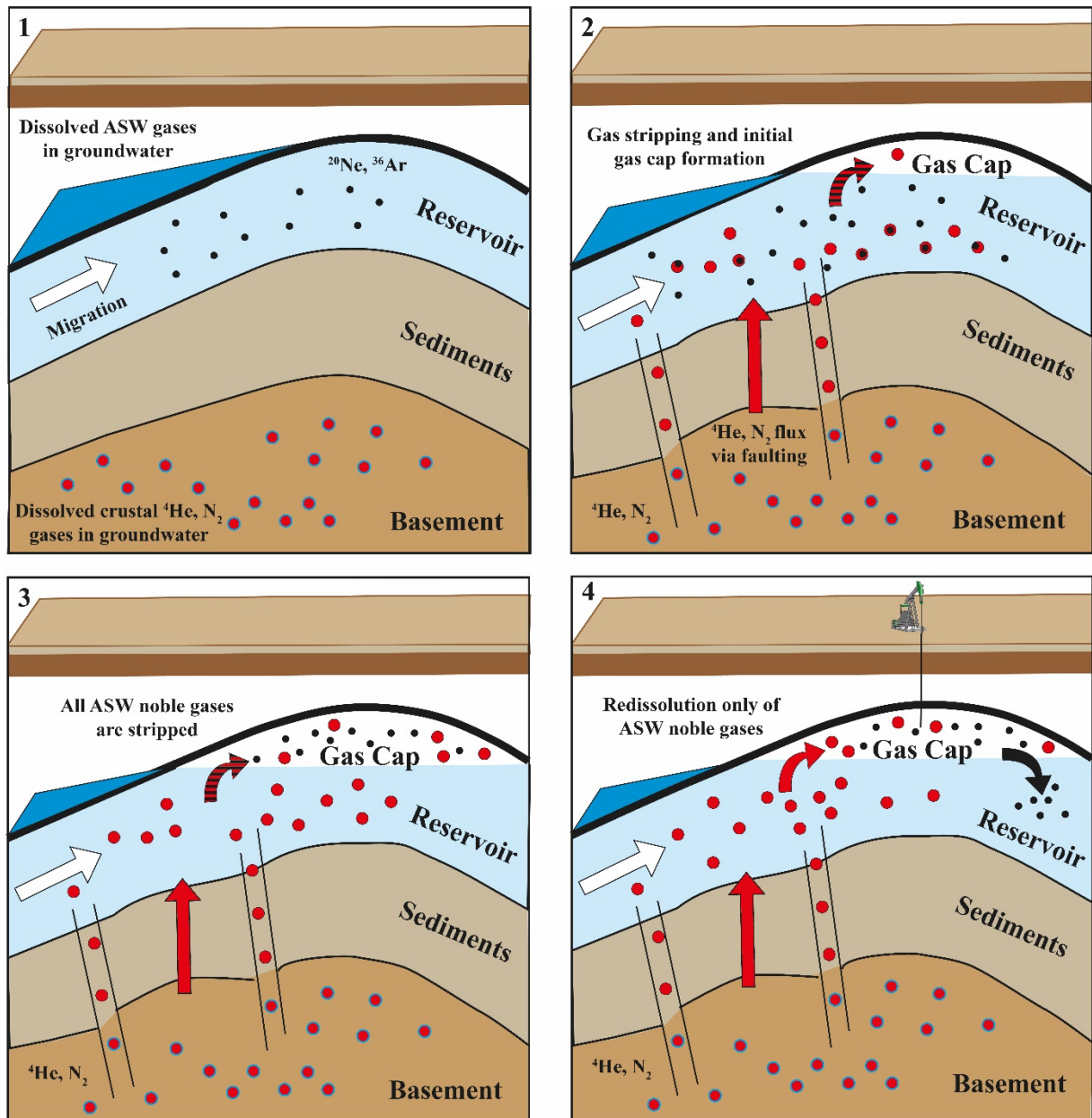


Figure 2.11: Schematic illustrating the conceptual four-stage decoupled model which explains He signatures (advective fluid flow) and highly fractionated $^{20}\text{Ne}/^{36}\text{Ar}$ values (partial redissolution) of the Navajo Springs, Pinta Dome, and Dineh-Bi-Keyah fields. Stage 1 represents the initial conditions where groundwater ^{20}Ne and ^{36}Ar contents (black dots) are in equilibrium with the atmosphere during the initial recharge conditions, and N_2 and ^4He are dissolved in basement groundwater (red dots outlined in blue). Stage 2 signifies basement faulting and flux of N_2 and ^4He (advective fluid flow). N_2 and ^4He are degassed due to decompression, migrate into the reservoir and begin to strip the groundwater of atmospheric noble gases, forming a gas cap above the water column. Stage 3) gases continue to exsolve into the gas cap in the reservoir and eventually all ASW-derived noble gases are stripped and the groundwater is saturated in N_2 and ^4He . Stage 4) the gas cap begins re-equilibrating with the degassed water (lateral gas migration or pressure change), and ASW-derived noble gases redissolve into groundwater, however ^4He and N_2 dissolution is prevented by oversaturation through continuous flux from the basement.

Stage 1 represents the initial conditions where groundwater ^{20}Ne and ^{36}Ar ASW contents are in equilibrium with the atmosphere during the initial recharge conditions, and crustal N_2 and ^4He are

dissolved in basement groundwater. The acquired concentrations of He and N₂ at atmospheric pressure are low and considered negligible relative to the concentrations acquired during the secondary equilibration at depth (N₂ carrier gas with He enrichment). Stage 2 signifies a period where the basement has been faulted and uplifted (as a result of inversion tectonics on the Colorado Plateau) (Davis and Bump, 2009) and a subsequent flux of N₂ and ⁴He (advective fluid flow) is introduced into the overlying sedimentary column. N₂ and ⁴He are degassed due to decompression, before migrating into the reservoir where the groundwater is stripped of its atmospheric noble gases, forming a gas cap above the water column (Sorenson, 2005; Torgersen, 2010; Danabalan et al., 2022). Gas cap calculations are in the appendix (section 2.A.6). The gases continue to exsolve into the gas cap in the reservoir and eventually all ASW-derived noble gases are stripped and the groundwater is saturated with respect to N₂ and ⁴He (Stage 3). Finally, the gas cap begins re-equilibrating with the degassed water, likely through lateral gas migration or pressure change, and ASW-derived noble gases re-dissolve into groundwater, however ⁴He and N₂ dissolution is prevented by oversaturation through continuous flux from the basement. The re-dissolution process only affects the atmospheric noble gases because their total budget in the subsurface is determined by equilibration with the atmosphere during water recharge (crustal fluids have no additional sources of ²⁰Ne and ³⁶Ar, therefore water will not be saturated in respect to these gases), while basement-sourced N₂ and He may occur in much higher volumes (depending on the volume of basement where fluids are liberated from) and therefore fully saturate the water column.

Several alternative mechanisms of ²⁰Ne/³⁶Ar fractionation are discussed (and ultimately discounted) in the appendix (section 2.A.5). These involve (1-2) oil contributions, (3) non-equilibrium diffusion, (4) multi-stage phase equilibrium fractionation, and (5) partial ASW redissolution with nitrogen as the carrier gas. Regarding option (3), there is little evidence for diffusion controlled isotopic fractionation in our samples (appendix section 2.A.5) (Figure 2.A.4), and thus we treat these subsurface systems as primarily advection-controlled systems (Caracausi and Paternoster, 2015; Buttitta et al., 2020; Lowenstern et al., 2014; Brown, 2010; and Tolstikhin et al., 2010).

2.5.5 Helium Mass Balance

To understand a regional helium system, we need to account for the amount of helium formed in different regions of the crust: 1) reservoir, 2) reservoir + underlying sediments, and 3) basement down to 10 km depth, as ~90% of the Earth's ^4He is generated in this interval (Ballentine and Burnard, 2002) (Figure 2.12).

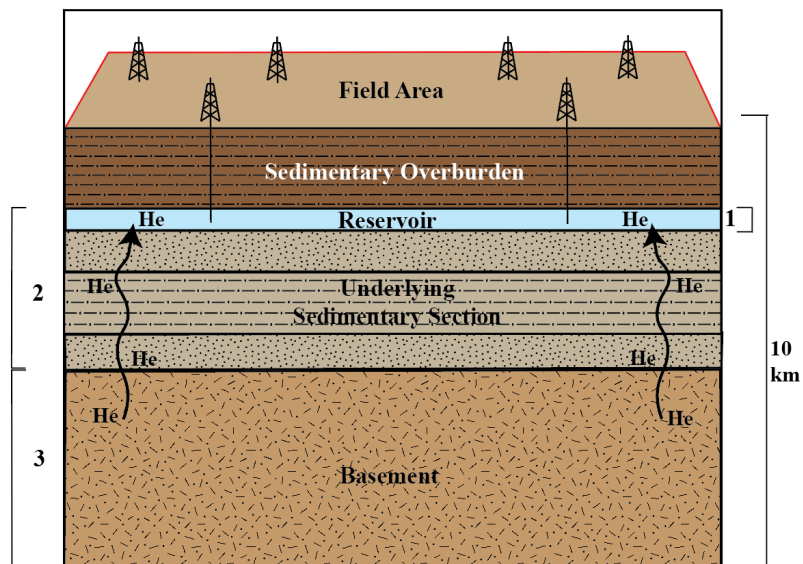


Figure 2.12. Simplified illustration showing volumes of rock beneath the field, which were utilized for the mass balance calculations: 1.) reservoir, 2.) reservoir + underlying sediments, and 3.) basement. Figure not to scale.

In order to better constrain the volume of helium that could be sourced internally from the reservoir or externally, helium mass balance calculations were made for the area directly under the field. By utilizing the average crustal occurrences of uranium (U) and thorium (Th) over discrete time intervals, we postulate the volume of the source rock required to generate the observed helium accumulations in the reservoirs.

2.5.5.1 In-Situ Helium Production

To investigate the volumes of rock required to produce crustal gases that are needed to saturate the water and explain the observed helium signatures, we calculate the possible contribution of helium from the reservoir itself. As an aside, to supplement these calculations, additional hybrid models tying the in situ mass balance models back to the multi-phase fractionation models to

investigate required volumes of rock and required reservoir water are presented in the appendix for the hydrocarbon-rich fields (Tables 2.A.9 and 2.A.10).

Initial volumetric calculations, original gas in place (OGIP) and original helium in place (OHIP), are calculated for each field (Equation 2.3; Tables 2.A.11 and 2.A.12). OGIP is defined as:

$$\text{Equation 2.3: } OGIP = \frac{Ah\phi(1-S_w)}{1} \times \frac{T_s P_i}{P_s T_f Z_i}$$

where OGIP cubic feet [meters³], A is the reservoir area ft² [m²], h is the net pay thickness ft [m], ϕ is the porosity, S_w is the water saturation, T_s is the base temperature standard condition Rankine [Kelvin], P_i is the initial reservoir pressure psia [kPa], P_s is the base pressure standard conditions 14.65 psia [101.35 kPa], T_f is the formation temperature Rankine [Kelvin], Z_i is the compressibility at reservoir pressure and temperature of the dominant gas (Robinson and Peng, 1976), and $(T_s P_i / P_s T_f Z_i) = B_{gi}$, which is the initial conditions gas formation volume factor (Mireault et al., 2007). We assume that the volumes are at ambient temperature of 15 °C/ 60 °F and convert them to 0 °C/32 °F STP (based on the Ideal Gas Law).

In order to determine the in-situ helium contribution of each reservoir, the in-situ ⁴He production is calculated based on the work of Ballentine and Burnard, 2002; Zhou and Ballentine, 2006; Danabalan, 2017; Karolytė et al., 2019; and Buttitta et al., 2020 (Equations 2.4 and 2.5). The amount of ⁴He produced in atoms/grams for a specified time interval is defined as:

$$\text{Equation 2.4: } {}^4He \frac{\text{atoms}}{\text{grams}} = X_R[R] \left(\frac{N_A}{A_R} \right) \times 10^{-6} (e^{\lambda t} - 1) \times \text{yield}_r$$

where X_R is the fractional natural abundance of isotope R, R is the concentration of R in ppm, N_A is the Avagadro's number (6.023×10^{23}), A_R is the molar mass of R (g), λ is the decay constant of R per year, t is the age in years, and yield_r is the number of alpha particles emitted (Ballentine and Burnard, 2002). The amount of ⁴He produced in-situ is defined as:

$$\text{Equation 2.5: } ^4\text{He atoms in situ} = p \times \Lambda \alpha \times (1 - \phi) \times V$$

where ^4He in-situ is the ^4He atoms, p is the average crustal rock density 2.7g/cm^3 , α is the ^4He atoms grams^{-1} , Λ is the efficiency of release, assumed to be 1, ϕ is the porosity, and V is the volume cm^3 (Buttitta et al., 2020).

Average crustal U and Th concentrations of 2.8 and 10.7 ppm are assumed (Burwash and Cumming, 1976; Danabalan et al., 2022). The residence time of all the fields, which is assumed to correlate with the time period after when the seal was deposited ($\pm$ several million years), is assumed to be 300 Mya for the Ratherford, Tocito Dome, and Dineh-Bi-Keyah Barker Creek, 235 Mya for the Navajo Springs and Pinta Dome fields, 370 Mya for the Dineh-Bi-Keyah McCracken interval, and 30 Mya for the Dineh-Bi-Keyah sill. We assume a 100% efficiency in the release (e.g., Holland et al., 2013; Warr et al., 2018), migration, and trapping of helium in the reservoirs; this generates a minimum area value to source helium.

Helium production in-situ contributes $\sim 12\%$ of the helium in the Ratherford Field, and for the remaining fields the contribution is $< 1\%$ (Table 2.A.12). Therefore, externally sourced helium (i.e., from sediments outside the field area or from the basement beneath the field area) must account for nearly 88% for Ratherford helium and $\sim 99\%$ for the remaining helium. Based on rock volumes beneath the field area, the factor by which the volume area is required to be increased to source 100% of its helium from in situ production is summarized in Table 2.A.12 (Ratherford 8x; Tocito Dome 107x; Navajo Springs 145x; Pinta Dome 116x; DBK Barker Creek 325x; DBK McCracken 700x, and DBK sill 3,275x).

Based off these initial calculations concerning the helium production from within the reservoir and known field boundaries, coupled with the fact that it is geologically unlikely to achieve 100% release, migration, and trapping even in the most fortuitous scenarios (especially when considering closure temperatures and thermal gradients), leads us to conclude that in-situ reservoir helium production is insufficient to explain the observed reservoir helium occurrences.

2.5.5.2 External Helium Production

Examining helium production from external sources consists of calculating the helium generating potential of the underlying sedimentary column and the basement at specific time intervals (Tables 2.A.13- 2.A.15). The Precambrian time interval (540 Mya) represents the lithologic interval immediately on top of the Precambrian granitic basement and we consider it to be impermeable to significant helium escape. The timing intervals of the sedimentary reservoirs correlate to sealing horizons that are stated in section 2.5.5.1.

Regarding the calculation of helium generated externally, Equations 2.4 and 2.6 were utilized to determine the helium generated from the entire sedimentary column and basement section up to 32,808 feet (10 km) beneath the respective fields. The external flux of ^4He atoms is defined as:

$$\text{Equation 2.6: } ^4\text{He atoms external} = (q_{^4\text{He}}^c) \times S$$

where $q^c ^4\text{He}$ is the average external crustal ^4He flux (atoms) / (cm^2) = $(p \times \alpha \times H \times (1-\phi))$, where p is the average crustal rock density $2.7\text{g}/\text{cm}^3$, α is the ^4He atoms grams^{-1} (Equation 2.4), H is the crust thickness in cm, ϕ is the porosity, and S is the gas bearing or field area cm^2 (Buttitta et al., 2020).

As the basement porosity is largely unknown in this region, we have retained the average porosity of the reservoirs for the entire sedimentary column and have assumed an average porosity of 1% for the basement with granite as the dominant lithology (Flawn, 1956; Bickford et al., 1981; Sherwood-Lollar et al., 2014).

Regarding the mineralogy within the basement, we consider several minerals (apatite, zircon, and titanite), which are known to contain helium within their structure (Ballentine and Burnard, 2002; Danabalan, 2017; Halford 2018; Danabalan et al., 2022). For our study we only assume: 1) the minimum threshold of helium release of 55°C of apatite and 2) that temperatures above 55°C will yield 100% of helium flux from minerals (Ballentine et al., 1994; Wolf et al., 1996; Ballentine and Sherwood-Lollar, 2002; Shuster et al., 2006; Reich et al., 2007; Hunt et al., 2012; Danabalan, 2017, Danabalan et al., 2022). Utilizing apatite represents a conservative approach, while other minerals would result in even higher helium estimates. Based on the reservoir temperatures in Table 2.A.2, and

an average gradient of 1.4°F/100 ft (~25 °C/km) (Reiter et al., 1979), the sedimentary columns and basement portions have been adjusted for the intervals that lie within the proper closure temperature interval (i.e., > 55°C) (Table 2.A.13). Helium amounts have not been affected for the Tocito Dome Field as it is above the closure temperature release interval for apatite. Based on the proximity to basement faults, we also assume that there are mechanisms that will allow helium flux from the basement as granitic rocks are relatively impermeable to helium (i.e., helium released remains trapped within the basement without release mechanisms).

Examining the mass balance model of ^4He from sedimentary external sources (reservoir + underlying sedimentary column), we observe the low helium producing Ratherford Field is the only area which can be reasonably explained by sedimentary contribution alone at a timescale of 300 Ma (which represents the assumed sealing horizon), requiring 12% of ^4He generation from the sediments needed to fill the reservoir volume of the field (i.e., to account for the OHIP) (Table 2.A.14). Additionally, for the Tocito Dome, Navajo Springs, Pinta Dome, and Dineh-Bi-Keyah fields, we conclude that ^4He cannot be derived solely from the entire sedimentary column beneath the field outline as the potential helium producing zones are largely outside of the closure temperature interval.

Examining the mass balance model of ^4He from basement external sources with an assumed sealing horizon of ~540 Ma and within the proper helium release temperature interval, we observe much more realistic percentages of ^4He generation needed from basement required to fill the reservoir volume (to account for OHIP) for the hydrocarbon-rich fields (Ratherford: 0.3%, and Tocito Dome: 3.6%). Regarding the helium-rich fields in the proper helium release temperature window, we also calculate more reasonable percentages of ^4He generation needed from the basement to fill the reservoir with Navajo Springs at 5.98%, Pinta Dome at 9.38%, and the Barker Creek, McCracken and sill intervals of the Dineh-Bi-Keyah Field at 47.63%, 91.32%, and 47.05% respectively (Table 2.A.15). It is important to note that these calculations are only for the volume of rock directly underneath the field area.

An observation from the mass balance model is that the sedimentary column cannot supply adequate volumes of helium to match OHIP calculations given shorter time scales, thus suggesting long stable intervals that could allow the helium to be generated from the basement. This basement

generated helium is ultimately released due to tectonic activity (i.e., uplift of the Colorado Plateau and activation of associated basement faults/shear zones) and then subsequently migrates and is trapped in a reservoir. Therefore, the most plausible explanation suggests either an old dominant basement source with a helium flux due to tectonic activity or various episodes of extensive migration from areas several orders of magnitude larger than the fields of interest, consistent with the degree of water contact required.

2.6 Conclusion

Helium is a valuable economic resource, which is in increasing demand and of short supply. Here we investigate the nature of He-rich systems on the Colorado Plateau by combining bulk gas analyses and isotopic analyses of noble gases, hydrocarbons, and non-hydrocarbons. This approach allows us to classify different helium systems. Nitrogen and helium ratios indicate similar transport mechanisms and sources. Integrating $\delta^{15}\text{N}$ isotopes with noble gas isotopes and bulk nitrogen suggests a crustal origin for He and N_2 gases in He-rich samples. Hydrocarbon-rich samples are explained by oil/water equilibrium models with air admixture. Utilizing a decoupled advective transport model, the highly unfractionated $^4\text{He}/\text{N}_2$ signatures (i.e., the crustal $^4\text{He}/\text{N}_2$ production ratio that has not been diluted by hydrocarbons) of high-helium samples are explained by primary gas migration from the basement via active tectonics. A multi-phase water gas model (open system Rayleigh fractionation), which indicates migration transport over large distances, accounts for the extremely fractionated $^{20}\text{Ne}/^{36}\text{Ar}$ values of the helium-rich samples, but does not affect $^4\text{He}/\text{N}_2$ due to water saturation with crustal gases released from the basement. Quantitative helium mass balance models examining helium production from various lithological intervals and time periods of the field area reveal that: 1) external (non-reservoir) helium sources are required, 2) long stable periods are favourable for helium accumulations, and 3) the predominant helium source in the Four Corners area is likely to be from the shallow crust (i.e., Precambrian granitic basement) utilizing a large area beneath the field (i.e., crustal gas mobilization and transport via fracture zones), consistent with the degree of water contact.

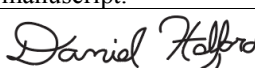
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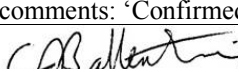
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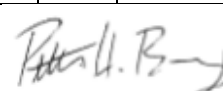
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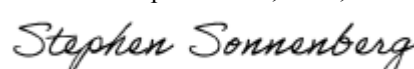
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Contribution to the Paper	I hereby give permission to Daniel T. Halford to use our joint work as contribution towards his DPhil thesis to be submitted for examination at the University of Oxford. I confirm that to the best of my knowledge, the author contribution statement below is accurate and Daniel T. Halford's contribution towards the work is greater than that of any other co-author. Chapter author contribution statement: The project was conceived by DTH, RK, PHB, JJC, SAS, and CJB. DTH managed the project, and prepared the first draft of the manuscript. CJW and THD collected and analysed the samples. Noble gas models and mass balance models were developed by DTH, RK, PHB, and CJB. All authors contributed to the final manuscript.
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Chapter 3

Examining the Effect of Heat from the Yellowstone and Surrounding Environs on the Release of Helium Gases from the Crust

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Abstract

The coherence between helium (He) and heat flow in certain geologic environments has been well established, but few studies have specifically focused on studying the natural system with implications to He exploration to test the validity of how igneous processes influence gas release/storage from crustal rocks. Here we show quantitatively the relationship of thermal aureoles and He signatures using heat flow data coupled with bulk gas and noble gases geochemistry data (n=43) gathered from hot springs in and around Yellowstone, USA, to quantify gas origin and fluid flow in a regional context and to assess the validity of a distance to heat source sweet spot He indicator. We observed from noble gas heat models that the likely dominant processes controlling most Yellowstone samples and non-Yellowstone sample's heat and volatile input are likely convective and degassing processes in the hydrothermal system which are being influenced by air saturated water (ASW) dilution and also various boiling episodes. Utilizing noble gas solubility fractionation models, we confirm that open system degassing events (i.e., gas stripping) with minor amounts of redissolution are likely responsible for isotopic signatures for ASW noble gases as well as radiogenic He and Ar with some degree of influence from diffusion. Relationships of ^4He and ^{20}Ne have been reaffirmed as well as the role that groundwater plays in transporting dissolved ^4He until it is effectively degassed/gas stripped. Insight from a geospatial analysis of heat flow values and the distance to the active Yellowstone caldera shows a 1) narrow range of heat flow values for non-Yellowstone samples, and 2) no significant patterns exhibited for heat flow, He% and distance to the Yellowstone caldera. Examining the effect of localized heat patterns, 1-D heat diffusion modelling quantifies elevated temperatures around theoretical intrusions which exceed closure temperature of He-bearing minerals at much shallower depths compared to normal geothermal gradient. Migration processes either by diffusion or advection have been highlighted, with advection (via buoyancy driven mass transport) considered a possible dominant force supplemented by diffusion based on the noble gas fractionation models and the neotectonic history of the area. Therefore, we report that an universal approach of only using distance from an active volcanic centre is ill-advised for an He exploration strategy to find He sweet zones, and instead exploration strategies should incorporate models focusing on localized heat flow and isotopic geochemistry to constrain groundwater interactions.

3.1 Introduction

Helium (He), which is a critical resource in the 21st century, is now being actively explored for as a primary resource in a variety of geologic scenarios from active volcanic centres to quiescent basins to everything in between (Boreham et al., 2018; Cheng et al., 2021; Danabalan et al., 2022; Halford et al., 2022; Karolyte et al., 2022; National Research Council, 2010). While anomalous He occurrences have been postulated to be the result of various geologic components and advective based fluxes in igneous areas (Boles et al., 2015; Buttitta et al., 2020; Danabalan et al., 2022; Lowenstern et al., 2014; Mtili et al., 2021), extensive studies focusing on the relationship between He and heat flow have not specifically focused on developing exploration frameworks to test the validity of how igneous processes influence He gas release from crustal rocks and also provide information on the relative storage capacity of the crust. The observation of a coherence between He and heat flow (Kennedy et al., 2000) served as a catalyst to develop the concept of utilizing empirical data to quantify the relationship of thermal aureoles and He to assess the validity of a sweet spot indicator or

predictive model for He exploration put forth in Danabalan et al., (2022). Yellowstone and its surrounding area (Fig. 3.1) is an ideal natural laboratory to test the hypothesis that heat flow coupled with bulk gas and noble gases geochemistry gathered from hot springs in and around Yellowstone, USA, can be utilized to quantify gas origin and fluid flow in a regional context and provide insight to explore for He resources, which may be translated to other areas of interest for He exploration.

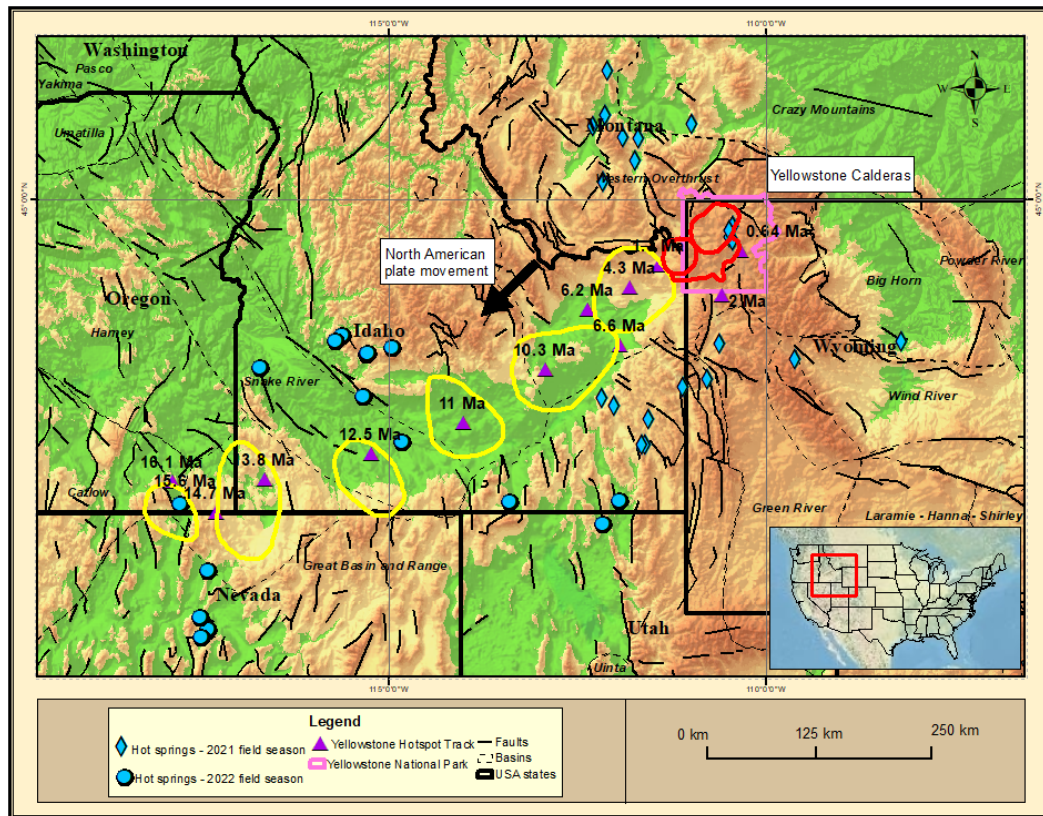


Figure 3.1: Location map showing hot springs sample locations in and near Yellowstone, USA (Berry et al., 1980). The track of the Yellowstone hotspot along with associated ages (from Smith and Siegel, 2000) and the relative direction of the North American plate (Smith and Sbard, 1974) are shown. The older silicic volcanic centres are represented in yellow, and the more recent volcanic centres are outlined in red. Green areas represent topographically lower areas and brown represent higher areas. Basin provinces are shown with dashed black lines, and faults are shown with solid black lines.

3.2 Geologic History

The Yellowstone complex, which is currently located in the north-western corner of Wyoming with some small overlap in Idaho and Montana, USA, is the more recent expression of mantle upwelling and magmatism due to the Yellowstone hotspot (YSH). Due to the relatively stagnant position of the YSH and the overall movement of the oceanic and continental lithosphere due to plate tectonics, progressively older calderas and volcanic fields associated with the YSH are

observed traveling southwest through Idaho into eastern Oregon and northwest Nevada. Magmatism associated with the evolution of the YSH and the tectonic effects of the YSH go well beyond the potential tracks of the Yellowstone plume itself into the adjacent geologic provinces (Murphy, 2016). In general, the YSH's history of progressive crustal melting can be described as a collection of tectonomagmatic stages that record the effects of a long-lived hotspot as it moves from beneath the oceanic to continental lithosphere (Camp and Wells, 2021; Murphy, 2016).

The evolution of the YSH across the Siletzia oceanic plateau to the North American plate can be traced back at least 56 Ma (Camp and Wells, 2021; Murphy, 2016). From roughly 56-49 Ma (late Paleocene to Eocene) there was volcanism and accretion of the Siletzia oceanic lithosphere and the creation of a subduction system from 48-45 Ma (Camp and Wells, 2021; Gao et al., 2011; Schmandt and Humphreys, 2011; Wells et al., 2014). As subduction conducted, the North American Plate continued to override the YSH from 42-34 Ma (Camp and Wells, 2021; Chan et al., 2012; Parker et al., 2010; Simpson and Cox, 1977; Wells et al., 2014). From 30-20 Ma, there was Farallon slab uplift and heating which resulted in volcanism in the Oregon backarc region along with coeval adakite volcanism resulting from the melting of oceanic crust and thermomechanical erosion of the Farallon slab, which was followed by a brief cessation of volcanism activity from 20-17 Ma in the backarc region (Camp et al., 2017; Camp and Wells, 2021; Campbell, 2005; Coble and Mahood, 2012; Murphy, 2016). After the volcanic hiatus ended there was slab rupture/dismemberment and significant tholeiitic flood basalt (Nevada-Columbia Basin magmatic Belt and Columbia River Basalt Group) and bimodal rhyolitic volcanism along the YSH trace (Benson et al., 2017; Camp, 1995; Camp et al., 2015; Coble and Mahood, 2012, 2016; Glen and Ponce, 2002; John et al., 2000; Kasbohm and Schoene, 2018; Liu and Stegman, 2012; Sleep, 1996; Obresbski et al., 20210; Wolff and Ramos, 2013). Also, during 17-15 Ma, the initiation of Basin and Range expansion could be attributed to active mantle upwelling beneath the Nevadaplano (Camp et al., 1995; Camp and Wells, 2021; Colgan and Henry, 2009; Dickinson, 1997; Morriss et al., 2020). Following this time from 14-10 Ma, there was a transition from broad-based volcanism to age-progressive volcanism along the Eastern Snake River Plain (Benson, 2017; Camp and Wells, 2021; Coble and Mahood, 2016; Pierce and Morgan, 1992, 2009; Shervais and Hanan, 2008). Lastly, there are recorded coeval rhyolite migration and volcanism

from 10 Ma to recent times to the WNW (Lava Plains) and to the ENE along the Eastern Snake River Plain (Anders et al., 2019; Camp, 2019, Camp and Wells, 2021; Christiansen et al., 2002; Foulger et al., 2015; Hawley and Allen, 2019; Jordan et al., 2004; Long et al., 2009; Long, 2016; Wagner et al., 2010; Wells and McCraffrey, 2013).

3.3 Methods

3.3.1 Sample Collection Procedures

Natural gas was sampled between 2021 - 2022 from natural hydrothermal springs ($n = 43$) in the Yellowstone National Park and the surrounding environs in Nevada, Utah, Oregon, Wyoming, Montana and Idaho, USA (Figure 3.1). Gas samples were collected in the field using thick-walled refrigerator grade copper tubes, which are 40.6 cm (15.98 in) long, and have a 0.95 cm (0.374 in) outside diameter. Copper tubing was connected via plastic tubing to an inverted funnel that was submerged in the hydrothermal pool over locations that were showing signs of effervescence (Hilton et al., 2002; Barry et al., 2013). Duplicate samples were collected at each site by linking up multiple copper tubes to the sampling line, allowing for the simultaneous collection of copper tubes. To minimize contamination, the end of the flow lines that were connected to the copper tubes were placed in a bottle of water. The flow lines were purged for approximately 10 tube volumes of gas to negate air contamination (Weiss, 1968; Darrah et al., 2015b; Kang et al., 2016). Once the samples were successfully flushed to remove air, the copper tubes were sealed with stainless steel clamps with a 0.762 mm gap (Darrah et al., 2013; Darrah et al., 2015b; Kang et al., 2016; Barry et al., 2016). Additionally, at sites with low flow gas bubble seeps, the water-displacement method was utilized (Craig, 1953, Mazor and Wasserburg, 1968; Barry et al., 2022) which involved submerging the whole sampling apparatus, inverting the funnel, and capturing gas bubbles underwater. In theory, over time the gas bubbles displaced all the water in the copper tube and the stainless steel clamps were closed as described above (Barry et al, 2022).

3.3.2 Geochemical Analyses

The analyses were divided into: noble gas isotopes at the University of Oxford Noble Lab, bulk gas components at the University of Oxford Noble Lab and in the field, and laboratory noble gas isotopes at Woods Hole Oceanographic Institution (WHOI) Barry Lab.

For the noble gas isotopic analyses of helium, neon, argon, krypton and xenon (He, Ne, Ar, Kr, and Xe), a Thermo Fisher Helix Split Flight Tube (SFT) static vacuum mass spectrometer and an Argus VI static vacuum mass spectrometer were utilized at the University of Oxford to measure gas samples (n=27) from the 2021 field season. The noble gas procedures for the purification (i.e., removal of hydrogen, hydrocarbons and reactive gases) and analyses of gas samples are described below. Overnight standards and blanks were utilized to ensure instruments were leak free, monitor overall sensitivity, and track background levels. Procedure air samples taken from University Parks, Oxford, UK, were used to normalize samples by comparing standard signal sizes and sample signal sizes normalized to pressure within the same expansion volume. The average precision for noble gas concentrations from the Oxford Lab that are based on standard reproducibility for noble gas isotope concentrations are: ^4He (0.54%), ^{20}Ne (1.89%), ^{36}Ar (1.76%), ^{84}Kr (1.18%), and ^{130}Xe (1.13%).

In the Oxford Noble Laboratory, to measure the major gas components, a miniRUEDI portable mass spectrometer system was utilized to rapidly quantify ion-current peak heights (Brennwald et al., 2020). The miniRuedi is capable of measuring and quantifying the mass/charge ratio of He, Ne, Ar, Kr, N₂, O₂, CH₄, H₂ as well as other gas components in both water and gases (Brennwald et al., 2020). Calibration of gas samples was possible by comparing peak heights to a gas standard with well-known partial pressures (Brennwald et al., 2020). The final standard errors for major gas concentrations were all less than 1% for 2021 measurements in the Noble Lab (n=27), and <3.4% for 2022 measurements in the field (n=16).

For the noble gas analyses from the 2022 field season, a Nu Instruments multi-collector Noblesse HR mass spectrometer was utilized at WHOI to measure gas samples (n=16). The mass spectrometer is equipped with a unique zoom optics system that permits detectors to be fixed (enhancing reliability) (Barry et al., 2022). The whole spectrometer is connected to a noble gas fully automated processing and purification inlet system (Barry et al., 2022). Noble gas procedures for

purification (i.e., removal of hydrogen, hydrocarbons and reactive gases) and analyses of gas samples are described in Barry et al. (2022). Procedure air samples taken from the roof of the Clark Laboratory building at WHOI were used to calibrate the gas samples. The average precision for noble gas concentrations from the Barry Lab that are based on standard reproducibility for noble gas isotope concentrations are: ^4He (2.16%), ^{20}Ne (4.65%), ^{36}Ar (2.94%), ^{84}Kr (10.15%), and ^{130}Xe (1.65%).

3.3.2.1 Oxford Noble Gas HELIX and ARGUS Systems Procedures

Before 2021 field season gas samples could be accurately analysed on the HELIX and ARGUS mass spectrometers, the gas samples first needed to undergo a series of purification or cleaning steps. The Oxford purification line was kept at a low vacuum pressures $\sim 10^{-6}$ mbar with a turbomolecular pump, $\sim 10^{-3}$ mbar with a rough pump, and 10^{-9} mbar with ion pump. The sample held in copper tubes was attached to the extraction line (based off of Gilfillan et al., 2008) using a metal ferrule and connection port. Once the sample tube was attached, the line was leak checked by spraying He while all the valves to the quadrupole mass spectrometer (QMS) were open so that He's signal was monitored. Once the line was leak free, a portion of the copper tube was expanded into the extraction line. A baratron gauge measured pressure of the gas sample and then a small aliquot of gas was allowed into the clean-up portion of the line. For the first portion of reactive gas clean up, the gas sample was first exposed to a titanium furnace operating at 950 °C. The titanium furnace was subsequently cooled to remove hydrogen before letting the gas into two getters kept at 523 °K and 295 °K, which effectively removed leftover active gases and hydrogen. After these steps, a small amount of gas was let onto the QMS, which provided a preliminary inspection into the components of the gas (Warr, 2013). This step was critical in determining which workflows and splits to run for the sample so as to not oversaturate a particular cup and damage the mass spectrometer.

Next, the noble gases were separated using cryogenic traps cooled with He compressors. A 24 °K Janis Closed Cycle Refrigerator trap adsorbed the heavy noble gases (Ar-Kr-Xe) onto a stainless steel trap at 31 °K, and the light noble gases (He-Ne) were adsorbed onto a charcoal trap at 15 °K using a 10 °K Janis Cycle Refrigerator. To release He adsorbed onto the charcoal trap, the temperature was raised to 31 °K, which was inlet into the Helix SFT mass spectrometer for He isotopic analysis.

Following the quantification of He isotopes, the charcoal trap temperature was raised to 90 °K which releases the Ne, which is analysed by the ARGUS mass spectrometer. Following a series of stepwise heating and cooling episodes, the heavy noble gases (Ar-Kr-Xe) are released and analysed by the ARGUS. More specifically, Ar is released by setting the trap to 60 °K followed by cycles of heating and cooling from 375 °K to 60 °K. Kr and Xe are released simultaneously by heating the trap to 200 °K. Peak centring for He, Ne and Ar was manual, while Kr-Xe peak centring was automatic. After all noble gas isotopes were measured, the traps were warmed to 300 °K to ensure the lines were cleaned.

Procedural air samples were analysed in the same method as described for samples. To process samples, the sample signal, the procedural air signal, the procedural air pressure, the sample pressure and the atmospheric concentration values were required (Equation 3.1). Since the volumes are kept similar, we can effectively ignore them for the calculation. To account for the degrees of uncertainty associated with blank, procedural air samples, and gas samples, the relevant errors were calculated by Equation 3.2. Blank samples were also analysed to ensure a consistent baseline threshold throughout the laboratory run and to monitor for potential leaks or equipment problems. In the event that blank levels were high, the line was baked overnight with a series of heat controlled wires (and foil to insure insulation) that were wrapped around the stainless steel portions of the system, ultimately to clean out any residual gas.

Equation 3.1: Sample cm³ STP = $\frac{\text{sample signal intensity}}{\text{proc air signal intensity}} \times \frac{\text{proc air pressure}}{\text{sample pressure}} \times$
atm concentration

Equation 3.2: Sample error cm³ STP = Concentration sample cm³ STP × $\left[\left(\frac{\text{sample err signal intensity} + \text{blank err signal intensity}}{\text{sample signal intensity} + \text{blank signal intensity}} \right)^2 + \left(\frac{\text{proc air err signal intensity} + \text{blank err signal intensity}}{\text{proc air signal intensity} + \text{blank signal intensity}} \right)^2 + \left(\frac{\text{proc air pressure err}}{\text{proc air pressure}} \right)^2 + \left(\frac{\text{sample pressure err}}{\text{sample pressure}} \right)^2 \right]^{1/2}$

3.3.2.2 Oxford MiniRUEDI Field Protocol

The Oxford MiniRUEDI, which is a small portable mass spectrometer that takes dynamic measurements, is useful for quick field analysis of bulk gas from gas and water samples due to its

relatively compact size and light weight (80 cm by 52 cm by 32 cm and ~32 kg). Although there can be interferences on some peaks that requires deconvolution methods, for the most part the miniRUEDI allows the quantification of He, Ne, Ar, Kr, along with other gases such as nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), methane (CH_4), and hydrogen (H_2) (Brennwald et al., 2020). The main components of the MiniRUEDI involve a rough pump, a turbomolecular pump, a long capillary, and a quadrupole mass spectrometer (QMS).

In the field, the miniRUEDI was utilized to measure bulk gas samples from hot springs in Yellowstone, USA and around its plume track during the field season of 2022. Gas bag samples for major gas analyses were collected at the same locations where copper tubes were collected for noble gas measurements. The latitude and longitude coordinates of each measurement were recorded. After copper tubes were closed, silicone hosing connecting copper tubes to the funnel was pierced with a syringe, collecting a sample of residual gas and injecting into a gas bag through a septum. Gas bags were collected in duplicates. The samples were measured using miniRUEDI on the collection day. The field campaign moved between different locations (and therefore altitudes) each day, and measured signal intensities were expected to vary between days due to elevation changes, therefore samples were corrected using standards measured only on the same day of the collection. Between 1 and 6 standards (42 in total) were run each day, and mean reproducibility was calculated for each day.

Details on calculating mean weight standard errors are described below. After obtaining the raw intensity data from an analysis run, standard deviations were calculated for each day. The first step is to multiply the gas species standard deviation value by the total number of measurements per day. Next, we took the sum of all the values of standard deviation multiplied by the measurements per day for each day of the field season and then divided it by the total number of samples. This was done because the measured signal intensities were expected to vary between days (i.e., different conditions/elevations), but should be consistent the same day. The final mean weighted error was taken from all the standard deviation by weighting them by the number of measurements that day.

Mean weighted standard reproducibility for the 2022 field campaign period was: N_2 (0.24%) and CO_2 (0.51%). Additionally, final machine reproducibility, determined by repeat measurements of the same samples, was 3.4% for N_2 and 2.9% for CO_2 .

3.3.2.3 Oxford MiniRUEIDI Laboratory Procedures

The Oxford MiniRUEIDI, was used in the Oxford Noble Laboratory to measure hot spring gas samples collected from the field season of 2021. The setup of the machine is similar to described in section 3.3.2.2 with the exception of an additional rough pump that was attached to the sample inlet line to allow for pumping down of atmospheric air that occurs when changing samples.

To add a gas sample to the system, we first modified an attachment to allow direct connection from the sample copper tube and the capillary, which slowly feeds the gas sample to the mass spectrometer. Once the sample tube is attached to the inline system, the line was leak checked to ensure minimal contamination and pressure was monitored. An attached barometer was used to monitor and record pressure for each step of the analysis. First, a blank sample was run to determine the baseline of the system. As an aside, several experiments were run to check the pump down time to blank levels of various gas mixtures under different pressures. This quality assurance step was completed to mitigate gas contamination from previous samples. Next, a measurement was taken from a gas bag, collected in University Parks, Oxford. This step was completed at the beginning and end of each day the mass spectrometer was operated which essentially served as a method to ensure the system was acting normally (i.e., monitor the reproducibility of results and the performance of the mass spectrometer) and measurements were within a reasonable range of the previous day's measurements. Finally, the sample was let into the system and was measured by the QMS. Typical workflow included running two short scans (Faraday and Multiplier cups), followed by a longer analysis (via customized script), and followed by two short scans (Faraday and Multiplier cups). This sandwich pattern of scan-analysis-scan allowed us to pinpoint certain components we were most interested in in the analysis, but also to have the whole spectrum from m/z 0-100 as well. The customizable analysis script allowed us to define specific peaks that miniRUEIDI should measure multiple times, which allowed relative uncertainty calculations. Procedural air samples of different compositions (air from University Parks, Oxford, a relatively pure CO₂ endmember, and a 50/50 mix of the two) were also analysed to enable adequate processing, which is similar to that described above regarding the Oxford HELIX and ARGUS procedures (Section 3.3.2.1). The mixing of University

Park air and a relatively pure CO₂ endmember was accomplished by a modified inlet sample apparatus that allowed the inlet and measurement of each gas phase separately.

The miniRUEDI is not designed to handle samples at pressures other than 1 atmosphere, so a specialized workflow was developed to measure procedural air standards for a range of sample pressures. Calibration curves for various gases and gas mixtures (N₂-rich and a CO₂-rich) were generated that allowed us to determine the signal output at the relevant pressures for N₂, CO₂ and O₂ (Figs. 3.2 and 3.3). A 50/50 mixture of air from University Parks, Oxford and a relatively pure CO₂ endmember was also used to create a calibration curve, but was determined to be superfluous as all samples could be adequately processed with only a N₂-rich or CO₂-rich procedural air standard. As the relationship between pressure and intensity is not exactly linear, it is important to use multiple data points to attempt and create an accurate curve. We would recommend for any future work to take multiple measurements in this step especially for gas species with expected low % in the procedural air sample. In summary, this step was critical in that the miniRUEDI software is not designed to work effectively for gases that are above or below 1 atmosphere in pressure (1.01 bar), and because all of our samples ranged from ~0.20-0.30 bar, the calibration curves were essential in ensuring the pressures could be matched during processing with procedural air samples.

Equation 3.3 was used to convert the raw sample signal intensity into a percentage value for the bulk gases. Procedural air standard air reference values for gas components were taken from Porcelli et al., (2002). Approximate values for the CO₂-procedural air were determined from scans on the Multiplier and Faraday cups, but only the Faraday cups were utilized for final processing. Air corrections for N₂ and CO₂, were completed using the ratio of N₂ to O₂ in air followed by the subsequent adjustment of the percentages given the effective removal of O₂.

$$\text{Equation 3.3: Sample cm}^3 \text{ STP} = \frac{\text{sample signal intensity}}{\text{proc air signal intensity}} \times \text{atm concentration}$$

$$\text{Equation 3.4: Sample error cm}^3 \text{ STP} = \text{sample intensity} \times$$

$$\sqrt{\left(\frac{\text{sample intensity err}}{\text{sample average intensity}}\right)^2 + \left(\frac{\text{proc air A intensity err}}{\text{proc air A average intensity}}\right)^2 + \left(\frac{\text{proc air B intensity err}}{\text{proc air B average intensity}}\right)^2 + \dots}$$

Where the first term under the square root describes the error for the sample, and the next two terms describe the error of the procedural error. There could be more of the procedural error terms

depending on how many points were involved in the procedural error curve calibration, in this instance we had 4-5 points.

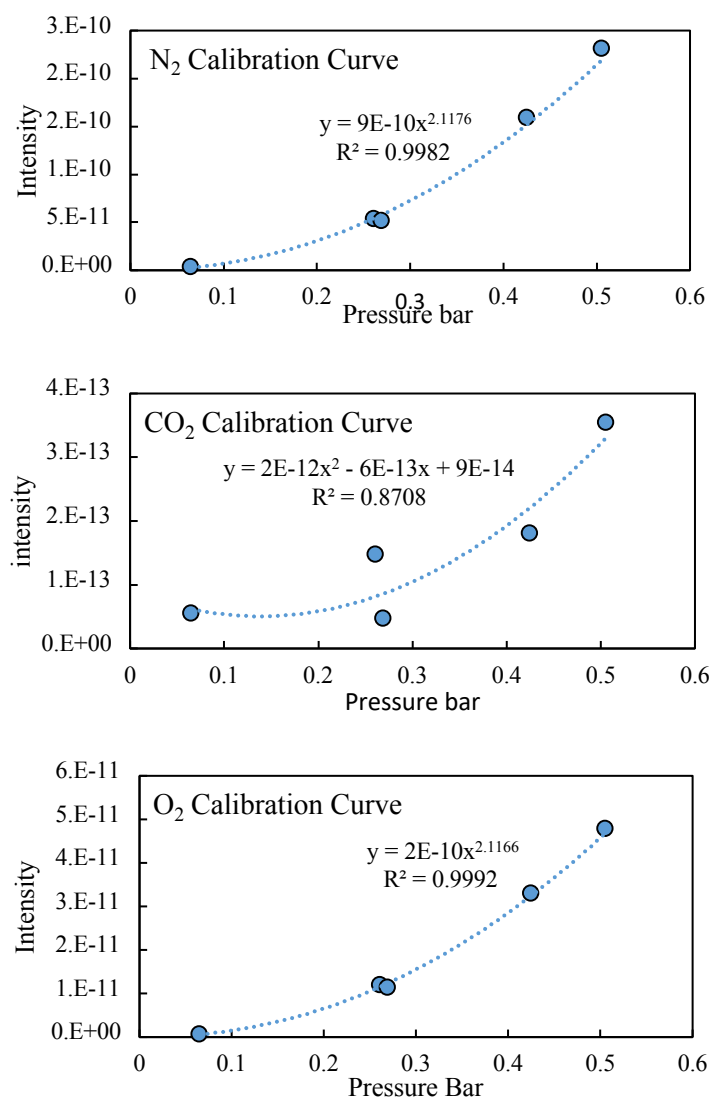


Figure 3.2: Calibration curves of a N₂-rich gas collected from University Parks, Oxford for N₂, CO₂ and O₂ using the Faraday cup to measure intensities. The relevant equations are also shown which allows the calculation of intensity given a pressure. These allow us to effectively match sample pressures with procedural air pressures.

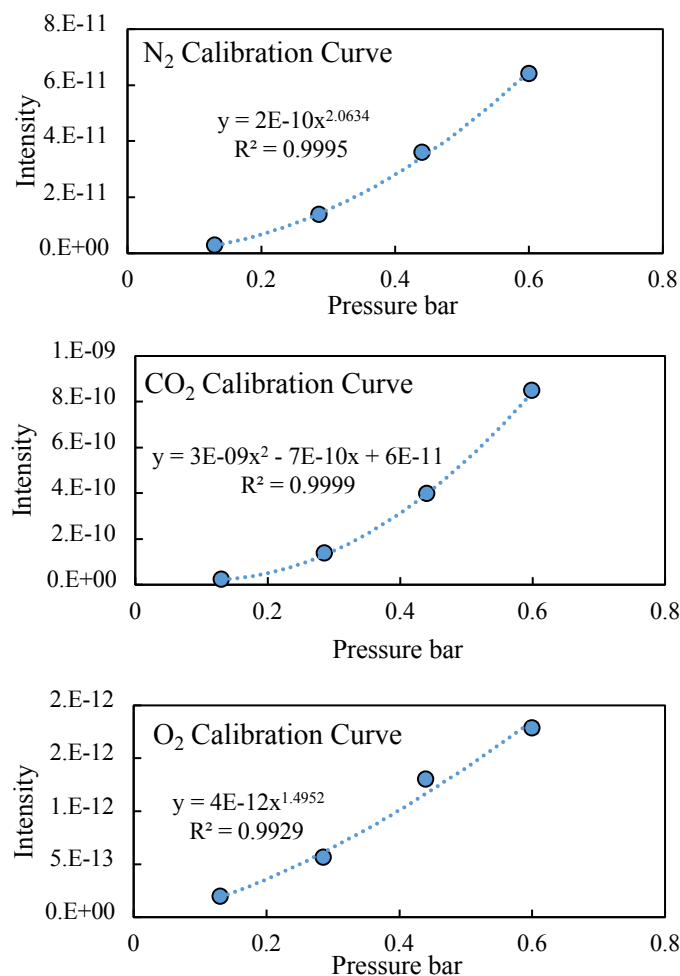


Figure 3.3: Calibration curves of a carbon dioxide-rich gas collected from a pressurized CO₂ cylinder in the Oxford Noble Laboratory, Oxford for N₂, CO₂ and O₂ using the Faraday cup to measure intensities. The relevant equations are also shown which allows the calculation of intensity given a pressure. These allow us to effectively match sample pressures with procedural air pressures.

Regarding the errors that we propagate into the final error value, there are two main components, 1) the sample signal intensity reproducibility, and 2) procedural standard intensity reproducibility. The sample signal intensity was measured for each sample five times. This enabled us to take a standard deviation and average value of those measurements. For the most part, all five measurements were utilized with the exception of instances where there were abnormally large deviations as a result of low values of a gas being measured. The second component of the error propagation focuses on the procedural air measurements that went into developing the calibration curve. Each calibration curve is comprised of 4-5 points each with five entries/measurements. An initial pass over the data was completed to remove abnormally high deviation values especially for low amounts of CO₂ in the University Park sample (N₂-rich). Next, the standard deviations were

calculated for each of the entries. Next, we combined the sample reproducibility values with each of the calibration curve procedural air reproducibility values. The equation used for error propagation is shown in Equation 3.4. The raw signal analytical uncertainty range for N₂ averaged at 0.79%, CO₂ at 1.03%, and O₂ at 5.52%. Raw intensity signals, processed values and air corrected processed values are presented for N₂, CO₂ and O₂ in the appendix along with their respective errors (Table 3.A.1).

Another approach for calculating the average reproducibility of sample errors was calculated by taking the mean weighted error from all the standard deviations and weighting them by how many measurements occurred in total. This is similar to the technique described in section 3.3.2.2 for procedural errors with the main difference that we are not looking at averages per day rather averages per sample. The average results of the mean error weighted by number of measurements in each day for sample analyses in the laboratory are as follows: N₂ (0.78%), CO₂ (0.80%), and O₂ (5.56%), which are comparable to error values obtained previously in section 3.3.2.3.

3.4 Results

Complete gas results for noble gas isotopes are presented in Table 3.1. The exact coordinates of samples collected along with records and estimated surface temperatures are presented in Tables 3.A.2-3 in the appendix. The data ranges for ⁴He (cm³/cm³) are from 1.82E-06 to 1.14E-02. The data ranges for ²⁰Ne (cm³/cm³) are 1.22E-08 to 4.67E-04. The data ranges for ⁴⁰Ar (cm³/cm³) are 4.04E-08 to 1.18E-04. The data ranges for ⁸⁴Kr (cm³/cm³) are 5.97E-09 to 1.23E-06. The data ranges for ¹³⁰Xe (cm³/cm³) are 2.45E-10 to 2.19E-07. The 2022 samples with blank contributions >5% are excluded.

The complete gas results for noble gas isotopic ratios and isotopic-bulk gas ratios are presented in Table 3.2. There are large fluctuations of the R/R_a corrected data from near crustal endmember values of 0.02 to elevated values of ~16 inside Yellowstone (Andrews, 1985; Ballentine and Burnard, 2002; Boreham et al., 2018). The ²⁰Ne/²²Ne values and ²¹Ne/²²Ne values are from 9.73 to 10.3, and 0.008 to 0.033, respectively. The ⁴⁰Ar/³⁶Ar values range from 294 to 547. ⁴He/N₂ ratios range from 3.91E-6 to 4.52E-2 and CO₂/³He ratios vary from 1.06E6 to 1.85E11. The majority of samples collected outside of Yellowstone are N₂-rich, while the majority of samples collected within Yellowstone's active caldera area are CO₂-rich.

Table 3.1: Noble gas concentrations and their error values for hot springs; n.d. = no data, * = 2021 field season, ** = 2022 field season.

Sample	⁴ He cc/cc	±	²⁰ Ne cc/cc	±	³⁶ Ar cc/cc	±	⁸⁴ Kr cc/cc	±	¹³⁰ Xe cc/cc	±
ALK*	9.57E-06	3.51E-08	2.55E-06	6.90E-09	7.52E-06	3.48E-08	1.91E-07	1.76E-09	3.41E-08	2.93E-10
ALP*	5.80E-06	2.58E-08	1.55E-05	5.72E-08	3.00E-05	1.56E-07	5.71E-07	5.46E-09	8.04E-08	7.24E-10
AST*	4.99E-03	1.56E-05	2.14E-06	2.64E-08	9.45E-06	7.89E-08	2.43E-07	5.80E-09	5.57E-08	1.33E-09
BLZ*	4.41E-03	7.02E-05	3.27E-06	5.92E-08	1.19E-05	1.97E-07	3.43E-07	6.22E-09	5.94E-08	1.07E-09
BOL*	9.05E-04	5.13E-06	1.40E-05	8.21E-08	3.99E-05	2.77E-07	8.83E-07	9.36E-09	1.25E-07	1.26E-09
BRI*	5.95E-05	1.01E-06	8.90E-06	1.70E-07	2.02E-05	3.56E-07	4.76E-07	9.36E-09	6.88E-08	1.31E-09
CH1*	1.40E-05	7.98E-08	1.08E-07	6.04E-09	3.70E-07	3.62E-09	6.30E-08	6.98E-10	2.76E-09	3.16E-11
CH2*	3.86E-06	2.74E-08	1.22E-08	6.83E-10	4.04E-08	2.26E-09	5.97E-09	6.71E-11	2.45E-10	3.09E-12
ENN*	1.14E-02	3.78E-05	6.85E-06	2.51E-08	2.95E-05	1.55E-07	8.13E-07	7.78E-09	1.56E-07	1.40E-09
FSP1*	2.41E-05	1.43E-07	8.03E-08	4.50E-09	4.97E-07	2.78E-08	9.69E-08	1.08E-09	4.72E-09	5.44E-11
FSP2*	1.95E-05	1.15E-07	4.43E-08	2.48E-09	1.61E-07	9.00E-09	2.64E-08	2.96E-10	1.13E-09	1.32E-11
HNR*	9.02E-06	1.87E-08	1.67E-06	1.49E-08	4.13E-06	1.90E-08	9.54E-08	8.60E-10	1.43E-08	1.24E-10
JAK *	2.50E-03	5.31E-06	3.50E-06	9.23E-09	9.12E-06	4.17E-08	2.03E-07	1.87E-09	2.87E-08	2.47E-10
KEL*	1.62E-04	3.53E-07	4.65E-06	1.25E-08	1.18E-05	5.41E-08	2.68E-07	2.48E-09	4.28E-08	3.70E-10
MV1*	1.70E-05	1.18E-07	1.80E-08	1.01E-09	7.32E-08	4.11E-09	1.29E-08	1.53E-10	6.21E-10	8.04E-12
NOR*	1.06E-04	3.20E-07	5.71E-07	5.26E-09	1.71E-06	1.19E-08	4.44E-08	4.12E-10	6.75E-09	6.09E-11
POT*	8.46E-05	4.43E-07	4.84E-06	2.65E-08	1.34E-05	8.93E-08	2.90E-07	7.11E-09	6.02E-08	4.28E-10
PUL*	1.96E-04	3.74E-07	1.04E-07	9.24E-10	3.27E-07	4.36E-09	1.10E-08	9.90E-11	2.32E-09	2.03E-11
REN1*	5.51E-03	1.87E-05	1.26E-05	4.72E-08	4.48E-05	2.35E-07	9.47E-07	5.56E-09	2.14E-07	1.25E-09
REN2*	7.50E-03	3.09E-05	1.20E-05	1.51E-07	4.42E-05	3.87E-07	9.52E-07	2.28E-08	1.85E-07	4.44E-09
SILV*	9.94E-04	1.96E-06	9.01E-06	2.28E-08	3.95E-05	1.76E-07	9.63E-07	8.86E-09	2.19E-07	1.91E-09
SODA*	1.82E-06	7.77E-09	4.12E-08	3.30E-10	2.55E-07	6.03E-09	1.55E-08	1.28E-10	2.58E-10	2.24E-12
STEA*	4.98E-06	1.18E-08	3.53E-07	3.18E-09	1.80E-06	9.72E-09	6.97E-08	6.33E-10	1.81E-08	1.57E-10
THER*	3.25E-03	7.49E-06	6.70E-07	6.03E-09	3.01E-06	1.46E-08	1.00E-07	9.19E-10	2.08E-08	1.82E-10
WB1*	9.28E-05	2.18E-07	2.28E-07	1.28E-08	9.26E-07	8.95E-09	1.74E-07	1.94E-09	8.78E-09	1.01E-10
WB2*	5.89E-05	1.53E-07	1.45E-08	8.09E-10	7.52E-08	4.21E-09	1.40E-08	1.57E-10	7.14E-10	8.47E-12
YAN*	7.33E-06	1.95E-08	8.48E-06	2.77E-08	1.80E-05	4.63E-08	4.05E-07	1.35E-09	2.31E-09	7.86E-12
BB**	2.93E-04	6.34E-06	6.63E-06	3.08E-07	2.52E-05	7.41E-07	8.66E-07	8.79E-08	4.88E-09	8.03E-11
BS**	1.47E-04	3.18E-06	7.29E-06	3.39E-07	2.77E-05	8.13E-07	1.05E-06	1.07E-07	6.51E-09	1.07E-10
FS**	8.57E-04	1.85E-05	n.d.	n.d.	1.12E-04	3.30E-06	1.23E-06	1.24E-07	5.85E-09	9.63E-11
GV**	1.53E-04	3.30E-06	2.47E-06	1.15E-07	1.09E-05	3.21E-07	3.35E-07	3.40E-08	1.80E-09	2.95E-11
LF**	6.17E-04	1.34E-05	n.d.	n.d.	1.18E-04	3.47E-06	8.69E-07	8.82E-08	3.69E-09	6.06E-11
MD**	1.43E-05	3.09E-07	9.10E-06	4.23E-07	2.35E-05	6.91E-07	6.59E-07	6.69E-08	3.31E-09	5.45E-11
PA**	2.36E-04	5.11E-06	5.77E-06	2.69E-07	2.85E-05	8.38E-07	1.15E-06	1.17E-07	6.21E-09	1.02E-10
PE**	4.54E-04	9.84E-06	4.67E-04	2.17E-05	1.14E-04	3.35E-06	8.70E-07	8.83E-08	3.73E-09	6.13E-11
PV**	4.11E-04	8.89E-06	2.21E-06	1.03E-07	2.03E-05	5.95E-07	6.54E-07	6.63E-08	3.10E-09	5.10E-11
RC**	2.26E-05	4.88E-07	n.d.	n.d.	6.18E-06	1.82E-07	1.33E-07	1.35E-08	1.10E-09	1.81E-11
RH**	3.01E-06	6.51E-08	8.88E-06	4.13E-07	2.21E-05	6.50E-07	3.50E-07	3.55E-08	2.03E-09	3.34E-11
SC**	4.31E-05	9.33E-07	7.72E-06	3.59E-07	2.66E-05	7.81E-07	9.69E-07	9.84E-08	4.70E-09	7.73E-11
SQ**	1.79E-04	3.87E-06	n.d.	n.d.	2.22E-06	6.51E-08	4.49E-08	4.56E-09	3.21E-10	5.28E-12
TS**	4.20E-05	9.10E-07	8.52E-06	3.96E-07	2.92E-05	8.58E-07	1.14E-06	1.16E-07	7.07E-09	1.16E-10
UD**	1.13E-03	2.44E-05	2.24E-04	1.04E-05	8.52E-05	2.50E-06	5.89E-07	5.98E-08	2.39E-09	3.93E-11
ZR**	1.79E-04	3.87E-06	2.14E-06	9.93E-08	1.86E-05	5.47E-07	7.71E-07	7.83E-08	4.70E-09	7.74E-11

Table 3.2: Noble gas and bulk gas ratios and their error values for hot springs; n.d. = no data, * = 2021 field season, ** = 2022 field season.

Sample	R/Rac (corrected)	±	²⁰ Ne/ ²² Ne	±	²¹ Ne/ ²² Ne	±	⁴⁰ Ar/ ³⁶ Ar	±	⁴ He/N ₂	±	CO ₂ / ³ He	±
ALK*	0.55	0.006	9.83	0.04	0.029	0.0001	298.93	1.93	1.24E-05	1.07E-07	1.54E+10	1.36E+08
ALP*	0.36	0.009	9.79	0.05	0.029	0.0002	298.92	2.20	9.00E-06	8.08E-08	7.22E+07	6.61E+05
AST*	0.03	0.003	9.80	0.17	0.029	0.0005	327.42	3.85	3.54E-02	2.98E-04	3.79E+09	3.26E+07
BLZ*	0.20	0.008	9.78	0.25	0.030	0.0008	357.14	8.33	5.01E-03	8.88E-05	6.04E+07	1.08E+06
BOL*	0.14	0.006	9.80	0.08	0.029	0.0002	300.86	2.95	1.03E-03	9.91E-06	1.06E+06	1.04E+04
BRI*	0.15	0.007	9.83	0.27	0.029	0.0008	458.23	8.34	8.75E-05	1.64E-06	4.61E+09	4.93E+07
CH1*	10.74	0.168	10.03	0.79	0.031	0.0024	312.81	4.37	n.d.	n.d.	1.63E+10	1.60E+08
CH2*	11.01	0.119	10.11	0.80	0.032	0.0025	349.33	11.74	n.d.	n.d.	1.63E+10	1.60E+08
ENN*	0.28	0.032	9.79	0.04	0.030	0.0001	363.57	2.32	1.24E-02	1.06E-04	1.27E+06	1.10E+04
FSP1*	11.40	0.180	9.94	0.79	0.031	0.0025	316.79	25.08	n.d.	n.d.	2.53E+09	2.52E+07
FSP2*	11.40	0.180	9.98	0.79	0.031	0.0025	344.98	27.32	n.d.	n.d.	3.12E+09	3.11E+07
HNR*	2.36	0.027	9.83	0.12	0.029	0.0004	298.55	1.91	1.28E-05	1.03E-07	9.01E+09	7.44E+07
JAK*	0.07	0.008	9.79	0.04	0.029	0.0001	317.89	2.04	2.77E-03	2.24E-05	1.72E+08	1.42E+06
KEL*	0.04	0.003	9.81	0.04	0.029	0.0001	299.56	1.93	1.78E-04	1.44E-06	4.95E+07	4.11E+05
MV1*	15.92	0.266	10.27	0.82	0.032	0.0026	526.02	41.75	n.d.	n.d.	2.57E+09	2.72E+07
NOR*	0.60	0.022	9.88	0.13	0.029	0.0004	303.72	2.60	1.12E-04	9.35E-07	1.51E+08	1.29E+06
POT*	0.25	0.004	9.79	0.08	0.029	0.0002	300.75	2.81	8.85E-05	8.31E-07	4.55E+07	4.35E+05
PUL*	0.21	0.008	9.88	0.12	0.030	0.0004	360.18	5.08	2.59E-04	2.08E-06	3.22E+07	2.65E+05
REN1*	0.15	0.017	9.81	0.18	0.029	0.0005	311.24	2.30	8.07E-03	7.12E-05	3.50E+07	3.15E+05
REN2*	0.11	0.012	9.80	0.05	0.029	0.0002	311.02	3.84	1.09E-03	8.79E-06	1.97E+08	1.62E+06
SILV*	0.13	0.005	9.77	0.03	0.029	0.0001	302.05	1.90	6.13E-03	5.22E-05	5.92E+06	5.15E+04
SODA*	2.05	0.018	9.94	0.11	0.029	0.0004	300.11	3.51	5.17E-05	4.59E-07	1.85E+11	1.68E+09
STE*	1.94	0.030	9.89	0.13	0.029	0.0004	301.08	2.14	3.80E-04	3.10E-06	7.18E+10	6.00E+08
THER*	0.04	0.005	9.83	0.13	0.030	0.0004	363.69	2.42	4.54E-02	3.70E-04	4.82E+09	4.02E+07
WB1*	0.65	0.017	10.01	0.79	0.030	0.0024	315.03	4.16	n.d.	n.d.	1.15E+10	9.58E+07
WB2*	0.65	0.017	9.91	0.78	0.033	0.0026	547.45	43.35	n.d.	n.d.	1.82E+10	1.53E+08
YAN*	0.30	0.004	9.81	0.00	0.029	0.0000	298.97	7.33	3.91E-06	3.22E-08	2.18E+09	1.84E+07
BB**	1.62	0.04	9.77	0.04	0.029	0.0004	299.26	0.004	3.08E-04	1.24E-05	5.72E+06	1.82E+05
BS**	0.89	0.02	9.73	0.04	0.029	0.0004	300.30	0.004	2.21E-04	8.89E-06	2.09E+06	6.66E+04
FS**	0.15	0.00	n.d.	n.d.	n.d.	n.d.	303.79	0.005	1.54E-03	6.20E-05	2.07E+07	6.59E+05
GV**	1.46	0.04	9.79	0.04	0.029	0.0004	299.49	0.004	1.56E-04	6.28E-06	1.64E+06	5.22E+04
LF**	1.05	0.03	n.d.	n.d.	n.d.	n.d.	296.57	0.003	7.25E-04	2.92E-05	5.89E+06	1.88E+05
MD**	0.42	0.01	9.82	0.04	0.029	0.0004	299.00	0.004	1.64E-05	6.61E-07	3.91E+07	1.25E+06
PA**	0.66	0.02	9.85	0.04	0.029	0.0004	298.58	0.004	2.34E-04	9.43E-06	7.86E+06	2.50E+05
PE**	0.13	0.00	n.d.	n.d.	n.d.	n.d.	294.11	0.004	9.61E-04	3.87E-05	5.56E+08	1.77E+07
PV**	0.26	0.01	9.93	0.04	0.030	0.0004	298.65	0.004	6.25E-04	2.52E-05	7.98E+08	2.54E+07
RC**	0.15	0.00	n.d.	n.d.	n.d.	n.d.	299.60	0.004	2.64E-04	1.06E-05	1.72E+11	5.48E+09
RH**	1.01	0.03	9.85	0.04	0.029	0.0004	299.03	0.004	1.68E-03	6.77E-05	1.41E+11	4.49E+09
SC**	0.56	0.01	9.77	0.04	0.029	0.0004	298.62	0.004	4.51E-05	1.82E-06	2.50E+07	7.96E+05
SQ**	0.13	0.00	n.d.	n.d.	n.d.	n.d.	351.05	0.004	2.75E-03	1.11E-04	2.61E+10	8.31E+08
TS**	1.12	0.03	9.78	0.04	0.029	0.0004	299.28	0.004	4.99E-05	2.01E-06	7.20E+06	2.29E+05
UD**	0.29	0.01	n.d.	n.d.	n.d.	n.d.	296.57	0.003	n.d.	n.d.	n.d.	n.d.
ZR**	0.17	0.00	9.98	0.04	0.029	0.0004	299.22	0.004	4.63E-04	1.87E-05	1.08E+10	3.44E+08

Data for He was corrected for air contamination following the methods of Mackintosh and Ballentine (2012) with Equations 3.5 and 3.6. Data for ^{21}Ne and ^{40}Ar were additionally corrected to remove air contamination with Equations 3.7-3.8 to arrive at a purely crustal contribution value (Ballentine et al., 2002; Moore, 2018; Zhang et al., 2019). The relative proportions of $^3\text{He}/Q$ (heat) were calculated from Equation 3.9 based on previous published work (Burnard et al., 1999; Han et al., 2022; Turner and Stuart, 1992). Additional heat flow data was acquired through SMU Geothermal lab (Blackwell et al., 2011) and was compiled with the geochemical data presented in the manuscript.

$$\text{Equation 3.5: } A = [({}^3\text{He}/{}^4\text{He})_{\text{sample}} ({}^4\text{He}/{}^{20}\text{Ne})_{\text{sample}} / ({}^4\text{He}/{}^{20}\text{Ne})_{\text{air}}] - ({}^3\text{He}/{}^4\text{He})_{\text{air}} \\ B = [({}^4\text{He}/{}^{20}\text{Ne})_{\text{sample}} / ({}^4\text{He}/{}^{20}\text{Ne})_{\text{air}}] - 1$$

$$\text{Equation 3.6: } A/B = ({}^3\text{He}/{}^4\text{He})_{\text{corrected}}$$

$$\text{Equation 3.7: } {}^{21}\text{Ne}^* = ({}^{21}\text{Ne}/{}^{22}\text{Ne})_{\text{measured}} - ({}^{21}\text{Ne}/{}^{22}\text{Ne})_{\text{air}} \times ({}^{22}\text{Ne})_{\text{measured}}$$

$$\text{Equation 3.8: } {}^{40}\text{Ar}^* = (({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{measured}} - ({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{air}}) \times ({}^{36}\text{Ar})_{\text{measured}}$$

$$\text{Equation 3.9: } {}^3\text{He}/Q = ({}^3\text{He}/{}^{36}\text{Ar}) \times ({}^{36}\text{Ar})_{\text{ASW}} / (C_p \times E)$$

Where the E= is the excess of the surface temperature compared to atmospheric temperature in °C and C_p is the heat capacity of water at $4.4\text{J k}^{-1}\text{g}^{-1}$

3.5 Discussion

3.5.1 General Relationships

Prior to examining relationships between He and heat, we must first identify the sources of He and associated fluids. Various sources of fluids exhibit different and characteristics ranges of $(R/R_a)_c$ values, such as crustal sources with 0.02; convective depleted MORB mantle with 8 ± 1 ; and hotspot signatures >10 (Allegre et al., 1995; Lupton et al., 2012; Oxburgh et al., 1986). Examining the He isotopic ratios $(R/R_a)_c$ compared to ^4He and ^{20}Ne allow us to establish the relative portions of mixing between mantle endmembers to air and crustal endmembers to air.

We observe that for samples taken within Yellowstone, most plot along a high $(R/R_a)_c$ signature ~ 11 -12 mixing trend indicating dominant input from the Yellowstone hotspot (with the exception of two samples), while the samples taken outside of Yellowstone are much more crust dominated with some mantle influence indicated with a $(R/R_a)_c$ of 0.02 to 1-2 $(R/R_a)_c$ (Fig. 3.2A). The

samples outside of the Yellowstone caldera are evidence for heterogeneous mixing of He sources from the mantle and crust with dominantly radiogenic crustal input from the sedimentary column and granitic basement. The relative concentrations of ^4He are much greater and have a wider range for samples outside of Yellowstone compared to those taken with the active caldera. As $^4\text{He}/^{20}\text{Ne}$ ratios can be a proxy for determining groundwater involvement as ^{20}Ne is a noble gas which is introduced into the subsurface via groundwater recharge. The samples outside of Yellowstone have a greater degree of groundwater influence than those within the caldera (Fig. 3.4B).

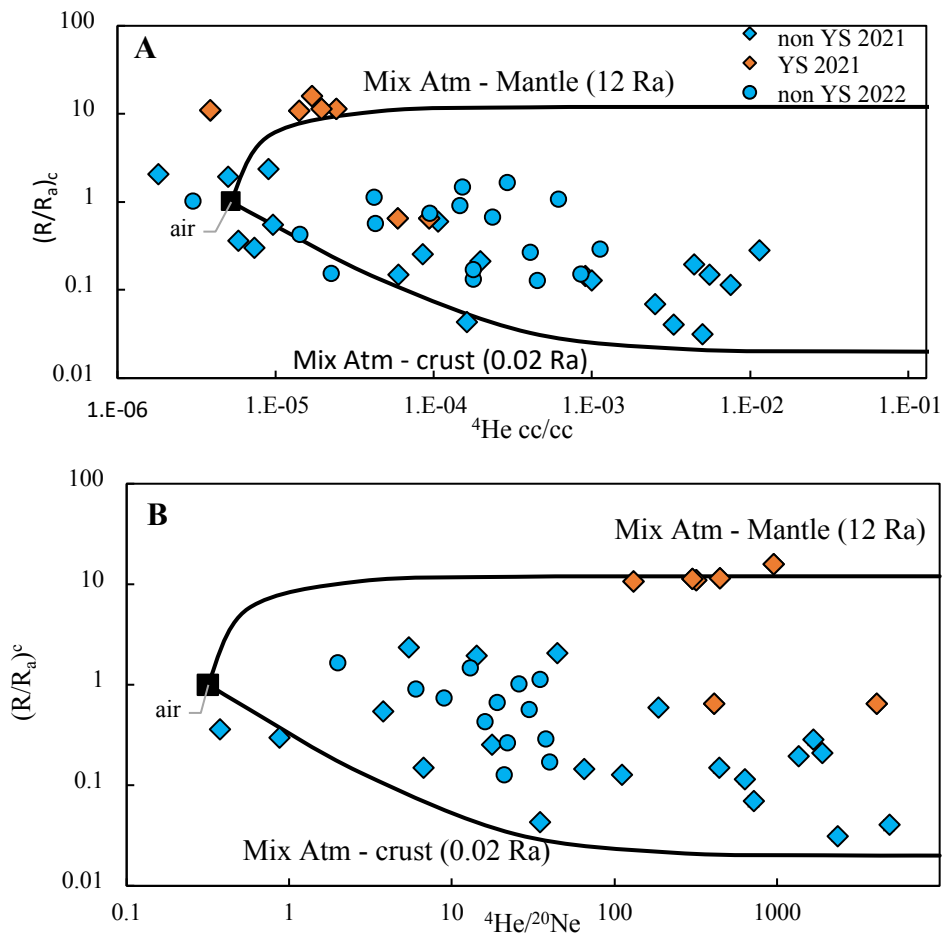


Figure 3.4: A) $(R/R_a)_c$ versus ^4He , and B) $(R/R_a)_c$ versus $^4\text{He}/^{20}\text{Ne}$ which shows general mixing trends with air, mantle and crustal endmembers with Yellowstone samples mostly plotting on the mantle-air binary mixing trend, while the non-Yellowstone samples plot along the air-crust mixing line with some degree of influence from the mantle endmember as some samples are shifted up. Generally, the non-Yellowstone samples are more ^4He enriched than the samples obtained from within Yellowstone. The non-Yellowstone samples have on average a lower $^4\text{He}/^{20}\text{Ne}$ signal than the Yellowstone samples, indicating that the non-Yellowstone samples have had more groundwater interaction than the Yellowstone samples.

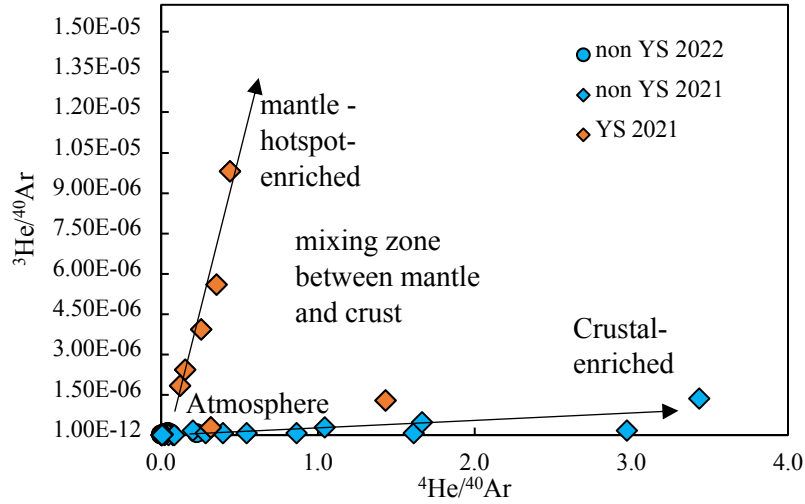


Figure 3.5: Plot showing $^3\text{He}/^{40}\text{Ar}$ versus $^4\text{He}/^{40}\text{Ar}$ that shows a clear distinguishing grouping of the mantle/hot spot enriched Yellowstone samples compared to the crustal enriched non-Yellowstone samples. The atmospheric value is not visible as it is behind non-Yellowstone samples $^4\text{He}/^{40}\text{Ar} = 1.58 \times 10^{-4}$ and $^3\text{He}/^{40}\text{Ar} = 2.21 \times 10^{-10}$ at 25°C (Han et al., 2022; Ozima and Podosek, 2002). The non-Yellowstone samples stretch from atmosphere value for both $^3\text{He}/^{40}\text{Ar}$ and $^4\text{He}/^{40}\text{Ar}$ to elevated $^4\text{He}/^{40}\text{Ar}$ values.

To further differential He sources, a theoretical model of $^3\text{He}/^{40}\text{Ar}$ versus $^4\text{He}/^{40}\text{Ar}$, is put forth which shows general mixing between air, mantle and crustal endmembers (Fig. 3.5). The atmospheric endmember, which likely represents a meteoric water endmember, has values of $^4\text{He}/^{40}\text{Ar} = 1.58 \times 10^{-4}$ and $^3\text{He}/^{40}\text{Ar} = 2.21 \times 10^{-10}$ at 25°C (Han et al., 2022; Ozima and Podosek, 2002). Since both axes have the common denominator of ^{40}Ar , a straight line should represent mixing between two theoretical endmembers (air and mantle or air and crust) (Han et al., 2022; Matsuda and Marty, 1995). We observe crustal systems with points plotting to the lower-right side of the plot (i.e., more crustal contribution), which is indicative of the addition of crustal helium (^4He). Likewise, increases in ^3He derived from mantle sources can be distinguished within the bulk of the Yellowstone samples. There are two samples from the Yellowstone grouping that do not plot with the rest along the mantle-hot spot enriched trend. These outliers from the Yellowstone group can be attributed to mixing with crustal enriched subsurface fluids. We consider the amount of ^3He that is sourced from the crust to be negligible (Pinti and Marty, 1998). Thus, when using our data, the plot also shows a similar pattern of a strong mantle influence regarding the Yellowstone samples via an air-mantle mixing trend, and a more dominant crustal signature for the samples outside of Yellowstone via an air-crust mixing trend (Fig. 3.5).

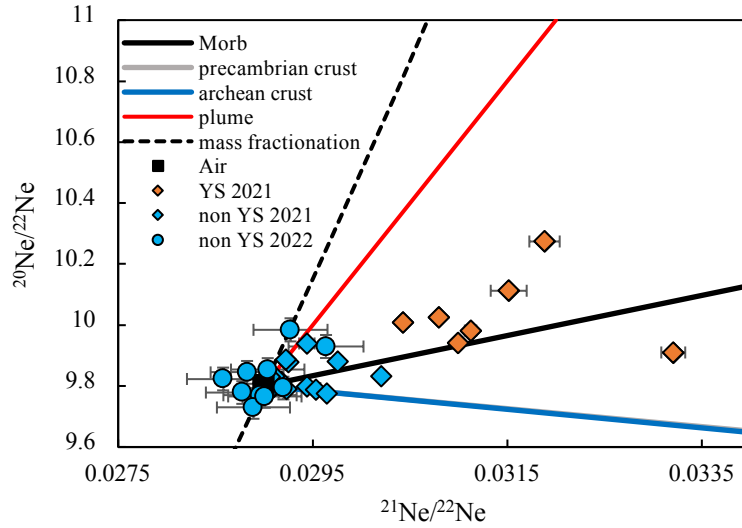


Figure 3.6: Plot consisting of $^{20}\text{Ne}/^{22}\text{Ne}$ versus $^{21}\text{Ne}/^{22}\text{Ne}$, which shows a strong influence of the air endmember and fractionation along the mass dependent fractionation trend from non-Yellowstone hot spring samples. The Yellowstone samples largely plot in between the MORB and plume mixing trends with air. Several of the non-Yellowstone samples plot along the Precambrian crust and Archean crust trends, as well as the MORB and plume trends as well, but their respective levels of fractionation in the $^{21}\text{Ne}/^{22}\text{Ne}$ and $^{20}\text{Ne}/^{22}\text{Ne}$ space is less compared to the Yellowstone groups. Endmembers are from Ballentine (1997), Ballentine and O’Nions (1992) and Ballentine and Holland (2008).

Considering the neon isotopes of ^{20}Ne , ^{21}Ne and ^{22}Ne , we observe largely a plume-mantle mixing for most Yellowstone samples, while samples collected outside of Yellowstone are largely dominated by air signatures and various degrees of crustal mixing (Figure 3.6). There is one Yellowstone sample that plots in between the MORB and Archean crust mixing line, is the same sample in Fig. 3.5, which showed a strong crustal influence despite being within the Yellowstone caldera. Some of the non-Yellowstone samples lie on the Archean crust and Precambrian crust line indicating a mixing between air and these crustal endmembers. Several of the non-Yellowstone samples lie along the mass dependent fractionation line indicating fractionation on purely mass alone. Most of the non-Yellowstone samples from the 2022 field season, appear to lie (within error) clustered around the air endmember. Overall, the trends observed corroborate the mixing between air, mantle and crustal sources observed via He and Ar isotopes.

3.5.2 Heat Transfer and Fluid Mixing

In theory, radiogenic ^4He and heat should be uniquely coupled being that uranium (U) and thorium (Th) produce 50% of Earth's heat and all of the ^4He (Kennedy et al., 2000). Historically, ^3He has been observed to have a strong relationship with areas of elevated heat flow (fluid enthalpy) (Q) especially at mid-ocean ridges, where values are similar to predicated theoretical values (Burnard et al., 1999; Han et al., 2022; Kennedy et al., 2000; Tuner and Stuart, 1992). Moving from oceanic environments to more complicated continental regions, the relative proportion of heat derived from different sources (i.e., mantle or crust) can be assessed studying the He-helium relationship and quantifying $^3\text{He}/^4\text{He}$ (R/R_a) values (Kennedy, et al., 2000).

Considering the isotopic values associated with He in a crustal environment, they are often characterized by values of 0.02 R/R_a (Andrews, 1985; Ballentine and Burnard, 2002; Boreham et al., 2018). This low R/R_a value dominated by input from ^4He derived from radioactive decay of U and Th from crustal rocks, corresponds to a Q/He ratio of $\sim 1 \times 10^{15}$ Joule/ccSTP (Kennedy et al., 2000). In contrast, a volcanic environment which has experienced episodes of mantle partial melting exhibits a R/R_a value of $\sim 10 R_a$ or greater for some areas associated with hotspot volcanism such as Hawaii, USA ($\sim 32 R/R_a$) (Kenney et al., 2000). The associated Q/He signature for a MORB endmember of $\sim 2 \times 10^{12}$ Joule/ccSTP is significantly lower than the crust source signature. These differences can provide a mechanism to quantify and extrapolate province and geologic history of an area and more importantly differentiate the proportions of crustal and mantle heat ultimately driving geothermal systems (Kennedy et al., 2000; Han et al., 2022).

By plotting $Q/^3\text{He}$ versus $^4\text{He}/^{36}\text{Ar}$, we can examine the processes involved in the transfer of heat and subsequent fractionation of He, heat, and volatiles in the Yellowstone and surrounding area systems (Fig. 3.7). By utilizing Equation 3.9, we calculate $Q/^3\text{He}$ ratios for each of the samples at the surface. A first-order observation of our data is there is a wide fractionation range in both the $Q/^3\text{He}$ and $^4\text{He}/^3\text{He}$ axes. If no fractionation had occurred the samples would likely plot close to the expected melt sources for continental hydrothermal systems, which are the mid ocean ridge basalts ranging from 5×10^{12} to 1×10^{13} JccSTP⁻¹ (Baker and Lupton, 1990; Burnard and Polya, 2004; Han et al., 2022; Kennedy et al., 2000; and Lupton et al., 1989), another which represents melts generated

beneath continents (2% partial melting) of $1-2 \times 10^{12}$ JccSTP⁻¹ (Burnard and Poly, 2004; Han et al., 2002; and Martel et al., 1989), and another which represents a hot spot endmember 4.2×10^{10} JccSTP⁻¹ (Alonso et al., 2019; Kennedy et al., 2000). While examining Fig. 3.7 closely, we observe two deviations away from the hot spot endmember. The first, which is labelled as conduction/ASW dilution/boiling is characterized by an increase in the $Q/^3\text{He}$ ratio coupled with a decrease in $^4\text{He}/^{36}\text{Ar}$. This trend patterns fits most the non-Yellowstone and Yellowstone samples and leads from the hot spot endmember to a meteoric water endmember. The second, which is labelled advection (convection)/magma degassing, is characterized by a decrease in the $Q/^3\text{He}$ ratio and an increase in the $^4\text{He}/^{36}\text{Ar}$ ratio. The samples that make up this group are one Yellowstone sample and a subset of the larger non-Yellowstone samples. It should be noted that addition of radiogenic crustal He should shift values to the right portion of the plot.

Concerning the first trend (conduction/ASW dilution/boiling), this describes a physical process of magma cooling in which magmatic volatiles are not transferred into a hydrothermal system, but magmatic heat is transferred (Burnard and Poly, 2004). The rationale behind this is that if there is an influx of meteoric water into the system, it will increase ^{36}Ar , and it will decrease the $^4\text{He}/^{36}\text{Ar}$ ratio. Concerning the addition of meteoric water and ^3He , it has the potential to dilute the ^3He and increase the $Q/^3\text{He}$ ratio. This situation is difficult to explain, where there is a transfer of heat and not volatiles as this goes against evidence of magmatic He influencing R/R_a values. Conversely, we also see a small subset of samples that show a decreasing $Q/^3\text{He}$ trend in the broad conduction group. This might be evidence for interaction with an atmospheric source which adds small amount of ^3He relative to heat and ultimately lowers the $Q/^3\text{He}$ ratio (Han et al., 2022). The small subset of samples is also very close to the calculated range of meteoric water MAAT 12-22 °C, which could be affecting the observable fractionation pattern. Another plausible theory given the majority of the heat systems in Yellowstone are dominated by convective heat transport (Fournier et al., 1976; Lowenstern and Hurwitz, 2008; McMillan et al., 2018), is that we could be observing a more dominant convective trend showing the addition of heat with dilution of magmatic volatiles via meteoric water addition (Han et al., 2022). Moreover, it is also possible to explain a lower $^4\text{He}/^{36}\text{Ar}$ and higher $Q/^3\text{He}$ trend via boiling of hydrothermal fluids (Han et al., 2022). In this type of scenario for Yellowstone the

temperatures can be very high (i.e., systems can be boiling), Ar would be retained more so than He due to their differences in solubility, and He would be lost more efficient than heat (Han et al., 2022). However, this scenario is difficult to quantify for samples outside of Yellowstone, as although we know the surface temperature of springs (none are $>100^{\circ}\text{C}$ at the surface, except one), the exact geothermal gradients and fluid temperature at depth are unknown in the area.

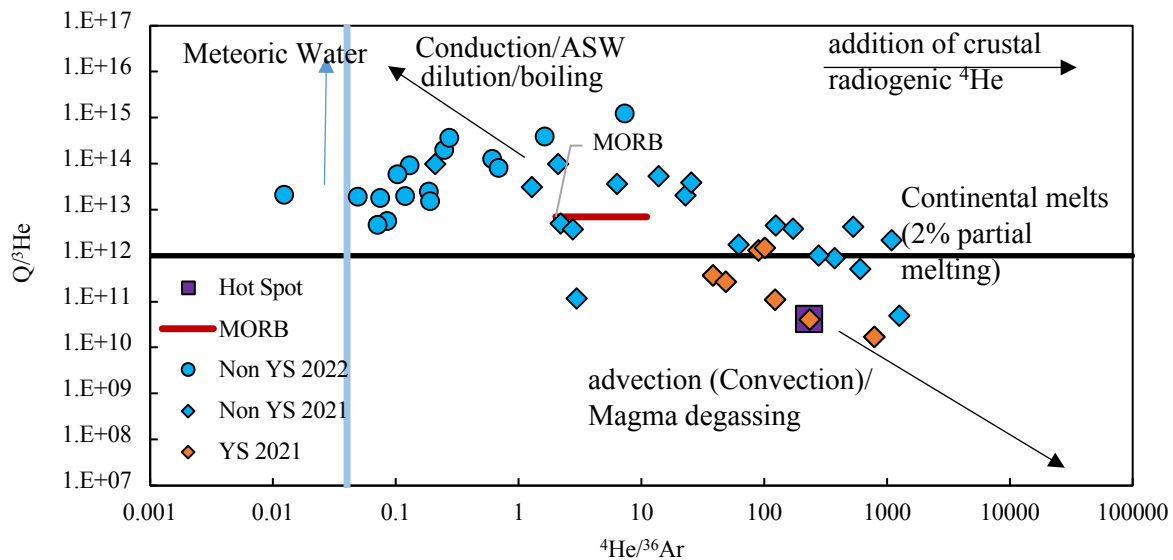


Figure 3.7: $Q^3\text{He}$ versus $^4\text{He}/^{36}\text{Ar}$ plot shows two main processes that are affecting samples, 1) the conduction/ASW dilution/boiling processes and 2) advection (convection)/magma degassing processes). Since it is known convective systems dominate Yellowstone, we propose a convective system that adds heat and volatiles and is subjected to various ASW dilution and boiling episodes. Several of the non-Yellowstone samples and Yellowstone samples with elevated $^4\text{He}/^{36}\text{Ar}$ ratios fall along the heat-He range of a continental melt. Additionally, continental melt values are shown from Burnard and Polya (2004), along with ASW ranges calculated at $12\text{--}22^{\circ}\text{C}$ from Han et al., (2022). The shifting of value to the right of the plot could be influenced by the addition of crustal radiogenic ^4He .

Concerning the second trend (convection/magma degassing), it describes a physical process whereas heat and volatiles are transferred via convection from a cooling parent magma body into a hydrothermal system (Baker and Lupton, 1990; Burnard and Poly, 2004; Han et al., 2022). In this instance, He will be removed from the magma faster than heat is removed, so there will be more He in the system, which results in the characteristic decreasing fractionation signature. Not only can magma degassing fractionation He and heat, it can also affect the ratio of He/Ar by both solubility and diffusivity values with diffusion being a more dominant fractionation mechanism (Burnard, 1999, 2001). Since He is highly diffusive, it is much more likely to escape compared to other noble gases such as Ar, thus resulting in higher $^4\text{He}/^{36}\text{Ar}$ signatures (Matsuda and Marty, 1995; Gonnermann and

Mukhopadhyay, 2007). Interestingly, the lowest ASW influence is observed in the convection group of samples and this relates to the higher $^4\text{He}/^{20}\text{Ne}$ ratios observed in Fig 3.2B. Therefore, it is likely we are observing a regional trend that is largely controlled by convection and degassing of volatiles coupled with various degrees of ASW dilution and potential boiling episodes.

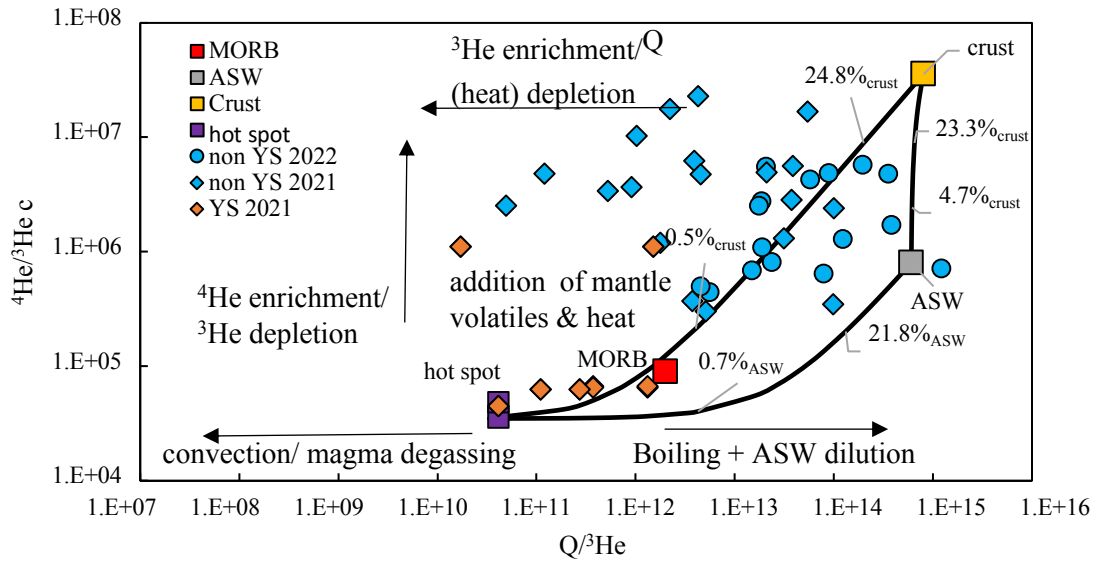


Figure 3.8: $^4\text{He}/^3\text{He}$ versus $Q/^3\text{He}$ plot showing mixing lines between crust, ASW and hot spot endmembers (Alonso et al., 2019; Kennedy et al., 2000; Han et al., 2022). Yellowstone samples plot near hot spot endmembers which is likely caused by boiling processes; most non-Yellowstone samples are likely influenced by ASW dilution processes. Several non-Yellowstone samples lie on the hot spot–crust mixing line. Non-Yellowstone samples lie between the ASW–crust mixing line and the hot spot–crust mixing line, which indicates more ASW influence. Heat depletion is observed for several Yellowstone samples and non-Yellowstone samples (plotting away from mixing lines).

Unfortunately, the determination of the various mantle versus crust components of $^4\text{He}/^{36}\text{Ar}$ is poorly constrained. Fortunately, the $^4\text{He}/^3\text{He}$ ratio is much more accurately defined and useful to differential sourcing bodies and determine their impact on heat in these systems (Ballentine et al., 2002; Han et al., 2022; Turner et al., 1993). By plotting $Q/^3\text{He}$ versus $^4\text{He}/^3\text{He}$, we can examine the relationship between heat and He and the contribution of various known endmembers on the subsurface system (Fig. 3.8). The MORB signature ($Q/^3\text{He} = 2 \times 10^{12}$; $^4\text{He}/^3\text{He} = 1 \times 10^5$), crust signature ($Q/^3\text{He} = 8 \times 10^{14}$; $^4\text{He}/^3\text{He} = 3.5 \times 10^7$), and ASW signatures ($Q/^3\text{He} = 6 \times 10^{14}$; $^4\text{He}/^3\text{He} = 8 \times 10^5$) are from Kennedy et al., (2000). The hot spot endmembers are from Alonso et al., (2019) and are $Q/^3\text{He} = 4.2 \times 10^{10}$; $^4\text{He}/^3\text{He} = 3.5 \times 10^4$ to 4.77×10^4 . As meteoric water (ASW) moves deeper into the crust, it will encounter ^4He via diffusion that has been released from host minerals rich in U and Th (Cheng et al., 2021). Ultimately, the He concentration is the result of the concentration of U and Th,

diffusion gradients, the presence or lack of concentration migration pathways (i.e., advective transport), and water residence time (Cheng et al., 2021; Danabalan, et al., 2022). The heat contribution is gained through conduction as a function of the geothermal gradient (Kennedy et al., 2000).

The interactions between the crustal and ASW endmembers should plot on the crustal-ASW binary mixing line, and we do observe points near the ASW endmember, which are some of the non-Yellowstone samples. Mixing between the crustal endmember and the hot spot/mantle endmember is the result of volcanism influencing deep crustal fluids and the transfer or addition of mantle volatiles and heat into the system (Han et al., 2022). For our samples, those collected within Yellowstone plot near the hot spot endmember and are likely influenced by ASW and boiling episodes with minor impact of convection/magma degassing processes. This process is characterized by the unfractionated nature of He isotopes compared to the fractionated $Q/^3\text{He}$ (Baker and Lupton, 1990; Lupton et al., 1999). The samples collected outside of Yellowstone plot broadly along the mixing trend from the hotspot endmember to the crustal endmember. Those samples that plot to the right of the crust-hot spot mixing line are likely influenced by ASW interaction. There is evidence to support boiling which would serve to increase $Q/^3\text{He}$ ratios by preferentially removing ^3He , while keeping the $^3\text{He}/^4\text{He}$ relatively constant and unfractionated (Saby et al., 2020). A significant portion of non-Yellowstone samples plot to the left and above of the crustal-hotspot binary mixing trend which indicates that they have experienced either ^4He enrichments and/or heat depletion. Temperature data collected on site confirms heat depletion as the left most points are significantly cooler than those on the right.

Comparing the heat and volatile relationships with other major gases such as CO_2 should produce a similar complex fractionation mixture of contributions from ASW, the crust and a hotspot/mantle endmember. Concerning $\text{CO}_2/^3\text{He}$ versus $Q/^3\text{He}$, we plot binary mixing trends between ASW, crust and hot spot endmembers (Fig. 3.9). We observe that the Yellowstone samples unsurprisingly plot near the hot spot endmember and a portion of the non-Yellowstone samples lie along a hot spot –ASW mixing line. Despite a known range of $\text{CO}_2/^3\text{He}$ in literature, the hot spot endmember is listed as 3.5×10^9 from the Galapagos hot spot (Taran et al., 2010). Several of the points lie along a crust-hot spot mixing line as well. Any deviation of points with higher $\text{CO}_2/^3\text{He}$ values

from the hot spot-ASW mixing line is considered to be due to crustal influence. The crustal endmember has been shown to range from 1×10^{12} - 1×10^{14} (O’Nions and Oxburgh, 1998). The majority of non-Yellowstone samples plot below the mantle endmember, which suggests that they have experienced some degree of CO₂ loss and dissolution, likely from precipitation and/or dissolution, but without CO₂ carbon isotopes it is difficult to say for certain.

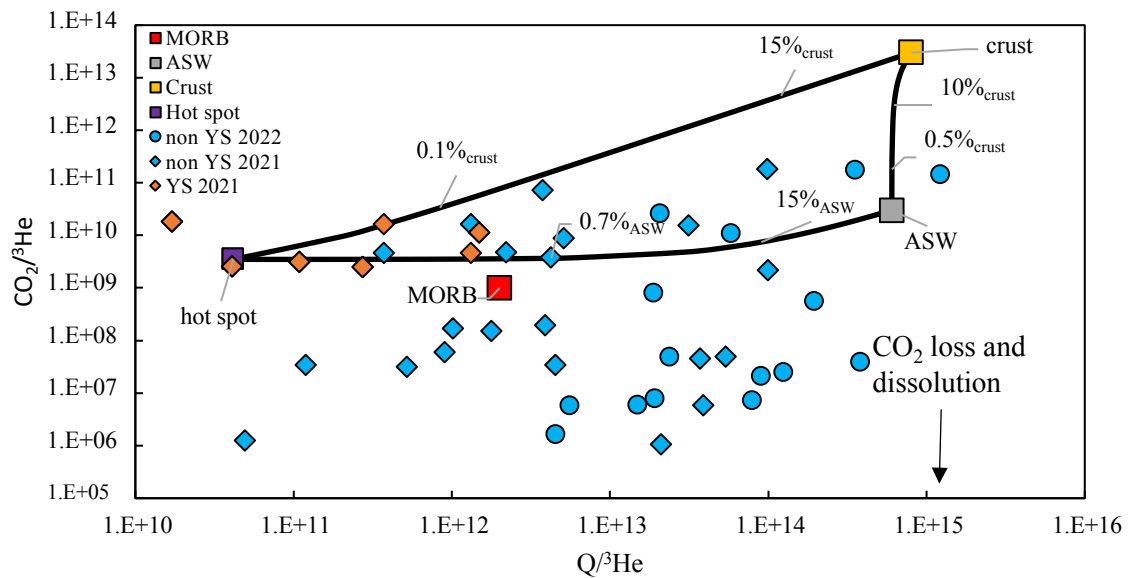


Figure 3.9: CO₂/³He versus Q/³He which shows mixing trends from ASW, crust and hot spot endmembers (Han et al., 2022; O’Nions and Oxburgh, 1998; Taran et al., 2010). The MORB endmember has been shown to range from 1×10^9 - 1×10^{10} (Gilfillan et al., 2008, 2009). The Yellowstone samples plot near the hot spot endmember. Several of the non-Yellowstone points plot within the three component mixing area. A large portion of non-Yellowstone samples plot below the mixing lines which indicates these samples are likely influenced by CO₂ loss and dissolution processes possibly from carbonate precipitation.

It is worth noting that the Q (heat) calculation discussed above was originally utilized to calculate the fluid enthalpy of geothermal reservoirs with known and well documented temperature parameters. As much of our current work deals largely with unknowns in this regard, we have substituted the reservoir temperature value with the surface temperature recorded value that were measured in the field for most samples and supplemented by historical reports to determine Q. Another reason to use the surface temperatures is because these are clearly advective systems and often surface temperatures of hydrothermal fluids are used as indicators of fluid temperatures at circulation depth. With this substitution, we are examining the Q of the shallow subsurface and not the heat associated with higher fluid temperature at depth. Additionally, this simplification was

adopted due to the vastly differing geothermal gradients encompassing the field area. This being said, the models in Fig. 3.7, 3.8 and 3.9 do allow the modification of surface temperature values, which shift values along the x axis. However, we noted that even altering the Yellowstone samples to have a hypothetical fluid temperature at depth of 150 °C and the non-Yellowstone samples to have a hypothetical fluid temperature at depth of 50 °C; the end results of establishing regional processes and mechanisms to explain heat and He signatures are comparable to those produced by using measured hot spring surface temperatures.

3.5.3 Noble Gas Fractionation Models

To more deeply solidify the understanding of the processes of ASW dilution noted for most of our higher He samples, we constructed numerous fractionation models focusing on ASW derived noble gases. More specifically, we primarily use atmosphere derived noble gases (i.e., ^{20}Ne , ^{36}Ar , ^{84}Kr , and ^{130}Xe) that are dissolved in groundwater (termed air saturated water or ASW) to extrapolate physical processes influencing the noble gases in these systems. These fractionation models were utilized based on noble gases solubilities and diffusivities (mass dependent). Noble gases from the atmosphere are dissolved into the groundwater at the surface based on their individual solubilities and the groundwater is subsequently circulated into the subsurface due to the hydrological dynamics of aquifer recharge (Holland and Gilfillan, 2013). The noble gases are widely considered effective tracers due to their unreactive nature in the subsurface and unique geochemical signature (Ballentine and O’Nions, 1994; Pinti and Marty, 2000; Ozima and Podosek, 2002; Gilfillan et al., 2008; Zhou et al., 2012; Prinzhofer, 2013; and Byrne et al. 2017).

Firstly, we consider a fractionation model of $^{20}\text{Ne}/^{36}\text{Ar}$ versus $^{84}\text{Kr}/^{36}\text{Ar}$ and $^{20}\text{Ne}/^{36}\text{Ar}$ versus $^{130}\text{Xe}/^{36}\text{Ar}$ (Fig. 3.10). In this model we present an open system Rayleigh fractionation gas to water curve (Equation 3.10), an open system Rayleigh fractionation water to gas curve (Equation 3.11), and a closed system water to gas curve (Equation 3.12). Several assumptions were taken to construct the fractionation models, namely that the average surface temperature for the samples is considered the temperature we used to calculate Henry’s constants (324 °K). Henry’s constants were calculated with

known parameters for each gas listed in Ballentine et al. (2002). We also assume the gas phase fugacity coefficient and liquid phase activity coefficient to be ~1. We assume that the redissolution of noble gases occurs into groundwater with zero noble gases. Additionally, we use calculated ASW endmembers of 0.15 for $^{20}\text{Ne}/^{36}\text{Ar}$ (at 283 °K and 10% excess air Ne), 0.045 for $^{84}\text{Kr}/^{36}\text{Ar}$, and 0.00046 for $^{130}\text{Xe}/^{36}\text{Ar}$ (Gilfillan et al., 2008). Air endmembers utilized are 0.52 for $^{20}\text{Ne}/^{36}\text{Ar}$, 0.02 for $^{84}\text{Kr}/^{36}\text{Ar}$, and 0.00011 for $^{130}\text{Xe}/^{36}\text{Ar}$ (Gilfillan et al., 2008).

Equation 3.10 (open gas to water): $\left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]}\right)_g = \left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]}\right)_{og} P^{\left(\frac{1}{\alpha}-1\right)}$

where α is the fractionation coefficient = $(\gamma_{20\text{Ne}}/\phi_{20\text{Ne}} \times K_{20\text{Ne}}^{\text{groundwater}})/(\gamma_{36\text{Ar}}/\phi_{36\text{Ar}} \times K_{36\text{Ar}}^{\text{groundwater}})$, $\gamma/\phi \sim 1$, $([^{20}\text{Ne}]/[^{36}\text{Ar}])_{og}$ = original groundwater phase ratio, and P = the fraction of Ar remaining in the water phase.

Equation 3.11 (open water to gas): $\left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]}\right)_g = \left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]}\right)_{ow} P^{(\alpha-1)} \alpha$

Equation 3.12 (closed water to gas):

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

where $K_d = \frac{K \frac{\text{atm kg}}{\text{mol}}}{\text{gas constant} \frac{\text{atm kg}}{\text{mol K}} \times \text{temperature K}} \times \frac{Y_i}{\Phi_i}$

$$\left(\frac{[i]}{[Ar]}\right)_T = \text{original ratio}; \frac{V_g}{V_l} = \frac{\text{volume gas}}{\text{volume liquid}}$$

Equation 3.13 (mass dependent diffusion): $\frac{M_B}{M_{A\text{gas}}} = \frac{M_B}{M_{A\text{initial}}} P^{(\alpha-1)}$

where α is the fractionation coefficient for mass A and mass B: $M_A/M_B = \sqrt{\frac{M_B}{M_A}}$

Regarding Fig. 3.10, the theoretical framework of the open system approach is that at some theoretical point at the far left of the open system water to gas blue curve, there is an initial amount of groundwater with noble gases dissolved in the groundwater (i.e., initial ASW value). As one moves down the blue curve and to the right, that initial groundwater becomes progressively degassed. This process can be caused by a process called gas stripping where essentially another gas phase is near the groundwater, and the dissolved gases will be exsolved into the gas phase due to their relative solubility coefficients (Ballentine et al., 2002). Unsurprisingly, for the closed batch system fraction red curve the range of fractionation values is much smaller compared to the open system equivalent. Despite this smaller range, the closed water to gas red trend is essentially portraying a similar process

of degassing dissolved gases from an initial ASW starting value in groundwater. The second stage of the model involves the gas which has been exsolved, return to the groundwater. This is shown in Fig. 3.10 with the dashed black lines which start at the ASW endmember and move progressively to the right of the plot. As one moves right on this trend, more and more of the gas (in the gas phase), is returned or redissolved to the water phase. A second Kr and Xe enriched trend is presented in Fig 3.10, for instances of increased heavy isotopes potentially due to the influence of organic matter (Frink and Chang, 1977).

A first-order observation from Fig. 3.10 is that the majority of Yellowstone and non-Yellowstone samples can be explained by several known and well documented physical processes. There was surprisingly not a large degree of difference between the sample groups inside the physical boundary of Yellowstone compared to those taken outside the National Park. The majority of samples fall along or near a water to gas degassing curve. Both the Yellowstone and non-Yellowstone sample groups can be compatible with the open system degassing trend, but only the Yellowstone samples are compatible with the closed system degassing trend. Two outlier points of non-Yellowstone data have elevated $^{20}\text{Ne}/^{36}\text{Ar}$ ratios well beyond ASW and air endmembers at 2.6 and 4.1, and are considered to be influenced by some sort of redissolution process (e.g., migration) likely influenced by regional tectonic history (Gilfillan et al., 2008). There are several samples with lower $^{20}\text{Ne}/^{36}\text{Ar}$ values that exhibit potential patterns of gas redissolution (potentially due to migration) and they plot slightly below the degassing trends. This might be due to the fact that the exact temperature parameter is not well constrained and calibrated for each individual model, and/or because assumptions have been made for the relevant best-fit ASW endmembers due to a lack of consistency with elevation and temperature. Initial attempts were made to calibrate each model for each point, but as there are many sample points ($n=43$), with each having a different surface temperature and geothermal gradient, the decision was made to simply the model and use average temperatures for a regional generalized approach. For example, lowering the temperature for the model (which alters the Henry's constants) the blue water to gas degassing trend will shift right and most of the points currently sitting on the redissolution dashed line trend will switch to be on or closer to the water to gas trend. Thus, after several iterations of tests in which we lower the temperature of the model, we surmise that overall the

systems are heavily influenced by a degassing physical process.

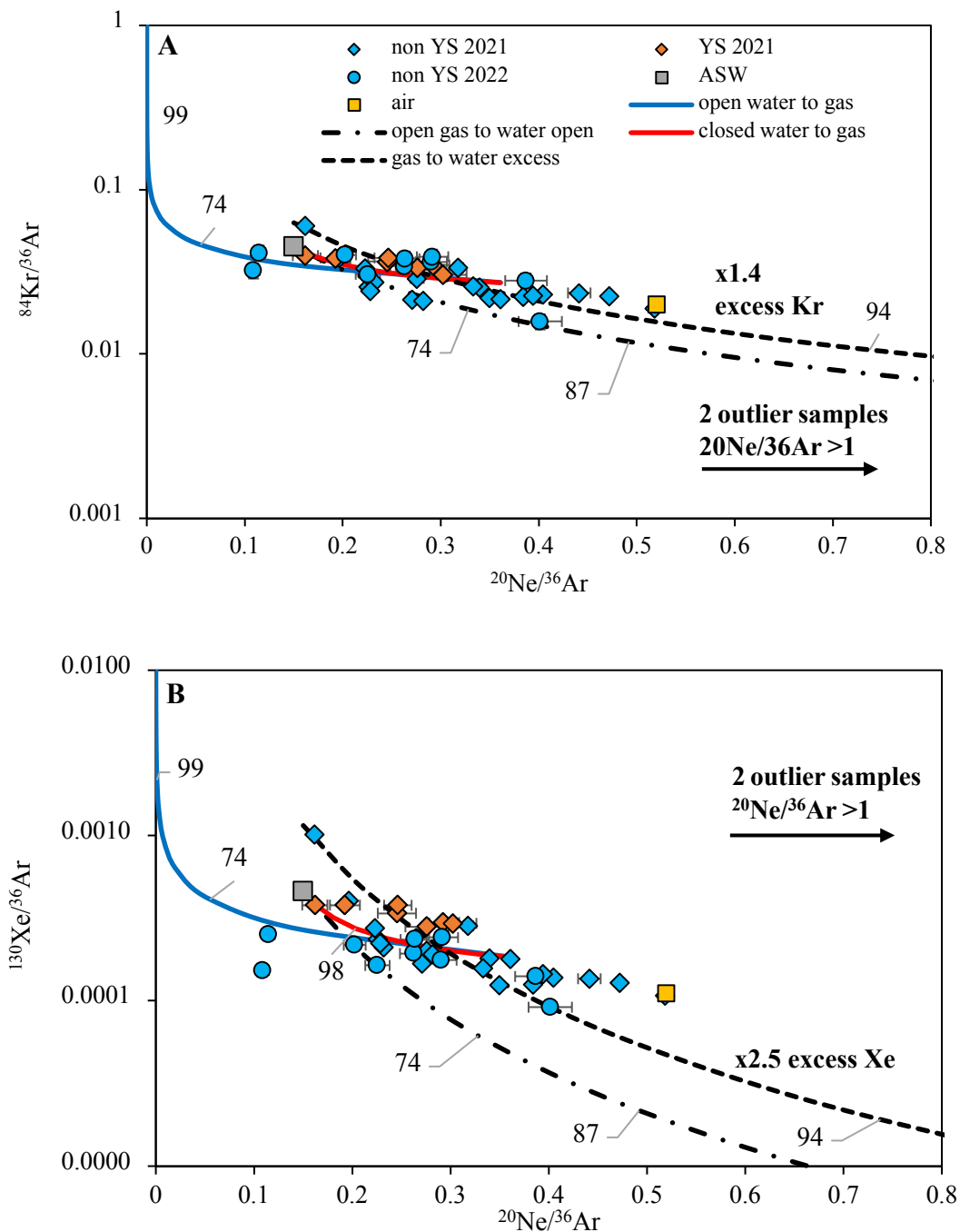


Figure 3.10: $^{20}\text{Ne}/^{36}\text{Ar}$ versus $^{84}\text{Kr}/^{36}\text{Ar}$ (A) and $^{20}\text{Ne}/^{36}\text{Ar}$ versus $^{130}\text{Xe}/^{36}\text{Ar}$ (B). On each plot, we show air and ASW values, along with calculated Rayleigh open water to gas (degassing curves), closed batch water to gas (degassing curves), and open Rayleigh gas to water (redissolution curves). The numbers associated with the open and closed system degassing trends are associated with the amount of Ar remaining in the groundwater phase, while the numbers associated with the open system redissolution curve represent the proportion of Ar lost from the gas phase. Most of the Yellowstone and non-Yellowstone samples plot can potentially be explained by a dominant degassing process from groundwater, with minor contributions of redissolution.

We also observe a well-documented feature (Gilfillan et al., 2008) that correlates the amount of ^{20}Ne to the relative portion of ^4He , namely in the case of the Yellowstone samples we observe they are relatively depleted in ^{20}Ne and likewise have lower amounts of ^4He , where the inverse is true for the non-Yellowstone samples. Additionally, when examining the data (Table 3.1), we observe that nearly all of the ^4He values are elevated beyond the ASW and air endmembers. This can be interpreted as groundwater interaction being responsible for ^4He concentration and enrichments (Danabalan et al., 2022). When a migrating free gas phase such as N_2 or CO_2 encounters groundwater with dissolved He, the He will be effectively exsolved from solution and subsequently transported in the gas phase (Brown, 2010). This process is called degassing or gas stripping and has been known to dilute amounts of ^4He in the groundwater in some cases, whereas in other cases the dilution remains minimal most likely due to a continuous oversaturation of ^4He (Danabalan et al., 2022). Another process that encourages exsolution of ^4He from groundwater is depressurization of subsurface systems caused by neotectonics (Danabalan et al., 2022; Halford et al., 2022). Thus, it is likely the act of groundwater degassing also plays a key role into the accumulation and concentration of He (Danabalan et al., 2022).

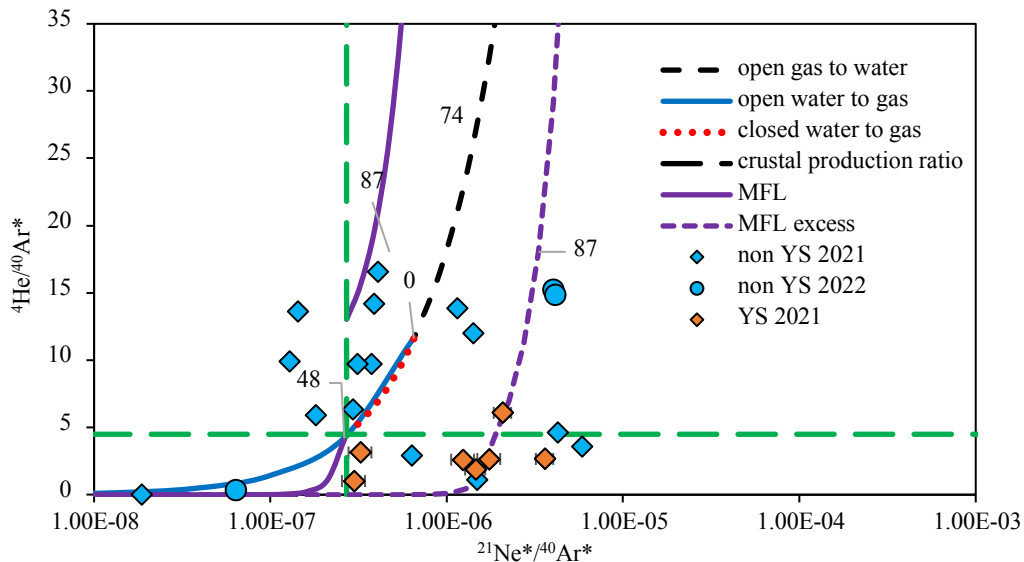


Figure 3.11: $^4\text{He}/^{40}\text{Ar}^*$ versus $^{21}\text{Ne}^*/^{40}\text{Ar}^*$ shows open and closed fraction water to gas fractionation curves, a regular and modified free molecule diffusion trend as well as crustal production ratio ranges. The Yellowstone samples plot near one or both of the crustal production ratios. The lower He non-Yellowstone signals can be explained as mixing between crustal endmembers (Li et al., 2022, Matsuda and Marty, 1995; Warr et al., 2019). Elevated crustal values might be explained with an Rayleigh fraction model or a mass fractional model. A portion of the higher Ne samples might be explained via a free molecule diffusion trend with an initial $^{21}\text{Ne}^*/^{40}\text{Ar}^*$ value of $2.7\text{E}-6$ ($\times 7$ elevated).

To understand the physical processes affecting the expected higher He beyond air and ASW values, we examine the relationship between $^4\text{He}^*/^{40}\text{Ar}^*$ and $^{21}\text{Ne}^*/^{40}\text{Ar}^*$ (Fig. 3.11). Corrections for ^{21}Ne and ^{40}Ar ($^{21}\text{Ne}^*$ and $^{40}\text{Ar}^*$) are described in the results (section 3.4), and they remove air contamination to arrive at a purely crustal component. For our fractionation models, the $^4\text{He}/^{40}\text{Ar}^*$ production value of 4.5 for the shallower crust is utilized (Warr et al., 2019), and a crustal endmember of $2.7\text{E}-7$ for $^{21}\text{Ne}^*/^{40}\text{Ar}^*$ is utilized (Rudnick and Fountain, 1995; Li et al., 2020).

We observe that the majority of samples plot within range of the crustal production ratios. The majority of Yellowstone points near/below the crustal production range for $^4\text{He}/^{40}\text{Ar}^*$ and above the crustal production range for $^{21}\text{Ne}^*/^{40}\text{Ar}^*$. Higher amounts of nucleonic ^{21}Ne are expected in volcanic rich gases (Craig and Lupton, 1976). The majority of non-Yellowstone points show near production ratios relative to $^{21}\text{Ne}^*/^{40}\text{Ar}^*$, but higher amounts of ^4He . The elevated ^4He of non-Yellowstone points can be potentially explained by groundwater/gas interactions: a water to gas open or closed system degassing curve. As an aside, if the $^4\text{He}/^{40}\text{Ar}^*$ ratio is increased by $\times 1.8$ (not shown), the gas/water curves account for most of the variability. The most enriched $^{21}\text{Ne}^*/^{40}\text{Ar}^*$ sample could be the result of an artefact during QA/QC at WHOI, as the blank contribution for the sample is near 4%. Additionally, a broad positive correlation is to be expected as ^4He and $^{21}\text{Ne}^*$ are produced via the same decay chain from Th and U (Li et al., 2022). This relationship hints that the gases are well mixed in a groundwater solution, and experienced physical fractionation during migration.

A second major process possibly affecting the samples is free molecule diffusive fractionation (Ballentine et al., 2002). Using Graham's law of diffusion, the relative fraction/diffusive coefficient (ratio of the masses of gas A and gas B) can be calculated (Holland and Gilfillan, 2013). Because the values of the diffusive coefficient are based on relative masses of the gases, we consider them as independent of reservoir conditions (Holland and Gilfillan, 2013). We plot two trends: one with the initial values of crustal production ratios mentioned before and the second with an enriched $^{21}\text{Ne}^*/^{40}\text{Ar}^*$ endmember ($\times 7$) (best fit for elevated $^{21}\text{Ne}^*/^{40}\text{Ar}^*$ points). This process is likely occurring under non-equilibrium conditions as the ASW noble gas diffusion properties control the transfer of noble gases from water into the gaseous phase (Holland and Gilfillan, 2013).

Ultimately, it is likely that crustal derived He is largely controlled by the crustal production ratios coupled with stripping of gas from large areas as gas-water interactions occurring with small contributions from diffusion processes. Other factors which can also influence the elevated He ratios are the age of groundwater, porosity, tectonic history, and the amount of free gas phase carrier gas that all serve to enrich He, but these are outside of the scope of this work.

3.5.4 Geospatial Coherence of Helium and Heat Flow

In order to understand the potential impact of elevated heat flow on gas release, a geospatial analysis was conducted using heat flow data for the entire continental USA from the Southern Methodist University (SMU) geothermal laboratory (Blackwell et al., 2011) and the He isotope data collected from Yellowstone and the surrounding areas in the USA (Fig. 3.12). This was undertaken to quantify any He-rich locations and to see if those elevated He regions corresponded to any sweet spot zones related to heat flow values and distance from the Yellowstone caldera.

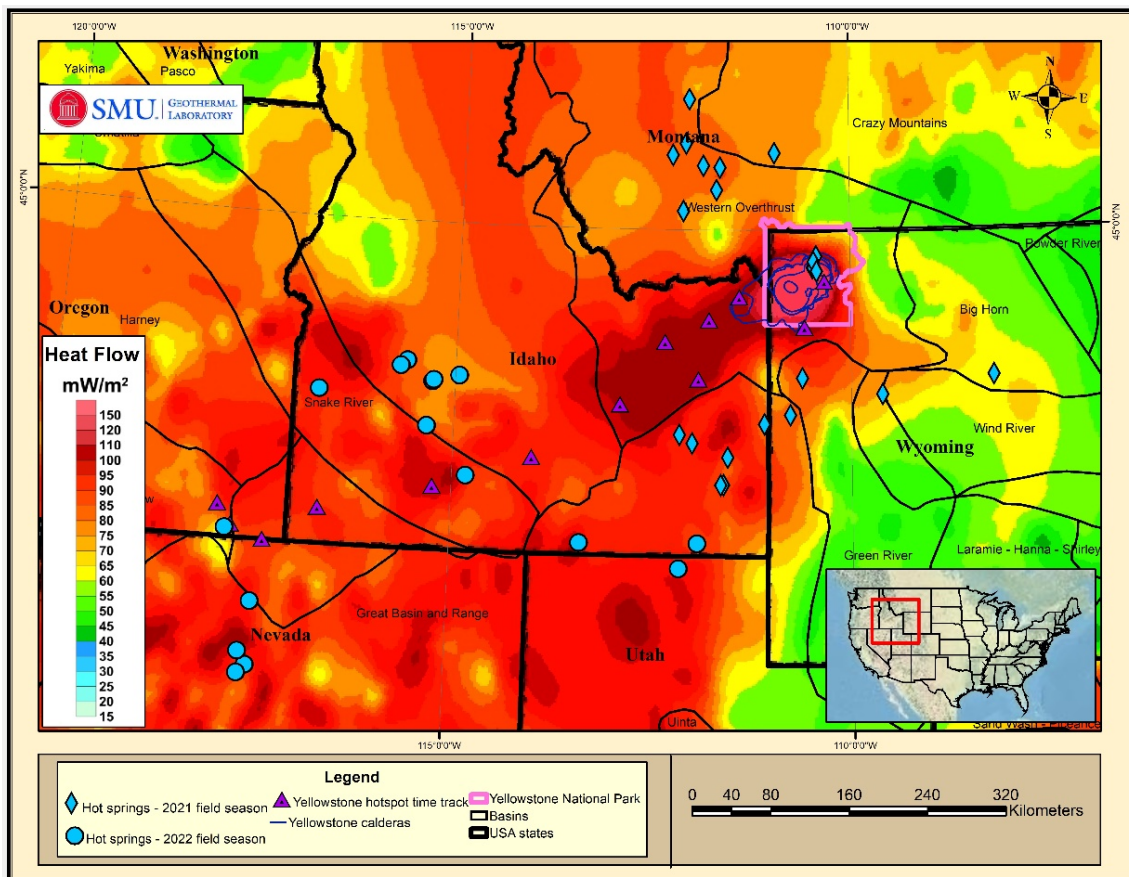


Figure 3.12: Location map showing the heat flow dataset from SMU geothermal lab (Blackwell et al., 2011) and the distribution of the hot spring sample sites. We observe a general elevated heat flow where the Yellowstone caldera is currently, and also along the previous Yellowstone hot spot track.

Our general observations from this dataset is that there is a large range of heat flow that relate to the R/R_a values of our samples (Figure 3.11) and no significant relationships were observed when comparing ^4He with heat flow, and ^3He with heat flow (Appendix Figure 3.A.1). The Yellowstone samples record elevated heat flow from 120 - >200 mW/m^2 , however, despite these ranges, the measured R/R_a values remained relatively constant at >10. Most samples that lie outside of the Yellowstone caldera have an R/R_a from ~ 0.3 -2.7 and have heat flow values that range from ~ 60 -100 mW/m^2 . Similar to the non-Yellowstone samples, data from the USGS also shows a narrow range relationship with He and heat flow in other environments, namely the Four Corners area, USA (Appendix Figure 3.A.2) (Craddock et al., 2017). Although there might be a relationship between $(R/R_a)_c$ and heat flow, it is difficult to examine the extent of the relationship due to heat flow data quality and the presence of higher heat flow endmembers from within Yellowstone (Fig. 3.13). In contrast, with previously published data in the Four Corners area, USA, we observe a clearer relationship (strong positive correlation) between R/R_a and heat flow with a difference being these samples are from subsurface reservoirs not surface samples (Gilfillan et al., 2008; Halford et al., 2022) (Appendix Figure 3.A.3).

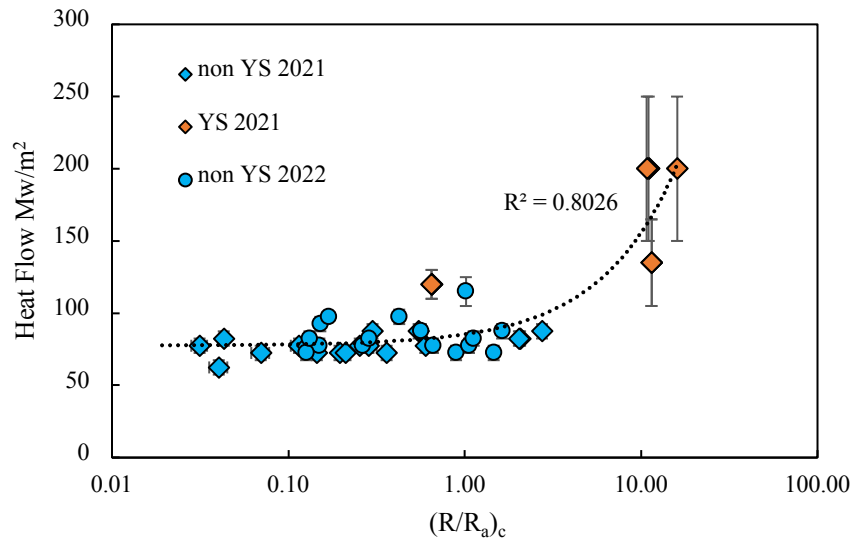


Figure 3.13: Plot showing the $(R/R_a)_c$ values with heat flow data obtained from Blackwell et al., (2011). There is a correlation, but it might be spurious as it is heavily driven by the outlier samples from Yellowstone. Removing the Yellowstone samples leaves a relatively narrow range between ~ 60 -100 Mw/m^2 that does not strongly correlate to R/R_a signatures.

There was an initial concern that the effects of determining a thermal aureole would be masked due to poor data control on the heat flow for areas surrounding Yellowstone. This concern was tested in the Four Corners area, USA (Appendix Figure 3.A.4). Essentially, a higher resolution heat flow dataset was obtained in the Four Corners area, and the results were that there is a similarly relative narrow range of moderate heat flow values associated with He anomalies both low and high (Appendix Figure 3.A.2 and 3.A.3). This mitigates our trepidations that we are missing significant data trends for the regional data surrounding the Yellowstone caldera.

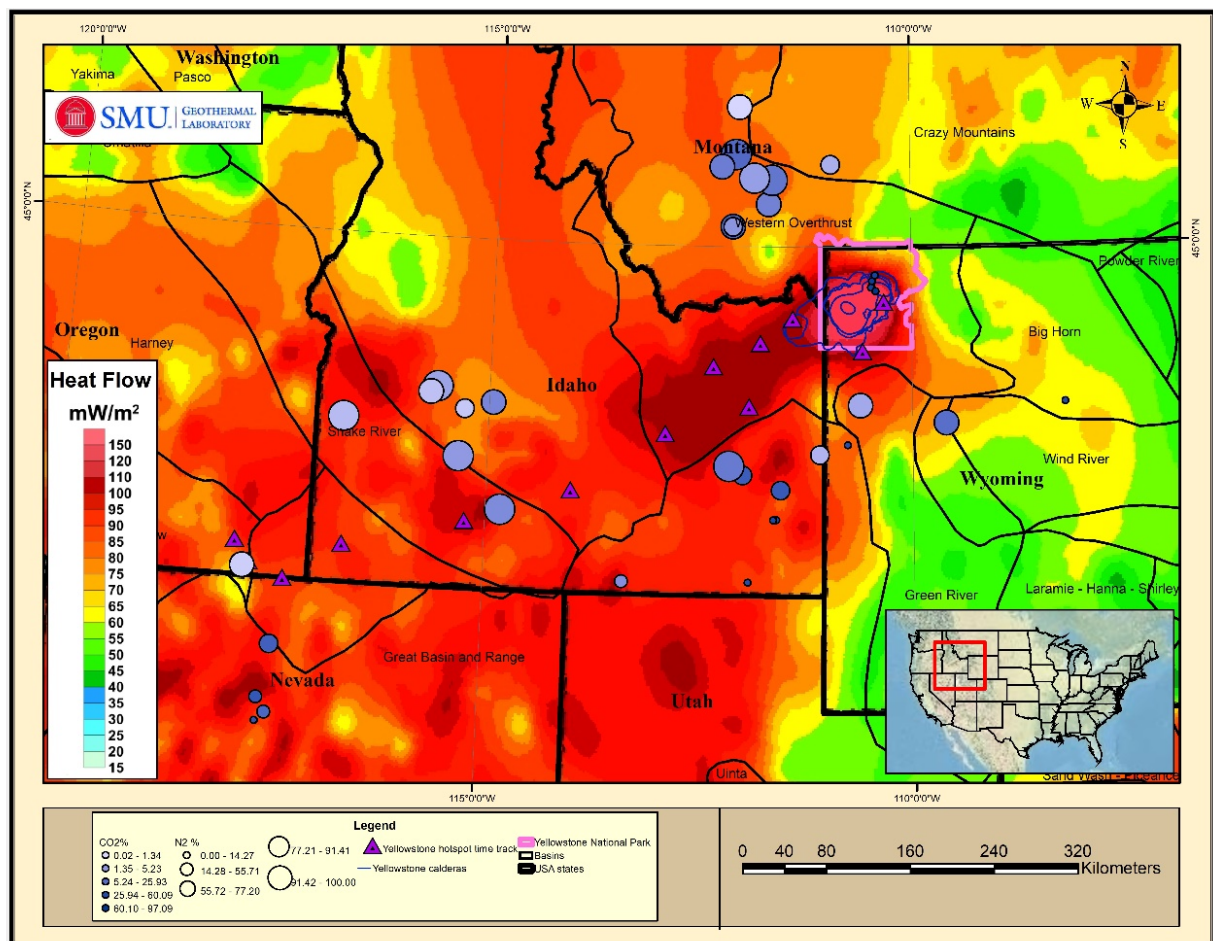


Figure 3.14: Location map showing the heat flow dataset from SMU geothermal lab (Blackwell et al., 2011) and the distribution of the CO₂ and N₂ bulk gas data from hot spring sample sites. The larger the circle is the more N₂ was measured, and the darker the circle, the more CO₂ was measured. We observe a CO₂-rich environment in the Yellowstone caldera and small pockets to the south west. Largely the Yellowstone surrounding environs are rich in N₂ gas.

Considering the general distribution of N₂ and CO₂ rich gases, we observe generally that CO₂-rich gases are the dominant species within Yellowstone and some small areas to the south west, and in large part, most of the non-Yellowstone samples from surrounding areas and the plume track are N₂-

rich (Fig. 3.14). No general patterns were observed concerning He and bulk gases as there is a mix of N₂ and CO₂ dominated sampled with >0.3 He%. Regarding the non-Yellowstone samples, we note small ranges of heat flow values with large ranges of CO₂ and N₂ values, and for the samples within Yellowstone, they exhibit high values of CO₂ and high values of heat flow. Observing the spatial distribution of sample's ⁴He and ³He values compared to the distance to the active Yellowstone caldera produced no significant results. Instead, a narrow pattern was observed in both instances (Appendix Figure 3.A.5). Similarly, the lack of a clear relationship was observed when studying the isotopic ratios of ³He/CO₂ and ⁴He/N₂ in relation to the distance to the active caldera (Figure 3.A.6). Unfortunately, the lack of a clear relationship indicates that higher areas of heat flow do not necessarily correspond with higher areas of He. This must indicate a complicated relationship involved in the gas release, possibly one with overprinting of various geologic processes.

The question of why does Yellowstone, despite having such high amounts of heat flow and high amounts of ³He relative to ⁴He, not have any indication of distance controlled sweet spots. One such possibility, is that the influence of magmatic controlled ³He is such a minor contributor into these systems even when they are active igneous zones, that the amount ⁴He essentially dominates the flux evidenced by the strong radiogenic He signatures immediately outside of Yellowstone where there should theoretically still be residual igneous activity on mantle gas release. Another possibility is that due to the link between groundwater and He observed in early sections, that the crustal ⁴He source is dwarfing the ³He mantle material, simply because the systems have experienced significant groundwater migration and thus significant water stripping (degassing) episodes that over time increases the amount of ⁴He in the system. Lastly, perhaps even more localized heat flow patterns, which are missed by the higher level regional USA heat flow data, are responsible for the degassing signatures. To explore the localized heat theory, we examine the impact of small intrusions and the expected local heat anomaly.

There are many variables influencing the release and transportation of gas in the crust (Ballentine et al., 2002). Examining the potential mineralogy/lithology of potential He source rocks and the surrounding geology can provide useful information pertaining to the closure temperatures of various minerals (Danabalan et al., 2022; Farley, 2002) that are known to contribute He into the

subsurface via the decay of U and Th held within their mineral grains. Depending on the minerals, we see there is a broad range of temperatures affecting potential He gas release (Danabalan et al., 2022; Farley, 2002). We observe that given a slightly elevated geothermal gradient (35°C/km), most closure temperatures are met/partially met within 6 km of the upper crust. Using the program, SILLi – a 1D numerical tool for quantifying thermal effects of sill intrusions, thermal diffusion profiles were computed with hypothetical intrusions for south-western Montana (Iyer et al., 2018). Using stratigraphic inputs from Ruppel and Lopez, (1984), general porosity estimates for certain lithologies, and a geothermal gradient of 35°C/km, these profiles illustrate that the closure temperatures can be reached given a presence of an intrusive body at much shallower depths (Figure 3.15).

Thus, depending on the number of intrusive bodies, their timing of emplacement and their relative temperatures, intrusive bodies are likely significantly controlling geologic factors that control the gas release of He from the crust. It is important to not forget that the presence of an intrusion will not only provide heat to liberate trapped He in mineral grains, but also it will follow preferential zones of weakness in the crust and additionally can create additional intervals of shallow fracturing (Halford et al., 2023), which can serve as potential migration channels concentrating He fluxes from depth.

Therefore, we advocate that the area in and around Yellowstone is significantly more complex, and a simple expectation that one would be able to easily find a He sweet spot around a volcanic centre, such as that presented in Danabalan et al., 2022, is not a universal exploration approach. We can however argue that looking for areas of moderate heat flow rather than those of high heat flow or areas with known localized heat flow to release trapped crustal He are more advantageous for encountering He anomalies.

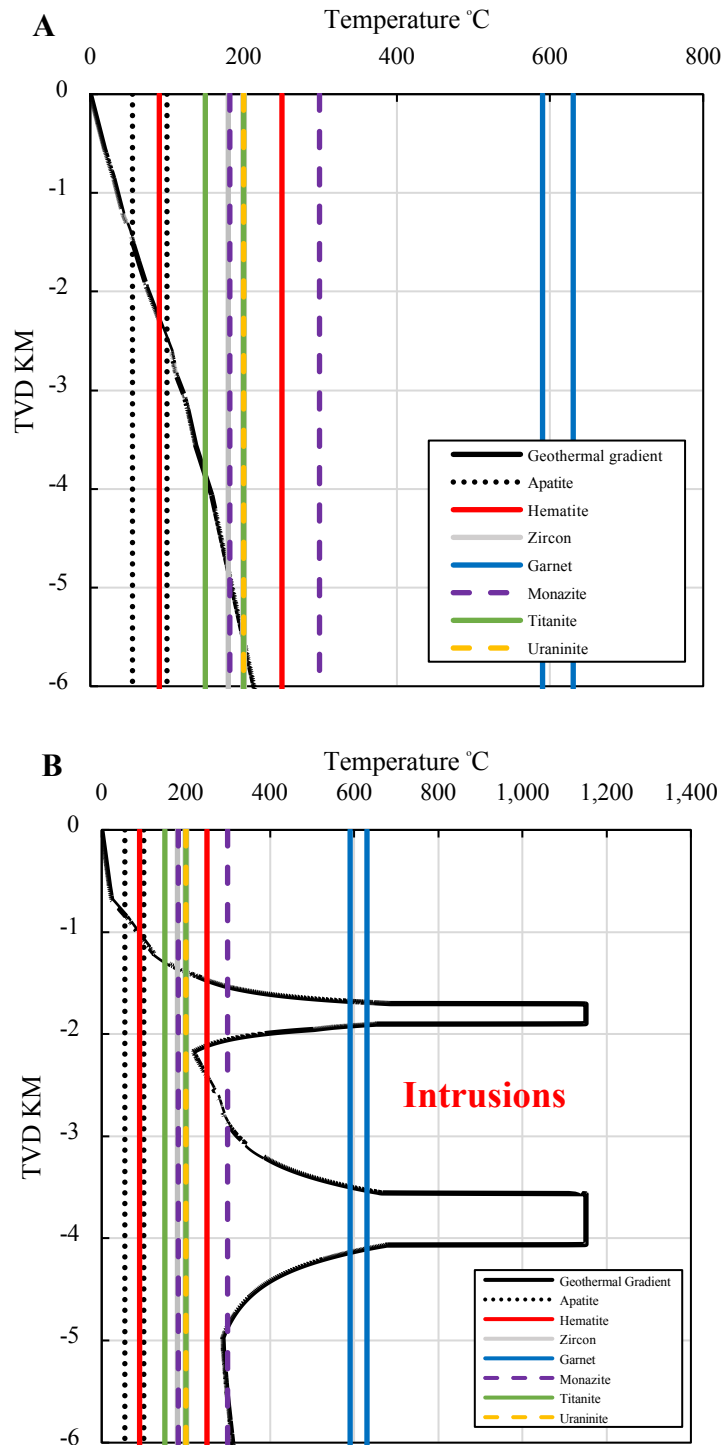


Figure 3.15: A) Showing the approximate ranges of He closure temperatures for several minerals (Danabalan et al., 2022; Farley, 2002) along with a hypothetical geothermal gradient of 35 °C/km, and B) a modified geothermal gradient (starting with the same hypothetical 35°C/km gradient) that has been influenced by two intrusions (1150 °C) that rapidly heats the immediate rock. The modified geothermal gradient was created using the program, SILLi (Iyer et al., 2018). The model was constructed using stratigraphic inputs for south-western Montana, USA, from Ruppel and Lopez, (1984), and general porosity estimates for certain lithologies.

3.5.5 Gas Release and Transport

It has been shown that several non-Yellowstone data points fit diffusive trends and are likely driven purely by diffusive gradients, so diffusion is most likely occurring over this area in some parts similar to how it has been shown to theoretically account for observed He signatures to the north east from our area of interest in the Canadian Williston Basin (Cheng et al., 2021, 2023). The question then becomes how significant is this process outside of a theoretical standpoint, and given the extremely geologic active nature of the Yellowstone and surrounding environs, it seems unlikely diffusion would be the only transport mechanism at work. Previous work by Brown (2010), advocates for a departure from relying on traditional diffusion based models and advocates a primary reason is the extremely slow speed of the diffusive fluxes. Moreover, finding areas on Earth with the extreme stability required (i.e., absolutely no fault/fractures) becomes problematic as even the most quiescent basins have some degree of fracture networks. All points aside, if we assume that diffusion is a universal process that is slowly contributing to He fluxes worldwide, let us then assume that there must be, another faster process that can facilitate large amounts of gas release over faster timescales.

Previous work has argued that gas release is likely heavily influenced by the presence of fault and fracture networks (Boles et al., 2015; Buttitta et al., 2020; Craddock et al., 2017; Danabalan et al., 2022; Halford et al., 2022; Karolytè et al., 2022; Mtili et al., 2021; Tardani et al., 2016). Faults have been mapped extensively in the area in and around Yellowstone (Garrity and Soller, 2009), and the known record of earthquake swarms monitored through various monitoring programs (Chochlaki et al., 2018) corroborates that there are numerous known and hidden faults all throughout the region. Previous work by Caracausi et al., 2022, has shown how critical earthquakes (even low magnitude) are in controlling crustal He degassing episodes. The study reports there is a quantitative relationship between the volume of fault zones and the crustal output of He (Caracausi et al., 2022). Another study by Rice et al. (2022), states the presence of advective fluid flow zones (i.e., faults) can provide pathways for buoyancy driven mass transport. As an aside, within the realm of buoyancy driven bubble ascent microseepage, there are several competing theories that can be applied to He gas migration such as the steady ascent of bubble water in a vertical fracture, isolated bubble ascent in

fracture, bubble ascent without concentration or wall effects, and continuous gas phase flow in fractures (which the author advocates is the most important) (Appendix Section 3.A.5) (Brown, 2000).

Additionally, when examining relative stress fields and $SH_{\max}$ orientations, information as to whether or not mapped faults might be open or closed conduits might be extrapolated. Quantifying whether or not faults are completely sealed/blocked or have experienced patterns of chemical alteration, can be extremely challenging and often quite costly. However, in theory, increased dilation of faults as a function of tectonic and lithostatic pressures as well as fluid pressures can potentially be studied using regional stress fields as a proxy (Lundstern and Zoback, 2020). Following this line of thought, it is reasonable to infer that if fault orientation aligns with current regional stress fields, this could be a proxy for an active He fluxes from the crust via open faults and associated fractures and resulting in a broader and fuller ranges of continuous He anomalies. Moreover, using the relative length of faults and fault displacement as proxies to understand how fault geometry changes over multiple scales (i.e., how it affects the area faults could be influencing) has been put forth by Kim and Sanderson (2005). Therefore, as no fault experiences homogeneous deformation given these are complex geologic systems, it is critical to understand how fault stress (i.e., relative dilation tendency and slip tendency) can be used as a predictor of fault deformation behaviour, which can also elucidate information about He conduit transport versus sealing functionality of faults (Ferrill et al., 2019).

3.6 Conclusion

Heat flow data combined with bulk gas and noble gases geochemistry data gathered from hot springs in and around Yellowstone, USA, were utilized to quantify gas origin and fluid flow in a regional context. We observed from noble gas heat models that the dominant processes controlling most Yellowstone and non-Yellowstone sample's heat and volatile input are convective and degassing processes influenced by episodes of boiling and ASW dilution. Utilizing noble gas solubility fractionation models, we confirm that degassing events (i.e., gas stripping) with minor amounts of redissolution episodes are likely responsible for measured isotopic signatures for ASW derived noble gases. Radiogenic He and Ar signatures from mostly crustal production input along with contributions

from solubility based degassing curves and minor influence from diffusion are also evident. General relationships of ^4He and ^{20}Ne have been reaffirmed and the role that groundwater plays in transporting dissolved ^4He until it is effectively degassed/gas stripped has been highlighted. Insight from a geospatial analysis of heat flow values and the distance to the active Yellowstone caldera shows a 1) relatively narrow range of heat flow values for non-Yellowstone samples, and 2) no significant patterns in regard to heat flow, He% and distance to the Yellowstone caldera. However, in conjunction with previously published data in other parts of the USA, the narrative that He anomalies are present with relatively moderate levels of heat flow persists. Examining the effect of localized heat patterns that are missed by the large-scale heat flow data, 1-D diffusion modelling shows how intrusions can elevate the subsurface temperatures to exceed closure temperatures of minerals bearing He at shallow depths. Migration processes either by diffusion or advection have been highlighted, with advection (via buoyancy driven mass transport) considered a possible dominant force supplemented by diffusion based on the previously mentioned noble gas fractionation models and the neotectonic history of the field area. Lastly, we report that an approach of only using distance from an active volcanic centre is ill-advised for an He exploration strategy to find He sweet zones, and instead exploration strategies should incorporate models focusing on areas with localized moderate heat flow combined with isotopic geochemistry models to constrain groundwater interactions.

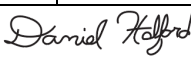
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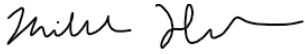
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Contribution to the Paper	I hereby give permission to Daniel T. Halford to use our joint work as contribution towards his DPhil thesis to be submitted for examination at the University of Oxford. I confirm that to the best of my knowledge, the author contribution statement below is accurate and Daniel T. Halford's contribution towards the work is greater than that of any other co-author. Chapter author contribution statement: The project was conceived by DTH, RK, PHB, MB, MH, KL, BM, and CJB. DTH managed the project, and prepared the first draft of the manuscript. DTH, RK, AE, DVB, CJR, AMS, CW, TD, RT, PHB, and CJB collected the samples. DTH, RK, DJH PHB, RT analysed the samples. Noble gas models were developed by DTH, RK, and CJB. Four Corners heat flow data visualization was prepared and made available by MA, BC, MC, and JD. All authors contributed to the final manuscript.	
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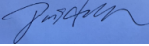
Karolyte, R.  September 28, 2023

Hudak, M.  September 28, 2023

Barry, P.  September 28, 2023;

Bakaert, D.  September 29, 2023

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Chapter 4

Probabilistic determination of the role of faults and intrusions in helium-rich gas fields

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Abstract

Natural gas fields with economic helium (>0.3 He%) require the radioactive decay of crustal uranium (U) and thorium (Th) to generate He and tectonic and structural regimes favourable to releasing and concentrating He. A key unknown of the He system is determining the role of faults and structural features in focusing deep-seated He sources to shallow accumulations. We test the

correlation between high-He wells (n=94) and structural features using a new high-resolution aeromagnetic survey in the Four Corners area, USA. A depth-to-basement map with basement lineaments/faults, an intrusion map, and a flattened basement structural high map, were created using Werner deconvolution algorithms by combining magnetic, gravity, and topography data, with magnetic and gravity depth profiles. We show quantitatively (via ANOVA) that a non-random process controls the relationship between He (>0.3%) and both basement faults and intrusions: 88% of high-He wells occur <1 km of basement faults; and 85% of high-He wells occur <1 km of intrusions. As He % increases, the distance to the structural features decreases. Strong spatial statistical correlations of He wells to both basement faults and intrusions suggest advective transport via faults/intrusions facilitates He migration. The role of gas phase buoyancy and structural trapping is confirmed: 88% of high-He occurs within basement structural highs; and 91% of the remaining wells are <1 km from intrusions (potential local structural high). We present a composite map to illustrate how a probabilistic approach can be used as a predictive model to improve He exploration success by targeting zones of intersection of basement faults and intrusions within basement structural highs.

4.1 Introduction

Helium (He), a natural resource derived from the radioactive decay of subsurface uranium (U) and thorium (Th), is irreplaceable in medical applications, low-carbon technologies, science and engineering, nuclear power, and the aerospace industry (e.g., Boreham et al., 2018; National Research Council, 2010). The Four Corners area, USA, has natural gas with high He (>10%) in some areas (Brennan et al., 2021; Casey, 1983). Originally, He was discovered serendipitously through hydrocarbon exploration, but now He is a primary exploration target (Danabalan et al., 2022). The shift of He to a primary exploration target is crucial to support He's increased global demand and dwindling supply (Olafsdottir and Sverdrup, 2020).

The helium system is defined as any subsurface natural gas system, and its associated geological processes and elements that allows the accumulation of economic levels of He (>0.3% for direct and secondary extraction, >0.04 for LNG operations), in the gas stream beyond the ubiquitous trace amounts found within Earth's mantle, atmosphere, and crustal sources (Boreham et al., 2018; Danabalan et al., 2022; Halford, 2018; Halford et al., 2022). In order to establish a significant He reservoir, there are several major variables that must be considered: 1) source rocks, 2) heating and fluid interactions, 3) migration pathways, 4) seals/traps, and 5) time (Boreham et al., 2018; Cheng et al., 2021, 2023; Danabalan et al., 2022; Halford, 2018; Halford et al., 2022; Karolytè et al., 2022).

In the Four Corners area, He discoveries (n=94) are often near structural features (i.e., Precambrian basement sutures or mapped surface traces of structures) (Craddock et al., 2017; Halford

et al., 2022). Previous work of the observed constancy of $^4\text{He}/\text{N}_2$ in the Four Corners gas fields ratios to argue for fault controlled advective free-gas He migration from the crystalline basement to trap (Halford et al., 2022). While high-He gas has been postulated to be correlated with structural features such as faults and intrusions (Boles et al., 2015; Buttitta et al., 2020; Craddock et al., 2017; Danabalan et al., 2022; Halford et al., 2022; Karolyt  et al., 2022; Mtili et al., 2021; Tardani et al., 2016) the data, until now, to quantifiably test this concept for high-He gas field formation, has not been available. Using newly acquired high-resolution geophysical data (Fig. 4.1) combined with geochemical datasets within the Four Corners area, we test the hypothesis that faults and intrusions are spatially correlated with high He, which may be translated to regions outside of the Four Corners area. By comparing observed He occurrences and synthetic datasets of randomly located points to investigate the spatial relationship to structural features, we find their relative density distributions are statistically different, suggesting a non-random process is controlling their relationship.

4.2 Geologic Background

The Four Corner's area of the USA, which is where the states of Colorado, New Mexico, Utah and Arizona converge, has experienced a complex geologic history pertaining to basement features and igneous activity. The larger Southern Rocky Mountain region, which includes the Four Corners area, records lithospheric assembly during the Paleo-Proterozoic time (1.8-1.6 Ga), intracratonic magmatism during the Meso-Proterozoic (1.44-1.35 Ga), incipient rifting (1.1-0.5 Ga), ancestral Rocky Mountain development during the Paleozoic (350-290 Ma), Laramide tectonism during the Cretaceous-Paleogene (75-45 Ma), and Paleogene-Neogene extension, magmatism, and uplift (Gilfillan et al., 2008; Karlstrom and Humphreys, 1998).

The heterogeneous Paleoproterozoic and Mesoproterozoic crystalline basement underlying the Colorado Plateau contains numerous basement suture zones, which are commonly marked by diffuse fault systems and/or discrete shear zones (Craddock et al., 2017; Davis and Bump, 2009). Shear zones deform various basement lithologies and are rooted in deep-seated zones of weakness (Davis and Bump, 2009; Whitmeyer and Karlstrom, 2007). Master shear zones are rooted in the deep seated zones of weakness within the basement and most are presumably originating along reactivated

deep-seated Neoproterozoic shear zones (Davis and Bump, 2009; Whitmeyer and Karlstrom, 2007). Thus, suture zones and shear zones represent deformational boundaries of the underlying Paleoproterozoic basement provinces in the area (Mojave, Yavapai and Mazatzal) (Karlstrom and Humphreys, 1998).

The field area within the Four Corners region consists of intrusive plutons, and Paleogene-Neogene mafic and ultra-mafic diatremes and lamprophyres that were emplaced along crustal extension zones (e.g., old and deep structural weak basement zones) (Gonzales and Lake, 2017; Re et al., 2015). Dikes and sills related to these diatremes and intrusive bodies intersect and crosscut the sedimentary section (Danie, 1978; Masters, 2000). More specifically, the Navajo Volcanic Field (NVF), which is the result of slab rollback of the Farallon plate (Gonzales and Lake, 2017; Hernández-Uribe and Palin, 2019), exists within the study area and consists of >80 mafic and ultra-mafic diatremes of Oligocene to Miocene age (28-19 Ma) and hundreds of intrusive plutons (Bélanger and Ross, 2018; Semken, 2003). Despite the volcanos of the NVF not being located along exposed faults, the magma ascent was likely aided by fractures at depth (Delaney, 1987).

4.3 Methodology

4.3.1. Aeromagnetic Geophysical Data Collection

The geophysical data was acquired by Earthfield Technology on behalf of the Navajo Nation Oil and Gas Company in 2021 using an airborne magnetometer, which measures and records the total magnetic field. By flying a Cessna C-180 aircraft at 152 m with a fitted tail-stinger which housed a Geometrics G823A Cesium-vapour Magnetometer System, 20,761-line km of high-resolution aeromagnetic data were collected. Flight lines and tie lines were spaced 400 m and 1,600 m, respectively. Ancillary airborne equipment and a ground-based magnetometer were also utilized.

4.3.2. Geophysical Pre-Processing

Quality control checks were completed prior to the profile data processing and levelling procedures by Earthfield Technology. Pre-processing procedures include the following listed below.

1.) Data Merging - Data traces (digital magnetic and ancillary) were recovered. The final position data from GPS time and related fiducial time marks (0.1 second intervals) were then merged with digital magnetic and ancillary data traces. Subsequently, a line location file and system log or lead time was produced from the conversion of the merged data.

2.) Data Editing – Merged data traces (i.e., the base magnetometer trace) were edited both for completeness and data spikes. The edited and merged data traces were then processed with profile-orientated data corrections.

3.) The International Geomagnetic Reference Field (IGRF) Correction – The magnetic data trace was processed with the IGRF correction.

4.) Diurnal Correction – The IGRF-corrected magnetic profile data was then processed with the IGRF-corrected diurnal data as a correction.

5.) Profile Levelling – An analysis of the network of line crossings was the first stage of levelling undertaken. To ensure that the sum of the square of the mis-tie errors in the network is minimized, the individual survey network lines were systematically shifted down or up. Further constraints were enacted on the systematic corrections to ensure that the sum of the systematic corrections was zero, which can eliminate DC shifts to the network. Virtual Network Analysis (VNA) was used in the micro-levelling process. The VNA is essentially a recursive process where a grid that has been based on the adjusted and edited data forms the starting point. Unadjusted and unedited data were readjusted and reconsidered in the procedure. Ultimately, the recovery of short-wavelength and map-coherent components in the data was made possible with VNA.

4.3.3. Geophysical Data Processing

A brief explanation of the raw geophysical data used to create the three different types of maps is presented below, divided by type: 1) topographic, 2) gravity and 3) magnetic.

1.) A Shuttle Radar Topography Mission (SRTM) 30 meter digital topography dataset was utilized to define potential shallow fracture zones in the survey area (NASA JPL, 2013).

2.) Gravity maps, from Earthfield's proprietary North American Gravity Compilation, were used to define density boundaries to illustrate sedimentary structures and fault zones at the basement

surface. Bouguer gravity maps processed with a 50, 25, and 25 thousand-feet (kft) wavelength high pass filters were used in enhancing subtle anomalies from shallower sources by removing long wavelength anomalies from sources at depth. A tilt derivation of the gravity data was compiled to enhance lithologic changes and/or fault zones (lateral boundaries anomalies). The tilt derivation and high pass filtered maps were used to define basement faults and trends using Werner deconvolution (Werner, 1953).

3.) High-resolution magnetic survey data was used to construct a total magnetic intensity map. Also, a Reduction-to-the-Pole (RTP) map was constructed from the total magnetic intensity map, which shifts magnetic anomalies directly over causative bodies by eliminating the Earth's magnetic inclination/declination effects. Various high pass filters were then applied to the RTP data at 25, 10, 6, and 3 kilo-feet (kft) wavelength, which enhances subtle anomalies from shallower sources by removing long wavelength anomalies from sources at depth. Additionally, using similar techniques to enhance magnetic anomalies from subtle sources, a RTP analytic signal map was created from the high-resolution magnetic RTP data to better identify shallower intrusive bodies. A tilt derivation of the magnetic data was compiled to enhance lithologic changes and/or fault zones (lateral boundary anomalies). The tilt derivation and high pass filtered maps were useful to define basement faults and trends using Werner deconvolution.

4.3.4. Geophysical Mapping Methods

The creation of the depth-to-basement with 1) basement lineaments, 2) igneous bodies, and 3) the structural high maps by Earthfield Technology LLC is described. Supplementary processing information related to Werner Deconvolution depth-to-source generation is in Appendix 4. In addition to the newly acquired high-resolution magnetic data, gravity data, topography data, and magnetic and gravity depth profiles were incorporated into the depth-to-basement mapping.

1.) Basement lineaments were generated during the depth-to-basement mapping using Werner Deconvolution analysis of the gravity and magnetic data. In areas where gradients in the gravity and magnetic data have been identified, basement faults were mapped. Tilt derivative Bouguer gravity data and high-pass filtered (50 kft and 25 kft) Bouguer gravity data along with tilt derivative RTP

magnetic data, and high-pass filtered (25 kft, 10 kft, 6 kft, and 3 kft) RTP magnetic data were used to qualitatively aid in the definition of basement faults and trends originally calculated using Werner deconvolution.

2.) The interpreted intrusive bodies and dikes map was produced from various filters and derivative maps of the magnetic data, and by using Werner Deconvolution depth estimation profiles. Shallow intrusive bodies were identified using a RTP analytic signal map, which enhances shallow magnetic anomalies at the expense of longer wavelength magnetic anomalies (deeper sources). The new smaller grid spacing allowed delineation of more discrete igneous bodies compared to regional magnetic data.

3.) First using Werner Deconvolution depth analysis, the depth-to-basement map was created. This map was subsequently used to create a residual basement map. More specifically, the residual flattened basement map was created via frequency filtering to remove regional dip for the purposes of isolating the local basement high features, and enhancing subtle basement structures. Subsequently, we windowed local high areas at the steepest gradients in that flattened surface to only keep the local highs. Since this residual basement was created using a high pass filter of the original depth-to-basement surface, the units are arbitrary.

4.3.5. Probability Density Mapping

Statistical tests were used to determine whether the spatial relationship between basement faults and intrusions, to observed economic He gas ($>0.3\%$) ($n=138$) (Brennan et al., 2021; Halford et al., 2022), is significant. Several of the 138 economic He producing wells have multiple He measured values at the same well location. To mitigate data duplication causing confirmation bias, we condensed the original 138 entries into 94 by averaging He values at the same location and within the same formation/substage. To determine whether the distribution of economic He wells ($n=94$) and structural features (basement faults/intrusions) are spatially correlated, five synthetic grids of randomly generated points ($n=94$) were created in the study area. Distances to structural features were calculated for each of the synthetic and observed (He-rich gas) data grids. One-way analysis of

variance (ANOVA) tests were conducted on the observed and synthetic data grid distances to He occurrences (McKillup and Dyar, 2010) (further discussed in Methods 3.6 and Appendix 1).

Probability density maps, which represent the relative probability of He occurrences in relation to a structural feature, were created based on the horizontal distance from observed economic He wells to basement lineaments/faults, and intrusions. To create the maps, the distance from all wells containing economic He to the nearest structure was determined. Igneous body locations were calculated from an intermediate depth to produce a simple polygon footprint, when in reality an igneous body can be complex (i.e., interleaved contact zone). Similarly, faults are seldom single linear features and often complex fracture zone systems. To represent these complexities, half-normal distributions were chosen to resemble geologic conditions. When examining the possibility that the relationship between the observed economic data and the synthetic data has arisen from chance or not, we observed the synthetic data broadly fits a half normal distribution. Thus, in order to compare the synthetic data to the observed economic data, we also utilized a half normal distribution approach when constructing our probability density models with the observed economic data. Thus, a normalized histogram of the distances with a half-normal distribution fit for faults and intrusions was then constructed.

A blank grid of 20,000 equally spaced points was created for the study area. The distance from each of the grid points to the different structural features (e.g. fault or intrusion) was determined. Using a Gaussian equation fit to the half normal curve generated for the observed data, we inputted the distance to the structural features as the X variable value, and we calculated the Y variable (relative probability), which is a value from 0 to 1. Points were then assigned a 0-1 probability value and contour maps with an inverse distance weighted (IDW) interpolation were created.

4.3.6. Statistical Tests

Pearson's and Kendall's correlations were used to determine the first order relationship concerning the distances between (n=94) economic He wells (>0.3 He %) and basement faults and igneous intrusions (Kendall, 1938; McKillup and Dyar, 2010). The Pearson correlation coefficient (r) examines the extent that two variables are linearly related (McKillup and Dyar, 2010). General

assumptions of Pearson's correlation are that the data is generally normally distributed, a linear relationship is present, variables should be continuous, and there should be no significant outliers (McKillup and Dyar, 2010). Kendall's (τ) correlation is a non-parametric measure of the correlation between ranked data that operates under the assumptions of a monotonic relationship and continuous scale or ordinal scale data (Kendal, 1938). The coefficients and their respective p-values comparing economic He and basement faults are: $r = -0.41 \mid p < .001$; and $\tau = -0.19 \mid p < .006$. The coefficients and their respective p-values comparing economic He and igneous bodies are: $r = -0.53 \mid p < .001$; and $\tau = -0.34 \mid p < .001$.

The generalized linear model (GLM), which is a type of general class of linear model for independent data, is made up of three components, random, systematic, and a link function (McCullagh and Nelder, 1989). Regarding the residuals, the GLM allows distributions from the exponential family to be permissible (McCullagh and Nelder, 1989). Regarding the relationship between the response and explanatory variables, a linear relationship is required via the link function (McCullagh and Nelder, 1989). Utilizing a Gaussian family distribution and an identity link function, a GLM with the dependent variable as He % and covariates as distance to faults and distance to intrusions, showed that basement faults ($p < .001$) and igneous bodies ($p < .001$) were statistically significant predictor variables concerning He % (Table 4.A.1).

A one-way Analysis of Variance (ANOVA) tests for significant differences between multiple independent groups. Although the ANOVA test relies on assumptions of independence, normality, and similar variance, it is nonetheless robust with respect to violations of its normality and variance assumptions especially with larger sample sizes and equal sample sizes (Blanca et al., 2017; Glass et al. 1972; Harwell et al. 1992). The initial hypothesis of the test states that the means are always equal according to the null hypothesis and at least one mean is different according to the alternative hypothesis. Essentially, the ANOVA test examines between group and within group variation to calculate the F statistic. The calculated F statistic is compared to a critical F statistic. When the calculated F statistic is greater than the critical value (critical F statistic) the null hypothesis is rejected (the sample populations are different, i.e., they do not have the same mean), and the alternative hypotheses adopted (McKillup and Dyar, 2010).

The synthetic dataset represents randomly distributed pseudo-wells, while the observed data points are observed economic He wells. To keep sample sizes similar to the economic data ($n=94$), 94 locations were randomly selected from each of the synthetic grids. The ANOVA single factor statistical tests were conducted to check for any significant variations when comparing the synthetic grids ($n = 94$) and no significant differences were found (Tables 4.A.2 and 4.A.5). Additionally, ANOVA tests were conducted with the five synthetic grids and the economic data sets. This second ANOVA test showed there was a significant difference present in the economic and synthetic data sets for both faults and intrusions ($F \text{ statistic} > F \text{ critical value}$; $p < .001$). A Games-Howell post-hoc test, which is a non-parametric approach that does not rely on homogeneity of variances, was used to examine combinations of group differences (McKillup and Dyar, 2010; Ruxton and Beauchamp, 2008). Comparing the economic data to the synthetic data for both faults and intrusions produced a Games-Howell post-hoc test p value of $< .001$, which can be interpreted as the economic He data was significantly different from the synthetic data and thus the economic He data was not randomly distributed (Tables 4.A.3, 4.A.4, 4.A.6 and 4.A.7). Despite heteroscedasticity (non-homogenous variances) in our datasets reducing the statistical power of the one way ANOVA test, the ANOVA tests still produced a significant effect, thus we were not concerned about heterogeneity of variance skewing our results.

4.4 Results

4.4.1 Spatial correlations between structural features and high-He occurrences

Statistically significant relationships between high-He fields and structural features (basement faults, igneous intrusions, and basement structural highs) are observed in coupled high-resolution geophysical and geochemical datasets (Fig. 4.1). These correlations were not observed utilizing proprietary interpretations of low-resolution geophysical data.

Within the Four Corners area, all economic He observations occur within 0 to ~ 2.5 km and ~ 4.5 km of faults and intrusions, respectively. In contrast, synthetically generated data points occur within 0 to 6 km of these features (Fig. 4.2, 4.3). Figs. 4.2 and 4.3 were constructed to test the assumption that the geospatial distributions of basement faults and intrusions are the dominant

contributors to economic (<0.3 He %) He plays. Histograms (Fig. 4.2B and 4.3B) illustrate the striking inverse relationship between wells with observed economic He gas values and the lateral distance from He wells to basement faults and intrusions. As He molar % increases, the distance to the structural feature decreases, indicating higher He concentration is correlated with shorter distances to basement faults and intrusions.

Examining distances to structural features, the data of the economic He wells shows that 88% are <1 km from basement faults, and 85% of economic He wells (>0.3 He %) are <1 km from intrusions (Figs. 4.2B and 4.3B). The observed economic He wells are left skewed with most data points restricted to <1 km from both faults and intrusions, while the synthetic data are evenly distributed (Fig. 4.2C, 4.3C). ANOVA F statistics (F - faults 7.11, $p < .001$; F - intrusions 17.48, $p < .001$) > F critical values (2.23 for both) and post-hoc tests (Appendix 1) show the spatial relationships between economic He and faults and intrusions are not controlled by random processes (Appendix Tables 4.A.2-4.A.7). Thus, by comparing observed and synthetic datasets we find their relative density distributions are statistically different suggesting a non-random process is controlling their relationship.

We found no observed correlation between high-He occurrence and other structural features, including basement depth, dike cluster locations, reservoir depth compared to basement depth, position on structural basement structure, distance to basement structural highs, and sealing intervals. Additionally, it was not possible to test any intrusion depth correlation with He occurrence due to low data density. A topological analysis was completed to examine the relationship between He occurrence and fault connectivity/geometry, however we found that He is not strongly correlated with fault connectivity compared to basement faults shown in Fig 4.1. (Appendix 4.A.2).

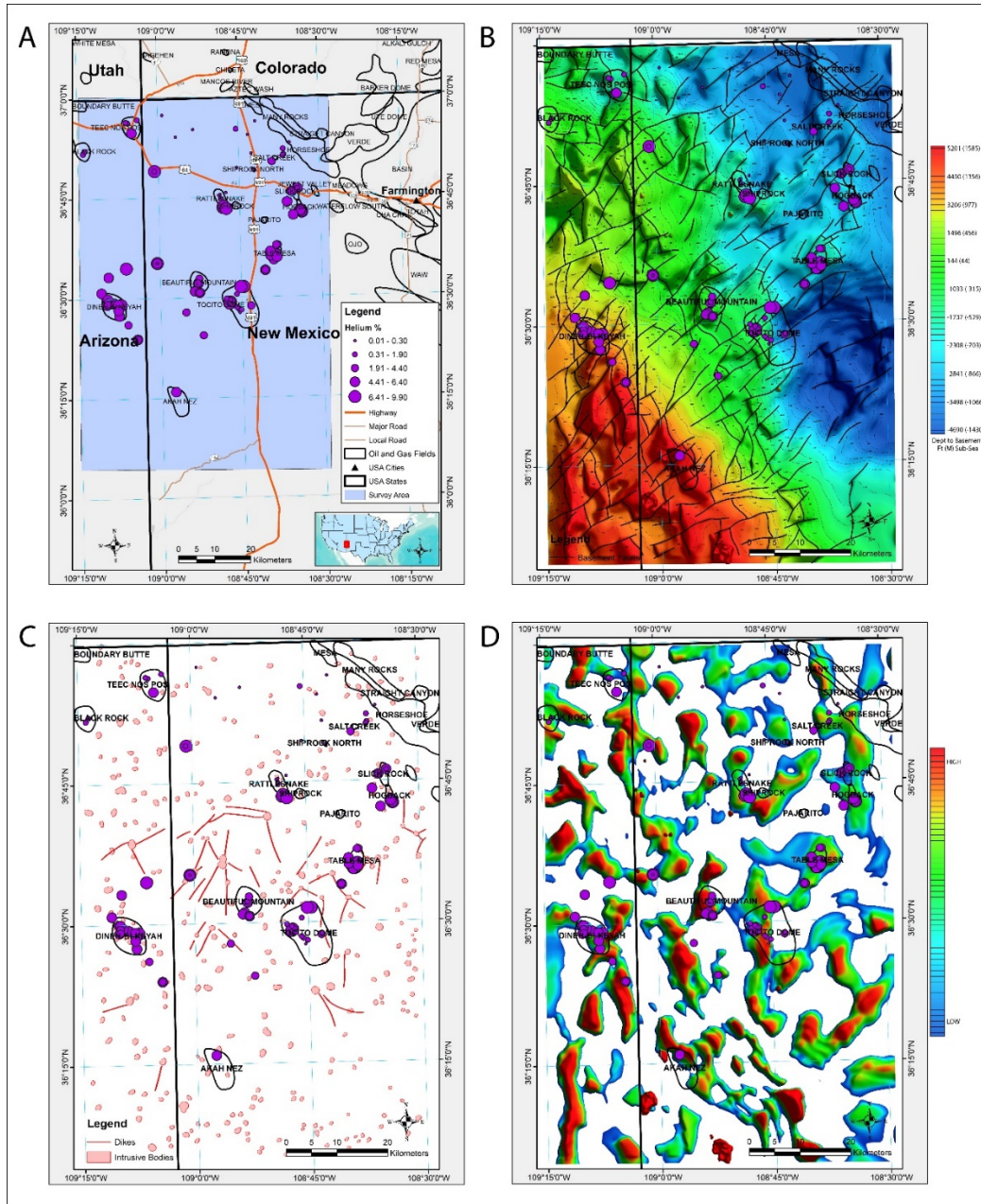


Figure 4.1: A) Location map with the study area (blue rectangle). Maps calculated from the high-resolution geophysical data: B) Depth-to-basement map with interpreted basement faults/lineaments as black lines, C) intrusions (red polygons) and dikes (red lines) map, D) localized basement structure map from flattened depth-to-basement map illustrates structural highs with an arbitrary scale from red (high) to blue (low). He molar % is overlain on all maps as purple circles (Brennan et al., 2021; Halford et al., 2022).

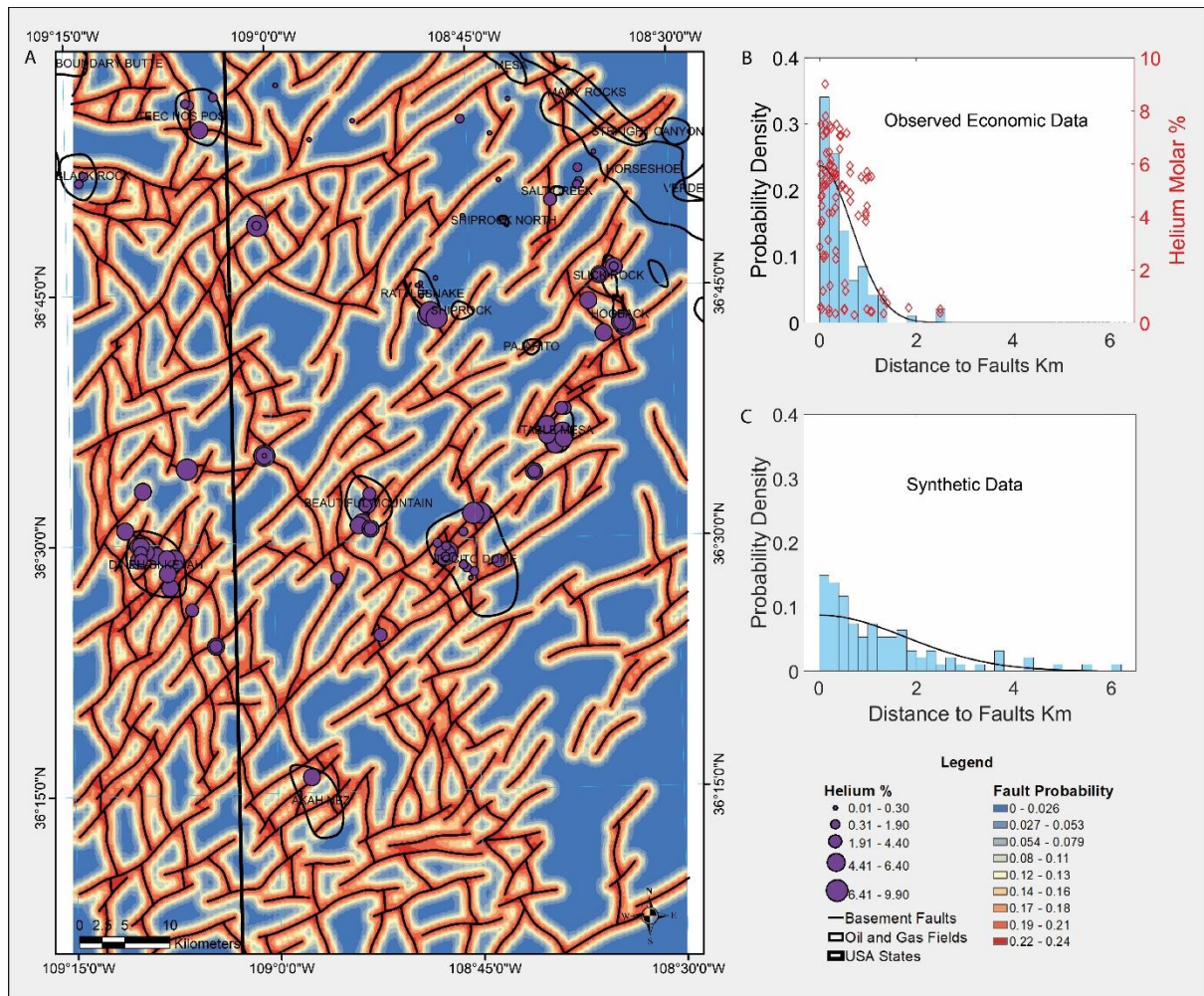


Figure 4.2: A) Probability density map for He occurrence with basement faults. B) Histogram with a half normal distribution (black curve) showing distances from basement faults to economic He wells (n=94). Economic He data (n=94) is overlain (red diamonds). C) Synthetic grid data, which is shown with a half normal distribution (black curve), has a statistically different distribution (F value 7.11 > F critical value 2.23 in Appendix 1) when compared to the economic data (B) shows a non-random process controlling the relationship between He and faults.

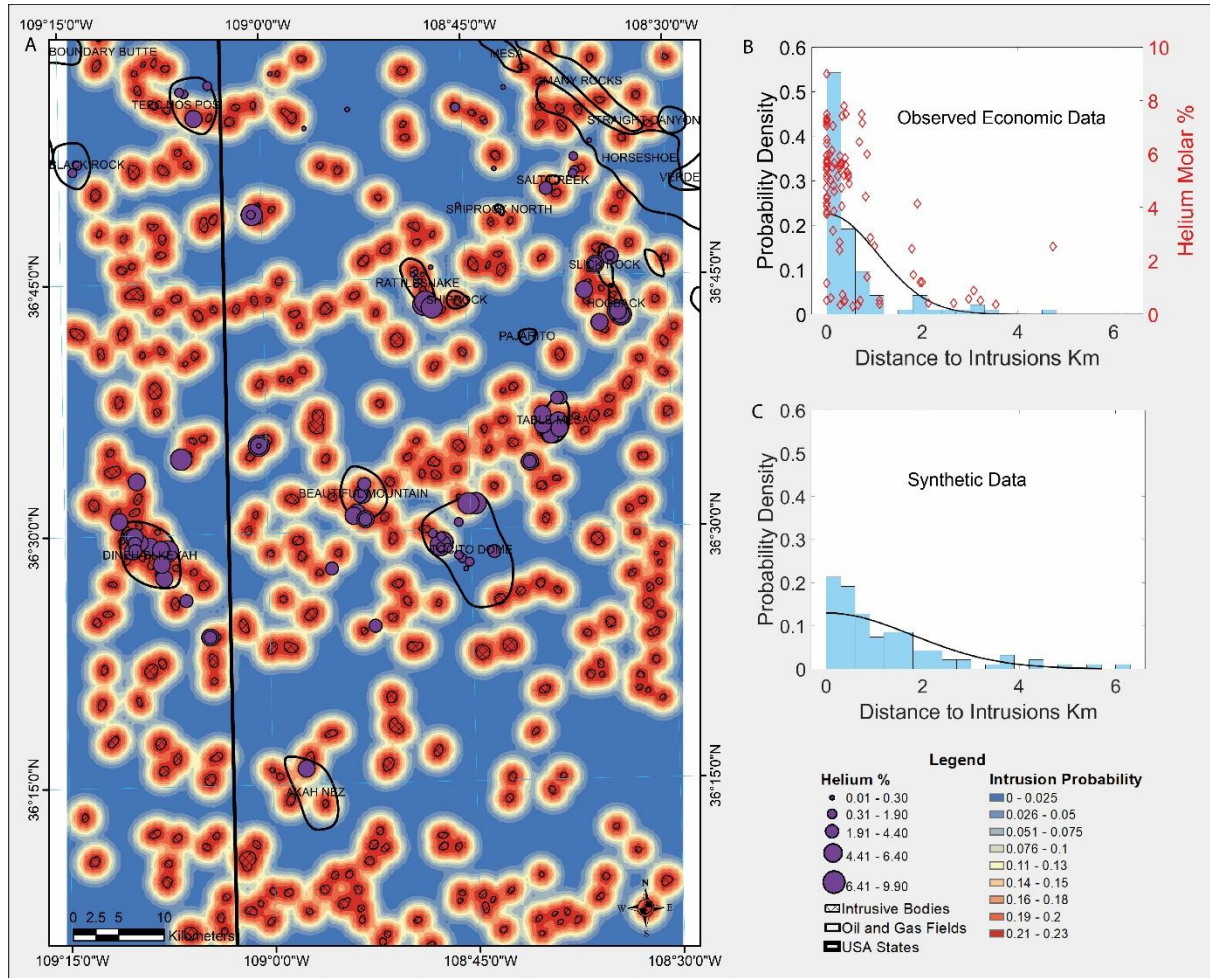


Figure 4.3: A) Probability density map for He occurrence with intrusions. B) Histogram with a half normal distribution (black curve) showing distances from intrusions to economic He wells (n=94). Economic He data (n=94) is overlain (red diamonds). C) Synthetic grid data, which is shown with a half normal distribution (black curve), has a statistically different distribution (F value 17.48 > F critical value 2.23 in Appendix 1) when compared with the economic data (B) shows a non-random process controlling the relationship between He and intrusions.

To summarize, using a spatial and statistical analysis of He occurrence with faults and intrusions from high-resolution geophysics, our results demonstrate that a non-random process indeed controls the relationship between He and faults and intrusions. Additionally, there is a strong relationship between He and faults/intrusions that can be quantified and utilized for He exploration as a primary target.

4.5 Discussion

4.5.1 He-System Processes Related to Faults and Intrusions

Migration of He from its source to the surface is likely enhanced by a thermal perturbation (i.e., geothermal setting) of the crust (Cheng et al., 2021, 2023; Danabalan et al., 2022; Lowenstern et al., 2014; Torgersen, 2010). This has an effect on multiple scales. An increase in thermal gradient will enhance He release from minerals by exceeding the closure temperature, and promote the release of related gases such as nitrogen (N_2) by low-grade metamorphism (e.g. Ballentine and Sherwood Lollar, 2002). Interconnected fractures and pore space, perhaps enhanced by the He and N_2 -rich fluid pressure exceeding lithostatic confining pressure, promotes advective movement of He from the source rock (Danabalan et al., 2022; Warr et al., 2018). Zones of enhanced porosity and permeability such as faults, reasonably act to focus the fluids released. Basement faults act as migration conduits, allowing the He and nitrogen-rich fluids to migrate updip, driven by gas buoyancy or pressure differentials (Danabalan et al., 2022; Halford et al., 2022). Whether the deep-seated basement faults propagate all the way to the reservoir is unknown, but due to their interpreted dimensions at depth, their presence remains critical. Thus, basement faults are interpreted to be the controlling agent aiding in primary migration (i.e., He advective transport) from the source rock into the overlying sedimentary column as well as in secondary migration (Danabalan et al., 2022; Halford et al., 2022).

In principle, intrusions may provide local heating and some He release from minerals. Intrusions will also enhance any fracture network by increasing hydrothermal fluid and magma pressures, likely following pre-existing zones of weaknesses as well as providing supplemental shallow radial and concentric fracturing (Gonzales and Lake, 2017; Halford, 2018; Koide and Bhattacharji, 1975; Re et al., 2015). Like faults, intrusions then also provide a focus for He and N_2 -rich fluid collection at depth in the crust and a transport pathway to the near surface (Ballentine et al., 2002; Broadhead and Gillard, 2004; Halford, 2018). Similarly, whether the intrusion invades the reservoir or breaches the basement is yet to be determined based on the inherent challenges (i.e., processing costs, different igneous body geometries, different mineral compositions, etc.) of calculating exact intrusion depth. Since most He occurrences lie <1 km of an intrusion, we interpret this as evidence to support a strong component of primary and secondary vertical migration

(depending on how far the intrusion invades) coupled with a weak component of lateral secondary migration (Halford et al., 2022).

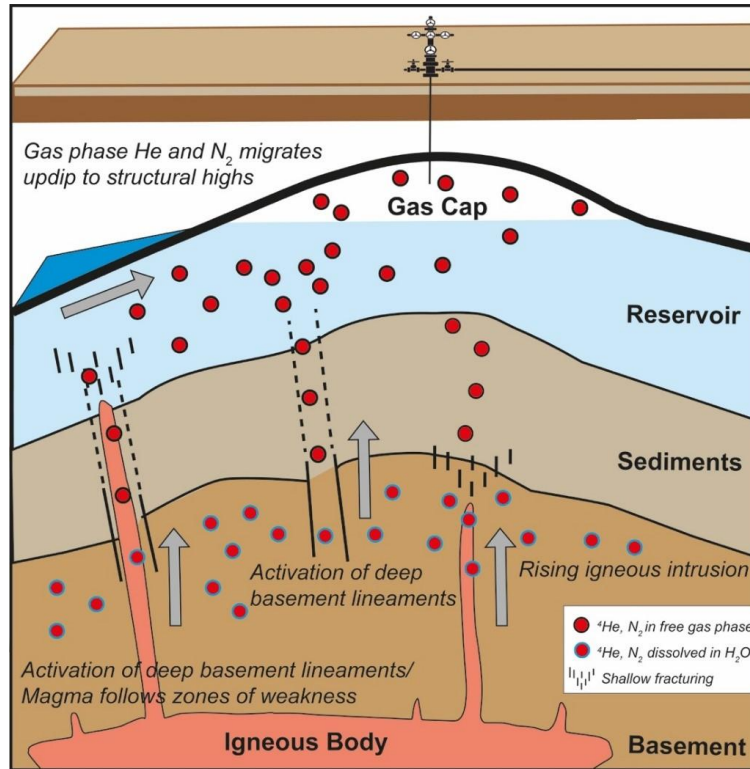


Figure 4.4: Schematic illustrating the conceptual model showing the activation of deep basement lineaments/faults, and continued igneous activity which equates to an increased supplemental shallow fracturing followed by He migration upwards along the zones of weakness, and He migration updip to structural highs. Regarding shallow fracturing, when hydrothermal fluid and magma pressures are lower (but higher than lithostatic stress), there is the formation of predominant radial fractures. Additionally, when there is an increase in hydrothermal fluid and magma pressures, we predict an increase in peripheral radial fractures and concentric fracture patterns (not shown) surrounding intrusions (mod. from Halford et al., 2022; Koide and Bhattacharji, 1975; Van Zalinge et al., 2022).

In summary, to update the role of faults and intrusions in relation to He's migration and trapping, a schematic is presented that describes how basement faults and igneous intrusions or a combination of both can act as migration/focusing conduits (Fig. 4.4). Intrusions can also provide local heating to release He from minerals, as well as providing supplemental fracturing which likely enhances fluid flow. Thus, the strong spatial statistical correlation of He wells to both basement faults and intrusions suggests advective transport via faults/intrusions facilitates He flow/transport (primary and secondary migration) of basement derived He into the overlying sediments where the He can accumulate over time (Fig. 4.4).

4.5.2 Combined Predictive Probability Mapping for Helium Occurrence

The close proximity of economic He wells and structural features is reflected in the relative probability density maps, which show areas of higher probabilities (coloured as red intervals) of encountering economic subsurface He based on basement fault and intrusion data (Fig. 4.2 and 4.3). Figs. 4.2 and 4.3 show both faults and intrusions correlate with high-He, and to a similar magnitude. We created a composite map to consider the combined relative probabilities of both faults and intrusions (Fig. 4.5). Because there is no a-priori reason to differentially weight these features, we use the multiplication rule with faults and intrusions equally weighted as independent variables. The composite map, with an IDW interpolation and normalized to 1, illustrates low (blue) to high (red) areas of inferred probability of high-He occurrences (Fig. 4.5).

Of all the identified economic He wells, 88% lie within the structural high zones (Fig. 4.1D), with 91% of the remaining He points plotting near (<1 km) igneous bodies, which are likely creating subsurface domes as the igneous body moves through the subsurface enhancing structural trapping. Local structural maps, which highlight the strong relationship of He to relative structural highs, are presented in Appendix 3 for the He-rich Dineh-Bi-Keyah, Tocito Dome and Teec Nos Pos fields (Figs. A.2- A.6). While structural highs are an essential component of the trapping mechanism, we do not consider them a feature that enhances He migration via transport from the crystalline basement. Therefore, to visualize where the He (focused via faults and intrusions) could be trapped, we overlay the structural high boundaries (Methods 4.3.4) onto the composite map (Fig. 4.5) rather than include the structural highs within the combined He occurrence probability.

The highest likelihood of an economic He accumulation is where the combined probability of the influence of basement faults and intrusions is closest to 1 (the intersections of the red coloured intervals), providing proximity to both of the pathways that would appear to promote He transport to the near surface. The presented combined probability map (Fig. 4.5) treats faults and intrusions as independent events, however, there is a natural propensity of both to exploit zones of crustal weakness. Both faults and intrusions play a part in He release, mobilization, and transport, and some of the effects may be overlapping – and are provided an equal weighting.

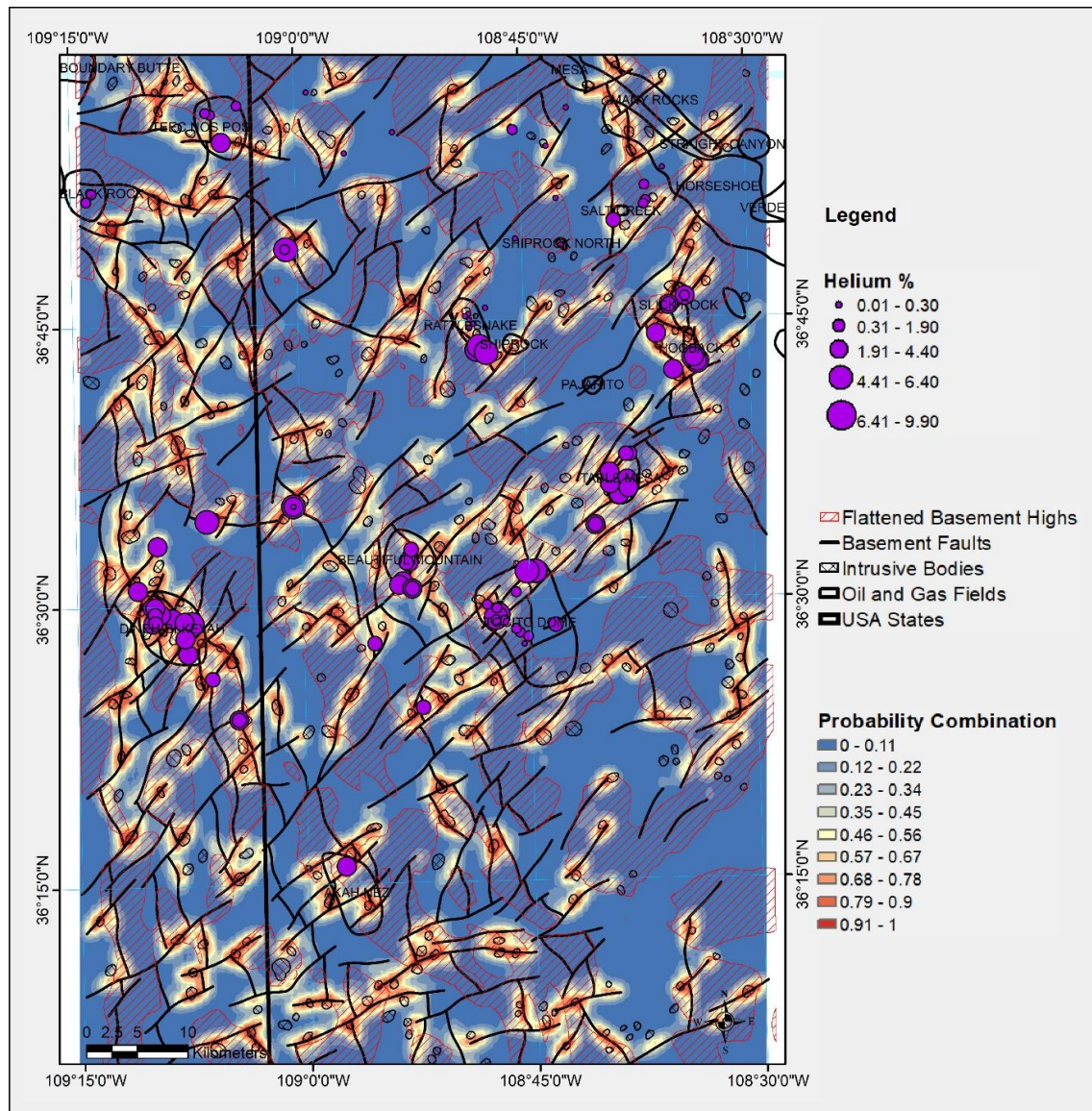


Figure 4.5: Composite probability map combining the basement fault and the intrusion He occurrence probabilities along with an outline of localized basement structural highs. The predictive exploration model shows the intersection of faults/intrusions (He transport mechanism) and basement highs (He trapping mechanism) are the zones of interest.

To summarize, by constructing a probabilistic relationship as a function of distance from basement faults and intrusions, we have developed a predictive model for high-He gas field occurrence. The probability analysis highlights the importance of targeting zones with the intersection of basement faults and intrusions, as well as provides confirmation of the role of gas phase buoyancy and structural trapping. In regards to He exploration, the predictive exploration model can be translated to other areas to generate He prospects, especially near regional/local thermal perturbations and active tectonics.

4.6 Conclusion

The importance of dominant structural mechanisms such as basement faults and intrusions in the transport of He from a deep crustal source to reservoir has been speculated before (Danabalan, et al., 2022; Halford et al., 2022; Karolyte et al., 2022), together with circumstantial evidence of basement fault control (Boles et al., 2015; Buttitta et al., 2020; Craddock et al., 2017; Mtili et al., 2021; Tardani et al., 2016). Using a spatial analysis of He occurrence with faults and intrusions from high-resolution geophysics we show that a non-random process indeed controls the relationship between He and faults and intrusions and, further, there is a strong relationship between He and faults/intrusions that can be quantified and utilized. By constructing a probabilistic relationship as a function of distance from these features, we have developed a predictive model. The probability analysis highlights the importance of targeting zones with the intersection of basement faults and intrusions. The significance of this study is threefold. It 1) provides a quantitative spatial analysis of basement faults and intrusions for He exploration, and 2) presents the predictive exploration model that can be translated to other areas to generate He prospects, especially near regional/local thermal perturbations and active tectonics, and 3) updates geologic elements and processes of the He-system (migration and structural trapping of He).

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Contribution to the Paper	I hereby give permission to Daniel T. Halford to use our joint work as contribution towards his DPhil thesis to be submitted for examination at the University of Oxford. I confirm that to the best of my knowledge, the author contribution statement below is accurate and Daniel T. Halford's contribution towards the work is greater than that of any other co-author. Chapter author contribution statement: The project was conceived by DTH, RK, MWA, JJC, JTB, KJWM, JGG and CJB. DTH managed the project, and prepared the first draft of the manuscript. BC and MC collected and processed the geophysical data. Geophysical data visualizations were produced and made available by BC, MC, JCC, and JD. Structural maps were constructed by DTH, JJC, and SS. Probabilistic geospatial and statistical models were developed by DTH, RK, AC, and CJB. All authors contributed to the final manuscript.		
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Chapter 5

Applications in Utilizing Soil Gas Geochemistry to Calibrate Helium Exploration Models on the Four Corners Platform, USA

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Abstract

A key unknown of helium (He) systems is if surface soil surveys can be an effective exploration tool for He when combined with other datasets. Here we present the results of seven new soil gas He gas surveys (n=1974) at the Akah Nez Field, Beautiful Mountain Field, Porcupine Dome area, Rattlesnake Field, Tom area, Tohache Wash area, and White Rock area, on the Colorado Plateau, Four Corners area, USA. Utilizing 2D seismic, well logs, and geophysical potential field data

we construct structural maps of potential He reservoirs at depth and examine relationships. Given we are examining geospatial relationships using the soil gas survey data, it is important to understand the mechanism that allows subsurface He to migrate upwards into the soil. We find that in several fields (Rattlesnake, Beautiful Mountain, Porcupine Dome, and Tom) interpreted basement faults act as migration conduits from the basement to the surface (i.e., leaky reservoir seals), and in other cases there is evidence for reservoir flank/crest fracturing likely due to differential compaction (Tohache Wash, Beautiful Mountain, Porcupine, Tom, Akah, and White Rock). Using internal and external He production rates and original gas in place calculated volumes, we calculate approximate ages of reservoirs and realize the average age of 30 mya corresponds to a known age of tectonic/igneous activity on the Colorado Plateau. Using a 1-D diffusion loss model, we calculate the amount of He dissolved in water that is lost through diffusion only and conclude it that for the Tohache Wash, Akah Nez, and Tom fields, diffusion appears to play a more dominant role. We propose diffusion loss systems are most ideal for preserving He (based on the rate of loss) once an accumulation has already formed. Additionally, based on the Tohache Wash data (most prospective He area) we present an effective and risk-reducing novel technique to calibrate a predictive He exploration model utilizing soil gas geochemistry, high-resolution geophysical data, well data and seismic data) using Bayesian regression techniques, which may be translated to areas outside of the Four Corners Area, USA.

5.1 Introduction

The utility of soil gas geochemistry as an exploration tool to distinguish geochemical anomalies is a cost-effective and relatively rapid method to search for surficial natural gas seepages, quantify lateral extent of anomalies and obtain clues about potential subsurface accumulations (Rice, 2022). Given soil gas sampling's extremely cheap overall cost, it can be employed on a larger scale and cover wide swathes of land. Despite the inability to differentiate isotopes compared to more advanced isotope geochemical analysis (which can be useful in determining information about sourcing, mixing and migration of subsurface fluids, Ballentine et al., 2002; Macintosh and Ballentine, 2012), the utility of soil gas geochemistry is more focused on geospatially marking the boundaries of gas anomalies (areas with signatures above background) and quantifying the lateral extent of a subsurface reservoir.

There are numerous models describing the migration pathways of He from its predominately basement source rock upwards into overlying sediments (Halford et al., 2022, 2023; Boreham et al., 2018; Buttitta et al., 2020; Cheng et al., 2021, 2023; Karolyte et al., 2020), but none focus specifically on the mechanism that can explain mass transport of He from a reservoir to the surface given realistic geologic timelines for a tectonically active area. This is important because understanding the mechanism can allow a deeper understanding on the migration and trapping mechanisms of He-systems. Therefore, understanding the migration of He from subsurface reservoirs to the surface can

aid in the refinement of pre-existing exploration models and the creation of new approaches to obtain information about reservoirs without costly drilling (Rice, 2022). In this study we test the hypothesis that He soil gas geochemistry surveys can be a cost-effective asset when combined with subsurface geophysical and geology parameters to define/de-risk He-rich regions (i.e., test overall He reservoir potential), which may be translated to other areas beyond the immediate area of the soil gas data.

5.2 Geologic Background and Production History

The field area (i.e., Four Corner's area) is located on the Colorado Plateau, USA and despite the plateau's relative stability throughout geologic history, it has experienced its fair share of neotectonism associated with the subduction of the Farallon plate and the subsequent Laramide orogeny (Davis and Bump, 2009). These tectonic episodes have produced structural features such as folds, faults, shear zones, and monoclines along with igneous zones in and around the plateau (Craddock et al., 2017; Gonzales and Lake, 2017; Re, 2017). Generalized San Juan structural province stratigraphy is shown in the appendix Fig. 5.1A. Working from north to south, we further describe the geology of the areas of interest below.

The Tohache Wash area, which has He % up to 6%, is located in north-eastern Arizona on the southwest edge of the Four Corners Platform (Spencer, 1978) (Fig. 5.1). Its discovery well, which was drilled and completed in 1967, was originally completed in the Devonian, Aneth Formation (oil) and later recompleted in the Mississippian Leadville Limestone where it encountered non-flammable gas. The well produced 1.09×10^7 m³ of gas over 1.5 years and was recently re-entered in 2015 which resulted in 7% He at 238 atm (2.412×10^7 Pa) of pressure. The reservoir rocks are generally uniform with the Aneth consisting of 12 meters (gross thickness) of dolomites and the Leadville consisting of 67 meters of dolomite and limestone (gross thickness). The porosity of the Aneth ranges from 4-6% (matrix), while the Leadville limestone porosity ranges from 5-9%. Structural closure dominates the reservoirs (Spencer, 1978).

The Rattlesnake Field, which had He up to ~7%, is located in north-western New Mexico on the Four Corners Platform (Baars, 1983) (Fig. 5.1). Its discovery well for He was found in 1942 (total depth 2144 m) and produced non-flammable gas from the Mississippian Leadville Limestone-

Devonian Ouray dolomites. Water production overtook the He-producing wells less than 2 years after production, and thus final production was only 2.8E7 to 5.7E7 m³ of gross gas. The reservoir rocks (gross thickness of 26 m) are porous limestone and dolomite consisting of blanket deposits. The porosity is estimated to range from <3% to 13%. Structural closure (northwest–southeast trending anticline) dominates the reservoir (Baars, 1983).

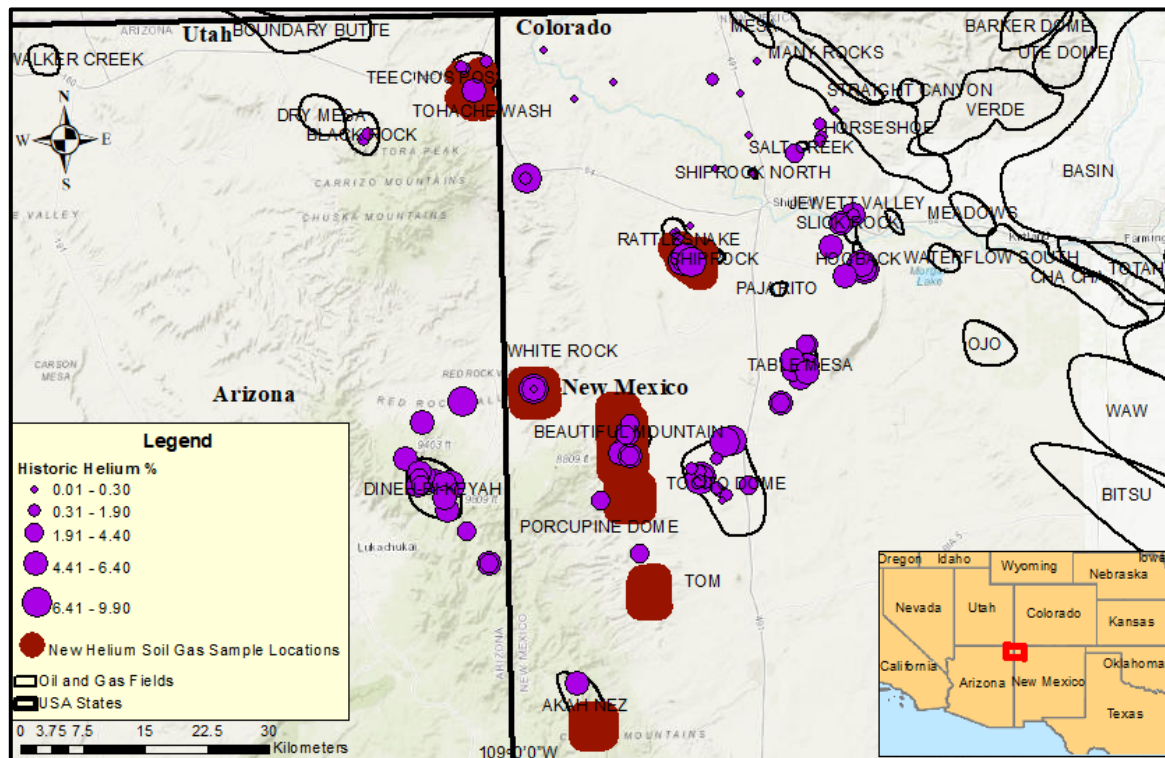


Figure 5.1: A) Field area showing the seven areas that soil gas surveys were collected in Arizona and New Mexico, on the Navajo Nation, USA.

The White Rock area is located 1.6 km east of the Arizona-New Mexico state border in San Juan County, New Mexico. Very little is known about the geology of the field. No production has occurred in this area and the only indication of He are from He shows (i.e., well tested 7.8% He from the Precambrian basement in 1966; and 5.2% He from the Pennsylvanian Barker Creek carbonate). Potential reservoirs are the Precambrian granitic basement and the Pennsylvanian Barker Creek carbonates. Based on geophysical data, Precambrian structural control is very poor.

The Beautiful Mountain Field, which had He up to 5.5% for the Permian reservoir, 5.35% for the Barker Creek reservoir, and 7% for the Leadville reservoir, is a large north-south structurally closed anticline located on the eastern flank of the Defiance Uplift in New Mexico (Fig. 5.1). There are three main He reservoirs, 1) Mississippian Leadville Limestone, 2) Pennsylvanian Barker Creek

carbonate, and 2) Permian Organ Rock Sandstone. Production from the Leadville began in 1975 and produced $7.3\text{E}7 \text{ m}^3$ of gross gas with $\sim 5.4\text{E}6 \text{ m}^3$ of He, production from the Barker Creek began in 1979 and produced $7.4\text{E}6 \text{ m}^3$ of gross gas with $\sim 4.4\text{E}5 \text{ m}^3$ of He, and production from the Organ Rock began in 1981 and produced $9.0\text{E}7 \text{ m}^3$ of gross gas with $\sim 2.8\text{E}6 \text{ m}^3$ of He. Lesser amounts of He have been measured from the deeper Devonian McCracken Sandstone at 4%, but this zone was never produced. All wells were plugged and abandoned by 2011. The Leadville is 46 meters in gross thickness and it is comprised of white, buff, dense, and finely crystalline limestone which is fractured and oolitic in parts (Brown, 1978). The geometry of the Leadville is uniform throughout and the trap is a well-developed structural nose (Brown, 1978). Little is known about the exact parameters of the Barker Creek horizon regarding its geology, mineralogy and thickness/extent. The Permian Organ Rock, which is a member of the Culter Formation (continental red beds), is comprised of poorly indurated sandstones with interbedded red shales (Broadhead and Gillard, 2004). A high angle reverse fault through the Organ Rock Sandstone bounds the field on the eastern flank of the structure.

The Porcupine Dome area is located 3.2 km south of the Beautiful Mountain Field in San Juan County, New Mexico (Fig. 5.1). Very little is known about the geology of the field. A well drilled in 1970 tested gas from the Leadville, but was eventually abandoned and the exact He% from the test is unknown. Several kilometres away, the Beautiful Mountain Field has 7% He values reported from the Leadville Limestone. Potential reservoirs with mapped structural closures (4-way and 3-way) are the Leadville Limestone and the Permian Organ Rock sandstones. Two high angle reverse faults through the Leadville Limestone cross cut the field on the eastern flank of the structure creating separate structural blocks.

The Tom area, which is located on the southernmost portion of the Four Corners Platform, is located 8 km south of the Porcupine Dome area in San Juan Country and which had He up to 7%, New Mexico (Fig.5.1) (Malinowski, 1983). Historically, the producing formation for oil was the Devonian McCracken Sandstone member of the Elbert Formation (Malinowski, 1983). Although there is no He production for the Tom area, it is in close proximity to wells that has high-He shows of 2.9% He in the Devonian and Mississippian sections; and has a 1976 oil/gas well that producing from the Devonian McCracken sandstone (although the exact He % is not known). The reservoir rocks of

the McCracken are relatively uniform throughout the area, have 3-8% porosity, and they consist of a gross thickness of 23 meters of fine to medium grained, poorly sorted, light grey to red, glauconitic sandstones with thin units (stringers) of sandy dolomite (Malinowski, 1983). Another potential reservoir with mapped structural closures (4-way and 3-way) is the Leadville Limestone. A high angle reverse fault through the Leadville Limestone cross cuts the field on the eastern flank of the structure.

The Akah Nez Field, which is located on the eastern portion of the Defiance Uplift and had He up to 6%, is located 14.5 km southwest of the Tom area in San Juan County, New Mexico (Fig. 5.1). The only indication of a possible He accumulation is from a He show located ~5 km to the northwest of the area from the Devonian McCracken sandstone. In the Akah Nez Field, there are two oil/gas wells (1967, 1970) producing from the McCracken Sandstone, but the exact gas He % is unknown. Overall structural control is very poor. Based on geophysical data, Precambrian structure is observed implying there could be structural closure further up the sedimentary column. Historically, the producing formation for oil was the Devonian McCracken Sandstone member of the Elbert Formation with a gross thickness of 74 m (Dawson, 1983).

5.3 Methods

5.3.1 Sample Collection

To measure responses over known He accumulations, we sampled the Tohache Wash area (6% He). To measure responses over partially depleted reservoirs, we collected samples over the Rattlesnake Field (7% He). To measure responses over relatively unknown and sparsely drilled areas (i.e., 1-2 wells per area), we sampled areas over the Akah Nez (6% He), Porcupine Dome (He unknown), Tom (5% He), and White Rock 5% He areas. Also, we collected gas samples over the Beautiful Mountain Field (5.5-7% He) because it represents an area with both a depleted reservoir (Leadville) and also a potential undrained discontinuous Organ Rock sandstone reservoir.

Using a modified engine powered soil auger probe, we collected He soil gas samples over seven natural gas fields of interest along transects at every 200 meters to establish an even grid. Once the soil auger probe was at its desired depth (~0.5-1 meter), 20 cc of soil gas was withdrawn with a syringe and discarded which effectively flushed the previous samples from the probe as the 20 cc gas

volume is 1.5 times the sample volume. Next, another 20 cc of new soil gas was collected with a syringe. This sample was subsequently injected into an evacuated glass sample bottle and stored for no more than 2 weeks before measurements were made. General quality assurance tests include testing for leaks to mitigate air contamination, replacing the septum on the sample collection port, and conducting routine background atmospheric gas measures to monitor background He levels.

5.3.2 Laboratory Analysis

Geochemical analysis solely for He was completed with a model 120SSA mass spectrometer based on previous work completed by the USGS (Freidman and Denton, 1976; Reimer, 1976). Continuous measurement of ^4He is made possible by the fixed mass to charge ratio of the instrument. Using a modified inlet, an aliquot of soil gas was injected. Impurities were separated with a liquid nitrogen cooled trap, and the sample moved to the mass spectrometer where the gas was ionized and components were separated according to their mass/charge ratio. The system is designed to only detect He via a specific selection slit which allows helium ions to pass through to a collector and which produces a current that is proportional to the He interacting with the detector plate. He's signal was converted to a voltage and amplified before undergoing integration (i.e., summation of output peaks) to calculate peak areas. Known bracketed He standards were run to establish a threshold from which we calibrated and calculated soil gas helium concentrations for each sample (Holland, 1984).

5.4 Results

Here we report the He content of (n=1974) soil gas samples from seven different fields which were chosen to represent case studies of prospective areas and depleted areas for He (Fig. 5.2). Data roughly follows the normal distribution for all fields. In order to establish a robust He background value, air samples (n=30) are taken which provide a range of 5.24-5.4 ppm, with an average of 5.33 ppm. To produce the air corrected He measurement, the average air value of 5330 ppb is removed from each sample. Considering the range of background air values, we use the cut-off of not mapping <40 ppb (1σ) above air to differentiate background compared to anomalous areas. Complete soil gas data is presented in the appendix Table 5.A.1.

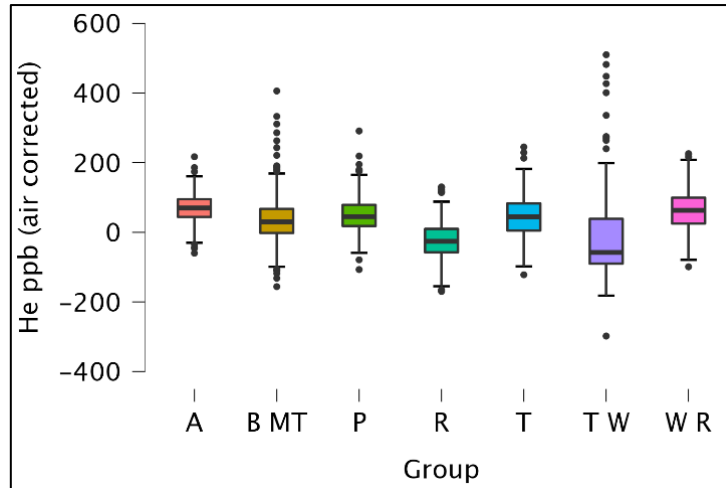


Figure 5.2: Boxplot showing the ranges of He that has been air corrected for each of the seven areas of interest. Sample size and standard deviations are as follows: A = Akah Nez ($n = 202$, $\sigma = 43.2$); B MT = Beautiful Mountain ($n = 644$, $\sigma = 59.7$); P = Porcupine Dome ($n = 262$, $\sigma = 54.2$); R = Rattlesnake ($n = 290$, $\sigma = 57.5$); T = Tom ($n = 221$, $\sigma = 59.8$); T W = Tohache Wash ($n = 88$, $\sigma = 162.9$); and W R = White Rock ($n = 267$, $\sigma = 56.6$). The upper and lower whiskers demarcate the range of data, with outliers represented as black points. The upper box represents the 75th percentile, the lower box represents the 25th percentile, and the thick black horizontal line represents the median.

5.5 Discussion

5.5.1 General Reservoir and Surface Gas Relationships

Here we present the details of the reservoir parameters and surface He signals for the fields of interest (Table 5.1). We notice that most areas have He surface signals in the 40-70s ppb above air range, with the one exception of the Tohache Wash area with an average He surface signal of 227 ppb above air. We propose that for He exploration, the higher the soil He signal is, the more likely a robust He accumulation is present in the subsurface. This approach coupled with data from historical He reservoir tests can provide information regarding He accumulations at depth.

Previous work by Halford et al., (2022) in chapter 2 and chapter 4 in the field area, illustrates the importance of tectonics (i.e., basement faults and igneous intrusions) in controlling He accumulations by providing and accentuating fault networks (Koide and Bhattacharji, 1975) which can serve as migration conduits for He transport via advective fluid flow. Going a step further, using high resolution geophysical data to examine basement fault patterns and potential fracture network intersections, we observe 1) faults aligned with the regional stress fields are longer and have a more complete range of He anomalies (Appendix Figure 5.A.2) and 2) a strong correlation with fracture network intersections (94%) and economic He wells (>0.3 He %) (Appendix Figure 5.A.3).

Additional information can be found in the Appendix section 5.A.2. Thus, understanding mechanisms (e.g., faults and fracture patterns) that can influence He accumulations is critical in understanding the He-system.

Table 5.1: Soil gas He concentrations (ppb above air), reservoir He concentrations, and recorded He reservoir information. Mc = McCracken Sandstone, Devonian; O = Organ Rock Formation, Permian; L = Leadville Limestone, Mississippian. All fields with the exception of Tohache Wash shows a He% that was tested several decades ago in the mid-1900s. (Baars, 1983; Brown, 1978; Dawson, 1983; Malinowski, 1983; Spencer, 1978). *= estimates; ? = no data.

	Akah Nez	Beautiful Mountain	Beautiful Mountain	Porcupine Dome	Rattle- snake	Tohache Wash	Tom	White Rock
Soil gas (avg.) ppb	68	59	59	52	42	227	45	76
Soil gas (avg.) %	6.8E-6	5.9E-6	5.9E-6	5.2E-6	4.2E-6	2.3E-5	4.5E-6	7.6E-6
Reservoir %	6	7	5.5	?	7	6	5	7.8
Formation	Mc	L	O	?	L	L	Mc	?
Depth m	1219.2	1828.8	1158.2	?	2133.6	1981.2	2011.7	1676.4
Press. atm	115.7	197.3	116	?	245.0	238.2	190.5	194.6
Field area km ²	30.4	23	23	10*	16.2	6.6	10*	10*
Gas bearing area km ²	0.2	6	3	0.2*	1.3	1.6	1.7*	0.2*
Gross thickness m	14.0	29.2	45.7	?	25.9	67.4	22.9	?
Net/gross	0.67	0.05	0.16	?	0.70	0.14	0.37	?
Porosity %	11	10	10	?	7*	7	5	?
Water saturation %	20	30	25	?	40*	40	43	?
Compressibility	0.009	.006	0.009	?	0.005	0.007	0.006	?
Temperature °K	323	323	311	?	323	334	326	?

5.5.2 Geologic Reservoir Controls

5.5.2.1 Differential Compaction

As the role of regional faults and fracture networks becomes more apparent, we have yet to investigate the localized structural controls/mechanisms that influence these migration conduits. To further explore the nature of structural geology's significance, we examine the role that differential compaction could have on He surface gas signatures.

Differential compaction, which is the process of uneven settling of sediments due to porosity loss, is critical in understanding reservoir architecture and connectivity (Meng and Hodgetts, 2020; Gay et al., 2006; Rusciadelli and Di Simone, 2007; Corcoran, 2008; Ireland et al., 2011). Differential compaction can occur either occur by dewatering episodes or by vertical loading (i.e., sedimentation). The concept of differential compact by sedimentation is relatively simple, in that after deposition of sediments as more and more overburden is added, the sediments will compact over the underlying rocks and form associated faults and fractures (Xu et al., 2015; Williams, 1987, Bjørlykke and Høeg, 1997, Buczkowski and Cooke, 2004). More specifically, if there are portions of the underlying

geology that protrude and create a circular feature, the weight of the sediments will create an isometric stress field around the protrusions flanks and ultimately lead to differential compaction radial fracturing (Xu et al., 2015; Mehl, 1920; Blackwelder, 1920; Moore, 1920; Merriam, 1999).

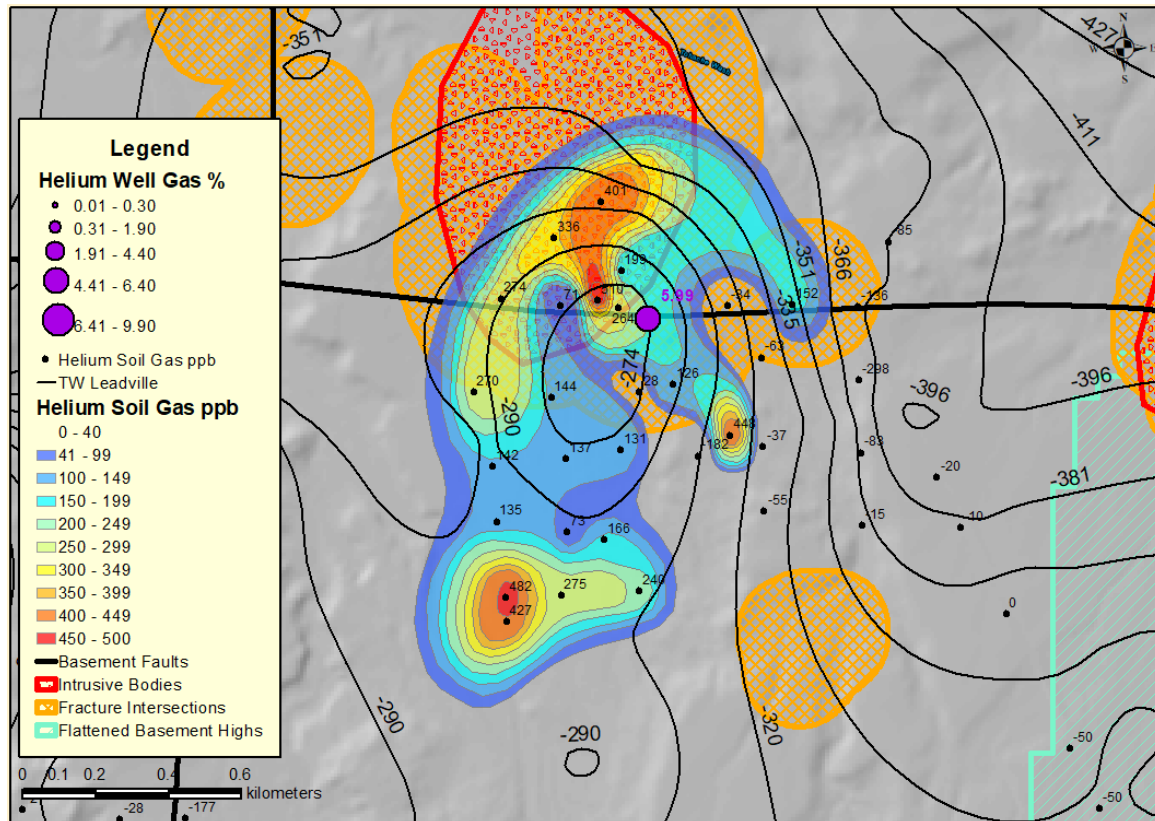


Figure 5.3: Tohache Wash area map showing the He soil gas coloured contours (via raster interpolation and manual techniques) of values above 40 ppb from background values of 5.33 pm along with structural elements, He data (Brennan et al., 2021) and structural contours (C.I. of 15 m) on top of the Leadville Limestone. There is strong correspondence between He soil gas anomalies and the reservoir structural flank and crest which could indicate apical (directly above) and halo (spill points) He microseepage.

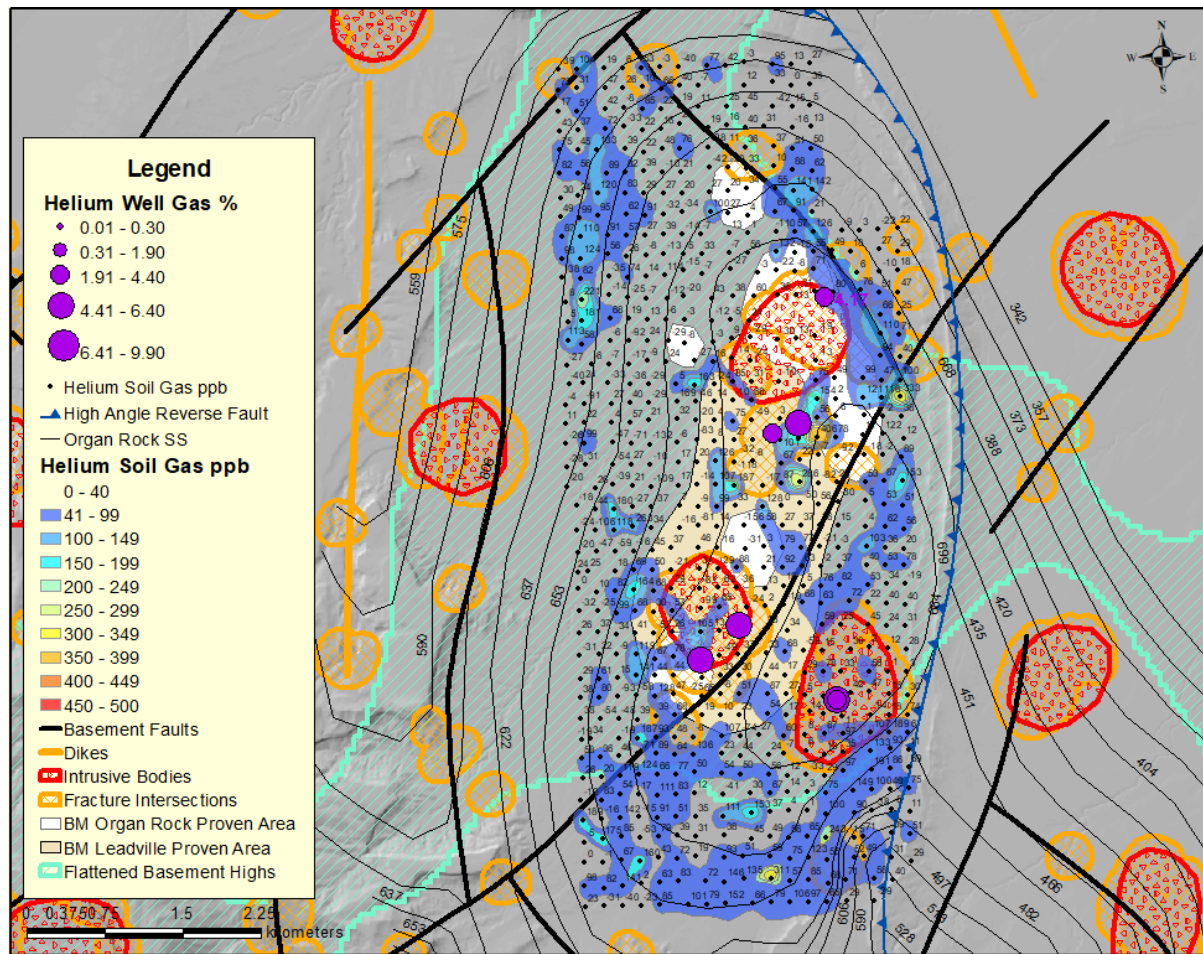


Figure 5.4: Beautiful Mountain Field map showing the He soil gas coloured contours (via raster interpolation and manual techniques) of values above 40 ppb from background values of 5.33 pm along with structural elements, He well data > 4% (Brennan et al., 2021), and structural contours (C.I. of 15 m) on top of the Permian Organ Rock sandstone. There is a correspondence between the He soil gas anomalies and a basement fault in the NE portion of the field which could indicate a pathway driven microseepage event. The previously depleted areas of the field are shown as white and tan polygons related to the Organ Rock and Leadville proven areas respectively. On the southern portion of the field, He soil gas anomalies occur over potentially undrained portions on the structural flanks of the reservoir, which could indicate halo (spill points) He microseepage.

We are proposing this mechanism as a contributing reason we observe He anomalies on structural crests and around the flanks of highs. By examining the structure maps of the potential He reservoirs at Tohache Wash, Beautiful Mountain, White Rock, Akah Nez and Tom, a first-order observation is that there are He soil gas anomalies overlying the flanks of reservoir highs along with several instances of strong crest signatures (Figs. 5.3-5.7). Traditional experience from the hydrocarbon industry tells us that in an ideal system that natural gas will migrate up dip into the crest of a structural high. Often times in reality, the natural gas accumulations can be offset from structural crest highs by various features (i.e., gas water contacts, tight lithologies, tectonic events,

fractures/faults, etc.). If we assume that the overlying fracture networks linking up the reservoir to the crust are more or less vertical with minor amounts of lateral offset, we can argue that this flank signature could be derived from differential compaction of sediments and the resulting fault or induced fracture pathways are either due to a basement high (Rattlesnake, Beautiful Mountain, White Rock, Akah Nez, Tom), a rising igneous body (Tohache Wash), or other underlying geologic features.

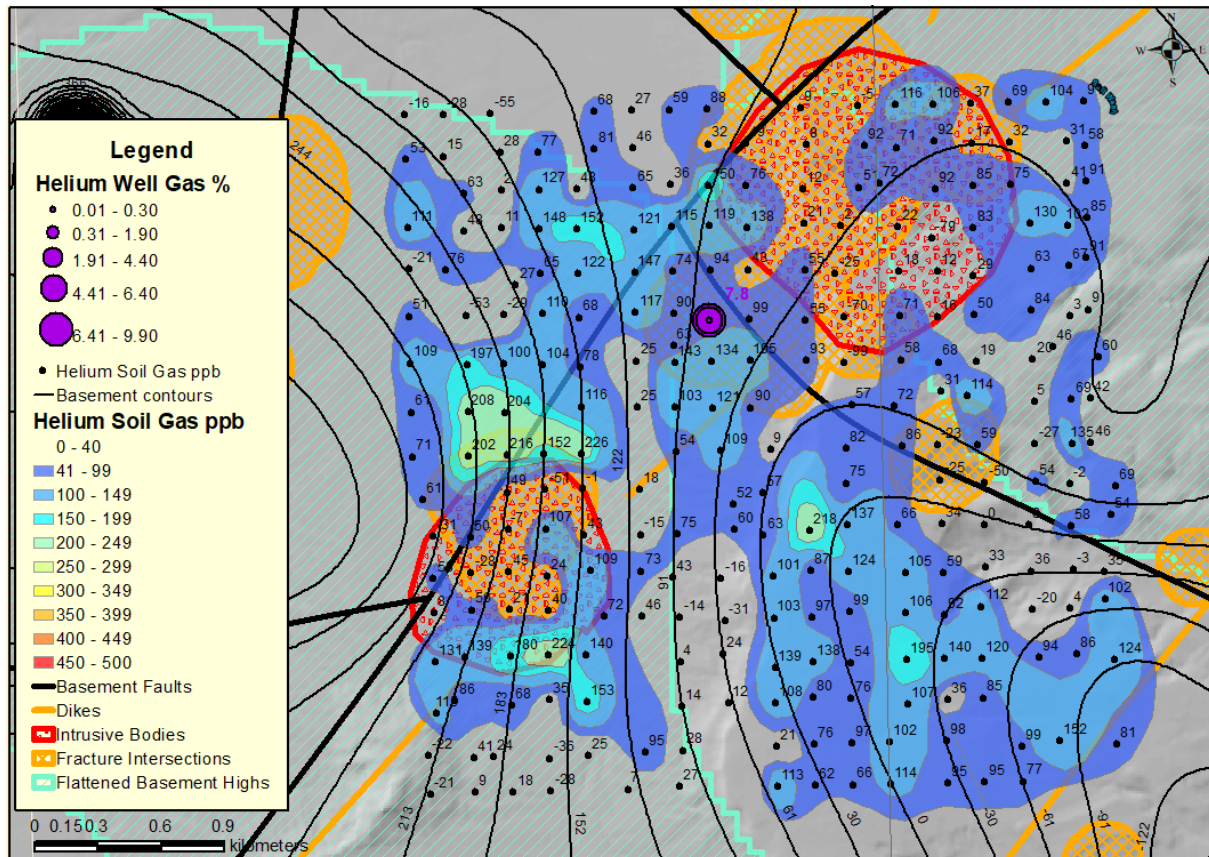


Figure 5.5: The White Rock area map showing the He soil gas coloured contours (via raster interpolation and manual techniques) of values above 40 ppb from background values of 5.33 pm along with structural elements, He well data (Brennan et al., 2021) and structural contours (C.I. of 15 m) on top of the Precambrian basement. There is strong correspondence between the He soil gas anomalies and the reservoir structural flank which could indicate halo (spill points) He microseepage.

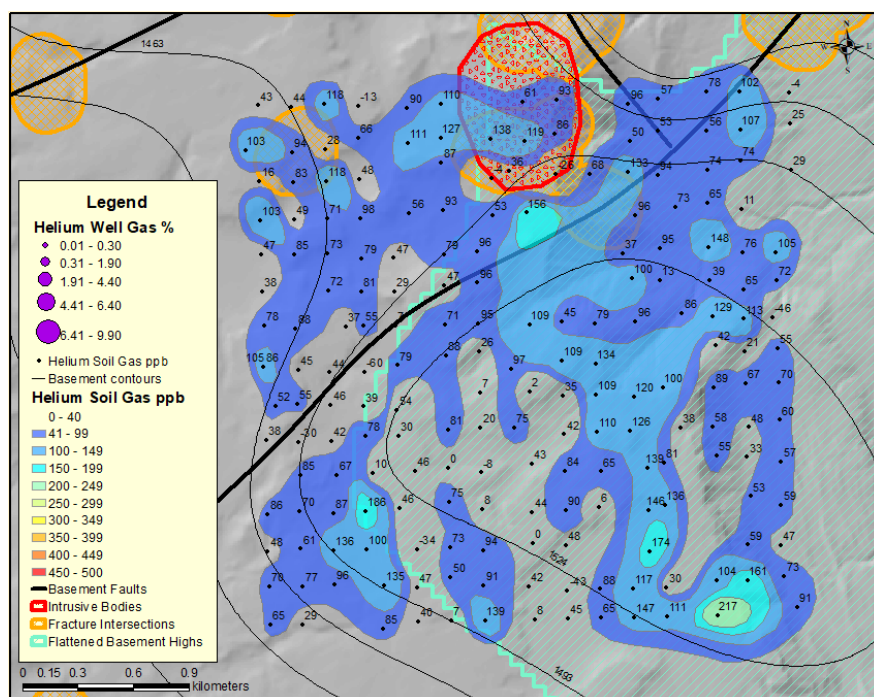


Figure 5.6: Akah Nez area map showing the He soil gas coloured contours (via raster interpolation and manual techniques) of values above 40 ppb from background values of 5.33 pm along with structural elements, He well data (Brennan et al., 2021) and structural contours (C.I. of 15 m) on top of the Precambrian basement. There is strong correspondence between the He soil gas anomalies and the reservoir structural flank which could indicate halo (spill points) He microseepage, and there is a strong signature in the centre of the Precambrian closure.

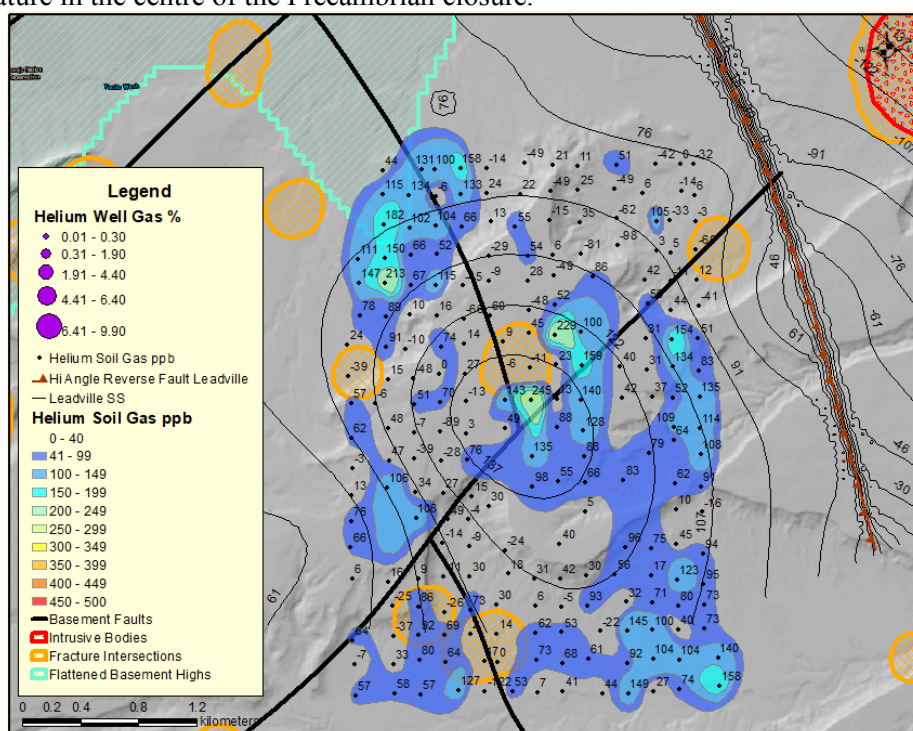


Figure 5.7: Tom area map showing the He soil gas coloured contours (via raster interpolation and manual techniques) of values above 40 ppb from background values of 5.33 pm along with structural elements, He well data (Brennan et al., 2021) and structural contours (C.I. of 15 m) on top of the Mississippian Leadville Limestone. There is strong correspondence between the He soil gas anomalies and the reservoir structural flank which could indicate halo (spill points) He microseepage, and there is a strong signature in the centre of the Mississippian closure. The high and flank anomalies could also be influenced by the presence of the basement faults.

5.5.2.2 Fault Leakage

It is well documented that surface hydrocarbon anomalies that are associated with faults often signify a connection to subsurface hydrocarbon reservoirs (Debnam, 1969; Ball and Snowdown, 1973; Dyck, 1976). Translating the principle of microseepage from hydrocarbons to He is a relatively straightforward step (Roberts and Roen, 1985). Whether this association is indicative of a larger accumulation or the tell-tale sign of a transient system with little gas potential is an ongoing debate in the literature (Danabalan et al., 2022, Mtili et al., 2021; Barry et al., 2013). As an aside, to fully understand how harmful or beneficial a surficial fault seep is, the surface flux of ^4He should be monitored over an extended period of time (to enable accurate mass balance calculations) and not sampled at a singular seep location for the best odds of success.

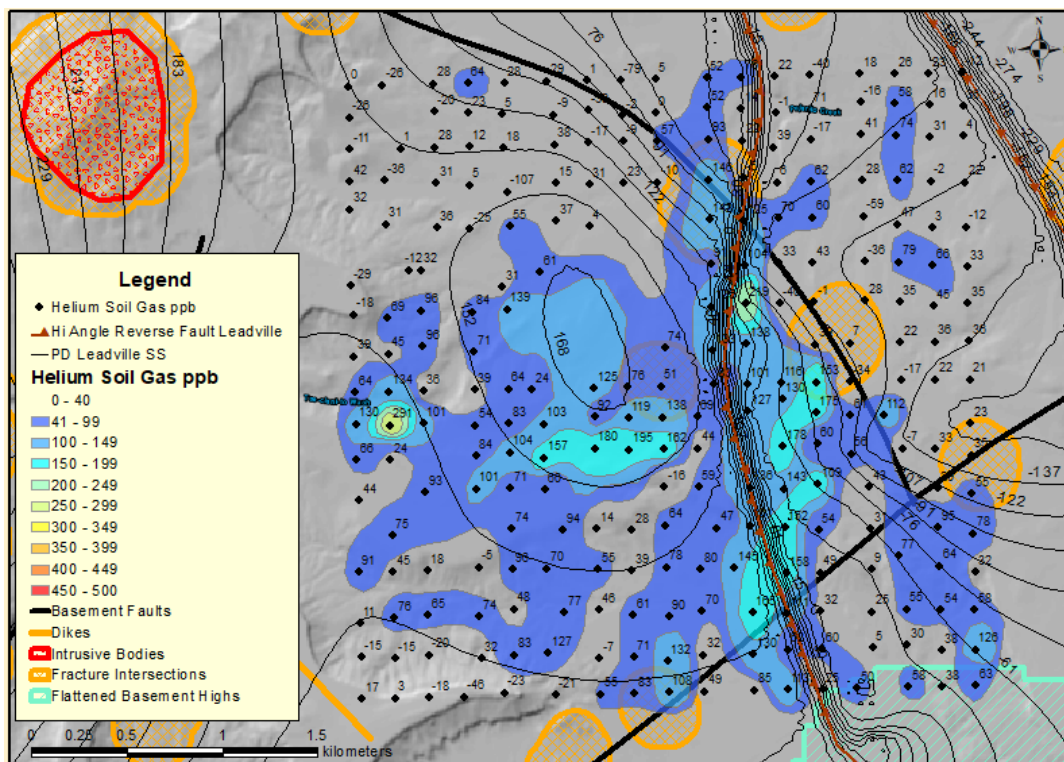


Figure 5.8: The Porcupine Dome area map showing the He soil gas coloured contours (via raster interpolation and manual techniques) of values above 40 ppb from background values of 5.33 pm along with structural elements, and structural contours (C.I. of 15 m) on top of the Mississippian Leadville Limestone. There is a correspondence between the He soil gas anomalies and a high angle reverse fault on the eastern portion of the field, which could indicate pathway driven advection He microseepage. Slightly elevated He anomalies around the crest and flank of the structure could also indicate a halo (spill point) He microseepage.

By examining the soil gas He signatures, we observe surface He anomalies that follow the outline of underlying basement lineaments/faults in the north east corner of the Beautiful Mountain

Field (Fig. 5.4), in the Tom area (Fig. 5.7), and in the Rattlesnake Field (Fig. 5.9). We also observe higher He soil signatures where a thrust fault cross cuts the Leadville Limestone in the Porcupine Dome area (Figs. 5.8). The presence of He anomalies at the surface indicates that these faults are relatively open and are acting as a migration conduit (i.e., leaky seal). Here we observe the depletion of the reservoirs is likely due to the leaky faults cross cutting the reservoirs (i.e., rapid advective fluid flow). This is a pathway driven mechanism where the seepage acts to focus He from the reservoir resulting in higher concentrations than surrounding areas. Therefore, we propose that He surface gas anomalies that closely resemble lineaments in conjunction with weak and disperse He surface signatures be regarded as a negative element in the He system as the faults are likely responsible for rapid advective loss of subsurface He accumulations.

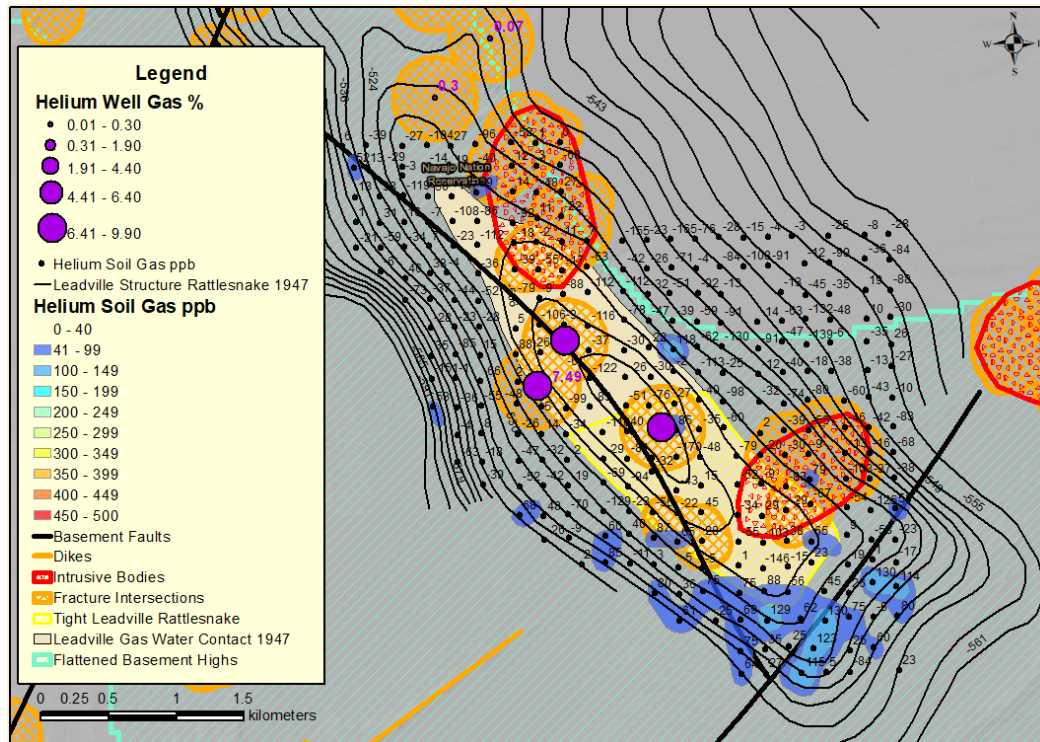


Figure 9: The Rattlesnake Field map showing the He soil gas coloured contours (via raster interpolation and manual techniques) of values above 40 ppb from background values of 5.33 pm along with structural elements, He well data > 4% (Brennan et al., 2021), and structural contours (C.I. of 15 m) on top of the Mississippian Leadville Limestone. There is a correspondence between the He soil gas anomalies and basement faults on the SE portion of the field, which could indicate pathway driven advection He microseepage. The overall depleted nature of the field is shown with tan and yellow polygons indicating theorized Leadville gas water contact and tight Leadville areas.

In addition to gas leakage due to faults, we consider a scenario of rapid He loss for Rattlesnake involving the depletion of the natural gas cap. Field reports show that the He-rich gas in

Rattlesnake Field was initially discovered in 1942 and then shut in <2 years after production began due to excess water production (Baars, 1983). In this scenario, it appears that the initial gas cap that was produced, which was dominantly nitrogen (73% N₂, 14% CH₄, 3% CO₂ and 7.6% He), could have been acting as a buffer effectively slowing down He loss. A proposed mechanism for this buffering is the larger N₂, CH₄, and CO₂ molecules blocking or impeding pore throats, effectively lowering permeability at the gas cap – reservoir seal boundary (Looney and Faulta, 2000). However, once production, and the gas cap barrier was removed, those pore throat pathways were left open, which resulted in an increase in permeability. This process could explain why despite such high initial He % tests in 1942, there are zero He-rich signatures where the pilot wells were drilled and produced as the He flux (e.g., vertical migration) leaving the reservoir exceeded that which was entering it.

5.5.3. Vertical Helium Migration from Reservoir to Surface

Vertical migration is an umbrella term describing the mass transport processes that facilitates the movement of gas from subsurface reservoirs to the surface (Rice, 2022). The idea of methodically tracing back surficial seeps to underground reservoirs has been a core approach from the beginnings of hydrocarbon exploration to the present day. More recently, this approach been adapted to He exploration (Barry et al., 2013; Danabalan et al., 2022). The transportation of natural gas that feeds seeps can be broken down into a slow and steady continuous diffusive flux (dissolved in water) (Cheng et al., 2023; Marschall et al., 2005) or a rapid continuous phase buoyancy driven flow dependent on tectonic history (Brown, 2000; Rice, 2022).

5.5.3.1 Diffusion Mass Transport

In the mid-20th century, diffusion, which is the process describing movement under a concentration gradient where mass transfer occurs from higher to lower concentrations, was regarded as the favoured mechanism to explain vertical migration especially for hydrocarbons (Rosaire, 1940; Horvitz, 1949; Price, 1986; Krooss and Leythaeuser, 1996). Since then, various authors (Hunt, 1979; Smith et al., 1971; Davis, 1967) advocate that diffusion for natural gas seepages would require hundreds of million years and considering the insufficient fluxes and levels of microbial degradation/gas evaporation to atmosphere, they argue diffusion is likely a non-crucial mechanism

(Rice, 2022). More recent work focusing specifically on He and N₂ (Cheng et al., 2021, 2023) argues that in an environment with extreme basin stability devoid of significant geological activity (i.e., >100 mya) diffusion can theoretically act a key transport mechanism for natural gases.

Examining Fick's first law of diffusion, the general relationship for a diffusive flux is controlled by a concentration gradient that is expressed in a concentration change (δC) and a position change (δx) (Crank, 1975) (Equation 5.1). The diffusion coefficient (D) represents the amount of time that a substance takes to travel through a medium and is dependent on molecular shape/size, viscosity of the solvent, and interactions with the solvent (Crank, 1975).

$$\text{Equation 5.1: } Flux(J) = -D \frac{\delta C}{\delta x}$$

Gas diffusion in pure water is a function of the gas mass, diffusion activation energy, diffusion constant, and temperature (Jahne et al., 1987; Ohsumi and Horibe, 1984; Ballentine and Burnard, 2002). Due to the monotonic nature and stable electron shell configuration, noble gases have little interaction with water (i.e., lower activation energy) and diffusion is mostly dominated by mass (Ballentine and Burnard, 2002). Equation 5.2 represents the diffusion coefficient of He dissolved in pure water as a function of temperature (Jahne et al., 1987).

$$\text{Equation 5.2: } D_{He_w} = 2.309 * 10^{-2} * e^{-1706/T}$$

Gas diffusion in a porous media is ultimately slower than diffusion in a pure water environment due to the constraints of porosity, tortuosity, and permeability (Ballentine and Burnard, 2002). In order to quantify these constraints, we incorporate a retardation factor of D_r (shown in Equation 5.3) into Equation 5.1 (Boving and Grathwohl, 2001). Diffusion coefficients are difficult to quantify due to non-homogeneous rock properties, temperatures, and medium (Liu et al., 2017), but here we make a macroscopic assumption of the continuity of average porosity values from literature for each of the fields of interest. Our calculated D_r for each of the fields are consistent with the reported value of 2E-06 cm²/s from Osenbruck et al. (1998).

$$\text{Equation 5.3: } D_r = \varphi^{2.2} D_{He_w}$$

Using Equation 5.4, the original gas in place (OGIP) for each reservoir was calculated (Q) using a volumetric approach based on geologic parameters for each field. Calculating the original He

in place (OHIP) was then relatively straightforward by multiplying the OGIP by the known historical He concentrations that were measured from well tests from Brennan et al. (2021). Using Equations 5.5 and 5.6, internal and external fluxes were calculated for the areas of interest. U and Th concentrations were assumed to be relatively constant for both and we used the U value of 2.8 ppm and Th value of 10.7 ppm (Danabalan et al., 2022). Using the calculated OHIP and the external and internal flux rate of He/year, we are able to calculate the approximate age of each gas accumulation (Table 5.2).

$$\text{Equation 5.4: } OGIP = \frac{Ah\phi(1-S_w)}{1} \times \frac{T_s P_i}{P_s T_f Z_i}$$

where OGIP cubic feet [meters³], A is the reservoir area ft² [m²], h is the net pay thickness ft [m], ϕ is the porosity, S_w is the water saturation, T_s is the base temperature standard condition Rankine [Kelvin], P_i is the initial reservoir pressure psia [kPaa], P_s is the base pressure standard conditions 14.65 psia [101.35 kPaa], T_f is the formation temperature Rankine [Kelvin], Z_i is the compressibility at reservoir pressure and temperature of the dominant gas (Robinson and Peng, 1976), and $(T_s P_i / P_s T_f Z_i) = B_{gi}$, which is the initial conditions gas formation volume factor (Mireault et al., 2007).

$$\text{Equation 5.5: } P_{\text{internal}} \text{ cm}^3 \text{ STP } ^4\text{He} = \rho \cdot 0.2355\text{E-}12 \cdot U [1+0.123(\text{Th}/U-4)] \cdot (1-\phi) \cdot V$$

Where ρ is the average crust density (g/cm³), U and Th are the concentrations of uranium and thorium in ppm, ϕ is the porosity, and V is the volume of rock in cm³.

$$\text{Equation 5.6: } P_{\text{external}} \text{ cm}^3 \text{ STP } ^4\text{He} = \rho \cdot 0.2355\text{E-}12 \cdot U [1+0.123(\text{Th}/U-4)] \cdot H \cdot S \cdot t$$

Where S is the gas bearing area cm², H is the depth cm, and t is time in years.

To address the significance of diffusion in porous media, we utilize a one-dimensional steady state diffusion model to investigate He diffusive loss from natural gas subsurface reservoirs (Equation 5.7) (Buttitta et al., 2020, Lui et al., 2017). We assume that He migration occurs in the subsurface due to a concentration gradient of He dissolved in pore water from the reservoir seal to the surface where the capillary pressure of the seal is exceeded by reservoir pressure. We also assume that the He concentration in surface water is 4.5E-8 cm³STP/ml (Kipfer et al., 2002). The model incorporates the partial pressure of He in natural gas and the Henry's constants for He in water to quantify the concentration of He dissolved in pore water. By integrating the function in regard to the approximate age of the gas accumulation (Table 5.2), we quantify the amount of He lost (cm³) per unit time. The calculation, which was calculated iteratively using defined time steps followed by summation, allows us to determine the amount of reservoir He (cm³) lost by diffusion (Table 5.2).

$$\text{Equation 5.7: } \int_0^t \frac{D_r}{Z} (C_{H_2O}(t) - 4.5 * 10^{-8}) * S * dt$$

$$\text{Where } C_{H_2O}(t) = \frac{22.4 * Q * C(t)}{G.B.V. * \phi * K_{H_2O}} * \frac{P_{NC} * T_{RC}}{T_{NC}}$$

Where T = time, D_r = diffusion coefficient for He with the retardation factor applied cm^2/time , Z = reservoir depth cm , Q = estimated original gas in place in the reservoir cm^3 using Equation 5.4, $G.B.V$ = the gross bulk volume cm^3 , ϕ = the porosity %, K_{H_2O} = Henry's constant for He in water $\text{atm} * \text{kg/mol}$, $C(t)$ = ^4He volume %, P_{NC} = the normal atmosphere (1 atm), T_{NC} is normal temperature (273 K), T_{RC} = reservoir temperature (K), and S = gas bearing area cm^2 .

General observations for the model are that 7-49% of He has been lost via diffusive mass transport given the calculated gas accumulation age based on the OHIP in place and external and internal flux calculations. Interestingly, the average formation age of all the accumulations was ~30 Ma, which represents an approximate on the documented Oligocene volcanism in the region (Gonzales and Lake, 2017; Halford et al., 2022). This is considered a maximum end value, as no seal was incorporated into the model, as this would hinder He lost. While considering the volumetric estimates of the OGIP and OHIP, we show that theoretically there should be a considerable amount of He remaining in the reservoirs of the Akah Nez, Beautiful Mountain, Rattlesnake, Tohache Wash, and Tom fields currently (i.e., 83%, 22%, 42%, 55% and 90%, respectively).

A characteristic of diffusion dominated processes is that generally diffusion has nearly spherical dispersion that can't be focused into localized anomalies (Price, 1986), which is not what we observe from the soil gas surveys for parts of the Rattlesnake and Beautiful Mountain fields (i.e., more linear trends demarcating basement fault zones) (Figs. 5.4 and 5.9). If diffusion was the only significant process acting in the Beautiful Mountain and Rattlesnake fields, our calculations show there should be a considerable amount of He left in the reservoir (Table 5.2), and this considerable amount of He should provide a slow stable He soil gas signature if the reservoir pressure exceeds the seal lithology capillary pressure. A strong surface signal is not reflected in the collected soil gas data, which indicates other processes are influencing the signals, such as pressure driven water migration (advective transport) and/or reservoir pressure is depleted compared to seal capillary pressure.

One scenario to explain the lack of a He surface signal involves the production/movement of groundwater. In the case of the Rattlesnake Field, it was produced until excessive water production

terminated gas production (Bars, 1983). The effect of excess water production indicates that a water cone or water fingering developed due to pressure differentials when producing the reservoir (Arthur, 1944). More specifically, the water that is drawn upwards from underlying/adjacent wet rock to the wellbore, can push the remaining unproduced reservoir gas to the fractured edges of the structural uplift. Once gas encounters these zones of higher permeability, the capillary pressure in the seal will be lower than the underlying reservoir, and the gas and adjacent fluid can migrate upwards via advection out of the reservoir (Rice, 2022). This scenario, which could result in He gas depletion depending on the influence of the groundwater pressure drive, is plausible as we only observe He soil gas signatures at the edge of the Rattlesnake structure where there are likely (micro)fractures due to high stress (point of maximum curvature).

Another explanation for the lack of a surface He signal at Rattlesnake is due to the lack of adequate reservoir pressure. Because the well was produced for a short amount of time, the reservoir pressure has fallen below the capillary pressure and no significant amounts of He is escaping the reservoir. This means the gas would not be forced through limited pathways in a seal (effusion zones) and not be subjected to subsequent diffusion or advection in the overlying sediments. If this scenario has occurred, our diffusion calculations could provide added insight as to the remaining potential for the reservoirs of interest beyond what the soil gas surveys are recording.

Although diffusion is likely occurring and we cannot rule it out, there is not strong evidence that diffusion alone for these depleted fields (Rattlesnake and Beautiful Mountain) is a significant mechanism. Therefore, given the regional tectonic history of the Colorado Plateau which has provided prevalent fracture and fault pathways, it seems unreasonable to assume diffusion loss would be a dominant process to explain vertical migration, and other mechanisms such as buoyancy driven advective mass transport should be considered such as those covered in Brown (2000) and Rice (2022) discussed in Chapter 3. An application for He exploration is that the absence of diffusive crest signatures combined with the presence of advective transport fault derived halo signatures could indicate a He gas accumulation with relatively low reservoir pressure (below capillary pressure), but there are many other variables to consider outside of the scope of this work.

The Tohache Wash area, which shows semi spherical surface He signatures in Fig. 5.3, a high He % remaining value, and the strongest He soil gas survey signatures can be a prime example of a partly diffusion dominated system where the reservoir pressure is greater than the capillary pressure. Given it has the highest He soil gas values measured, coupled with the fact that it has had consistent He% well tests over decades (1969 and 2016) despite having been produced (~13% of original gas), shows that there must be a slower process and not an active rapid loss mechanism, otherwise the accumulation would not exist with such high He values. Another indication are that some of the patterns observed on the surface are characteristic of diffusion dominated processes (i.e., spherical dispersion patterns), which is what we observe relatively at Tohache Wash and the Tom and Akah Nez areas as well (Price, 1986). Tom and Akah Nez areas have the largest amount of remaining He in place at ~90 and 83%, respectively. Diffusion is likely important in these areas because of a relatively good anomalous coverage of the He soil gas survey. The signatures, although not as strong as those measured in the Tohache Wash area, are relatively complete (i.e., don't exhibit large drawdown footprints of previously produced fields), and show moderate He values above air values. Additionally, it is likely these values at Akah Nez and Tom indicate a lower concentration of He % (compared to Tohache Wash) at depth.

Table 5.2: Reservoir, Diffusion coefficients, Henry's constant, historic He %, Original Gas in Place (Q), Original Helium in place (OHIP), produced He, lost he, % He produced, % He lost and % He remaining for the fields of interest, excluding Porcupine Dome and White Rock (no data). Mc = McCracken Sandstone, Devonian; O = Organ Rock Formation, Permian; L = Leadville Limestone, Mississippian. All fields with the exception of Tohache Wash shows a He % that was tested several decades ago in the mid-1900s. *= estimated. (Baars, 1983; Brown, 1978; Dawson, 1983; Malinowski, 1983; Spencer, 1978).

	Akah Nez	Beautiful Mountain	Beautiful Mountain	Rattlesnake	Tohache Wash	Tom
Reservoir	Mc	L	O	L	L	Mc
D_r cm ² /s	9.1E-7	7.4E-7	6.0E-7	7.4E-7	4.0E-7	1.7E-7
Henry's K atm kg/mol	3113.2	3113.2	3221.21	3026.7	3113.2	3113.2
Historic He %	6	7	5.5	7	6	6*
Q cm ³	1.71E+14	1.99E+14	1.02E+14	2.25E+14	8.70E+13	6.60E+13
OHIP cm ³	1.03E+13	1.19E+13	6.10E+12	1.35E+13	5.22E+12	3.96E+12
Prod. He cm ³	-	5.11E12	4.95E12	3.96E12	6.54E11	-
Lost He cm ³	1.72E+12	3.29E+12	4.07E+11	6.55E+12	1.69E+12	3.39E+11
% produced	0.00	42.87	81.19	29.39	12.53	0.00
% lost	16.77	27.63	6.67	48.59	32.47	8.55
% remaining	83.23	29.50	12.14	22.02	55.00	91.45
Gas age (mya)	19.4	29.6	15.2	47.8	45.1	22.4

5.5.3.2 Near Surface Migration Microseepage Model

Active seepages can be classified into two general systems, 1) episodic and 2) continuous. Episodic seepage describes system that are sporadic and advective in nature such as instances of venting or enhanced tectonic activity versus those that are continuous such as a steady diffusive flux (Abrams, 1992, 2020; Arp, 1992, Brown, 2000; Jones and Burtell, 1996; Klusman and Saeed, 1996, Brown, 2000, Rice, 2022). Additionally, seepages can be categorised either macroseepages (>100,000 ppm total gas) or microseepages (<10,000 ppm total gas) (Abrams, 2020). It is important to note that migration will follow the zones of least resistance based on pressure drive, buoyancy drive and capillary resistance, and observed seeps do not have to occur directly over a subsurface gas accumulation (Abrams, 2020).

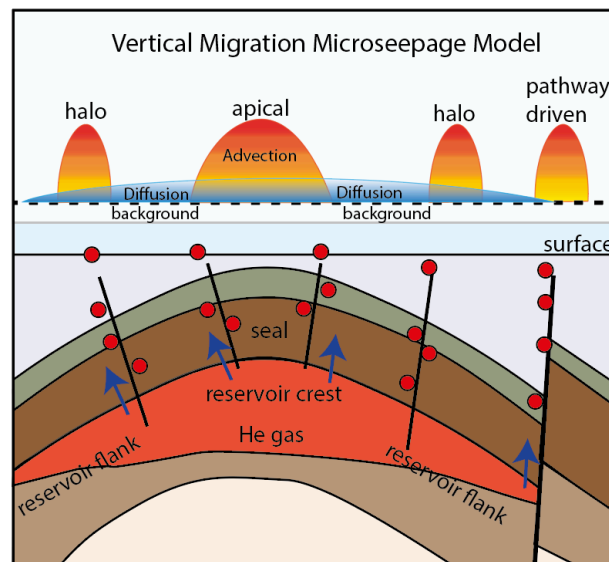


Figure 5.10: Schematic showing the main groupings of observable surface expressions of He, 1) pathway driven, 2) halo, 3) and apical (modified from Abram, 2020). Advection (yellow-red parabolas) is the likely transport mechanisms for vertical migration related to faults and fractures in and around the reservoir crest/flanks. Diffusion (blue parabola) is inferred to produce a spherical surface expression. The size of each parabola for advection and diffusion in the cartoon is not indicative of its importance, but rather a broad indication of the relative speed of each (i.e., diffusion is smaller, because it is much slower than advection). The far right of the schematic indicates a scenario where there is an active fault zone from depth to surface where advection dominates transport (Rice, 2022).

Upon analysing the structural and geochemical data, we present a schematic (Fig. 5.10), which highlights the main elements impacting vertical microseepage He migration from a gas reservoir to the surface. Patterns observed on the surface (quantified with soil gas He survey) can be used to distinguish characteristic geometries related to apical anomalies (immediately above a

subsurface gas body) and halo anomalies (spill points around subsurface gas body) (Abrams, 2020). Additionally, geological migration pathways (basement faults, thrust faults, diapirs, fractured basin carrier beds, etc.) can act as advection pathways allowing higher concentrations of He seepage on the surface. We observe pathway driven migration in the Beautiful Mountain Field, Porcupine Dome area, Tom area, and Rattlesnake Field; partial vertical halos are observed in the Tohache Wash area, Beautiful Mountain Field, White Rock, Porcupine, Akah Nez and Tom areas; and vertical apical anomalies are observed in the Tohache Wash and Tom areas.

Regarding exploration frameworks, it appears the evidence of diffusion dominated systems is favourable compared to more advective signatures to describe the process of He escape from a reservoir. This is because a diffusive flux is significantly slower than advective fluid flow enabling the preservation of gas accumulations over longer amounts of time given there is an adequate seal/capillary pressure in place.

5.5.4 Bayesian Statistical Models

Following on the work presented in chapter 4, which argued for the significance of regional structural features impacting He-system migration and accumulation, we present a statistical approach examining the impact of locally controlled structural features in relation to measured He values from surficial soil gas surveys. More specifically, we use the soil gas survey points to observe the effect of several structural features with more precision (higher resolution) than previously possible in Halford et al., (2022) and chapter 4, which only had access to a regional He % well dataset. We utilize a Bayesian linear regression to determine which geologic features are the most significant in explaining the soil gas anomalies at Tohache Wash (most He prospective area with characteristics of both advective and diffusive loss) and then test the approach on the areas surrounding Tohache Wash.

The Bayesian linear regression model, which is a type of conditional modelling, is used to analyse model comparisons and determine the most optimal combination of covariates influencing He anomaly soil occurrences. Bayesian regression differs from the standard linear regression model in that it utilizes probability distributions and not point estimates (Bergh et al., 2021; Faulkenberry and Wagenmakers, E.-J., 2020; van Doorn et al., 2021). More specifically, a Bayesian linear regression

model utilizes a linear combination of other variables to describe the mean of one variable to determine the posterior probability of regression coefficients (Bergh et al., 2021). This allows out-of-sample predictions and uncertainty quantification of the dependent variable that is based on observed values of the independent variables (i.e., what the model derived from the data) (Bergh et al., 2021).

In our case, our response variable (i.e., dependent variable) are the He soil gas values, and the explanatory variables (i.e. independent variables) are the structural features of interest (i.e., intrusions, basement faults, fracture intersections, reservoir high, reservoir flank, and previous He wells). The soil gas values utilized are those >25 ppb above 5.33 ppm due to the average air value at Tohache Wash being 5.355 ppm. Each of the soil gas points records dummy variables of either 1 or 0, to mark the presence or absence of a geologic feature at that exact location. For zones demarcating a structural high or flank of a high, approximations are made to correspond to the highest structural contour representing the structural high; whereas the flanks are represented by the area from the base of the structural high to the upper most contour (generally up to 1 km). Upon observations that 94% of all previously recorded economic He anomalies occur within a fracture intersection node, we add the fracture intersection variable to the null model as a control variable. For our model, we assume a uniform distribution for the model prior (i.e., probability of the model before observing the data). Assumptions of homoscedasticity, linearity, multicollinearity, and normality were considered and generally found to have been met (Bergh et al., 2021). We also assume the soil gas He signatures are not being overly influenced by lateral transport and more or less are experiencing near vertical He migration.

We observed the best model is comprised of the intrusion and reservoir flank predictors $P(M|\text{data}) = 0.098$, Bayes Factor $(BF)_M = 3.354$, Bayes Factor $(BF)_{10} = 1$, and $R^2 = 0.328$. $P(M|\text{data})$, which denotes the posterior probability of the models after observing data, shows us that “intrusion + reservoir flank” has the highest posterior probability of 0.098. The odds in favour of the model containing “intrusion + reservoir flank” as predictors have increased by a factor of 3.354 after observing data. The second best fit model is comprised of the intrusion, reservoir highs and reservoir flank predictors ($P(M|\text{data}) = 0.096$, $BF_M = 3.291$, $BF_{10} = 0.983$, and $R^2 = 0.39$) (Table 5.3). The odds in favour of the model containing “intrusion + reservoir high + reservoir flank” as predictors have

increased by a factor of 3.291 after observing data. Considering the BF_{10} (relative predictive adequacy), the observed data are 1.017 times as likely to occur under the “intrusion + reservoir flank” model than they are under the “intrusion + reservoir high + reservoir flank” model. Thus, the best model based on the posterior probability of the model after observing the data $P(M | \text{data})$, BF_M and BF_{10} is the “intrusion + reservoir flank” model (Table 5.3).

Examining the BF inclusion factor, which is a quantification designed to aid in determining whether to include the predictor in the model or not, we observe that reservoir flank has the highest value of 4.06, followed by intrusion at 2.056 (Table 5.4). The BF inclusion factors are computed by dividing the posterior odds by the prior odds. More practically this can be thought of dividing the posterior inclusion ($P(\text{inclusion} | \text{data})$) by the posterior probability of excluding data ($P(\text{excluding} | \text{data})$) following by dividing prior inclusion ($P(\text{inclusion})$) by prior exclusion ($P(\text{exclusion})$).

Table 5.3: Bayesian linear regression comparison of best models & Bayesian coefficients (via JASP). The first two columns populated by numerical data are $P(M)$ and $P(M|\text{data})$, which the former denotes the prior probability of each model and the latter denotes the posterior probability of each model. The next columns represent the Bayes factors with BF_M describing the Bayes factor on the model odds, and BF_{10} describes the relative predictive adequacy of the model compared to the best fitting model.

Models	P(M)	P(M data)	BF_M	BF₁₀	R²
Intrusion + Reservoir flank	0.031	0.098	3.354	1.000	0.328
Intrusion + Reservoir high + Reservoir flank	0.031	0.096	3.291	0.983	0.390
Intrusion + Reservoir flank + Previous He	0.031	0.091	3.117	0.936	0.386
Intrusion + Reservoir high + Reservoir flank + Previous He	0.031	0.078	2.617	0.797	0.430
Reservoir flank + Previous He	0.031	0.052	1.687	0.528	0.267
Basement Fault + Intrusion + Reservoir high + Reservoir flank	0.031	0.050	1.647	0.517	0.390
Basement Fault + Intrusion + Reservoir flank	0.031	0.050	1.618	0.508	0.329
Basement Fault + Intrusion + Reservoir flank + Previous He	0.031	0.049	1.585	0.498	0.387
Basement Fault + Intrusion + Reservoir high + Reservoir flank + Previous He	0.031	0.043	1.382	0.437	0.430
Reservoir flank	0.031	0.038	1.223	0.389	0.161

The most critical migration element of the He-system in the Tohache Wash area are intrusive bodies. These bodies can behave similar to basement faults as they act as migration conduits that support advective buoyancy driven transport from basement granitic source rocks into overlying sediments (Danabalan et al., 2022; Halford et al., 2022, 2023). Regarding the most critical trapping

variable, reservoir flank, the presence of He surface anomalies on reservoir flanks suggest that there are likely faults and associated fractures as a result of differential compaction of the reservoir. This has implications in understanding the trapping potential of the reservoir and deciphering potential prospectively of an area. Although the statistical analysis (Table 5.3) presents the best model as only intrusions + reservoir flanks, by examining real world geologic data we have noticed often times the elements of a He-system are not standalone, rather they build off each other. Namely, the presence of an intrusion as a migration conduit/pathway, and a reservoir flank structure to aid in trapping is often not enough to produce a He-anomaly. Following this line of reasoning, we use the BF inclusion factors as a means to quantifiably rank each variable in our updated probabilistic He model.

Table 5.4: Posterior summary of coefficients for the Bayesian linear regression model (JASP, 2023).

								95% Credible Interval	
Coefficient	Pincl	Pexcl	Pincl data	Pexcl data	BF_{inclusion}	Mean	SD	Lower	Upper
Intercept	1.0	0.0	1.000	0.000	1.000	227.375	26.901	171.155	280.614
Base Fault	0.5	0.5	0.364	0.636	0.572	4.876	42.310	-79.695	133.730
Intrusion	0.5	0.5	0.673	0.327	2.056	73.093	74.295	-4.471	227.830
Fracture nd	1.0	0.0	1.000	-2.220e-16	1.000	-22.337	64.511	-149.91	102.991
Res. high	0.5	0.5	0.438	0.562	0.780	24.454	56.399	-63.658	174.672
Res. flank	0.5	0.5	0.802	0.198	4.060	87.488	63.956	-3.399	201.744
He well	0.5	0.5	0.476	0.524	0.910	33.494	62.113	-50.438	194.337

5.5.4.1 Predictive Framework Model

Building off the initial probability predictive modelling in chapter 4, we utilize a similar approach to determine He-gas rich areas but with the addition of He soil gas data, high density fracture networks, and structural mapping of reservoirs of interest (from 2D seismic and well control). In order to construct an updated predictive model from the Bayesian linear regression models using Tohache Wash area variables and data, we utilize the computed BF inclusion coefficients to act as our weighting factors for our predictive model. The Tohache Wash area was chosen because of the availability of geologic data, high He% well tests (1969 and 2016), high He % soil gas signatures, and likely slow diffusion dominated He leakage in some areas (i.e., greater He preservation). The primary objective is to identify key He-system criteria, understand what combination of He system variables

are most favourable and subsequently search for He-potential in extended areas mapped around Tohache Wash in the Mississippian Leadville Limestone reservoir.

To initiate model construction, we created a fishnet equally spaced point grid every 200 m to reflect the initial spacing of the soil gas survey. Concerning each of the shapefiles and polygons representing the structures of interest, a new field was added to each attribute table with the respective BF inclusion coefficient. For the attributes that are recorded as polygons (i.e., intrusions, fracture intersection nodes), a spatial join tool was used to assign values from the fishnet grid only in areas where polygons overlay the fishnet. For basement faults, a 200 m buffer was constructed around the feature to mirror the soil gas geochemistry survey spacing followed by a spatial join. Concerning the reservoir highs, manual areas were determined based on the highest level of structural contour mapped at a 15 meter contour interval. Regarding reservoir flanks, areas were determined based on the structural geology of the Leadville Limestone to distances ~1km from the crest of the reservoir high. Additionally, areas around previous wells were determined by a 200 meter radius in each direction as the drainage area for each well is unknown. Next, we utilize the computed BF inclusion coefficients to act as our weighting factors for our predictive model and add each factor based on if a structure is physically present at a specific point. We then use the inverse distance weighted (IDW) interpolation method to create a contour map showing probability values, which represents the He probability production map. Therefore, from predictions (using Bayesian coefficients) we compute a probability prediction model, which has been calibrated with historical data, that inputs the predicted variables and translates them into a visual representation of areas where there is lower and higher probabilities of He occurrence.

Upon examining, the predictive model we observe there are two areas with the highest likelihood of encountered He based on the BF inclusion coefficients. The first region corresponds directly with the area of the Navajo Z-1 well (API: 02001053090001) which has produced 6% He. This shows the model is well calibrated with real world data producing a He hot zone where we would likely expect it. The second area, which is ~2.5 km immediately west of the Navajo Z-1 well, is an area of high-He potential. There is likely a third area on the eastern flank of the reservoir high with

a fracture intersection and intrusion presence on the southwest portion) of Fig. 5.11, but due to well/seismic control the accuracy of the Leadville Limestone structure cannot be accurately mapped.

The exact buffer zones around each variable can be adjusted and updated (e.g., when more data is acquired), which allows the model to be highly versatile and adaptable. The significance of this approach is that it allows a site by site specific model that can be calibrated with real world data in order to extrapolate subsurface He gas plays. This approach would be beneficial where there is well control/seismic control to produce reservoir structure maps plus geochemical and geophysical data to integrate/tie data from the surface to the basement and to assess the viability of a He-system. The utility of this predictive model in areas outside of the Four Corners Plateau can be great especially in areas that have experienced some level of geologic and tectonic activity.

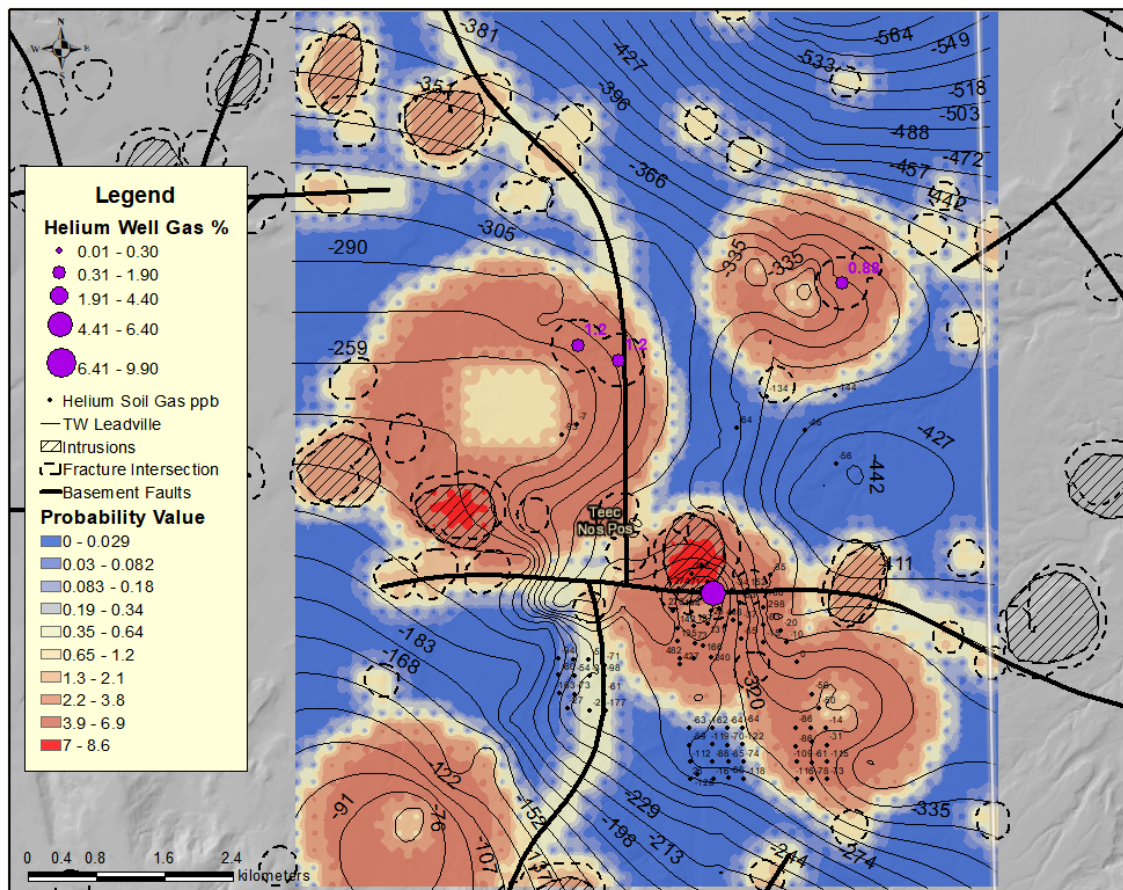


Figure 5.11: Probability model derived from Bayesian linear regression inclusion coefficients shows He-potential in extended areas mapped around Tohache Wash on the Mississippian Leadville Limestone (C.I. 15 m). The model highlights two zones where the model predicts the highest likelihood of encountering subsurface He-rich gas. One zone being the immediate area around a well that produced 6% He, and the other just to the west which indicates a potential new prospect area.

5.6 Conclusions

The importance of structural features influencing advective based migration pathways for subsurface He accumulations has been established in Chapter 4, but these observations were drawn from a widely scattered database of historical He%. Until now, the He data to determine exactly how vital each individual or combination of features is in controlling a He accumulation was not available. Fortunately, we have access to seven soil gas surveys to examine geospatial relationships. By combining historical geochemical data, well log data, 2-D seismic data and potential field geophysical data, we identify structural features and subsequently test their relationship to closely spaced measured He soil concentrations taken at each of the seven areas of interest.

Given we are examining geospatial relationships within the soil gas survey data, it is important to understand the mechanisms that allow the He in the subsurface reservoir to migrate into the soil. We find that in several fields interpreted basement faults act as migration conduits from the basement to the surface (i.e., leaky reservoirs) producing He microseepages, and in other cases there is evidence that He surface signatures are controlled by reservoir flank/crest fracturing likely due to differential compaction. Using a 1-D diffusion loss model, we calculate the amount of He dissolved in water that is lost through diffusion and advocate that for several fields, diffusion appears to play a more dominant role. We propose diffusion loss systems are most ideal for preserving He (based on the rate of loss) once an accumulation has already formed. Given the Tohache Wash area has the highest soil gas signatures, likely partially diffusion dominated leakage, and multiple high He well tests, we conclude it is the most prospective area to be modelled. Thus, we utilize Bayesian linear regression models to predict the most significant variables controlling He occurrences (i.e., flank of the reservoir and intrusions). Using Bayesian inclusion coefficients, we compute a probability prediction model using weighted variables, which has been calibrated with historical data that inputs predicted variables and translates them into a visualization of areas where there are probabilities of high and low He. This model produced an output that matched historical records of anomalous zones and also highlighted an additional area of interest for future He exploration.

Thus, in order to more effectively explore for subsurface He accumulations at a finer scale, surficial soil gas surveys can be effective to provide a closer examination of He's response to

structural features in hopes of finding and developing future He plays when combined with other techniques such as well data, seismic data, geochemical data, and potential field geophysical data. The significance of this approach is that it ties geologic data throughout various depths of the crust (basement, reservoir, and surface) to examine He-systems. Translating this predictive model into other areas where there is sufficient well control and seismic data to map reservoirs can be a powerful tool to mitigate exploration risk.

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Contribution to the Paper	I hereby give permission to Daniel T. Halford to use our joint work as contribution towards his DPhil thesis to be submitted for examination at the University of Oxford. I confirm that to the best of my knowledge, the author contribution statement below is accurate and Daniel T. Halford's contribution towards the work is greater than that of any other co-author. Chapter author contribution statement: The project was conceived by DTH, RK, MWA, and CJB. DTH managed the project, and prepared the first draft of the manuscript. MWA and GR collected the samples. DTH and MWA analysed the samples. Noble gas calculations and models were developed by DTH, RK, and CJB. Structural mapping was completed by DTH and MWA. Geophysical data was produced and made available by BC, MC, and JD. All authors contributed to the final manuscript.
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By signing the Statement of Authorship, you are certifying that the candidate made a substantial contribution to the publication, and that the description described above is accurate.

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Chapter 6

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Conclusions

6.1 Summary and Impact

Helium's usefulness goes far beyond the stereotypical party balloon application, in fact it is a critical element that is involved either directly or indirectly in the medical industry, and many facets of science and engineering due to helium's unique chemical and physical properties. Dwindling supply/reserves of He coupled with the ever-increasing demand of these modern luxuries has created an increased demand for He and subsequently steady increase in price. This surge in prices over the last decade plus multiple projections that He demand will outstrip supply in the near future, has prompted several exploration companies to target He as a primary resource. This is a large departure to the old business model, which was to explore and produce hydrocarbons first and foremost, and any accidentally He found along the way was merely an added bonus. Thus, the primary motivation for this dissertation is to provide an updated framework pertaining to the sourcing and migration of subsurface He with the goal to mitigate risk when exploring for this resource and subsequently to aid in the development of economically viable projects that will contribute to meeting global demand of He and generate streams of revenue to aid local economies surrounding the project.

The noble gases (He, Ne, Ar, Kr, and Xe), which are highly unreactive elements, serve as excellent geochemical physical tracers when investigating the sourcing and migration of He-rich gases dissolved in subsurface crustal fluids (Ozima and Podosek, 2002; Ballentine et al., 2002; Gilfillan et al., 2008; Hunt et al., 2012; Darrah et al., 2014; Byrne et al., 2017; Barry et al., 2016, 2018). Noble gas contributions derived from the atmosphere/air saturated water, crust, or mantle are

distinct and are well documented (Prinzhofer, 2013), and thus allow scientists to quantitatively study the genetic fingerprinting of gas families, mixing between several endmembers, timing constraints, thermal maturity, fluid rock interactions, geological residence times of subsurface fluids, and mass balance calculations between gas, oil, and water phases (Pinti and Marty, 1995; Hunt et al., 2012; Prinzhofer, 2013; Warr et al., 2018). The utilization of noble gas geochemistry is best when combined with knowledge from structural geology and geophysics (aeromagnetic and gravity data). This combination of different branches of science has allowed the construction of quantitative models that have spurred further development of the He-system, namely that of the sourcing provinces and migration mechanisms. Below is a brief synopsis of the major conclusions from each of the chapters.

In Chapter 2, we focus on explaining why the Colorado Plateau, a moderately active tectonic zone (i.e., Four Corners area) in the southwestern USA has such anomalous high He values in its gas fields by utilizing bulk gas analyses and isotopes of non-hydrocarbons, hydrocarbons, and noble gases collected from oil/gas wells (n=31). A similarity of transport mechanisms and sources is inferred for N₂ and He based on their ratios. More specially, a crustal origin for He and N₂ gases in He-rich samples is described by integrating noble gas isotopes, bulk nitrogen values and $\delta^{15}\text{N}$ isotopes. Oil/water equilibrium models with various amounts of air admixture are used to explain hydrocarbon-rich samples. Highly fractionated ⁴He/N₂ values of He-rich samples are modelling with a decoupled advective transport model to understand the process of primary He/N₂ gas migration from basement upwards into the sedimentary section via active tectonics (i.e., crustal gas mobilization and transport via fracture zones). We observe a high level of fractionation in ²⁰Ne/³⁶Ar values of the He-rich samples utilizing a multi-phase water gas model with open system Rayleigh fractionation, which indicates migration over large distances. Interestingly, the fractionation observed with ASW gases, is not observed in regards to ⁴He/N₂ ratios due to fluxes of crustal gases released from basement rocks oversaturating the groundwater. Major observations resulting from He production and mass balance models indicate that external non-reservoir He sources are necessary, the dominant He source rock for these gas fields is likely from the shallow crust (i.e., Precambrian granitic basement) and the fields are likely sourcing gas from large areas beneath the field footprint. We rule out significant contributions from in-situ production of He from the reservoirs as the amount of He produced is too small given the

ages and sizes of the fields. Other observations from the mass balance modelling efforts are that long relatively stable periods to accumulation He are favourable.

In Chapter 3, we examine the impact that heat has on the release of He gases from the crust in an environment that is even more tectonically active than the Colorado Plateau. More specifically, using noble gas and bulk gas data gathered from hot springs ($n=43$) in Yellowstone, USA and the surrounding areas combined with heat flow data, we quantify gas origin and fluid flow in a regional context. Considering our noble gas heat models, we conclude that most Yellowstone samples and non-Yellowstone samples heat and volatile input are likely influenced by convective and degassing processes in the hydrothermal systems that have been influenced by air saturated water (ASW) dilution and also various boiling episodes. Degassing events are observed to be the dominant driver of the ASW noble gases based upon noble gas solubility fractionation models with only minor influence of redissolution. This degassing process seems to be responsible for some fractionation patterns observed for radiogenic He and Ar as well. We also observe minor potential evidence for free molecule mass dependent diffusion processes. A geospatial analysis of heat flow data, and our isotopic and bulk gas data shows that there is a relatively narrow range of moderate heat flow values for the non-Yellowstone samples, and that no singular and simple relationship exists between the heat flow, the distance to the Yellowstone caldera, and the amount of He in the sample. Most samples are located in zones of moderate levels of heat flow (i.e., relatively narrow range, with the exception of Yellowstone samples). Exploring the possibility that we have missed a relationship working with a larger regional heat flow dataset, we examine the effects of localized heating scenarios. To look closer at a localized level, we use a 1-D diffusion model to study the effects that intrusions can have on the geothermal gradient. We find that with small intrusions, the closure temperatures for He-bearing minerals can be reached at much shallower temperatures compared to the normal geothermal gradient. Additionally, we discuss both diffusion and advection migration mechanisms, and advocate that buoyancy-driven vertical transport is likely the dominant process based on the noble gas fractionation models and the area's tectonic history. We also advocate that utilizing a purely distance approach to find He-sweet spots around volcanic centres is ill-advised, and instead advocate that He

explorationists should employ models to understand localized heat flow to understand He release potential combined with the use of isotopic geochemistry to study groundwater interactions.

In Chapter 4, we transition back to the Colorado Plateau (i.e., Four Corners area) and show evidence for structural mechanisms controlling He transport from a deep crustal source into a shallow reservoir, namely basement faults and intrusions. This is the first study that incorporates high-resolution geophysical data (new aeromagnetic survey combined with gravity data) in the Four Corners area. The data corroborates our earlier work's claims of the importance of basement fault/shear zones for He-rich gas fields (Halford et al., 2022) in Chapter 2. Using a spatial analysis and statistical models, we show the relationship of basement faults and intrusions with high-He wells ($n=94$) is not random. We show that there are strong relationships between both the distances to basement faults, intrusions, and high-He occurrences. Moreover, we show that this strong geospatial distance relationship can be quantified and used to create probabilistic models to infer the likelihood of encountering He-rich gas in relation to structural features. We combine He-intrusions and He-faults probabilistic models as a function of distance into a single model to produce a combination basement fault and intrusion predictive probability map where the intersection of these two structural features produces hot regions and the absence of any overlap produces cool coloured regions. Various scenarios involving He-system processes related to faults and intrusion are explored, namely: the exploitation of zones of weakness in the crust (facilitating advective transport/ He migration), the creation of secondary supplementary fracturing by intrusions, and the addition of localized heating provided by intrusions. The significance of the study is broken down into three main points, 1) a quantitative spatial analysis of intrusions and basement faults for He exploration is provided, 2) a predictive framework is put forth that can be utilized in other He prospective areas, especially in zones of active tectonics, and 3) the processes and geologic elements associated with the He-system are updated that describes how basement faults and intrusions can act as migration/focusing conduits allowing basement derived He to migrate via advective buoyancy driven flow into the overlying sediments where the He can accumulate in structural highs.

In Chapter 5, we incorporate He soil gas surveys ($n=1974$) over seven fields taken on the Colorado Plateau (Four Corners area) to examine the utility of soil gas geochemistry and structural

geology at defining potential undiscovered He-plays and to produce an even higher resolution/finer scale predictive model than presented in Chapter 4. We recognize the important of structural controls for He-plays based on previous work (Halford et al., 2022) in chapters 2 and 4. We construct structural maps of reservoirs and examine the He soil gas signatures in relation to structural features. We find that there are localized signals along interpreted basement faults which can propagate to the surface (i.e., He microseepages). We find there are high He signatures over crests and flanks of structures (i.e., spill zones), and we propose that differential compaction induced fractures/faulting is a likely controlling process. We also use production rates for He (internal and external) combined with original He gas in place calculations, to estimate the age of the gas accumulations. We then use this age in a 1-D He diffusion loss model, which estimates the volume of He lost from the reservoir over a unit of time. Calculations reveal that several of the fields are likely influenced by diffusion fluxes, which is interpreted as a favourable factor for He plays because of the slow rate of loss. Other fields are characterized by linear microseepage features along faults, which shows evidence of advective leak driven systems. Taking all this into account, we develop a predictive model that we test on the most favourable area, Tohache Wash, that seems to be dominated by diffusive He loss (i.e., highest He soil gas). The model utilizes Bayesian linear regression models calibrated with historical data to predict the most important variables controlling He-rich plays. A probability prediction model was computed using Bayesian coefficients, which we translate into visual representations of zones of the highest probability of He-rich occurrences. The importance of this approach is that it unites geologic data from the deeper zones (basement), the shallower crust (reservoir) and the surface (soil gas measurements) to examine the He-system. This model can be applied to areas outside of the Colorado Plateau where there is sufficient well control and seismic data to map reservoirs, and we advocate that soil gas surveys can provide useful information about potential He-rich targets.

6.2 Future Work

Concerning recommendations for future work, the top promising areas that would benefit from further research related to He-system development are 1) source rock analyses, 2) fracture analysis models, 3) seal modelling, and 4) helium-hydrogen plays.

Source rock studies, which can be used to better understand the generation of He, are a critical and yet overwhelmingly under developed part of the He-system. In many places, the basement (considered an ample He source rock), is very poorly defined. This can lead to inaccurate model predications of He produced from the basement as the rock parameters such as uranium (U) and thorium (Th) content, porosity, water saturation, etc., are often heterogeneous. For example, more precise parameters of U and Th content beyond the estimates found in Ballentine and Burnard, (2002) and Danabalan (2017) can make substantial differences considering the large volume of the basement. Research concerning uranium deposits should also be incorporated to ensure shallow crustal fluxes of He be accounted for in the overall He flux model. Recently, work in the USA and Canada have utilized geophysical potential field data to map basement terrain and have observed an improved resolution of the basement. On a finer scale, research involving cores and outcrop samples to study the mineralogy and rock properties and provide information such as grain size, porosity, permeability, temperature/pressure regimes, and fracture networks, would be beneficial to understand the generative potential of certain rock types. Additionally, the conduction of additional step-wise heating experiments to observe how He is effectively released at different temperatures for different mineral and rock types is crucial to further quantify He release/retention processes for site-specific mineral assemblages (Lehmann et al., 2003). Given that cores from the basement are relatively rare and relatively pristine outcrop analogues are not always present makes this research challenging.

Various authors have shown how fracture networks can make or break potential gas accumulations (Hyne, 2001). Despite pessimistic views that fault/fracture networks studies are not helpful given the complexity and inherent unknowns associated with connectivity analysis, new advances in data science, artificial intelligence and machine learning challenges these notions. The development of mathematical models that harness new computing methods could be the quantitative tool needed to help constrain potential He migration pathways, understand the potential distribution of He after certain geologic events, and compile boundaries for certain plays (i.e., closed versus open faults). Another promising area that has been utilized in the hydrocarbon industry but needs development for He accumulations is that of assessing the structural integrity of accumulations looking at relatively connectivity of different traps. Combining structural geology approaches with

isotope geochemistry (i.e., noble gas isotopes) would be a powerful reservoir modelling tool (Kennedy et al., 2002). Another underutilized technique that has been used for geothermal exploration, is to interpret information about heat fluxes using satellite imagery (i.e., Landsat and ASTER data) to investigate which surficial expressions could be active and connected to deeper structures that are imaged via geophysical potential field data (i.e., magnetics/gravity data) (Sekertekin and Arslan, 2019). In theory, this could provide information as to whether the faults could be considered active transport conduits. Additionally, understanding the impact that regional stress regimes have on the overall pattern and distribution of lineaments at different scales (Lundstern, and Zoback, 2020) would also benefit studies investigating the nature of faults (i.e., open or closed), and how it would either benefit or hinder He accumulations.

Another useful application of core rock analyses would be more in-depth characterization of He caprocks. This type of modelling for seal analyses is of utmost importance to understand to timing constraints and potential viability of different lithologic units and their water content to effectively impede He fluxes out of a reservoir (Rice, 2022). Incorporating numerical simulations that can model multi-dimensional flow of various fluids and mixtures of those fluids through fractured and porous media can aid in quantifying which lithologies make adequate He seals (e.g., TOUGH3 by Lawrence Berkeley National Laboratory). TOUGH has been used as a screening tool for caprock imperfections with applications in CO₂ storage (Heath et al., 2009), but its utility as a computational program can be applied to He-systems directly. It is well documented that salt/evaporate layers which are extremely impermeable, make the best seals for both hydrocarbons and He (Broadhead and Gillard, 2004), however the dilemma is that many He-rich accumulations of gas are found in reservoirs without such a highly impermeable sealing layer. In fact, many He-rich accumulations have been found in the Four Corners area, with only tight mudstones, shales, and tight limes (Allen, 1978; Danie, 1978; Riggs, 1978; Spencer, 1978). This indicates that more permeable lithologies can slow down fluxes out of the reservoir, which begs the question of how permeable of a seal can support a He accumulation. Deciphering what the impact of a seal rock and its associated capillary pressure on fluid flow will mitigate He play development risk. Advances in the sealing capability of certain rocks for hydrogen storage has also been underway recently (Hassanpouryouzband, 2022; Muhammed, et al., 2022).

Lastly, there is a growing interest for geologic natural hydrogen (H_2) as society strives to implement greener energy initiatives (Zgonnik, 2020; Ellis and Gelman, 2002). This natural H_2 is found as a free gas through drilling activities in the sub surface. H_2 is commonly used in petroleum refining and fertilizer production as well as transportation and utilities (emerging markets) (Singh et al., 2015). Traditionally, H_2 gas has been produced as a by-product of the hydrocarbon industry (via steam methane reformation), but currently due to the large carbon footprint with this method, lower carbon and low-cost alternatives are being considered (i.e., natural H_2). There is speculation that the price of natural H_2 gas can be cheaper in the next decade to drill and produce than H_2 from steam reformation if found in high enough quantities and pure enough grade (IEA, 2022). There are several known H_2 shows in the USA, Australia, Africa and Europe, but the full commercial exploitation of these resources has not been fully developed due to multiple unknowns regarding key elements and processing driving natural H_2 systems (Milkov, 2022; Vidavskiy and Rezaee, 2022). Further work needs to be completed prior to this development to reduce exploration risk. Luckily, there is a strong overlap of several of the geologic processes that control the generation, accumulation, migration and storage of He and hydrogen in the subsurface. This commonality should be the foundation for the development of noble gas geochemical and numerical models to constrain the origin of H_2 (radiolysis, serpentinization, etc.), to understand H_2 fluxes and how to effectively monitor them, to understand how H_2 is interacting with other gas species in the subsurface, to extrapolate whether there is significant impact of microbial life (e.g. monitor reservoir parameters such as temperature, pressure and salinity), and ultimately to assess the long term storage potential of H_2 (i.e., study traps and seals).

Supplementary Information

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Chapter 2 Appendix

2.A.1 The Helium System

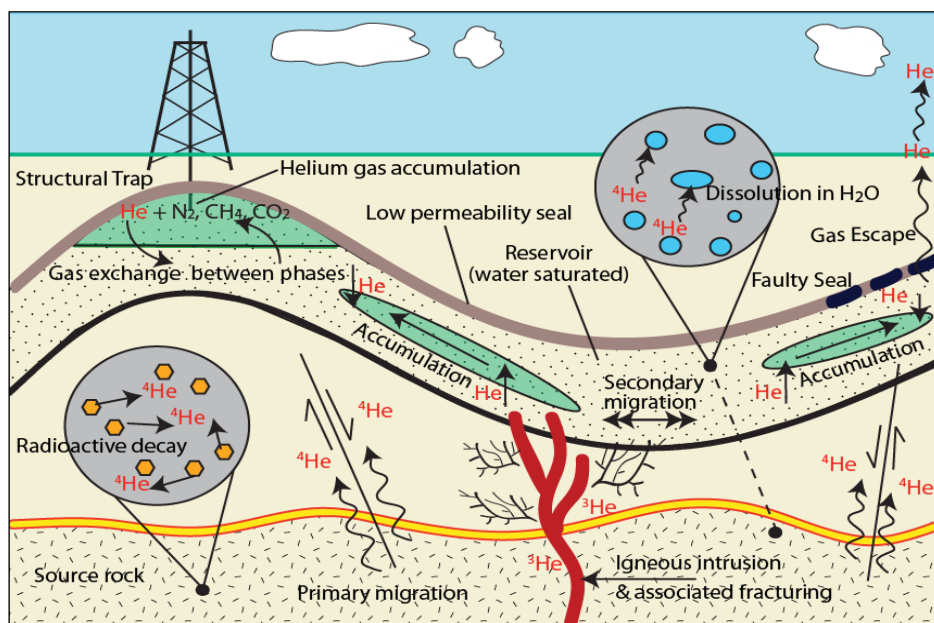


Figure 2.A.1: Geologic model of helium systems in the Four Corners area, southwestern USA. The model illustrates He sources, migration pathways, reservoirs, trapping, and sealing mechanisms. For a complete description of the components see Halford (2018).

Table 2.A.1: A comparison between petroleum and helium systems. Petroleum sources: Dow (1974), Demaison (1984), Meissner et al. (1984), Ulmishek (1986), Magoon (1987, 1992a, 1992b), Magoon and Dow (1994a, 1994b), Perrodon (1992), Magoon (1995), Magoon and Beaumont (1999). Helium sources: Broadhead and Gillard (2004), Brown (2010), Danabalan (2017), Danabalan et al., (2015, 2016, 2022), McDowell et al. (2017), Halford (2018).

Component	Helium System	Petroleum System
Source	Radioactive decay of $^{238,235}\text{U}$ and ^{232}Th	Organic material
Maturation	Time and volume controlled	Pressure and temperature
Primary migration (vertical)	Closure temperature, faulting, mineral degradation $\rightarrow$ expulsion of α particles from host minerals; dissolution into H_2O solution $\rightarrow$ advection	Pressure controlled
Secondary Migration (lateral)	Groundwater gas interactions/migration (dissolution and mobility of helium in pore water), stripping, buoyancy	Buoyancy controlled
Accumulation	Gas phase differentials (exsolution of helium from pore water into a gaseous phase), direct input (gas phase), degassing of oversaturated pore water	Buoyancy and capillary pressure boundaries
Reservoir	Porous and permeable matrix beneath caprock or trap	Porous and permeable matrix beneath a caprock or trap
Trap	Structural, stratigraphic, or combination	Structural, stratigraphic or combination
Seal	One of the most critical and rare components, must be extremely tight	Commonly a shale with limited permeability

A formal definition of a helium system based on previous works (Magoon and Dow, 1994; Broadhead and Gillard, 2004; Brown, 2010; Danabalan et al, 2012, 2015, 2016, 2022; Danabalan, 2017; McDowell et al., 2017; Halford, 2018) and based on isotopic analyses of this study, is any “subsurface natural gas system, and its associated geological processes and elements that allows the accumulation of economic levels of helium ($>0.3\%$ for direct and secondary extraction, >0.04 for liquefied natural gas operations dependent on the economics of the gas stream), in the gas stream beyond the ubiquitous trace amounts found within Earth’s mantle, atmosphere, and crustal sources” (Figure 2.A.1) (Grynja and Griffin, 2016; Boreham et al., 2018; Halford, 2018). Critical aspects of the helium system compared to a conventional petroleum system (Broadhead and Gillard, 2004; Brown, 2010; McDowell et al., 2017; Halford 2018; Danabalan et al., 2022) are summarized in Table A.1.

2.A.2 Generalized Stratigraphy

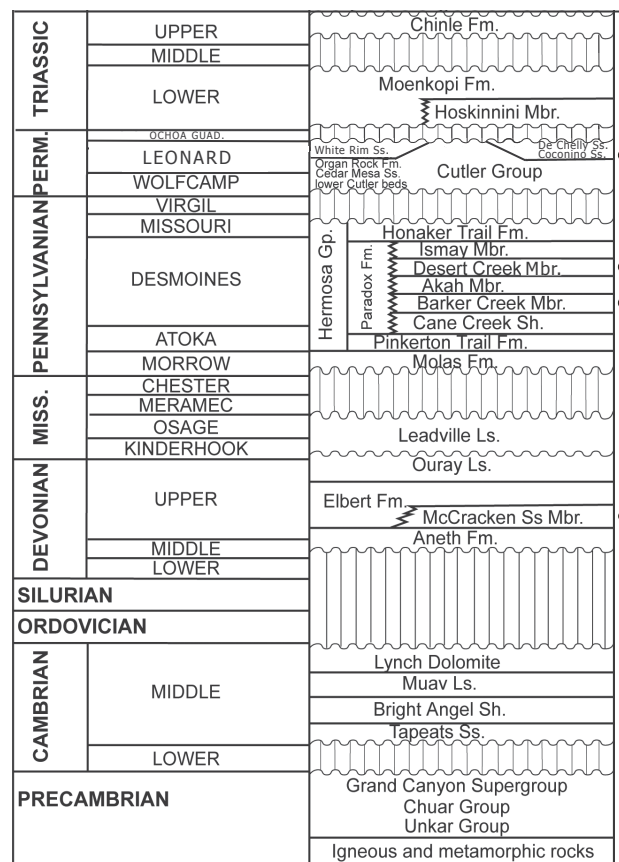


Figure 2.A.2.: Colorado Plateau stratigraphic column modified from Stevenson and Wray (2009) and Lillis et al. (2014). Yellow circles mark sampled intervals (i.e., Devonian McCracken Sandstone, Pennsylvanian Barker Creek Member, Oligocene sill intruded in the Pennsylvanian Barker Creek Member, Pennsylvanian Desert Creek Member, and the Permian Coconino Sandstone).

2.A.3 Groundwater Relationship

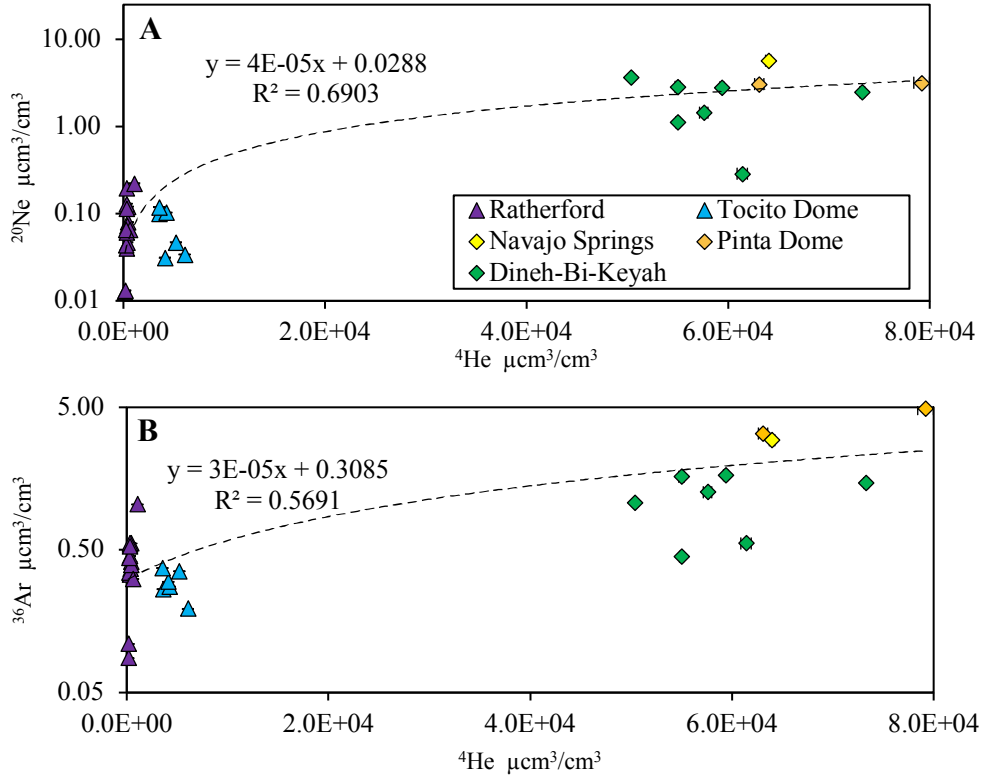


Figure 2.A.3: Plot showing A) ^{20}Ne versus ^4He and B) ^{36}Ar versus ^4He . The moderate positive correlations between ^{20}Ne and ^4He , and moderate to weak positive correlations between ^{36}Ar and ^4He suggest there is a connection between ^4He and groundwater interaction.

2.A.4 Fractionation Models

$$\text{Equation 2.A.1: } C_i^{oil} \text{ mol/kg oil} = \frac{C_i^{asw}}{\frac{v_o}{v_w} + \frac{K_i^{GO}}{(SG)(K_i^{GW})}}$$

where C_i^{asw} = asw concentration of i in mol/kg oil, $\frac{v_o}{v_w} = \frac{\text{volume oil}}{\text{volume water}}$,

K^{GO} = Henry's constant $\frac{\text{atm kg}}{\text{mol}}$ (gas from oil),

K^{GW} = Henry's constant $\frac{\text{atm kg}}{\text{mol}}$ (gas from water), SG = specific gravity g/cm^3

$$\text{Equation 2.A.2: } C_i^{oil} \text{ mol/kg oil} = \frac{C_i^{gas} \text{ GOR metric}}{(SG)(22.4)}$$

where $C_i^{gas} = \text{measured gas} \frac{\text{cm}^3 \text{STP}}{\text{cm}^3}$, $\text{GOR metric} = (\text{GOR}_{\text{imperial}} \times 0.028316) / (0.1589873)$ and $SG = (141.5) / (131.5 + \text{API})$

$$\text{Equation 2.A.3: Binary mixing} = \left(\frac{v_o}{v_w}\right)(i_1) + \left(1 - \frac{v_o}{v_w}\right)(i_2)$$

$$\text{Equation 2.A.4: } \ln f = \ln p + \left(b - \left(\frac{a}{RT}\right)\right) \frac{p}{RT}$$

where $a = 1.408 \text{ L}^2 \text{ atm mol}^{-2}$, $b = 0.03913 \text{ L mol}^{-1}$, p = pressure bar, T = temperature K, R = ideal gas constant, f = fugacity

Table 2.A.2: Field parameters of pressure, depth, temperature, GOR (gas to oil ratio), SG (oil specific gravity), and the Z compressibility factor (Pohlmann, 1967; Freeman, 1978; Spencer, 1978; Danie, 1978; Allen, 1978; Chidsey, 2006; Ballentine et al., 2002; Rutledge, 2010). Temperatures are estimates based on well data, or averages that are extrapolated based on previously published depth and pressure data with a 1.4F/100ft (0.03K/m) geothermal gradient where well data is scarce (Ballentine et al., 2002).

Field	P (psi)	P (bar)	Depth (ft)	Depth (m)	T (K)	T (°C)	GOR	SG _{oil}	Z
Ratherford	2,170	150	5,578	1,700	325	52	69	0.82	126.07
Tocito Dome	3,217	222	6,400	1,950	345	72	730	0.79	175.77
Navajo Springs	124	8.5	1,070	326	299	26	NA	NA	7.77
Pinta Dome	102	7	1,100	335	299	26	NA	NA	6.40
Dineh-Bi-Keyah Barker Creek & Sill	641	44.2	4,045	1,233	310	37	67	.81	38.95
Dineh-Bi-Keyah McCracken	1,314	91	4,582	1,397	312	39	NA	NA	79.67

Table 2.A.3: Table showing the noble gas concentrations in pure water at 283 K at sea level (Ozima and Podosek, 1983; Ballentine and Hall, 1999).

	Initial partial pressure in dry air at sea level (Gpa)	C _{asw} (mol)	C _{asw} mol/cm ³ (H ₂ O)	C _{asw} cm ³ / cm ³
²⁰ Ne	1.67E-09	1.50E-10	8.32E-12	1.86E-07
³⁶ Ar	3.18E-09	1.07E-09	5.95E-11	1.33E-06
⁸⁴ Kr	6.58E-11	4.29E-11	2.38E-12	5.34E-08
¹³² Xe	2.37E-12	2.93E-12	1.63E-13	3.64E-09

Table 2.A.4: Henry's constants K_i in water and light oil, approximate values for C (salinity), and the liquid phase activity and gas phase fugacity coefficients for Ratherford Field (325 K). *parameters for water (Freeman, 1978; Ballentine et al., 2002).

	K _i (Gpa)*	C (M)*	γ*	φ*	$\frac{\gamma}{\phi}$ K _i (Gpa)*	K (Gpa) (light oil)
He	14.43	2	1.62	1.05	22.2	3.69
Ne	13.51	2	1.63	1.05	21.0	3.14
Ar	5.66	2	1.82	0.96	10.73	0.68
Kr	3.43	2	1.87	0.85	7.57	0.23
Xe	2.28	2	1.96	0.80	5.57	0.07

Table 2.A.5: Henry's constants K_i in water and light oil, approximate values for C (salinity), and the liquid phase activity and gas phase fugacity coefficients for Tocito Dome Field (345 K). *parameters for water (Spencer, 1978; Ballentine et al., 2002).

	K _i (Gpa)*	C (M) *	γ*	φ*	$\frac{\gamma}{\phi}$ K _i (Gpa)*	K (Gpa) (light oil)
He	13.38	1.75	1.57	1.08	19.44	3.03
Ne	13.20	1.75	1.54	1.09	19.11	2.65
Ar	6.33	1.75	1.68	0.98	10.91	0.72
Kr	4.05	1.75	1.72	0.84	8.28	0.25
Xe	2.80	1.75	1.80	0.88	5.73	0.10

Table 2.A.6: Henry's constants K^d (dimensionless) in water, C (salinity), the liquid phase activity and gas phase fugacity coefficients, and the K_i in water for Pinta Dome & Navajo Springs fields (299 K) (Allen, 1978; Daniel, 1981; Battino et al., 1982; and Gevantman, 1992, Ballentine et al., 2002; Atkins and De Paula, 2006; Valderrama et al., 2016).

	K_d	C (M)	γ	ϕ	$\frac{\gamma}{\phi} K_i$ (Gpa)
He	106	0.35	1.09	1.01	15.77
Ne	91	0.35	1.10	1.01	13.72
Ar	30	0.35	1.12	0.98	4.72
Kr	17	0.35	1.13	0.94	2.76
Xe	10	0.35	1.14	0.85	1.83
N ₂	-	0.35	1.13	0.99	5.41

Table 2.A.7: Henry's constants K^d (dimensionless) in water, C (salinity), the liquid phase activity and gas phase fugacity coefficients, and K_i in water for the Dineh-Bi-Keyah Field (310 K) (Danie, 1978; Spencer, 1978; Battino et al., 1982; and Gevantman, 1992, Ballentine et al., 2002; Atkins and De Paula, 2006; Valderrama et al., 2016).

	K_d	C (M)	γ	ϕ	$\frac{\gamma}{\phi} K_i$ (Gpa)
He	103	1.75	1.51	1.03	21.69
Ne	92	1.75	1.57	1.03	20.08
Ar	34	1.75	1.73	0.97	8.67
Kr	20	1.75	1.78	0.89	5.63
Xe	12	1.75	1.85	0.83	3.96
N ₂	-	1.75	1.86	0.97	10.42

2.A.5 Discounted Models

Theoretically a single stage phase equilibrium fractionation where groundwater degasses (Equation 2.A. 5), could account for the $^{20}\text{Ne}/^{36}\text{Ar}$ signatures in the Ratherford samples, Tocito Dome samples, and for the lowest Dineh-Bi-Keyah and Pinta Dome samples. The maximum equilibrium fraction for $^{20}\text{Ne}/^{36}\text{Ar}$ in the gas phase is 0.84 under reservoir conditions. This takes into account air in excess of solubility equilibrium at recharge ($^{20}\text{Ne}/^{36}\text{Ar} = 0.52$), and the gas phase's maximum equilibrium fractionation ($^{20}\text{Ne}/^{36}\text{Ar} = 0.32$) under reservoir conditions (Equation 2.A.5) (Zhou et al., 2012). However, it is unlikely a single stage model is a dominant mechanism to explain extreme fractionation in that the majority of high measured $^{20}\text{Ne}/^{36}\text{Ar}$ samples are >0.84 .

$$\text{Equation 2.A.5: } \left(\frac{[i]}{[Ar]} \right)_{\text{gas}} = \left(\frac{[i]}{[Ar]} \right)_{\text{groundwater}} \frac{\frac{\gamma_i}{\phi_i} K_i^{\text{groundwater}}}{\frac{\gamma_{Ar}}{\phi_{Ar}} K_{Ar}^{\text{groundwater}}}$$

where K = Henry's constant $\frac{\text{atm kg}}{\text{mol}}$, $\frac{\gamma_i}{\phi_i}$ = $\frac{\text{liquid phase activity coefficient}}{\text{gas phase fugacity coefficient}}$

Oil Contributions

1) Equilibration with an oil phase and groundwater depends on whether or not there is evidence of significant oil interaction in the reservoirs. All of the new samples were taken from

intervals with known hydrocarbons with the exclusion of the Pinta Dome and Navajo Springs samples, for which we can exclude this model. Since argon is more soluble compared to neon in oil than water, further equilibration of the groundwater into the oil phase could increase the $^{20}\text{Ne}/^{36}\text{Ar}$ ratio in groundwater (Gilfillan et al., 2008). We calculate a Rayleigh open system model by plotting $^{84}\text{Kr}/^{36}\text{Ar}$ vs $^{20}\text{Ne}/^{36}\text{Ar}$ (Equation 2.A.6) where oil is migrating through water in an open system and noble gases are partitioned between the oil and water according to Rayleigh fractionation (Ballentine et al., 2002). We determine the magnitude of fractionation in a water phase that has interacted with an oil phase (in lieu of a gas phase). The model discussed only works by increasing Kr's % by several hundred percent. Kr and Xe enrichments are commonly associated with adsorption to organic-rich sediment (Torgersen and Kennedy, 1999). Although there are reasonable fits for the hydrocarbon-rich fields (Ratherford and Tocito Dome), we observe that the oil-water equilibration model presented is not able to comprehensively explain the extreme $^{20}\text{Ne}/^{36}\text{Ar}$ samples of the Dineh-Bi-Keyah, Navajo Springs and Pinta Dome fields.

$$\text{Equation 2.A.6: } \left(\frac{[i]}{[Ar]} \right)_g = \left(\frac{[i]}{[Ar]} \right)_o P^{(\alpha-1)}$$

$$\text{where } \alpha \text{ is the fractionation coefficient} = \frac{K_i^{\text{water}} K_{Ar}^{\text{oil}}}{K_i^{\text{oil}} K_{Ar}^{\text{water}}},$$

$$\left(\frac{[i]}{[Ar]} \right)_o = \text{original liquid phase ratio,}$$

$$p = \text{the fraction of Ar remaining in the water phase}$$

2) Organic-rich sediments/oil, which have essentially adsorbed and trapped atmospheric krypton and xenon, are capable of causing resolvable increases in $^{84}\text{Kr}/^{36}\text{Ar}$, $^{130}\text{Xe}/^{36}\text{Ar}$, and $^{132}\text{Xe}/^{36}\text{Ar}$ values (in excess of the groundwater water values) by releasing the atmospheric krypton and xenon (Frick and Chang, 1997; Zhou et al., 2005; and Gilfillan et al., 2008). ^{84}Kr vs ^{132}Xe (normalized to air) illustrates the effect of the heavier noble gases being trapped in sediments rich in organics (Equation 2.A.7) (Frick and Chang, 1977). By studying gas samples from coal's biogenic gas breakdown in the San Juan Basin, Zhou et al. (2005) provides evidence that excess of krypton and xenon can survive low degrees of thermal alteration and sedimentary consolidation. This option might have certain impact on this study's samples, as the Ratherford, Tocito Dome, and Dineh-Bi-Keyah reservoirs are adjacent to organic-rich source rocks for hydrocarbons and historically have produced hydrocarbons,

but ultimately since option 1 models do not fit the data, this mechanism for excess $^{20}\text{Ne}/^{36}\text{Ar}$ is not considered dominant.

$$\text{Equation 2.A.7: } (F) \text{ Noble gas ratio} = \frac{[(\frac{i}{^{36}\text{Ar}})_{\text{sample}}]}{[(\frac{i}{^{36}\text{Ar}})_{\text{air}}]}$$

Non-Equilibrium Diffusion

3) Non-equilibrium diffusion is another method that could fractionate $^{20}\text{Ne}/^{36}\text{Ar}$ and $^{84}\text{Kr}/^{36}\text{Ar}$ beyond gas/water phase equilibrium. Although because no significant fractionation (mass related) is observed in relation to the $^{20}\text{Ne}/^{36}\text{Ar}$, $^{20}\text{Ne}/^{22}\text{Ne}$, and $^{38}\text{Ar}/^{36}\text{Ar}$ (not shown) for He-rich fields, this method is probably not significant for the reservoirs for ASW components (Pinti et al., 1999; Ballentine et al., 2002; Holland and Gilfillan, 2013). Pertaining to other gas reservoirs, Gilfillan et al. (2008) notes that in situations where groundwater gases' mass dependent fraction is observable for $^{38}\text{Ar}/^{36}\text{Ar}$ and $^{20}\text{Ne}/^{22}\text{Ne}$ values, the fractionation has been largely controlled by solubility (Zhou et al., 2005). Concerning radiogenic noble gases migration, $^4\text{He}/^{40}\text{Ar}^*$ vs $^{21}\text{Ne}^*/^{40}\text{Ar}^*$ are plotted with a free molecule diffusion model (Equations 2.A.8 and 2.A.9) and no significant relationship with a diffusion-controlled fractionation gradient is observed (Figure 2.A.4).

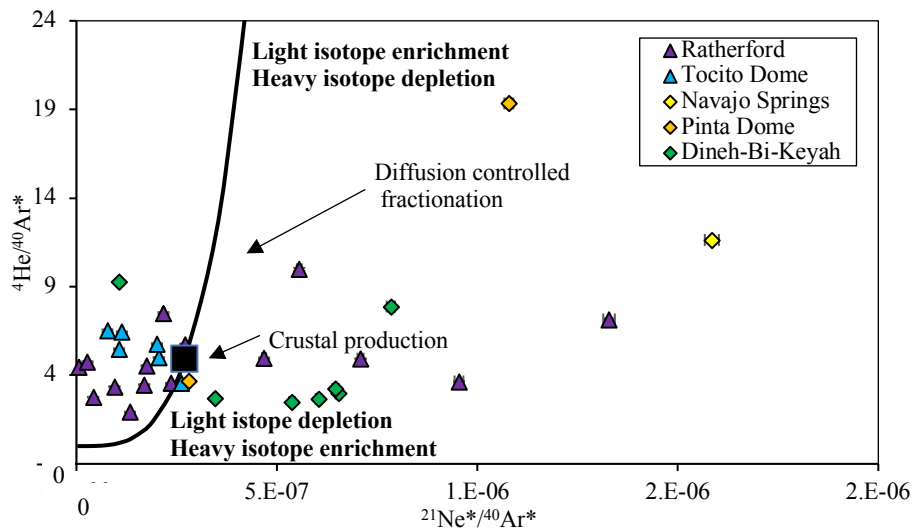


Figure 2.A.4: Plot showing $^4\text{He}/^{40}\text{Ar}^*$ vs $^{21}\text{Ne}^*/^{40}\text{Ar}^*$, which shows the expected diffusion- controlled fractionation gradient (Equations 2.A.8 and 2.A.9) with an average production ratio of $^4\text{He}/^{40}\text{Ar}^*$ of 4.92, and $^{21}\text{Ne}^*/^{40}\text{Ar}^*$ of 2.7×10^{-7} (Li et al., 2020; Ballentine and Burnard, 2002; Holland and Gilfillan, 2013). No significant diffusive gradient is observed in relation to our samples.

$$\text{Equation 2.A.8: } \left(\frac{[i]}{[\text{Ar}]}\right)_{\text{gas}} = \left(\frac{[i]}{[\text{Ar}]}\right)_o \times \alpha \quad \text{where } \alpha = \left[\left(\frac{\text{mass}_2}{\text{mass}_1}\right)^{\frac{1}{2}}\right]$$

$$\text{Equation 2.A.9: } \left(\frac{[i]}{[Ar]} \right)_{gas} = \left(\frac{[i]}{[Ar]} \right)_o \times \alpha \quad \text{where } \alpha = \left[\left(\frac{mass_1}{mass_2} \right)^{\frac{1}{2}} \right]$$

Multi Stage Phase Equilibrium

4) A multi-stage phase equilibrium fractionation (resolution and effervescence) model is theorized as a mechanism to elevate the $^{20}\text{Ne}/^{36}\text{Ar}$ ratio (Zartman et al., 1961; Ballentine et al., 2002). This method requires fluctuating salinity, temperature and pressure regimes (Gilfillan et al., 2008; Zhou et al., 2012). In theory this method, which would require multiple iterations of gas exsolution/redissolution and a low gas/water volume ratio, can be used to explain noble gas concentrations, which are in excess of a single step phase fractionation value (Gilfillan et al., 2008; Ballentine et al., 2002). Given that the process requires fluctuating physical conditions to allow the gas to exsolve and redissolve several times, this model seems implausible. Additionally, Ballentine et al., (2002) state the usual resulting fractionated gas volume is often too minor (in relation to the fluid water volume) to produce large-scale fractionation patterns that can be concisely recognized. Considering that this process requires exorbitant volumes of water (even compared to reasonable values in a dynamic system) and knowing the relative gas/water ratios of the high He fields, the multi-stage exsolution and dissolution model is not viewed as significant.

Nitrogen Redissolution of ASW Noble Gases

5) For the He-rich systems, utilizing an open system Rayleigh fractionation model (partial exsolution and dissolution) with N_2 as a primary carrier gas, can explain high $^{20}\text{Ne}/^{36}\text{Ar}$ ratios and high ^{20}Ne concentrations. Open system Rayleigh fractionation and closed batch models are calculated, with the assumption that noble gases have been directly degassed from water (Equations 2.A.10-A.14) (Zhang et al., 2019). We subsequently create a two-stage model where in stage one, noble gases that are dissolved in water partition into the pristine gas phase within a closed system (Equations 2.A.13 and A.14), and stage two, where N_2 dissolves back into groundwater solution (Rayleigh curves) concentrates the remaining gas (Ballentine et al., 2002) (Equation 2.A.15). Initial $^{20}\text{Ne}/^{36}\text{Ar}$ ASW composition (0.14) is at 10 °C with assumed recharge elevations ranging from ~1436m-2590m (4,714 ft -8,500 ft).

Nitrogen, which is modelled as the carrier gas, is chosen to be redissolved due to high quantities of measured gas from wellhead samples. Although this method is able to achieve increases in ^{20}Ne and $^{20}\text{Ne}/^{36}\text{Ar}$, it does so by redissolving extremely high amounts +90% of nitrogen back into solution. This extreme nitrogen redissolution is determined to be highly unlikely considering geologic conditions. It is also impossible to accurately extrapolate information related to helium concentration from this method, which is a primary goal of this manuscript. For these reasons, the nitrogen redissolution model with ^{20}Ne and $^{20}\text{Ne}/^{36}\text{Ar}$ is discounted to explain high helium occurrences.

$$\text{Equation 2.A.10: } \left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]} \right)_g = \left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]} \right)_{ow} P^{(\alpha-1)} \alpha$$

$$\begin{aligned} \text{Equation 2.A.11: } \left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]} \right)_w &= \left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]} \right)_{ow} P^{(\alpha-1)} & (36_{\text{Ar}})_w &= P (36_{\text{Ar}})_{ow} \\ (20_{\text{Ne}})_w &= (36_{\text{Ar}})_w \left(\frac{[^{20}\text{Ne}]}{[^{36}\text{Ar}]} \right)_w & (20_{\text{Ne}})_g &= \frac{[(20_{\text{Ne}})_w (K_d)]}{Z} \end{aligned}$$

where α is the fractionation coefficient = $\frac{\gamma_{\text{Ne}} K_{\text{groundwater}}^{20\text{Ne}}}{\gamma_{\text{Ar}} K_{\text{groundwater}}^{36\text{Ar}}}$, $(36_{\text{Ar}})_{ow} = asw \text{ cm}^3 / \text{cm}^3$,

$(20_{\text{Ne}})_w = asw \text{ cm}^3 / \text{cm}^3$, P = the fraction of Ar remaining in the water phase;

$$K_d = \frac{K \frac{\text{atm kg}}{\text{mol}}}{\text{gas constant} \frac{\text{atm kg}}{\text{mol K}} \times \text{temperature K}} \times \frac{\gamma_{\text{Ne}}}{\phi_{\text{Ne}}}$$

$$\text{Equation 2.A.12: } Z = \frac{(273.15)(P_R)}{T_R}$$

P_R = reservoir pressure (bar) and T_R = reservoir temperature (K)

$$\text{Equation 2.A.13: } \left(\frac{[i]}{[Ar]} \right)_g = \left(\frac{[i]}{[Ar]} \right)_T \frac{\left(\left(\frac{V_g}{V_l} \right) + \left(\frac{1}{K_d^i} \right) \right)}{\left(\left(\frac{V_g}{V_l} \right) + \left(\frac{1}{K_d^i} \right) \right)}$$

where $K_d = \frac{K \frac{\text{atm kg}}{\text{mol}}}{\text{gas constant} \frac{\text{atm kg}}{\text{mol K}} \times \text{temperature K}} \times \frac{\gamma_i}{\phi_i}$,

$$\left(\frac{[i]}{[Ar]} \right)_T = \text{original ratio; } \frac{V_g}{V_l} = \frac{\text{volume gas}}{\text{volume liquid}}$$

$$\text{Equation 2.A.14: } (20_{\text{Ne}})_g = (20_{\text{Ne}})_t \cdot \frac{1}{\frac{V_g}{V_l} + \frac{1}{K_{\text{Ne}}^d}} \cdot \frac{1}{Z}$$

where $(20_{\text{Ne}})_t = asw \text{ cm}^3 / \text{cm}^3$

$$\text{Equation 2.A.15: } \left(\frac{[^{20}\text{Ne}]}{[N_2]} \right) = \left(\frac{[^{20}\text{Ne}]}{[N_2]} \right)_o P^{\left(\frac{1}{\alpha}-1\right)} \quad \& \quad \left(\frac{[^{36}\text{Ar}]}{[N_2]} \right) = \left(\frac{[^{36}\text{Ar}]}{[N_2]} \right)_o P^{\left(\frac{1}{\alpha}-1\right)}$$

where α is the fractionation coefficient = $\frac{\gamma_i K_{\text{groundwater}}^{i}}{\gamma_{N_2} K_{N_2}^{\text{groundwater}}}$,

P = the fraction of Ar remaining in the water phase

2.A.6 Gas Gap

To determine if gas is moving in a free gas or solution state, calculations are completed to ascertain the presence or absence of a gas cap. Given that the Ratherford and Tocito Dome samples yielded high hydrocarbon content (dominantly CH₄) and the fields have produced hydrocarbons, oil bubble points are calculated with each reservoir conditions. The bubble point pressure is subsequently compared that to reservoir pressure to determine if the solution is undersaturated or oversaturated to establish if there is a gas cap (no gas cap/undersaturated: reservoir pressure > bubble point of oil; gas cap/saturated: reservoir pressure ≤ bubble point of oil). To calculate oil's bubble point, the Standing 1947 method is selected for its reliability and robustness. Utilizing the parameters in Table A.8, Ratherford Field and Tocito Dome Field do not have an initial hydrocarbon gas cap (i.e., undersaturated). The lowest GORs from each field are utilized to attempt to replicate initial reservoir conditions, however increases in GOR values can alter the oil bubble point pressure.

Concerning the dry gas fields (Dineh-Bi-Keyah, Navajo Springs and Pinta Dome) due to the lack of hydrocarbons, the saturation or unsaturation of nitrogen (i.e., dominant gas) is calculated in groundwater. By utilizing Henry's Law, we calculate the maximum concentration of nitrogen dissolved in water, compare the N₂ concentration to the total amount of water in the reservoir (based on volume, porosity and water saturation), and calculate the total number of moles of nitrogen in the reservoir. Utilizing the previously mentioned calculations, we determine the mole fraction of the N₂ that is in the groundwater solution. Thus, we have determined that there will most likely be a pristine nitrogen gas cap in all of the dry gas fields. It is assumed for the Navajo Springs and Pinta Dome samples there is a pristine gas cap in the upper parts of the reservoir while there is a water saturated interval in the lower portions of the reservoir (Ballard, 2018). The primary type of drive for the Navajo Springs and Pinta Dome is gas expansion with a northern titled gas water contact, which is a primary reservoir drive for a reservoir below the bubble point (i.e., an indication there is a likely gas cap) (Allen, 1978).

Regarding the Tocito Dome, if higher than minimum GOR values are used, the bubble point calculations indicate that there could have been a pre-existing gas cap. This introduces a confounding variable in our model as our data could in theory be supported by potential mixing with an elevated

$^{20}\text{Ne}/^{36}\text{Ar}$ endmember indicative of a gas cap or three component mixing (i.e., rightward shift of data on Figure 2.8B). Unfortunately, the assumptions with this line of reasoning are too abundant as we have no reasonable indication as to what this unknown gas cap endmember would be. To avoid scientific speculations and conjectures, we have excluded the three-component (water/oil/gas) mixing as significant at this point in time.

Table 2.A.8. Parameters utilized in gas cap calculations (Freeman, 1978; Spencer, 1978; and Danie, 1978). GORs are minimal values from well folder information.

Parameters	Ratherford	Tocito Dome
Gas specific gravity (SG)	0.82	0.79
Oil gravity (API)	40	44-47
GOR scf/stb (sm^3/sm^3)	69 (12)	730 (130)
Temperature °F (K)	125 (325)	161 (345)
Bubble point pressure psia (kPa)	256 (1,765)	1981 (13,659)
Reservoir pressure psia (kPa)	2170 (14,962)	3217 (22,180)
Initial gas gap	No	No
Gas drive	Solution gas	Water, gravity, solution gas

2.A.7 In-Situ Mass Balance Connection with Multi-Phase Fractionation Model

Hydrocarbon-rich

Tying the in situ mass balance models back to the multi-phase fractionation models, we compare the calculated in situ reservoir helium production to the moles of He dissolved in solution (oil/water) via calculated oil/water ratios (Figure 2.8A&B). In the Ratherford and Tocito Dome fields, we calculate the concentrations of helium (moles) dissolved in both water and oil. Once the maximum oil concentration has been calculated from Equation 2.A.2, it is then straightforward to use the original oil in place (OOIP; Equation 2.A.16) to determine the amount of helium dissolved in oil. Equation 2.A.17 is utilized to calculate the moles of helium dissolved in water (Table 2.A.9) (Lyons, 2010; Mireault et al., 2007; Ballentine et al., 2002). The volume ratios used in Equation 2.A.17 are taken from the values presented in Table A.10 (helium is assumed to have similar ratios to the atmospheric noble gases). These values of helium are then compared to in situ production of helium from the reservoir (Equations 2.4 and 2.5). The age of 300 Mya is used to calculate the in situ helium as it roughly corresponds to the time period after emplacement of the seal. Results indicate that the dissolved helium in oil and water for the Ratherford and Tocito Dome fields are larger than the

amount of reservoir helium produced in situ by roughly 10X and 18,522X respectively, which indicates either larger rock volumes are required or the reservoir has been subjected to extensive subsurface groundwater flow (Table 2.A.9).

$$\text{Equation 2.A.16: } OOIP_{imperial} = \frac{7758Ah\phi(1-S_w)}{B_{oi}}$$

Where $OOIP$ (STB), 7758 = API bbl per acre – feet conversion,
 A = reservoir area acre, h = pay interval thickness ft, ϕ = porosity,
 S_w = water saturation, and B_{oi} = oil formation volume factor (bbl/stb) (Standing, 1947)

$$OOIP_{metric} = \frac{Ah\phi(1-S_w)}{B_{oi}}$$

Where $OOIP$ (m^3), A = reservoir area m^2 , h = pay interval thickness m,
 ϕ = porosity, S_w = water saturation,
and B_{oi} = oil formation volume factor (m^3/m^3)

$$\text{Equation 2.A.17: } [i]_{oil} = [i]_T \left(\frac{V_{H_2O}}{V_{oil}} \times \frac{P_{H_2O}}{P_{oil}} \times \frac{K^M_{He\ Oil}}{K^M_{He\ H_2O}} + 1 \right)^{-1}$$

where p = density $\frac{g}{cm^3}$, K = Henry's constant in molality $\left(\frac{atm\ kg}{mol}\right)$,
 $i_T = i_{H_2O} + i_{oil}$

Table 2.A.9: Helium dissolved in oil and water for each of the hydrocarbon-rich reservoirs for stage 1. The last column (X) shows the total dissolved He (oil + water) for each field over the total in situ He reservoir production moles. He concentrations are averaged for each field.

Field	K H ₂ O $\frac{atm\ kg}{mol}$	K Oil $\frac{atm\ kg}{mol}$	Dissolved moles H ₂ O	Dissolved moles oil	In situ He moles	X
Ratherford	3941.26	654.87	3.31E+7	3.27E+7	6.84E+6	9.61
Tocito Dome	3451.89	551.57	8.26E+10	1.63E+9	4.55E+6	18,521.98

2.A.8 Water Oil Volumes

Hydrocarbon-Rich Gases

Regarding hydrocarbon-rich Ratherford and Tocito Dome fields, we assume the volume of initial gas is insignificant to alter the predicted oil/water ratios, and thus present a two-component exchange model of an oil/water system, as a minimum underestimate for noble gases dissolved in oil and V_w/V_o ratios. Reservoir volumes (litres) are: 3.27×10^{10} for the Ratherford and 1.80×10^{10} for the Tocito Dome. Reservoir volume, which represents the total amount of space available, is a maximum value (area, thickness, porosity), not including S_w . OOIP (original oil in place) in litres is: 2.33×10^{10}

for Ratherford and 9.68×10^9 for Tocito Dome (Equation A.16). We assume no significant compressibility for OOIP.

Table 2.A.10: Oil/gas average volumes (Ne, Ar) for hydrocarbon-rich samples (stage 1). %: of the total amount of H₂O required for each well/total volume.

Well	V_w/V_o	V_w	%
Ratherford: #12-23; #13-41; #20-66; #20-42; #20-44; #29-31; #15-33; #16-41; #10-14; #10-32; #17-11; #17-22; #13-12	5.0	1.17E+11	357
Ratherford: #9-34, #17-13	1.3	3.03E+10	93
Tocito Dome: U # 9; U #7; U #12; N #1; N #11; P #6	250	2.42E+12	13,447

For the hydrocarbon-rich samples, $V_{\text{water}}/V_{\text{oil}}$ (V_w/V_o) ratios (Table 2.A.10) are determined from the oil/water black dissolution curve presented in Figure 2.8A&B, which represents the complete degassing (^{20}Ne and ^{36}Ar) from a closed system groundwater solution (Equation 2.A.1). V_o/V_w ratios from the dissolution curve (Equation 2.A.1) provide the amount of water required for the oil to move through to acquire the observed noble gas signature during stage 1. Comparing the volume of water required to fully reconstruct the observed noble gas (^{20}Ne and ^{36}Ar) concentrations in oil and the reservoir volume with 100% open capacity, we observe that the amount of water needed to yield the observed gas compared to the entire reservoir water volume cannot be explained by the volumes of water present within the field/reservoir boundaries for Ratherford and Tocito Dome samples. This supports the statement that the amount of water in the reservoir itself is insufficient to produce the observed dissolved gas signatures in oil (Table A.10).

2.A.9 Mass Balance Model Tables

Considering the mass balance model, critical depths are the contacts of the overburden and reservoir, and the contact between the sediments underlying the reservoir and the basement. Fortunately, the first contact can be established from analysing perforation depths on well logs. Determining the basement contact is more problematic due to lack of data (with the exception of the Dineh-Bi-Keyah Field, which has well logs/files that record basement depth), and was therefore roughly estimated using average basement structure data relative to sea level from Butler (1991).

Table 2.A.11: Mass balance parameters: fields (reservoirs), B_{gi} formation volume factor, area in ft^2 and m^2 of the field, not including surrounding areas, thickness in feet and meters, ϕ porosity, S_w water saturation, original gas in place (OGIP) in cubic feet and meters³, He mol % are field averages. (Allen, 1978; Freeman, 1978; Spencer, 1978; and Danie, 1978).

Fields (Reservoirs)	B_{gi} rcf/scf	Area ft^2 (m^2)	Thickness ft (m)	ϕ	S_w	OGIP cf (m^3)	He %
Ratherford (Desert Creek)	153.46	5.66E+08 (5.26E+07)	20 (6.1)	0.102	0.25	1.18E+11 (3.33 E+09)	0.04
Tocito Dome (Barker Creek)	203.85	4.36E+08 (4.05E+07)	17 (5.19)	0.086	0.25	8.61E+10 (2.44E+09)	0.45
Navajo Springs (Coconino)	8.21	1.93+08 (1.79E+07)	32 (9.76)	0.16	0.32	4.88E+09 (1.38E+08)	6.4
Pinta Dome (Coconino)	6.75	2.15E+8 (1.99E+07)	61 (18.61)	0.14	0.29	7.77E+09 (2.20E+08)	7.0
Dineh-Bi-Keyah (Barker Creek)	47.18	2.27+08 (2.10E+07)	80 (24.4)	0.1	0.25	5.67E+10 (1.61E+09)	5.0
Dineh-Bi-Keyah (McCracken)	57.37	2.27+08 (2.10E+07)	60 (18.3)	0.135	0.2	7.45E+10 (2.11E+09)	7.3
Dineh-Bi-Keyah (sill)	47.18	1.52+08 (1.42E+07)	80 (24.4)	0.1	0.35	3.31E+10 (9.37E+08)	5.7

Table 2.A.12: Radiogenic production of 4He (atoms, feet³ and meters³) considering the relevant reservoir volumes (Table A.11) and time (300 Mya, except Pinta Dome & Navajo Springs 235 Mya, Dineh-Bi-Keyah sill 30 Mya, and Dineh-Bi-Keyah McCracken 370 Mya). Original helium in place (OHIP) is presented along with in situ He production from the reservoir as well as the percentage of external helium that would be required. The last column reports the increase in field area to supply roughly 100% of in situ He. Field and reservoirs are abbreviated: Ratherford (Desert Creek) = R, DC; Tocito Dome (Barker Creek) = TD, BC; Navajo Springs (Coconino) = NS, C; Pinta Dome (Coconino) = PD, C; Dineh-Bi-Keyah (Barker Creek) = DBK, BC; Dineh-Bi-Keyah (McCracken) = DB, Mc; and Dineh-Bi-Keyah (sill) = DBK, S.

Field, Res.	He (atoms)	He (ft^3)	He (m^3)	OHIP (ft^3)	OHIP (m^3)	He% _{in situ}	He% _{Ext.}	He _{in situ} 100
R, DC	4.12E+30	5.43E+06	1.54E+05	4.39E+07	1.24E+06	12.36	87.64	8.1x
TD, BC	2.74E+30	3.61E+06	1.02E+05	3.88E+08	1.10E+07	0.93	99.07	107x
NS, C	1.64E+30	2.16E+06	6.11E+04	3.12E+08	8.84E+06	0.69	99.31	145x
PD, C	3.56E+30	4.69E+06	1.33E+05	5.44E+08	1.54E+07	0.86	99.14	116x
DBK, BC	6.60E+30	8.71E+06	2.46E+05	2.84+09	8.03E+07	0.31	99.69	325x
DBK, Mc	5.90E+30	7.78E+06	2.20E+05	5.44E+09	1.54E+08	0.14	99.86	700x
DBK, S	4.37E+29	5.76E+05	1.63E+04	1.89E+09	5.34E+07	0.03	99.97	3275x

Table 2.A.13: The sedimentary column (reservoir + underlying sediments) and basement thicknesses (feet and meters) concerning volumes of rock directly under the field area are derived in part from Dunlap (1969); Allen (1978); Freeman (1978); Spencer (1978); Danie (1978), Butler (1991), and Halford (2018).

Field	Lithology	Total Column (ft)	Total Column (m)	Closure Depth (ft)	Closure Depth (m)
Ratherford	Sedimentary	1,835	559	1,406	429
Ratherford	Basement	25,395	7,740	25,395	7,740
Tocito Dome	Sedimentary	977	298	977	298
Tocito Dome	Basement	25,493	7,770	25,493	7,770
Navajo Springs	Sedimentary	1,699	518	0	0
Navajo Springs	Basement	30,047	9,158	27,998	8,534
Pinta Dome	Sedimentary	2,198	670	0	0
Pinta Dome	Basement	29,512	8,995	27,962	8,523
Dineh-Bi-Keyah (Barker Creek)	Sedimentary	763	233	0	0
Dineh-Bi-Keyah (Barker Creek)	Basement	27,991	8,532	27,205	8,292
Dineh-Bi-Keyah (McCracken)	Sedimentary	235	72	0	0
Dineh-Bi-Keyah (McCracken)	Basement	27,991	8,532	27,205	8,292
Dineh-Bi-Keyah (sill)	Sedimentary	763	233	0	0
Dineh-Bi-Keyah (sill)	Basement	27,991	8,532	27,205	8,292

Regarding the parameters laid forth in Table 2.A.13, approximate elevations and overburden thicknesses (depth to perforations) are utilized with discovery well information for the Ratherford, Tocito Dome, Navajo Springs, and Pinta Dome samples (Allen, 1978; Freeman, 1978; Spencer, 1978). The elevation for the Dineh-Bi-Keyah intervals is from the well Navajo Tract 88-2 (Halford, 2018). Overburden thicknesses for the Dineh-Bi-Keyah (sill), Dineh-Bi-Keyah (Barker Creek), and Dineh-Bi-Keyah (McCracken) are from the well files from the Arizona Oil and Gas commission for the Navajo Tract 88-2 well (Halford, 2018). The field elevations are treated as average values.

Table 2.A.14: Production of ^4He from sedimentary external sources (S) with an assumed 100% production and release. R = Ratherford, TD = Tocito Dome, NS = Navajo Springs, PD = Pinta Dome; DBK BC = Dineh-Bi-Keyah (Barker Creek), DBK MC = Dineh-Bi-Keyah (McCracken). The release window ^4He production, which represents ^4He production and release from intervals that lie above the closure temperature release interval for apatite (55°C), is calculated with the geothermal gradient of 1.4 °F/100 ft or (~25 °C/km).

Field (age Mya)	Produced ^4He (atoms)	^4He volume produced (ft ³)	^4He volume produced (m ³)	% of ^4He to fill the reservoir	Produced ^4He (atoms) in release window	^4He volume produced (ft ³)	^4He volume produced (m ³)	% of ^4He to fill the reservoir
R (300)	3.78E+32	4.98E+08	1.41E+07	8.81	2.90E+32	3.82E+08	1.08E+07	11.50
TD (300)	1.58E+32	2.08E+08	5.88E+06	186.61	-	-	-	-
NS (235)	8.69E+31	1.15E+08	3.24E+06	272.34	0	0	0	0
PD (235)	1.28E+32	1.69E+08	4.78 E+06	321.85	0	0	0	0
DBK BC (300)	6.30E+31	8.31E+07	2.35E+06	3,414.67	0	0	0	0
DBK MC (370)	2.31E+31	3.05E+07	8.62E+05	17,854.25	0	0	0	0
DBK sill (30)	4.17E+30	5.50 E+06	1.56E+05	34,308.26	0	0	0	0
DBK sill (300)	4.24E+31	5.59E+07	1.58E+06	3,373.69	0	0	0	0

Table 2.A.15: Production of ^4He from basement external sources (B) with an assumed 100% production and release. R = Ratherford, TD = Tocito Dome, NS = Navajo Springs, PD = Pinta Dome; DBK BC = Dineh-Bi-Keyah (Barker Creek), DBK MC = Dineh-Bi-Keyah (McCracken). The release window ^4He production, which represents ^4He production and release from intervals that lie above the closure temperature release interval for apatite (55°C), is calculated with the geothermal gradient of 1.4 °F/100 ft or (~25 °C/km).

Field (age Mya)	Produced ^4He (atoms)	^4He volume produced (ft ³)	^4He volume produced (m ³)	% of ^4He to fill the reservoir	Produced ^4He (atoms) in release window	^4He volume produced e (ft ³)	^4He volume produced (m ³)	% of ^4He to fill the reservoir
R (540)	1.05E+34	1.39E+10	3.93E+08	0.32	-	-	-	-
TD (540)	8.14E+33	1.07E+10	3.04E+08	3.61	-	-	-	-
NS (540)	4.24E+33	5.60E+09	1.58E+08	5.58	3.96E+33	5.22E+09	1.48E+08	5.98
PD (540)	4.64E+33	6.12E+09	1.73E+08	8.89	4.40E+33	5.80E+09	1.64E+08	9.38
DBK BC (540)	4.65E+33	6.13E+09	1.73E+08	46.29	4.52E+33	5.95E+09	1.69E+08	47.63
DBK MC (540)	4.65E+33	6.13E+09	1.73E+08	88.76	4.52E+33	5.95E+09	1.69E+08	91.32
DBK sill (540)	3.13E+33	4.12E+09	1.17E+08	45.73	3.04E+33	4.01E+09	1.13E+08	47.05

2.A.10 General Metadata: Sampled Well Gas

Table 2.A.16: Metadata of sampled well gas including name, well number, API, field name, state name, county name, basin, formation, and location data.

Name	Well #	API	Field Name	State	County Name	Basin	Formation Name	Latitude	Longitude
RATHERFORD UNIT	09-34	4303715711	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.231388	-109.285082
RATHERFORD UNIT	10-14	4303715713	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.230978	-109.275942
RATHERFORD UNIT	10-32	4303715714	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.238335	-109.266655
RATHERFORD UNIT	12-23	4303715846	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.236769	-109.343491
RATHERFORD UNIT	13-12	4303731127	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.226766	-109.348243
RATHERFORD UNIT	13-41	4303715856	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.229175	-109.334500
RATHERFORD UNIT	15-33	4303715718	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.219598	-109.266908
RATHERFORD UNIT	16-41	4303715725	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.227774	-109.280469
RATHERFORD UNIT	17-11	4303731169	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.226604	-109.311862
RATHERFORD UNIT	17-13	4303731133	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.220787	-109.312370
RATHERFORD UNIT	17-22	4303731170	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.224447	-109.308010
RATHERFORD UNIT	20-42	4303731051	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.209696	-109.298751
RATHERFORD UNIT	20-44	4303730915	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.202278	-109.298979
RATHERFORD UNIT	20-66	4303731592	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.211358	-109.310408
RATHERFORD UNIT	29-31	4303730914	RATHERFORD (GREATER ANETH)	UT	SAN JUAN	BLANDING	DESERT CREEK	37.198552	-109.303837
NAVAJO TRIBE-N	1	30045058090000	TOCITO DOME	NM	SAN JUAN	FOUR CORNERS PLATFORM	HERMOSA/BARKER CREEK	36.483044	-108.787862
NAVAJO TRIBAL-N	11	30045205830000	TOCITO DOME	NM	SAN JUAN	FOUR CORNERS PLATFORM	PENNSYLVANIAN/BARKER CREEK	36.493836	-108.786649
NAVAJO TRIBAL-P	6	30045217450000	TOCITO DOME	NM	SAN JUAN	FOUR CORNERS PLATFORM	PENNSYLVANIAN/BARKER CREEK	36.497188	-108.797301
NAVAJO TRIBE U	7	30045057510000	TOCITO DOME	NM	SAN JUAN	FOUR CORNERS PLATFORM	HERMOSA/BARKER CREEK	36.471811	-108.761363
NAVAJO TRIBAL -U-	9	30045201960000	TOCITO DOME	NM	SAN JUAN	FOUR CORNERS PLATFORM	PENNSYLVANIAN/BARKER CREEK	36.468198	-108.752375
NAVAJO TRIBAL-U	12	30045205800000	TOCITO DOME	NM	SAN JUAN	FOUR CORNERS PLATFORM	PENNSYLVANIAN/BARKER CREEK	36.475242	-108.765622
RANGER	31-1	02001204950000	NAVAJO SPRINGS	AZ	APACHE	MOGOLLON SLOPE	COCONINO	35.086639	-109.515664
RANGER	33-1	02001204940000	PINTA DOME	AZ	APACHE	MOGOLLON SLOPE	COCONINO	35.087864	-109.581479
RANGER	34-1	02001205000000	PINTA DOME	AZ	APACHE	MOGOLLON SLOPE	COCONINO	35.085974	-109.567138
NAVAJO-B	2	02001200100000	DINEH-BI-KEYAH	AZ	APACHE	DEFIANCE UPLIFT	HERMOSA/BARKER CREEK	36.471621	-109.131403
NAVAJO-C	2	02001200460000	DINEH-BI-KEYAH	AZ	APACHE	DEFIANCE UPLIFT	MC CRACKEN	36.484789	-109.123582
NAVAJO	4	02001200090000	DINEH-BI-KEYAH	AZ	APACHE	DEFIANCE UPLIFT	INTRUSIVE	36.486407	-109.132150
NAVAJO	15	02001200410000	DINEH-BI-KEYAH	AZ	APACHE	DEFIANCE UPLIFT	SILL /IGNEOUS SILL	36.493489	-109.157993
NAVAJO	24	02001202440000	DINEH-BI-KEYAH	AZ	APACHE	DEFIANCE UPLIFT	INTRUSIVE	36.489755	-109.145318
NAVAJO TRACT 88	2	02001200550000	DINEH-BI-KEYAH	AZ	APACHE	DEFIANCE UPLIFT	HERMOSA/SILL	36.499734	-109.166952
NAVAJO TRACT 88	3	02001200660000	DINEH-BI-KEYAH	AZ	APACHE	DEFIANCE UPLIFT	HERMOSA/SILL	36.485439	-109.166628

Chapter 3 Appendix

3.A.1 General Data

Table 3.A.1: The raw data from the 2021 field season analysed in the Oxford Noble Laboratory for bulk gas components of N₂, CO₂ and O₂, followed by the processed and air corrected values.

	Raw						Processed						Air corr.	
Samples	N ₂	err	CO ₂	err	O ₂	err	N ₂	err prop.	CO ₂	err prop.	O ₂	err prop.	N ₂	CO ₂
Alkali	4.56E-11	2.94E-13	1.71E-11	1.06E-13	3.87E-13	1.6E-14	81.69%	1.73%	11.54%	2.48%	0.92%	4.44%	77.20%	12.38%
Alpine	3.94E-11	3.06E-13	6.43E-14	8.49E-16	2.37E-12	2.2E-14	94.75%	1.78%	0.05%	2.74%	7.31%	1.87%	64.38%	0.05%
Astoria 1	2.52E-11	1.51E-13	3.06E-11	1.87E-13	3.36E-13	6.47E-15	16.18%	3.08%	80.92%	1.71%	0.08%	7.77%	14.27%	83.33%
Belz	4.53E-11	2.15E-13	7.14E-12	5.17E-14	3.17E-13	1.23E-14	91.40%	1.67%	5.04%	2.51%	0.81%	4.21%	87.96%	5.23%
Boulder	4.35E-11	2.99E-13	1.32E-14	7.07E-17	7.89E-13	1.17E-14	95.99%	1.75%	0.02%	2.46%	1.95%	2.19%	88.09%	0.02%
Bridger Canyon	3.67E-11	1.18E-13	2.9E-14	1.34E-15	2.1E-12	2.69E-15	93.37%	1.64%	0.05%	5.22%	5.93%	1.63%	68.01%	0.05%
Crater Hills 1	6.83E-12	9.66E-14	5.95E-11	2.56E-13	2.83E-13	1.73E-14	3.95%	3.33%	126.35%	1.65%	0.70%	9.70%	0%	96.97%
Crater Hills 2	7.26E-12	6E-14	6.24E-11	4.61E-13	3.98E-13	2.27E-14	3.86%	3.13%	119.53%	1.76%	0.09%	9.44%	0%	96.87%
Ennis Pool	5.12E-11	3.29E-13	4.69E-13	1.04E-14	3.04E-13	2.35E-14	94.19%	1.73%	0.54%	3.27%	0.66%	7.91%	91.41%	0.57%
Forest Springs 1	6.72E-12	8.95E-14	5.81E-11	1.4E-13	3.15E-13	1.66E-14	3.98%	3.30%	126.93%	1.61%	0.08%	9.18%	0%	96.96%
Forest Springs 2	5.51E-12	8.54E-14	4.66E-11	1.74E-13	2.95E-13	1.21E-14	4.00%	3.39%	127.95%	1.64%	0.09%	8.57%	0%	96.97%
Henry's	3.62E-11	8.85E-14	2.63E-11	1.74E-13	2.82E-13	1.94E-14	73.90%	1.62%	25.88%	2.49%	0.67%	7.08%	70.49%	25.93%
Jakeys Fork	4.26E-11	3.61E-13	4.06E-12	3.62E-14	2.62E-13	2.53E-14	92.92%	1.82%	4.08%	2.56%	0.67%	9.79%	90.15%	4.21%
Kelly	4.62E-11	2.33E-13	5.35E-14	8.49E-16	2.71E-13	1.43E-14	93.69%	1.68%	0.05%	2.88%	0.70%	5.54%	90.73%	0.06%
Mud Volcano 1	6.45E-12	1.13E-13	5.84E-11	3.9E-13	2.74E-13	2.43E-14	3.84%	3.49%	128.28%	1.73%	0.07%	11.63%	0%	97.09%
Norris	5.71E-11	4.43E-13	1.47E-12	1.86E-14	2.99E-13	1.34E-14	97.09%	1.78%	1.32%	2.71%	0.60%	4.77%	94.75%	1.34%
Potosi	6.39E-11	1.46E-13	1.69E-13	3.16E-15	2.99E-13	2.36E-14	97.74%	1.62%	0.14%	3.05%	0.54%	8.07%	95.62%	0.14%
Puller	3.17E-12	2.24E-14	2.02E-13	3.52E-15	8.11E-14	1.11E-14	88.20%	1.75%	0.16%	2.97%	2.62%	13.78%	75.67%	0.19%
Renova 1	6.3E-11	2.98E-13	4.21E-12	3.28E-14	3.01E-13	2.32E-14	93.21%	1.67%	3.45%	2.52%	0.53%	7.86%	91.03%	3.57%
Renova 2	4.5E-11	1.76E-13	2.94E-12	2.7E-14	2.23E-13	2.01E-14	95.08%	1.65%	4.19%	2.57%	0.56%	9.14%	92.86%	4.22%
Silver Star	6.81E-11	4.84E-13	8.05E-13	4.64E-15	3.32E-13	1.54E-14	92.31%	1.76%	0.64%	2.47%	0.57%	4.91%	89.84%	0.69%
Soda	9.34E-12	6.29E-14	8.38E-11	6.11E-13	3.73E-13	1.98E-14	4.67%	3.09%	121.92%	1.75%	0.07%	9.20%	0%	96.31%
Steamboat	1.07E-11	1.02E-13	9.07E-11	5.4E-13	3.13E-13	1.47E-14	5.13%	3.16%	125.03%	1.70%	0.06%	8.87%	1.72%	96.06%
Thermopolis	2.81E-11	9.92E-14	8.96E-11	8.32E-13	4.42E-13	2.25E-14	10.23%	3.04%	83.03%	1.85%	0.07%	9.09%	7.53%	89.03%
Washburn 1	6.14E-12	1.07E-13	5.4E-11	2.31E-13	3.05E-13	8.64E-15	3.95%	3.48%	129.84%	1.65%	0.08%	8.04%	0%	97.05%
Washburn 2	6.15E-12	7.12E-14	5.05E-11	2.67E-13	2.88E-13	1.69E-14	4.17%	3.23%	128.99%	1.68%	0.08%	9.54%	0%	96.87%
Yandell	4.24E-11	2.09E-13	7.92E-13	9.02E-15	2.26E-13	1.29E-14	96.44%	1.68%	1.22%	2.66%	0.60%	5.97%	94.07%	1.25%

Table 3.A.2: The location of sampled springs and their relevant surface water temperature from the 2021 field season. * denotes temperatures estimates (McCleskey et al., 2014).

Sample	Latitude	Longitude	Surface Water Temp. °C	pH
Alkali	43.03719	-112.00423	21.7	6.85
Alpine	43.21712	-111.09615	9.5	7.41
Astoria 1	43.30011	-110.76946	41.3	6.24
Belz	45.17214	-112.15102	39.4	6.85
Boulder	46.19895	-112.09399	41.5	8.56
Bridger Canyon	45.70762	-110.97536	25.1	7.47
Crater Hill 1	44.65327	-110.47756	75.0*	1.64
Crater Hill 2	44.653403	-110.48449	75.0*	1.46
Ennis Pool	45.36676	-111.72621	19.3	7.99
Forest Springs 1	44.708178	-110.47353	75.0*	No data
Forest Springs 2	44.708083	-110.47327	75.0*	No data
Henry's	42.91021	-111.5565	22.6	6.21
Jakeys Fork	43.48961	-109.60562	20.2	6.82
Kelly	43.63959	-110.61572	27.9	7.56
Mud Volcano 1	44.623115	-110.43232	75.0*	No data
Norris	45.57443	-111.68449	39.4	7.45
Potosi	45.58913	-111.89978	39.5	8.35
Puller	45.17142	-112.15279	47.0	7.15
Renova 2	45.79131	-112.12707	65.0	6.97
Renova 1	45.79093	-112.12695	43.8	6.9
Silver Star	45.68559	-112.29609	29.5	8.04
Soda	42.65756	-111.60511	20.3	6.35
Steamboat	42.65538	-111.64236	52.3	7.22
Thermopolis	43.65465	-108.1943	38.1	6.1
Washburn 1	44.75895	-110.43951	52.6	2.05
Washburn 2	44.7585	-110.43739	15.6	2.09
Yandell	43.11433	-112.16525	21.4	7.25

Table 3.A.3: The location of sampled springs and their relevant surface water temperature from the 2022 field season. * denotes temperatures estimates (McCleskey et al., 2014).

Sample	Latitude	Longitude	Surface Water Temp. °C	pH
BB	42.68871	-114.82671	56.2	8.98
BS2	43.53984	-115.28916	59.1	9.08
FS	42.10784	-113.39185	n.d.	8.02
GV	43.41366	-116.70737	50.6	9.08
LF	43.60339	-114.95269	46.4	8.95
MD	42.08096	-117.76051	53.2	9.08
PA	43.12967	-115.33838	55.7	8.83
PE	40.83812	-117.39013	53.2	6.72
PV	41.42233	-117.38749	54.1	6.69
RC	40.76124	-117.48877	94	7.3
RH	40.76101	-117.49151	82.2	7.82
SC	43.71965	-115.61815	59.6	9.08
SQ	42.11841	-111.93018	104	no data
TS	43.67096	-115.6968	65.5	9.15
UD	41.88513	-112.15779	35.9	6
ZR	40.96122	-117.49408	51.4	6.97

3.A.2 Heat Flow Supplemental Figures

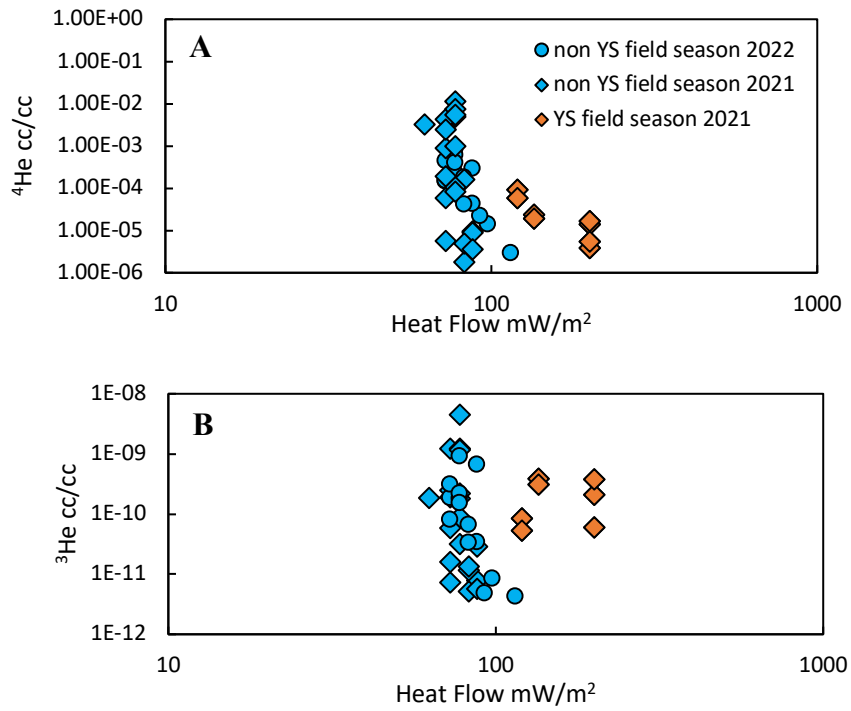


Figure 3.A.1: A) ^4He and heat flow, and B) ^3He and heat flow both show a relatively narrow range of heat flow values for non-Yellowstone samples in regards to heat flow which corresponds to various levels of measured ^3He and ^4He . Non-Yellowstone samples show a larger range in both ^3He and ^4He . No significant relationships regarding the amount of He and its corresponding heat flow value were observed for the non-Yellowstone samples. With increasing heat flow for the Yellowstone samples, we see a decrease in the amount of ^4He reported, but this trend could be due to the scarcity of data present and should be treated with caution.

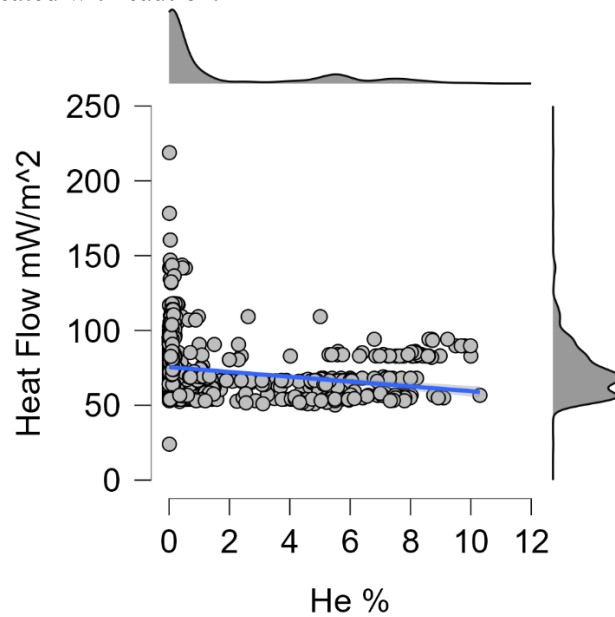


Figure 3.A.2. Scatter plot of heat flow versus He% showing Four Corners data (Brennan et al., 2021; Gilfillan et al., 2008; Halford et al., 2022) ($n=1,032$) along with relative density distributions and a linear regression line with confidence intervals of 95% (JASP, 2023).

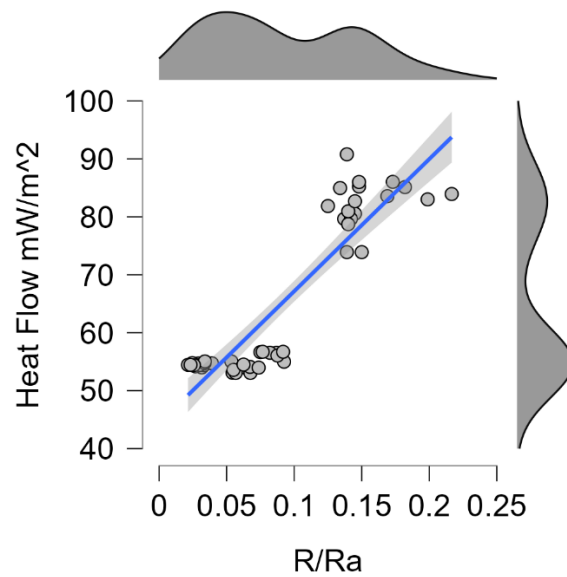


Figure 3.A.3. Scatter plot of heat flow versus R/R_a showing Four Corners area data excluding outliers from Doe Canyon and St. John's Dome (Gilfillan et al., 2008; Halford et al., 2022) ($n=46$) along with relative density distributions and a linear regression line with confidence intervals of 95% (JASP, 2023).

3.A.3 Four Corners Area Thermal Properties (Heat Flow) Analysis

In a boot-strap fashion we derived thermal properties by incorporating empirical relationships with depth to basement interpretations (with magnetic and gravity data) and open-file data (grids, stations, and results from previously published sources (e.g., Southern Methodist University's borehole temperature database, and University of Delaware terrestrial air temperature and precipitation database) with basic heat flow equations. Thermal and seismic refraction stations were used to provide measured control points for temperatures at various well depths, basin thermal conductivity, measured heat flow in the shallower section, and to determine the Moho/Curie point (Herrmann et al., 1966; Hoffman et al., 1977; Jaksha et al., 1984; Jaksha, et al., 1982; Lastowka et al., 2001; Leidig et al., 2005; Liu et al., 2011; Lutter et al., 1995; McCowan 1978; Molenaar and Halverson, 1969; Prodehl and Pakiser, 1980; Roller, 1965; Ryaboy et al., 2001; Sheehan et al., 1995; Shen et al., 2013; Slack et al., 1996; Snelson et al., 1998; Stankova et al., 2008; Steinhart and Meyer, 1961; Toppozada and Sanford, 1976; and Warren 1969).

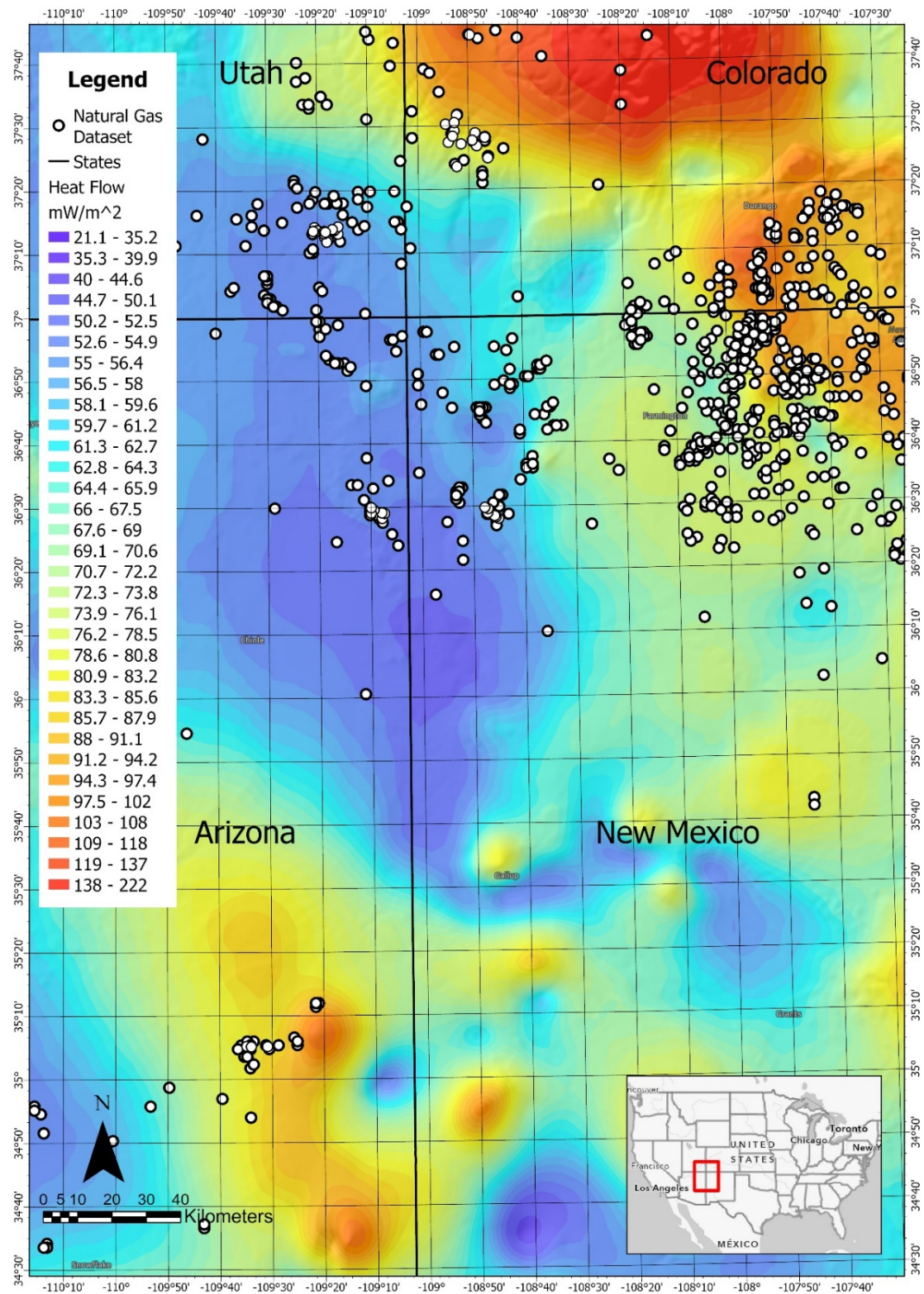


Figure 3.A.4: Calculated final heat flow courtesy of Earthfield Technology, LLC, which was calculated utilized the magnetic layer heat production and magnetic layer thickness as inputs into Fourier's Law. Maps are shown with previously collected samples from the USGS and other published works as small white circles (Brennan et al., 2021; Halford et al., 2022; Gilfillan et al., 2008).

The first equation is Fourier's Law, $Q_0 = k \cdot (\Delta T / \Delta z)$ where Q_0 is heat flow ($\text{m} \cdot \text{W} / \text{m}^2$), k is thermal conductivity ($\text{W} / \text{m} \cdot \text{K}$), ΔT is the temperature difference ($^{\circ}\text{C}$) over distance Δz (km). There was an assumption made that within Δz , sources and sinks do not exist. The second equation, which describes the continental crust heat flow that includes background heat and heat from radiogenic sources within the basement, is $Q_{\text{TOT}} = Q_{\text{BG}} + A_0 D$ where Q_{TOT} is total heat flow ($\text{m} \cdot \text{W} / \text{m}^2$), Q_{BG} is background heat flow, A_0 is heat produced by basement rocks ($\mu\text{W} / \text{m}^3$), D is thickness of the heat producing basement layer (km). As an aside, the product $A_0 D$ is flux (heat flow), which can be expressed as $\text{m} \cdot \text{W} / \text{m}^2$. The empirical relationship that, on average, Q_{BG} and $A_0 D$ are 3/5 and 2/5 of total heat flow (Q_{TOT}), respectively, was determined by Pollack and Chapman (1977).

From these relationships and equations, we have calculated the current temperatures at the topographic surface, the basement surface and the Curie Point/Moho. The generation of thermal gradients for the magnetic layer (top of basement to Curie point), background (Curie point to core of the Earth) and for the basin (topographic surface to basement surface) was made possible using temperature differences with depth (i.e., depth related temperature horizons). This allowed for the calculation of temperature at depth, and ultimately allowed the calculation of heat flow for the basin area, heat flow from the magnetic layers, background heat flow and total final heat flow.

A high-resolution thermal susceptibility study, building off previous work of Blackwell et al., 2011, is the culmination of background heat flow data, heat flow data from basement or magnetic layer, and heat flow data from the sedimentary section. This was used to produce the calculated final heat flow map. The final heat flow map represents present day conditions and areas of enhanced heat flow (Fig. 3.A.4). The zones of high heat flow correspond with volcanic activity associated with the areas of Rio Grande rifting and Basin and Range extension.

3.A.4 Distance Relationships

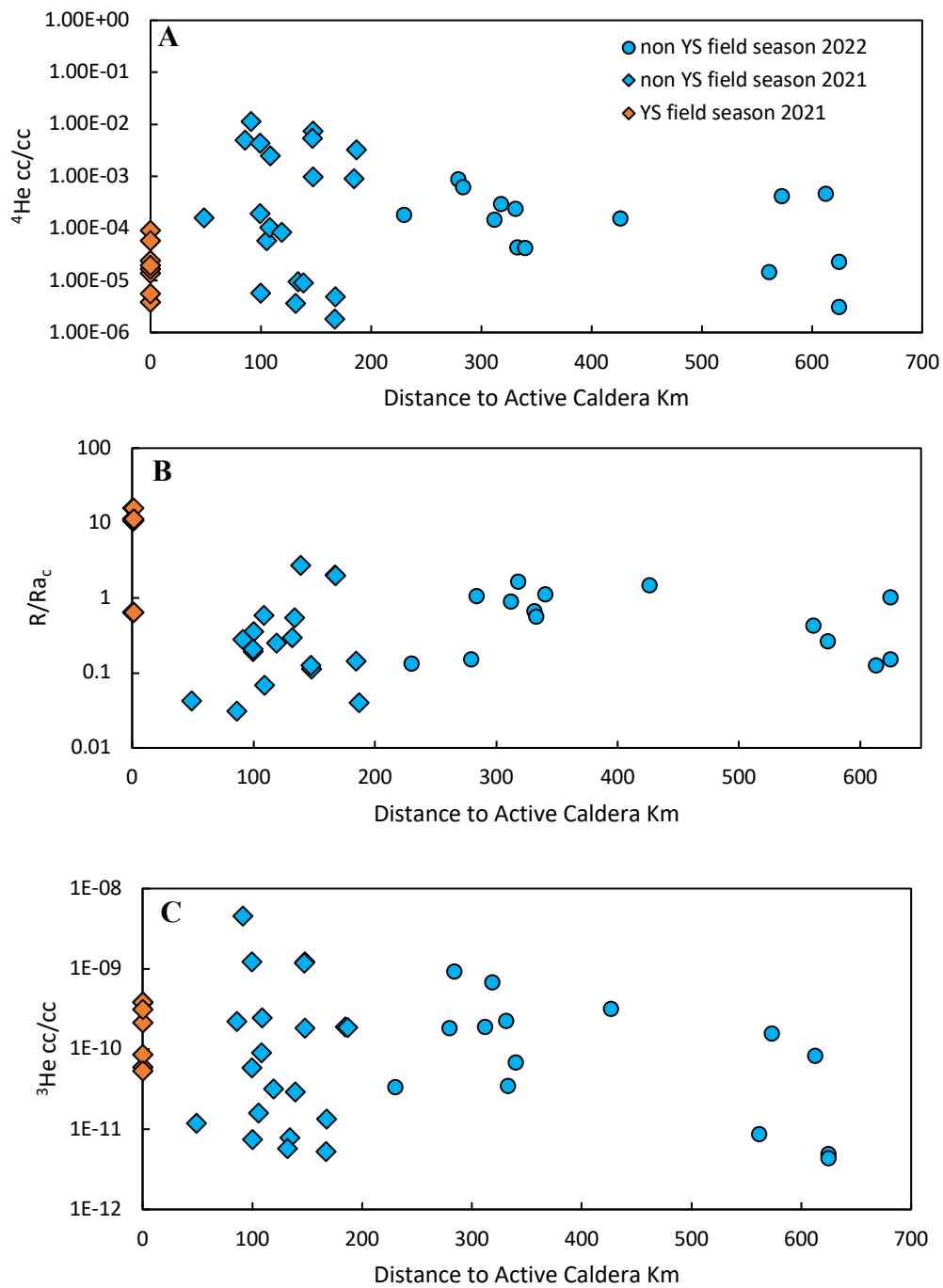


Figure 3.A.5: A) ^4He , B) R/R_{a_c} and C) ^3He all versus distance to the active Yellowstone caldera. R/R_{a_c} values within the Yellowstone caldera are significantly higher than outside the caldera. No observable patterns were observed regarding helium amounts and distance for non-Yellowstone data.

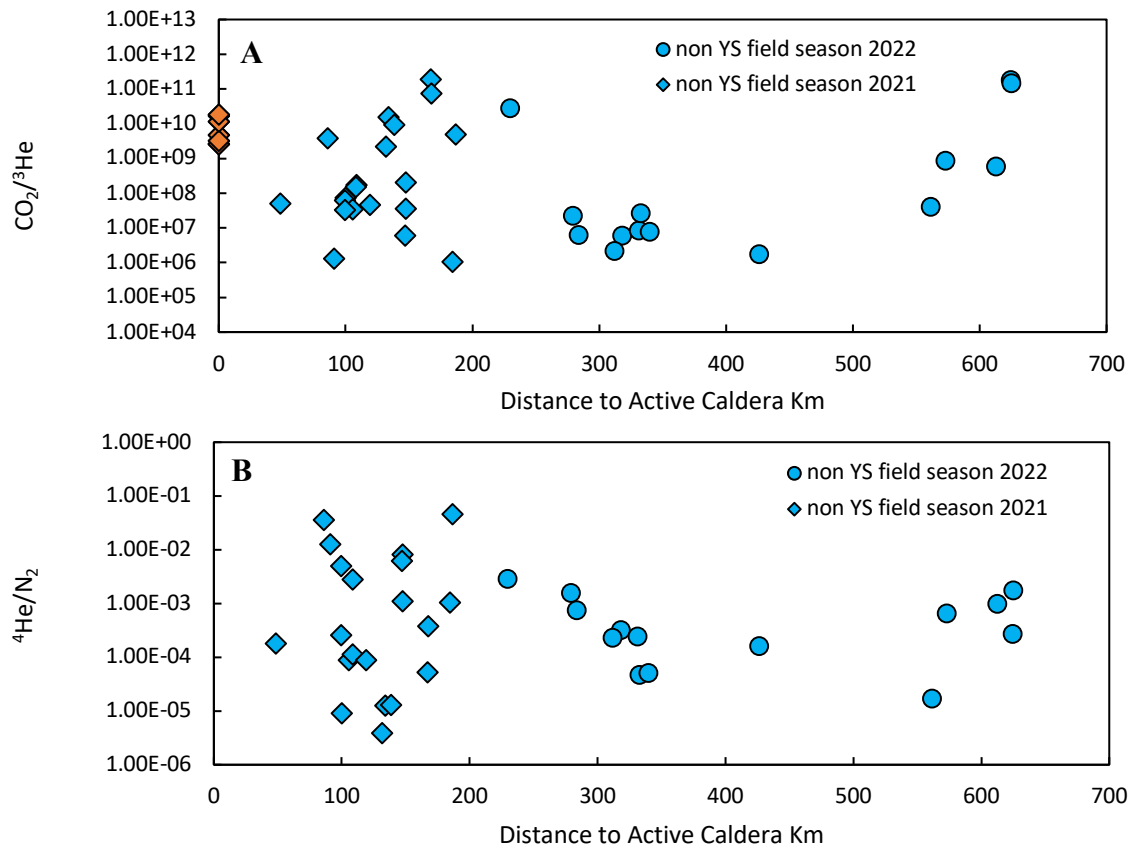


Figure 3.A.6: Plots of $\text{CO}_2/{}^3\text{He}$ (A) and ${}^4\text{He}/\text{N}_2$ (B) and distance to the active Yellowstone caldera (km). No significant observable pattern is observed between these plots indicating that utilizing distance alone to find zones of He enrichment is likely not an ideal method.

3.A.5 Buoyancy Mass Transport

Multiple authors have proposed models under the umbrella of buoyancy driven vertical migration mass transport to explain petroleum microseepage anomalies over accumulations (MacElvain, 1969, Price, 1986, Arp, 1992, Klusman and Saeed, 1996, Brown, 2000, Rice, 2022). One of the challenges is to determine a mechanism with a fast enough velocity to explain surface signatures, yet a slow enough flux to not drain the reservoir (Price 1986). Within the realm of buoyancy driven bubble ascent microseepage, there are several competing theories that can be applied to He gas migration such as the steady ascent of bubble water in a vertical fracture, isolated bubble ascent in fracture, bubble ascent without concentration or wall effects, and continuous gas phase flow in fractures.

$$\text{Equation 3.A.1: } U_s = \frac{2a^2(\sigma-\rho)g}{9\mu}$$

Where a = particle radius; μ = viscosity; σ and ρ = densities of gas and water; g = gravitational constant

The free bubbles (Equation 3.A.1) model is based on Stoke's law that quantifies the terminal Stokes' velocity (U_s). The assumption for this model is there are no other particles or walls in an infinite viscous medium, bubbles are spheres, and the Reynolds number is <1 (Brown, 2000). Additionally, water viscosity is utilized as the water is deformed around rising spheres of gas (Brown, 2000).

$$\text{Equation 3.A.2: } \frac{U}{U_s} = 1 - 1.004 \left(\frac{a}{l}\right) + 0.418 \left(\frac{a}{l}\right)^3 - 0.21 \left(\frac{a}{l}\right)^4 - 0.169 \left(\frac{a}{l}\right)^5$$

Where l = the fracture half width

The maximum bubbles (Equation 3.A.2) model considers the effect that proximity to walls has on velocity. The closer the bubble is to the wall will increase the viscous drag and slow migration (Happel and Brenner, 1965). The quickest normalized velocity is therefore at the midpoint between two walls. This model shows the fastest ascent velocity that can occur in a fracture (i.e., midpoint between two perfectly vertical walls) (Brown, 2000).

$$\text{Equation 3.A.3: } \frac{U_c}{U_*} = (1 - C)^n \text{ where } n = 4.65 + 20\left(\frac{a}{a_t}\right)$$

Where C = volume fraction concentration of spheres, a = sphere radius, a_t radius of the tube particles are rising, U^* = bubble terminal velocity in a fracture shown in equation A.5

$$\text{Equation 3.A.4: } \mu_e = \mu_w [(1 - C)^{-n}] \div [1 - 1.004 \left(\frac{a}{l}\right) + 0.418 \left(\frac{a}{l}\right)^3 - 0.21 \left(\frac{a}{l}\right)^4 - .169 \left(\frac{a}{l}\right)^5]$$

Where $n = 4.65 + 10a/l$ at $Re < 0.2$, μ_w = water viscosity, C = concentration, a = size of the sphere, l = fracture half width

The bubbly water model (Equation 3.A.3 + Equation 3.A.5 with viscosity from Equation 3.A.4) describes the interaction of bubbles entrained in a groundwater solution. The effects that concentration has on velocity, is that 1) as the concentration increases, there is particle interference ultimately decreasing terminal velocity, and 2) the bulk density decreases (Brown, 2000). The ascent velocity is determined by the relationship between viscosity and buoyancy.

The continuous gas phase flow model (Equation 3.A.5) describes a scenario where gas exists in a continuous body in the subsurface more than a singular bubble (England et al., 1987). In the event

that capillary pressures are exceeded, the fractures with apertures present are completely saturated (Brown, 2000). In the model, the assumption is made that the flow is between two parallel plates and the reservoir is normally pressured (Huitt, 1956).

$$\text{Equation 3.A.5: } velocity(U_f) = \frac{4l^2}{12\mu}(\sigma - \rho)g$$

U_f = velocity of fluid in a fracture perpendicular to width, μ = viscosity; l = fracture half width; σ and ρ = densities of gas and water; g = gravitational constant

The velocity rates for the aforementioned theories are estimated in a theoretical model (Figure 3.A.7). The additional parameters can be found in Table A.4 in the appendix. The horizontal axis is labelled as either fracture half width (for max bubble, continuous flow and bubbly water) and bubble radius (Stokes' law velocity). Several assumptions are considered, namely: fracture apertures are fixed, laminar flow is occurring, water drive assumption is made (i.e., water replaces lost gas to keep pressure in the leaking reservoir constant throughout leakage), and the fluid potential gradient is assumed to be buoyancy (Brown, 2000). As tortuosity, fracture sizes and roughness is generally unknown, these calculations only serve as rough approximations. Continuous gas phase flow, which is shown to have the highest velocity, is considered further.

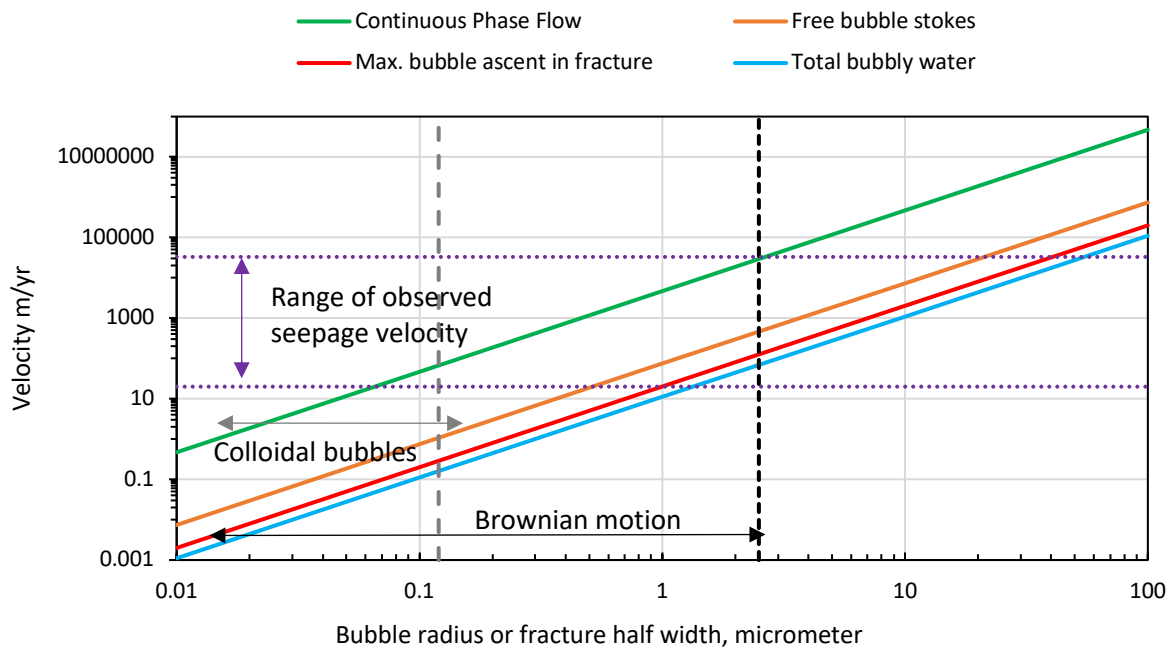


Figure 3.A.7: Comparison of several models (steady ascent of bubbly water in a vertical fracture, isolated bubble ascent in fracture, bubble ascent without concentration or wall effects, and continuous gas phase flow in fractures) as a function of bubble radius or fracture half width.

Brown (2002) provides a range of natural gas seepage velocities from >100 to $32,850$ m/year (Arp, 1992b; Jones and Burtell, 1996; Horwitz, 1969; and Ataktingi et al., 1984). A key observation is that the approximate range of Brownian motion, which is intrinsically linked to diffusion, cannot explain the observed range of natural gas seepage velocities, while continuous phase gas migration can migrate at these observed velocities.

Regarding sealing lithologies, rock properties alone are often incorrectly attributed to either the successful mitigation of He flux or not, when it is in reality the water inside those lithologies that is acting in combination with rock properties (i.e., porosity) as a hindrance to He migration. Migration will follow the most energetically favourable pathway. Using equations 3.A.6 and 3.A.7, we show that fractures require less capillary pressure for migration to occur compared to bubbles if the assumption that the area is completely water-wet (Fig. 3.A.8). In other words, the capillary pressure needed for a gas to form a bubble having a diameter equivalent to the fracture width is double compared to that needed to invade a fracture (Brown, 2000). The presence of a strong anomaly over a reservoir is not inherently indicative of a weak seal, because if leakage were to occur over the seal, one would expect to observe a non-localized signal over the accumulation due to the fact that the variations in capillary displacement pressure in overlying rocks would force gas to migration parallel updip with bedding (Brown, 2000).

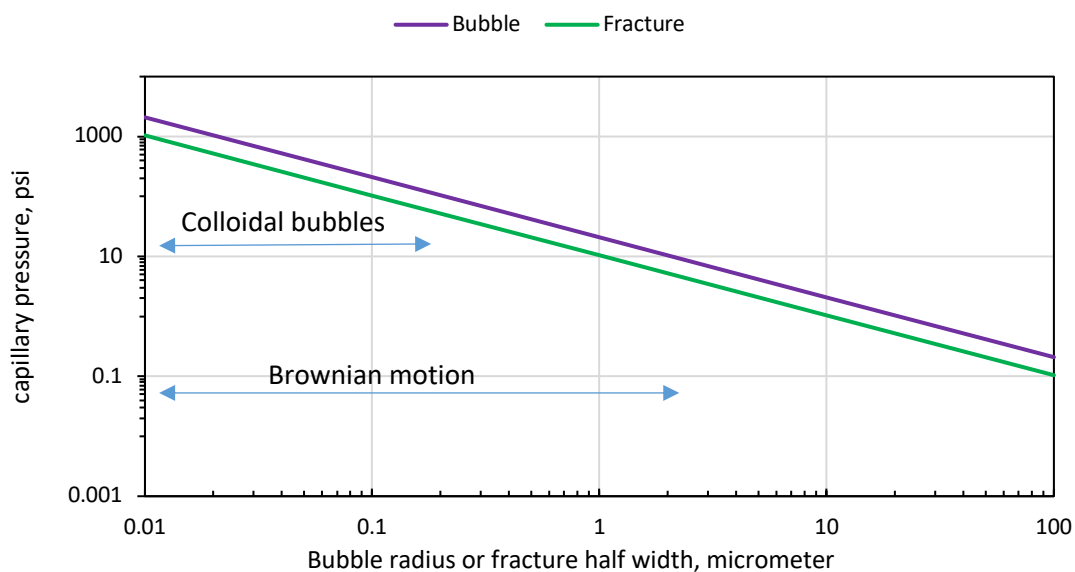


Figure 3.A.8: Capillary pressure as a function of bubble radius or fracture half width for bubbles and fractures.

Equation 3.A.6: Spheres: $P_C = \frac{2\gamma}{r}$
where r = bubble radius, and γ is the surface tension

Equation 3.A.7: Parallel plates: $P_C = \frac{\gamma \cos \theta}{l}$
where θ is the contact angles measured through the water phase ~ 1

$$\text{Equation 3.A.8: } \text{flux} \left(\frac{q}{L} \right) = \frac{W^3}{12\mu} \frac{dp}{dz}$$

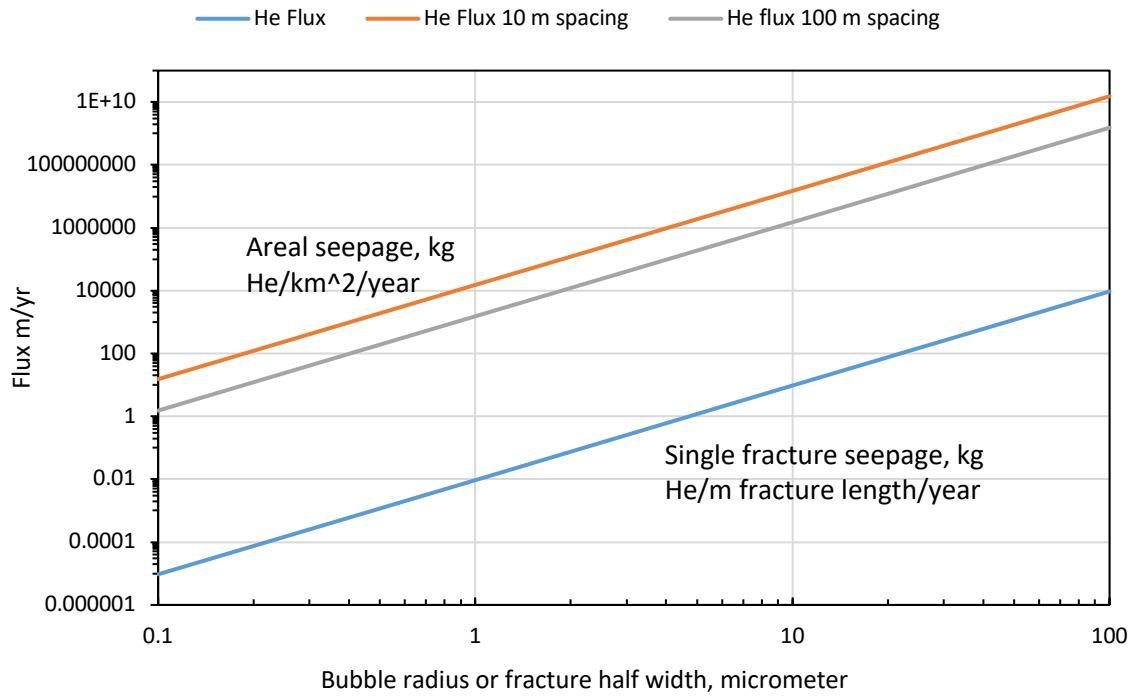


Figure 3.A.9: He mass flux reported from continuous phase flow in fractured rock. Two areal extent models are presented with various 10m and 100 m spacing along with a single fracture seepage flux.

A migration volumetric flux is calculated via Equation 3.A.8 along a single theoretical fracture seepage (Fig. 3.A.9). Adjusting different widths of fractures, we can produce a theoretical microseepage to macroseepage flux for a hypothetical field size $1.62\text{E}6 \text{ m}^2$. Comparing these theoretical fluxes at 10 and 100 meters spacing with ~ 0.2 and ~ 0.35 micrometer fracture half width would produce $\sim 75 \text{ He kg/km}^2/\text{year}$. If however there is any increase in the degree of fracturing, the continuous phase model is orders of magnitude more rapid than diffusion. Thus, vertical migration driven by buoyancy is likely a more dominant mechanism to explain the He microseepages.

Upon analysis of the various models and exploring the mechanism of continuous gas phase flow we are left with a quandary. One on hand the microseepage signals observed in reality could be

derived from an accumulation at depth which has gas escaping the reservoir through vertical migration as a continuous gas phase with a velocity fast enough to explain surface signatures, yet slow enough flux to not drain the reservoir (Brown, 2000). However, we could be interpreting the geologic framework incorrectly and ignoring the possibility that perhaps the distribution and complex network of micro fractures are indeed responsible for explaining the microseepage surface signatures more so than the actual distribution of He accumulations (Brown, 2000). Regardless, the applications for understanding a more rapid migration mechanism for exploration are that it would be possible to 1) monitor a potential reservoir pressure change in real time, 2) monitor the spatial extent as reservoirs as there would be little time for dispersion effects (Rice, 2022).

Table 3.A.4: Assumed fluid properties, reservoir properties and parameters that are utilized in He velocity and flux calculations. Hypothetical reference conditions are set at 323 °K and 3600 psi.

Parameter	Value	Units
Density of sphere (He gas bubble) (σ)	36.97	kg/m ³
Density of sphere (fluid water) (ρ)	996	kg/m ³
Gravity	9.8	m/s ²
Viscosity of Helium through which the spheres move 50 C	0.000021	Pa*s
Water gas surface tension	72	dynes/cm
C He concentration	10	%
Viscosity of water through which the spheres move	0.00089	Pa*s

Chapter 4 Appendix

4.A.1 Statistical Tests

Table 4.A.1: Coefficients from the generalized linear model comparing economic He (>0.3%) to distances to basement faults and igneous bodies. There is an inverse and significant relationship between He % and distance to basement faults and igneous bodies (JASP, 2023).

	Estimate	Standard Error	t	p
(Intercept)	5.649	0.285	19.793	9.82e-35
Basement Fault Distance Km	-1.527	0.415	-3.682	3.92e-04
Igneous Bodies Distance Km	-1.217	0.224	-5.435	4.55e-07

Table 4.A.2: Example showing ANOVA results comparing five variations of the synthetic grid distances to basement faults. Results indicate the grids are not significantly different.

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
Synthetic 1 Km	94	118.51	1.26	1.61		
Synthetic 2 Km	94	107.03	1.14	1.40		
Synthetic 3 Km	94	102.51	1.09	1.07		
Synthetic 4 Km	94	111.93	1.19	1.36		
Synthetic 5 Km	94	113.49	1.21	1.28		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	1.60	4	0.40	0.30	0.88	2.39
Within Groups	625.11	465	1.34			
Total	626.71	469				

Table 4.A.3: Example showing ANOVA results comparing five variations of the synthetic grid (n=94) data to the observed economic He (>0.3 He %) (n=94) distances to basement faults. Results indicate the datasets are significantly different.

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
Economic Km	94	43.81	0.47	0.24		
Synthetic 1 Km	94	118.51	1.26	1.61		
Synthetic 2 Km	94	107.03	1.14	1.40		
Synthetic 3 Km	94	102.51	1.09	1.07		
Synthetic 4 Km	94	111.93	1.19	1.36		
Synthetic 5 Km	94	113.49	1.21	1.28		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	41.27	5	8.25	7.11	1.83e-06	2.23
Within Groups	647.30	558	1.16			
Total	688.57	563				

Table 4.A.4: Table showing post-hoc (Games-Howell) results comparing five variations of the synthetic grid (n=94) data to the observed economic He (>0.3 He %) (n=94) distances to basement faults. Results (p values < .001) indicate the economic and synthetic grids are significantly different (JASP Team, 2023).

Comparison	Mean Difference	95% CI Lower	95% CI Upper	SE	t	df	p _{Tukey}
Economic - Synthetic 1	-0.80	-1.2	-0.39	0.14	-5.67	120.03	1.47e-6
Economic - Synthetic 2	-0.67	-1.06	-0.29	0.13	-5.09	123.70	1.93e-5
Economic - Synthetic 3	-0.62	-0.97	-0.28	0.12	-5.30	132.55	7.07e-6
Economic - Synthetic 4	-0.73	-1.10	-0.35	0.13	-5.55	124.61	2.39e-6
Economic - Synthetic 5	-0.74	-1.11	-0.37	0.13	-5.83	126.52	6.34e-7

Table 4.A.5: Example showing ANOVA results comparing five variations of the synthetic grid distances to igneous bodies. Results indicate the grids are not significantly different.

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
Synthetic 1 Km	94	195.47	2.08	2.22		
Synthetic 2 Km	94	184.91	1.97	2.96		
Synthetic 3 Km	94	171.94	1.83	1.54		
Synthetic 4 Km	94	163.96	1.74	1.48		
Synthetic 5 Km	94	204.84	2.18	2.29		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	11.84	4	2.96	1.41	0.23	2.39
Within Groups	975.14	465	2.10			
Total	986.99	469				

Table 4.A.6: Example showing ANOVA results comparing five variations of the synthetic grid (n=94) data to the observed economic He (>0.3 He %) (n=94) distances to igneous bodies. Results indicate the datasets are significantly different.

<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
Economic Km	94	52.93	0.56	0.82		
Synthetic 1 Km	94	195.47	2.08	2.22		
Synthetic 2 Km	94	184.91	1.97	2.96		
Synthetic 3 Km	94	171.94	1.83	1.54		
Synthetic 4 Km	94	163.96	1.74	1.48		
Synthetic 5 Km	94	204.84	2.18	2.29		
ANOVA						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between Groups	164.67	5	32.93	17.48	4.24e-16	2.23
Within Groups	1051.24	558	1.88			
Total	1215.92	563				

Table 4.A.7: Showing post-hoc (Games-Howell) results comparing five variations of the synthetic grid (n=94) data to the observed economic He (>0.3 He %) (n=94) distances to igneous bodies. Results (p values < .001) indicate the economic and synthetic grids are significantly different (JASP Team, 2023).

Comparison	Mean Difference	95% CI Lower	95% CI Upper	SE	t	df	p _{tukey}
Economic - Synthetic 1	-1.52	-2.04	-1.00	0.18	-8.44	153.42	4.06e-13
Economic - Synthetic 2	-1.40	-1.98	-0.83	0.20	-7.00	140.76	1.42e-9
Economic - Synthetic 3	-1.27	-1.72	-0.81	0.16	-7.99	170.04	2.86e-12
Economic - Synthetic 4	-1.18	-1.63	-0.73	0.16	-7.56	171.85	3.48e-11
Economic - Synthetic 5	-1.62	-2.14	-1.09	0.18	-8.89	151.96	6.30e-14

4.A.2 Basement Fault Connectivity Map

A geometric and topological analysis was completed using free software “NetworkGT” in ArcGIS (Nyberg et al., 2018). Rose diagrams, fault sets, and fault-size distributions were analysed for the geometric analysis. For the topological analysis, the basement fault network was either shortened or elongated within 150 meters to allow for a realistic distribution of fracture intersections (I – fracture tip, Y- splay node, X – cross-cutting node). Triangular ternary plots were generated showcasing IYX and branch topology, which indicates that within the major oil/gas and He fields in the field area, there is a large degree of connectivity between the fault segments (Fig. 4.A.1B).

Spatial analysis was also conducted in the form of grid sampling to produce maps with various topological parameters. Contour plots were generated of various network properties (i.e., degree of connectivity, and fracture abundances). Using a grid size of 10,000 equally distributed cubes, a weak relationship was noted when comparing calculated 2D connectivity values (i.e., intensity of fractures in an area) with economic He molar %. This could be significant, but should be mentioned that the correlation depends on the size of the grid, which is a significant bias and interpretations derived from such maps should be treated with caution. It is worth noting that 2D connectivity maps are dependent on the quality of the underlying fault map – if say a fault segment was missed or its intersection type wrongly attributed it would affect the outputs.

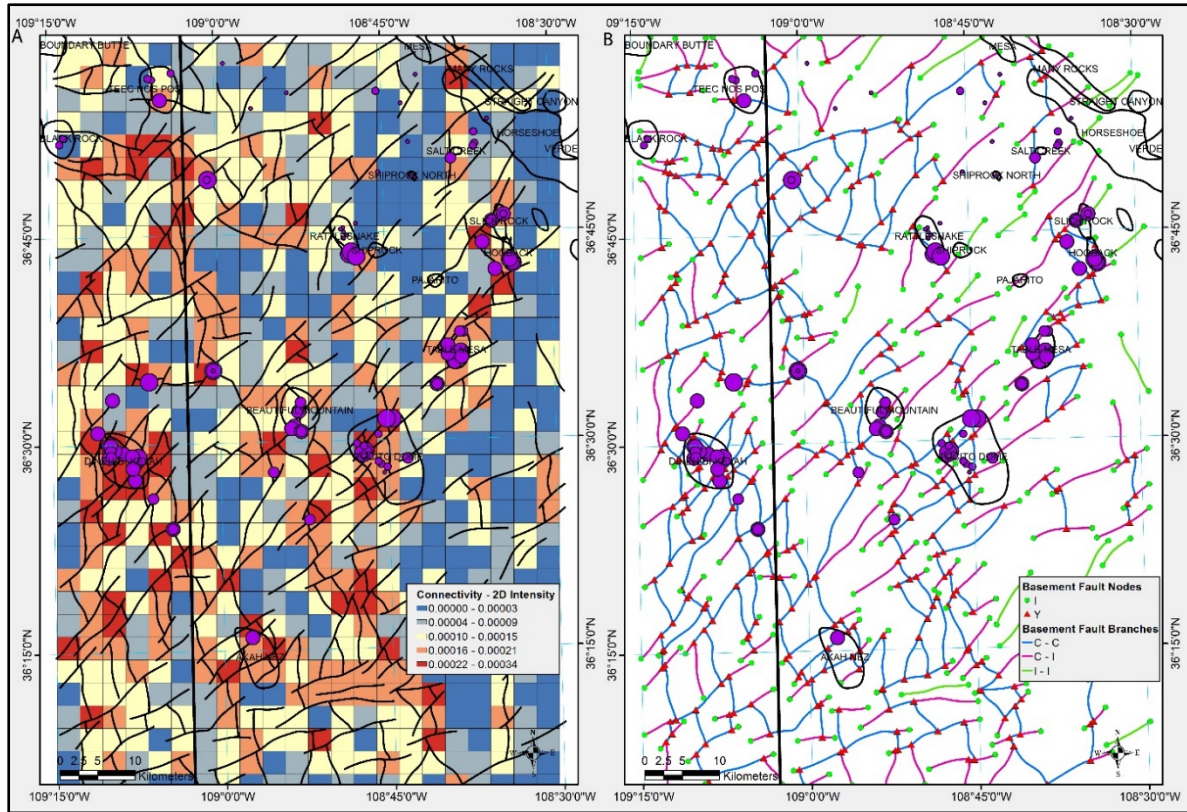


Figure 4.A.1: A) 2D fault connectivity map with 10,000 grids and B) basement fault nodes and branches are illustrated indicating a well-connected fault network in and around the prominent He clusters. Basement faults were manually adjusted within 150 m to create Y nodes and exclude X nodes. He % is overlain on maps as purple circles (Brennan et al., 2021; Halford et al., 2022).

A generalized linear model with the dependent variable as He % and covariates as distance to faults, distance to intrusions, distance to Y nodes and 2D connectivity values, produced the following p values of < .001 for basement faults, < .001 for igneous bodies, 0.009 for Y nodes, and 0.032 for 2D fault connectivity values. Considering an alpha value of 0.05, we observe that despite all covariates being significant, the Y nodes and 2D connectivity values are much larger values than those for basement faults and igneous bodies.

Therefore, a topological analysis was completed, which yielded a 2D fault connectivity map that could be utilized as a predictive tool for He occurrence based on fault connectivity and geometry (Fig. 4.A.1). However, as high-He is not strongly correlated with the 2D fault connectivity map compared with the basement fault map shown in Fig 4.1B, we do not pursue further 2-D connectivity mapping (Fig. 4.A.1A).

4.A.3 Localized Reservoir Structure Maps

Dineh-Bi-Keyah Field

The Dineh- Bi-Keyah (DBK) Field has historically produced hydrocarbons and He (Danie, 1978). The main producing interval for hydrocarbons and He is an igneous syenite sill that intrudes the Pennsylvanian Barker Creek Formation. The McCracken Sandstone is a Devonian reservoir that has been tested for high He, but not thoroughly produced. The Barker Creek is a poorly understood and non-productive He reservoir.

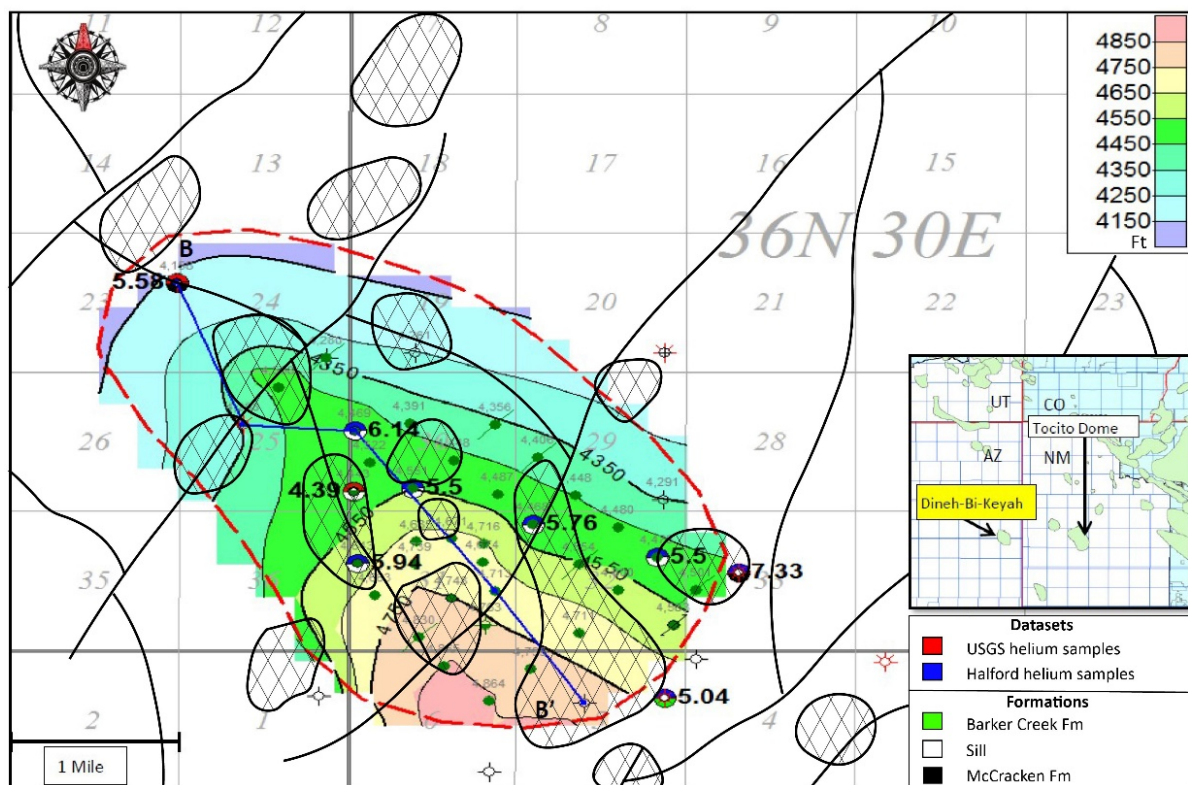


Figure 4.A.2: Structure map (datum: sea level ft) on the top of the sill in the DBK Field (C.I. 100 ft/30 m) with interpreted intrusions (cross hatched pattern) and basement faults (black lines). High He in the sill is found along the crest of the structure. There are stratigraphic pinchouts at the field boundary (red dashed line). No faults were directly observed in well logs, but are theorized to exist due to the presence of igneous bodies. He % is overlain on the map (Brennan et al., 2021; Halford et al., 2022). Cross section (B-B') is shown in Halford (2018).

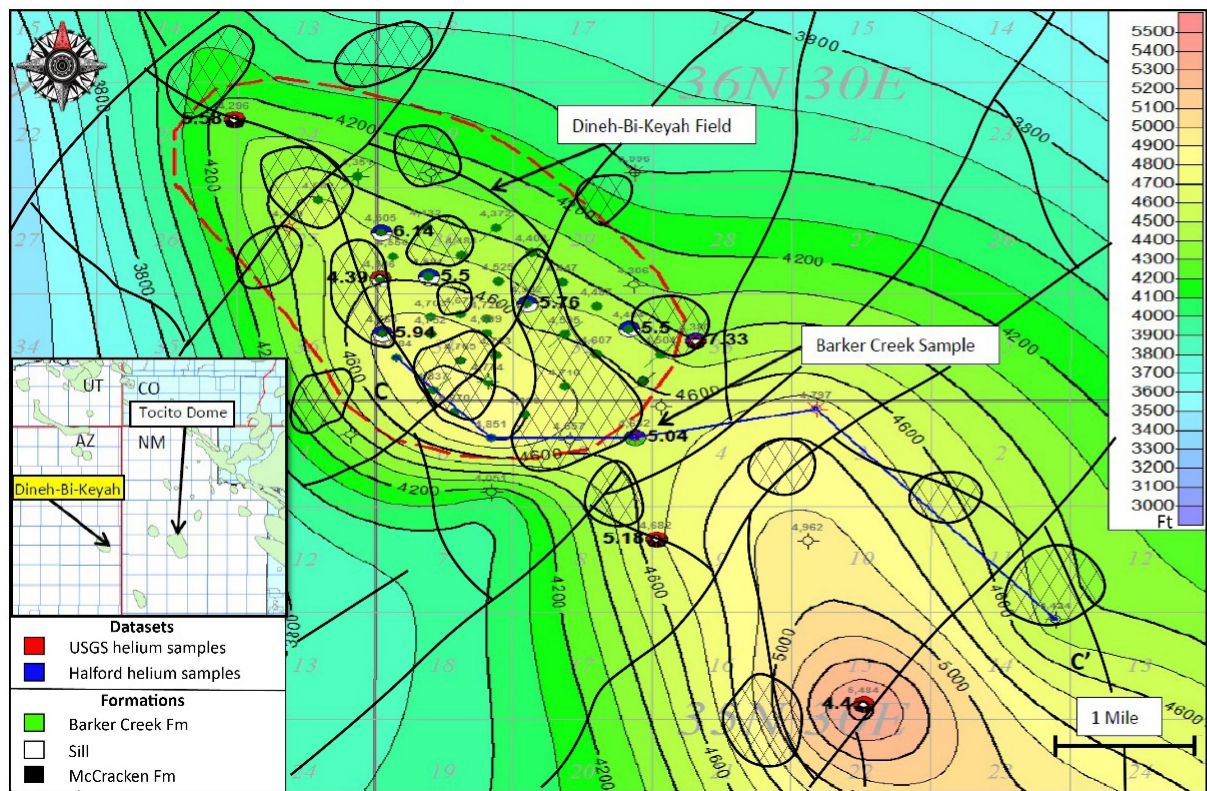


Figure 4.A.3: Structure map (datum: sea level ft) on the top of the Barker Creek in the DBK Field (C.I.100 ft/30 m) with interpreted intrusions (cross hatched pattern) and basement faults (black lines). Barker Creek sample is on a structural high. Barker Creek is a reservoir producing hydrocarbons and He in the Tocito Dome Field. He % is overlain on the map (Brennan et al., 2021; Halford et al., 2022). Cross section (C-C') is shown in Halford (2018).

Trapping in the DBK is a combination structural and stratigraphic trap. The primary reservoir (sill) appears to have 4-way closure due to stratigraphic pinch outs of the intrusion. The sill also has a structural component (plunging anticline) with a north-northwest trend (Fig. 4.A.2). Regarding the McCracken reservoir and Barker Creek reservoirs (Fig. 4.A.3 and 4.A.4), there is 4-way and 3-way structural domal closure with inferred stratigraphic pinchouts or hidden faulting as there are few wells drilled into the McCracken. Additionally, structural traps show updip He migration.

Although no faults were observed by well log analyses, hidden faults are considered responsible for influencing the dynamics of the field due to the presence of an igneous intrusion and recent geophysical data (i.e., basement faults and igneous bodies) (Fig.1). The intrusion is most likely causing secondary fracturing or it is following pre-existing faults/fracturing in the crust. Moreover, the DBK Field does lie within the basement structural high zone and where basement faults and igneous intrusions intersect (Fig. 4.1D, 4.4, 4.A.2-4).

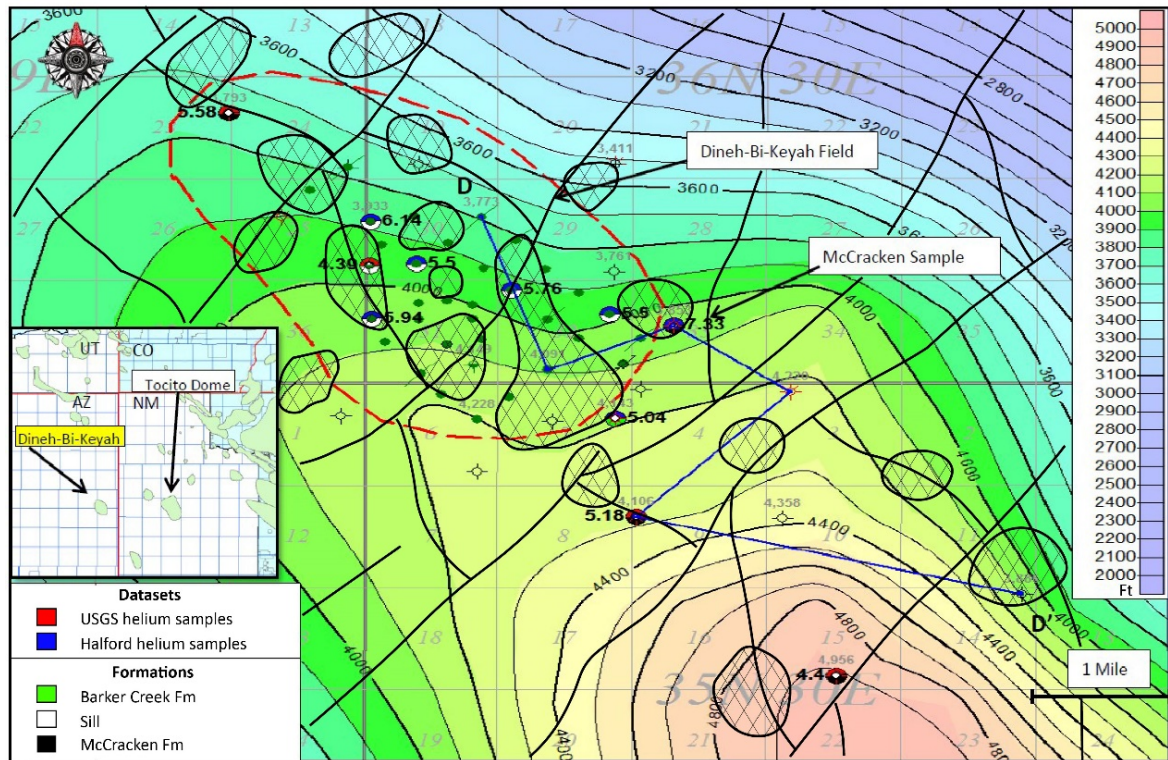


Figure 4.A.4: Structure map (datum: sea level ft) on the top of the McCracken in the DBK Field (C.I. 100 ft/30 m) with interpreted intrusions (cross hatched pattern) and basement faults (black lines). McCracken sample is near a structural high area. McCracken reports the highest He in the Dineh-Bi-Keyah area. He % is overlain on the map (Brennan et al., 2021; Halford et al., 2022). Cross section (D-D') is shown in Halford (2018).

Tocito Dome Field

There are two main He producing reservoirs in the Tocito Dome Field, the Pennsylvanian Barker Creek Member of the Paradox Formation and the Mississippian Leadville Formation. The Tocito Dome has a He accumulation at 0.3-0.5 He % in the Paradox Formation, which is composed of fossiliferous, calcareous boundstones, packstones, and grainstones (Spencer, 1978) with minor amounts of claystones, siltstones and phosphate, and around 7.0 He % in the Leadville Limestone, which is primarily composed of carbonates.

The geographic location of the He-rich samples (Fig. 4.A.5), for the most part, plot within the main structural dome of the Tocito Dome Field indicating that an efficient structural trap is present (four-way domal closure is apparent for the central portion of the field) for the Barker Creek structure and inferred Leadville structure. Although the Leadville structure is inferred due to the fact that it is difficult to accurately map the Leadville Limestone as most well logs don't record past Pennsylvanian strata, it is not unreasonable to assume a similar dome structure exists in the Leadville Formation. The

structural traps indicate the updip migration of He in the Barker Creek and inferred Leadville formations. The field is bounded by normal faulting on the east and several smaller faults are inferred on the northeastern portion of the field (Fig. 4.A.5) (Spencer, 1978). Additionally, the Tocito Dome high-He samples do for the most part lie within the basement structural high and at an intersection of basement faults and igneous intrusions (Figs. 4.1D, 4.4, and 4.A.5).

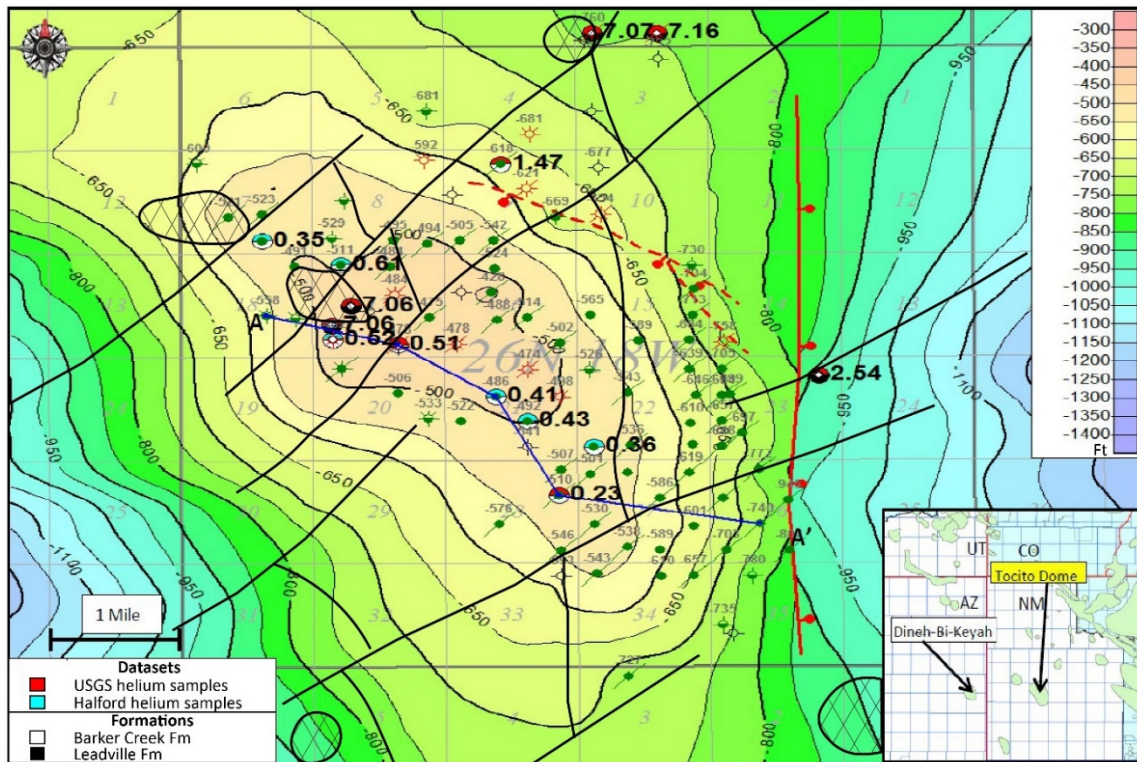


Figure 4.A.5: Structure map (datum: sea level ft) on the top of the Barker Creek (C.I. 50 ft/15 m) for the Tocito Dome with interpreted intrusions (cross hatched pattern) and basement faults (black lines). Labelled USGS He denotes previously published gas samples (Brennan et al., 2021), while labelled Halford He samples are from Halford et al., (2022). Four-way closure is observed as the Halford (2018) samples are found on the crest of the structure. Leadville USGS samples are also controlled by structure. Leaky seals are inferred based on the deeper He-rich gas from the Leadville. Cross section (A-A') is shown in Halford (2018).

Teec Nos Pos Field

In the Teec Nos Pos or Tohache Wash area, the Navajo Z-1 well (API: 02001053090001) was recompleted 1967, and temporarily shut-in in 1969 (Spencer, 1978). The Z-1 well was re-entered in the Leadville Limestone in 2016 and reported ~6% He. Historical bulk gas composition for the Z-1 well in the Leadville is: CH₄ <14.7%, C₂H₆ 1%, C₃H₈ 0.5%, N₂ 54.1 %, CO₂ 22.15%, and He 5.9%.

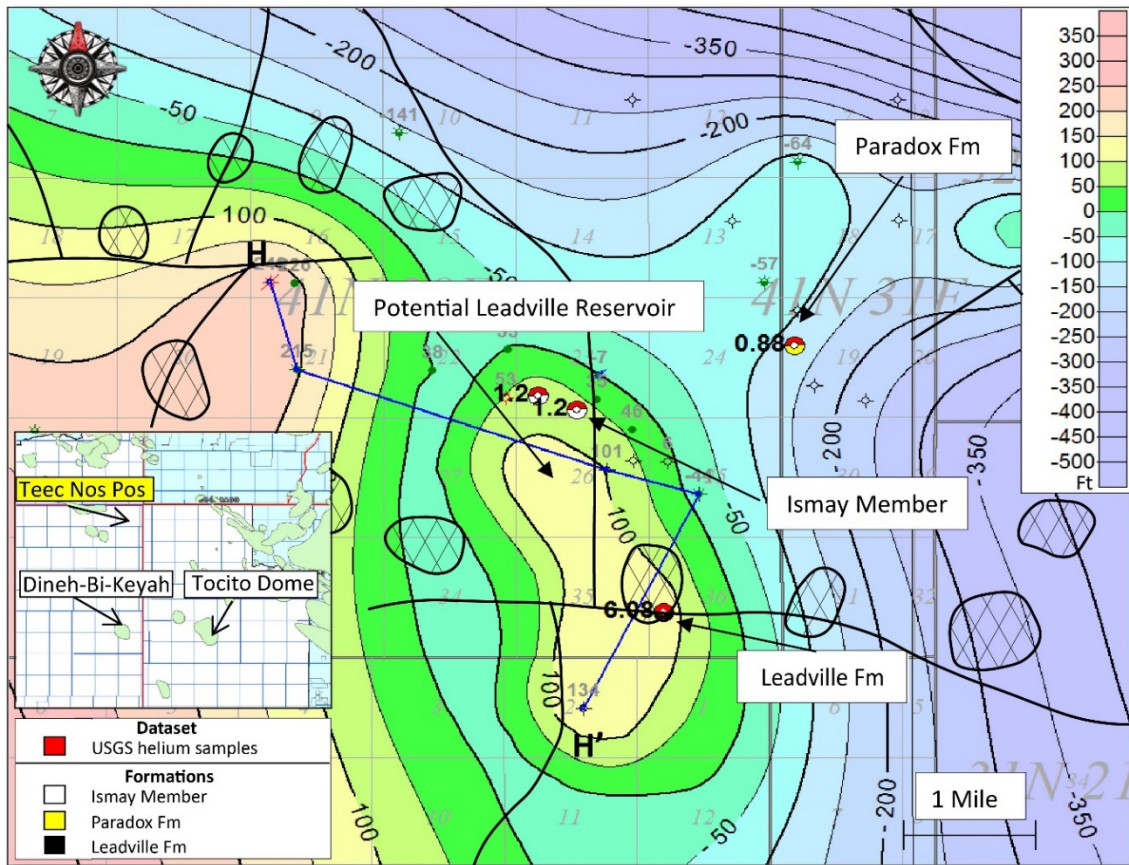


Figure 4.A.6: Structure map (datum: sea level ft) on the top of the Ismay (C.I. 50 ft/15 m) for the Teec Nos Pos area with interpreted intrusions (cross hatched pattern) and basement faults (black lines). The Ismay structure is very similar to the Leadville structure. The sample within the potential Leadville reservoir plots within a 4-way structural closure. Leaky seals are inferred based on the presence of smaller He values in the sediments (Ismay and Paradox) overlying and near to the primary Leadville reservoir. USGS legacy He samples are shown with their respective sampled reservoirs (Brennan et al., 2021; Halford, 2018).

The number of wells penetrating deep enough into the Leadville Limestone is extremely limited in the Teec Nos Pos area. A structure map on the top of the Ismay Member of the Paradox Formation serves as a proxy phantom map for the Leadville Limestone (Fig. 4.A.6). This map was created without calculated phantom values because previously published maps indicate a strong similarity between the shallower Desert Creek structure and the deeper Leadville structure. Thus, the Ismay Member structural map was assumed to roughly mirror the underlying structure of the Leadville Limestone. The largest concentrations of He at ~6.2 He % from the Leadville are observed at the top of the inferred structure (Spencer, 1978). He was measured from the Ismay Member of the Paradox Formation at ~1.2% and from sediments overlying the Ismay Member at ~0.88%. These He samples might be outliers or the result of a leaky seal. Overall, the trap appears to be structurally controlled as the high He samples are within high points of a dome (4-way closure) based on the

phantom structure map (Fig. 4.A.6). The sample's structural position on the dome highlights the updip migration of He. Interestingly, the Teec Nos Pos Field area does not lie within the basement structural high (Figs. 4.1D, 4.4, and 4.A.6), but it does lie at the intersection of basement faults and igneous bodies, which could be acting as sources of localized doming.

4.A.4 Werner Deconvolution Theory

To establish depth and structural configuration of the basement, aeromagnetic analysis was completed by Earthfield Technology, LLC and their methods are described in more detail below. More specifically, the magnetic data was processed and analysed using filtered residual maps, reduced to the pole (RTP) transform maps, and a qualitative review of total magnetic intensity contour maps. Additionally, a quantitative analysis of the previously mentioned data was completed by a generation and review of the Werner deconvolution (depth-to-source) estimates. The interactive analysis of the depth to and horizontal position of the source bodies as well as the related parameters of susceptibility and dip were conducted with Werner deconvolution-based algorithms (Werner, 1953) formatted in a PC-based program called MAGDEPTH © (Earthfield Technology's proprietary Werner deconvolution software package). The elimination of interference from adjoining/overprinted anomalies is achieved by a rigorous, iterative, and a two-dimensional inversion technique.

Parameters for thin, sheet-like bodies (e.g., sills, dikes, intruded fault zones, and basement plates of minor relief relative to the source-sensor separation distance) are generated from the analysis of the total magnetic intensity data. Similar patterns for geologic interface type features (e.g., major faults, slope changes of basement surfaces, prismatic body edges, and dipping contacts) are produced through horizontal gradient data analysis. The horizontal gradient data is computed each pass from filtered total intensity data. Two interferences bound all thin sheets. However, the two interferences are often indistinguishable as the anomalies are too close together to be distinguished from each other, thus the combination of the anomalies result in a single thin sheet anomaly. Interestingly, the horizontal derivative of the gravity/magnetic anomaly for an interface is often the same as the gravity/magnetic anomaly for a thin sheet that is similarly positioned. Therefore, it is simple to transform interface-type anomalies that are present in the total field data into sheet-type anomalies by

calculating the derivative of the total field data. The identification and calculation of interfaces and geologic parameters of thin sheet-type bodies is possible by combining the analyses of the gradient data and the total field data.

The interpreter performs six operator passes of the data in order to extract as much information pertaining to the structural and geologic environment. In each of the passes, the interpreter selects various parameters such as the order of the interference operator to be applied to the data, the order and terms of the filter to be used, and the sample spacing between adjacent data points forming the deconvolution operator. The detection of an anomalous source is dependent on the horizontal distance subtended by the observational array (i.e., the operator length). To ensure the deeper geologic sources that have broader magnetic signatures will be recognized, the distance must be increased. To allow for increasing operator sizes, the computation sequence previously mentioned can be run for up to six passes. The spacing parameter allows the operator length of each pass to be set. This process fundamentally specifies data decimation. It is not uncommon for an anomaly to be encountered on multiple passes if there is overlap between depth ranges for the passes.

A 1000-meter sample sampling protocol was used during each operator pass. The data spacing, the sub-sample interval, and the order of interference chosen for the pass (first second or third corresponding to a six, seven, or eight-point operator) determines the actual operator length. During deconvolution, the depth and along line position of the related source body can be determined from solving the set of simultaneous equations using the six, seven or eight equally spaced points along the said profile. Another calculation is made after the entire sequence of points is advanced by one point, so as to obtain as many X and Y pairs as there are data points along an anomaly. A statistical check for consistency is performed on the calculated positional coordinates and inconsistent depth calculations are disregarded. A central solution position can often be calculated if the operator is passing over an anomaly, as there should be a closely grouped set of depth points, which indicates an anomaly source. Subsequently, dip values and susceptibility values are computed. As an aside, manual techniques (e.g., half maximum slope) were attempted to calculate source depths in areas where the Werner deconvolution analysis failed.

Chapter 5 Appendix

5.A.1 General

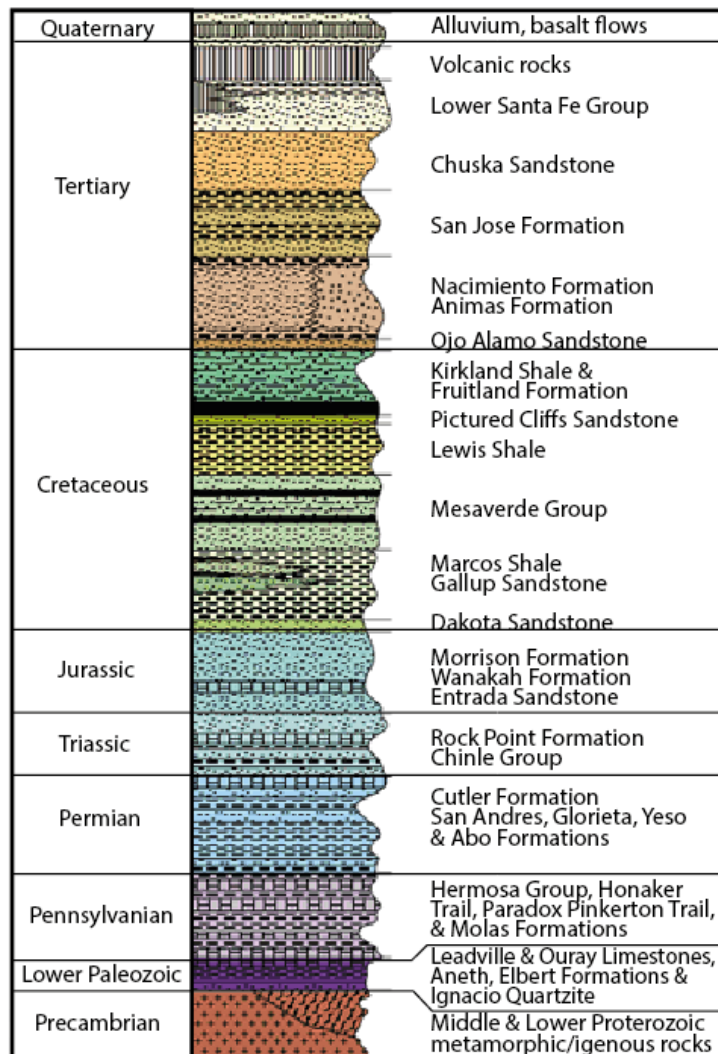


Figure 5.A.1: Generalized San Juan structural province stratigraphy (mod. Brister and Price, 2002).

5.A.2 Regional Fault and Fracture Patterns

Through examination of various transport mechanisms, the role of faults and fracture networks has been increasing apparent as the limiting factor for our field area in terms of migration conduits (chapter 4). To further explore the nature of regional fault significance, we examine regional basement fault and stress field orientation and fracture network connectivity.

Regional Stress Field Orientation

Using NetworkGT, an in-depth regional fault analysis is completed to examine two-dimensional basement fault networks (n=644) looking at both geometry and topology attributes

(Nyberg et al., 2018). We present the two fault sets and their respective orientations (Figure 5.A.2A). The orientations of basement faults are calculated from each individual fault segments (Nyberg et al., 2018). The dominant orientation, which is from the NE to SW, broadly aligns with the regional stress fields around the Colorado Plateau (Lunderstern and Zoback, 2020) (Figure 5.A.2B). Additionally, a maximum horizontal stress orientation of 35° was recorded from a wellbore image log near the Hogback NW of Farmington (Lorenz and Cooper, 2003). The dominant orientation hosts longer faults, which is illustrated by the rose diagram normalized to length (Figure 5.A.2C).

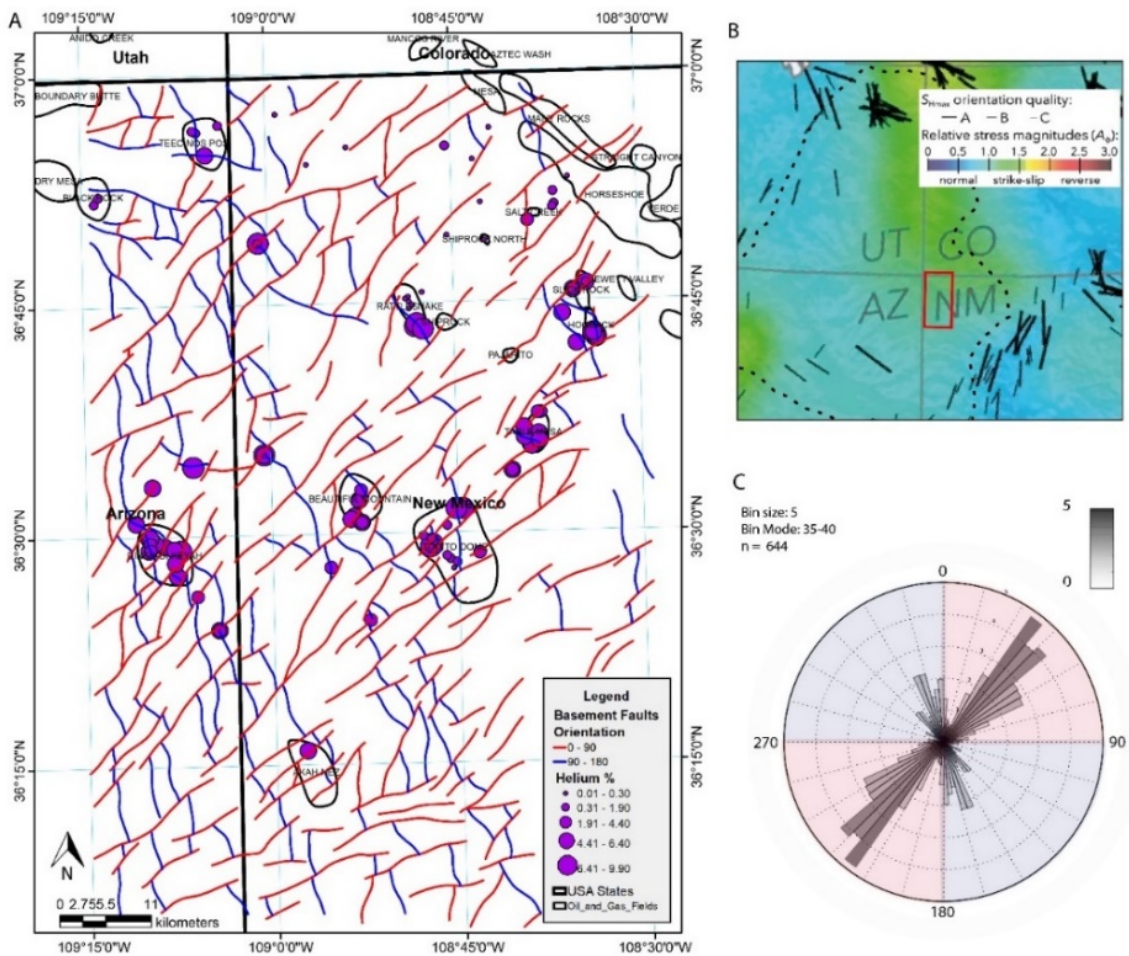


Figure 5.A.2.: A) Showing an orientation analysis conducted in NetworkGT (Nyberg et al., 2018) with red illustrating basement faults from 0°-90° and blue indicating faults from 90°-180° along with overlain He values (Brennan et al. 2021); B) Outline of the Colorado Plateau with a dashed black line and red box showing the field area on a state of stress map showing maximum horizontal stress (S_{Hmax}) orientations along with relative stress magnitudes (style of faulting) indicated by colour (Lunderstern and Zoback, 2020); C) length weighted fault orientation diagram shows the dominant and longer fault orientation is to the NE and SW.

To understand the spatial component of historical He wells and fault orientation we created a 1 km buffer around each of the fault legs (Chapter 4). Over 85% of all economic He data lie within

these buffers, and the remaining were manually assigned to the nearest basement fault. When looking at the distribution of He % and fault orientation, we observe two main groups corresponding to the dominant fault set (45°) and secondary set (150°) fracture orientations. The dominant fault orientation hosts ~60% of all the economic He points, while the secondary fault orientation hosts the remaining 40%. We observed that orientation as well as fault length does not correlate with high-He. Both have similar ranges of He data from 0.3 to ~8% He. One noticeable difference between the two data groupings is the dominant fault orientation has a continuous range from 0.3 to 8% He, while the secondary fault orientation group has a data hole (i.e., lack of data) from ~1.5-4 He%. This discrepancy might be due to disparities/biases within the actual data itself or patterns of chemical alteration, or it could be indicating increased dilation of faults as a function of tectonic stress and lithostatic pressures as well as fluid pressures (Lundstern and Zoback, 2020). Theoretically, active He fluxes from basement via open fractures and faults could be inferred in zones where the current regional stress fields align with the interpreted basement fault orientation. This could result in a broader and fuller ranges of continuous He anomalies.

High Density Fracture Network

In addition to the large basement faults, there is a pervasive fracture network throughout the field area which could be helping or hindering He accumulation potential. Fracture identification (i.e., areas of most pervasive fracturing) was made possible by a complex lineament analysis by combining and integrating lineaments from digital elevation models (topographic lineaments), well data and seismic data (formation lineaments), potential field data (magnetic and gravity lineaments), and basement faults/fractures (magnetic and gravity lineaments), courtesy of Earthfield Technology, LLC.

As geomorphology based analyses of surface expresses can often lead to insights about subsurface geology, a SRTM-30 meter digital elevation model is used to generate topographic lineaments. Bouger gravity lineaments, which have been generated using gridded Bouger gravity data, use subsurface density contrasts of lithologic units to infer information about potential fracturing/faulting. RTP magnetic lineaments, which have been generated using gridded RTP magnetic data, illustrate magnetic contrasts namely by the concentrations of ferromagnetic minerals in

the subsurface. Basement faults/lineaments have been generated by Earthfield's depth to basement mapping using Werner Deconvolution analysis of gravity and magnetic data (Werner, 1953). Also utilizing Werner Deconvolution along with filters and derivative maps of magnetic data, the locations and geometries of igneous bodies are derived from magnetic data (chapter 4). More specifically sharp and distinctive gradients were identified and mapped because they often represent faulting and fracturing that are key in constructing a lineament and intersection density map.

Ultimately a lineament and intersection density map, which ties surficial and subsurface lineament expression, is created by combing all the previously described lineaments and shows the number of lineaments predicted in an area. Areas of pervasive predicted fractures are illustrated by filtering to only illustrate areas where more than 3 datasets indicate possible fracturing. At this stage, directional data was filtered to capture and to enhance structural trends in a particular direction (i.e., N-S, E-W, NW-SE, SW-NE). The final product is produced by combining directionally filtered lineament data and by illustrating the junction of multiple fracture networks to highlight areas of potential increased natural porosity as a function of interpreted lineament intersection (Figure 5.A.3).

By closely analysing the distribution of He and the fracture network map, a first order observation is that 94% of economic helium wells lie on the intersection fracture node (Figure 5.A.3). Of the remaining 6%, half lie on or nearly on a fracture lineament. Fracture intersection nodes are likely zones of increased porosity and permeability, which is why we observe He at these localities. Interestingly, fracture node size does not correlation with higher amounts of He. When analysing these occurrences to be the result of a chance relationship, a synthetic random point grid was created and compared to the observed economic helium data, which showed they are significantly different distributions with only 7% of random points falling on a fracture intersection node.

Given there are many localities that have fracture intersection nodes but no He anomaly, this supports the statement that fracture nodes are likely important in the He system facilitating advection based transport, but are not likely the most important geologic feature in the transportation and accumulation of He in the subsurface. Another observation is the intricate nature of the predicated fracture network and fault intersection map. Even the Colorado Plateau which has experienced relatively little to moderate deformation compared to younger geologic regimes (i.e., Yellowstone),

the subsurface is likely extremely fractured. This should influence the assumptions scientists make in future mass transport models in areas that have experienced less dramatic forms of tectonic activity.

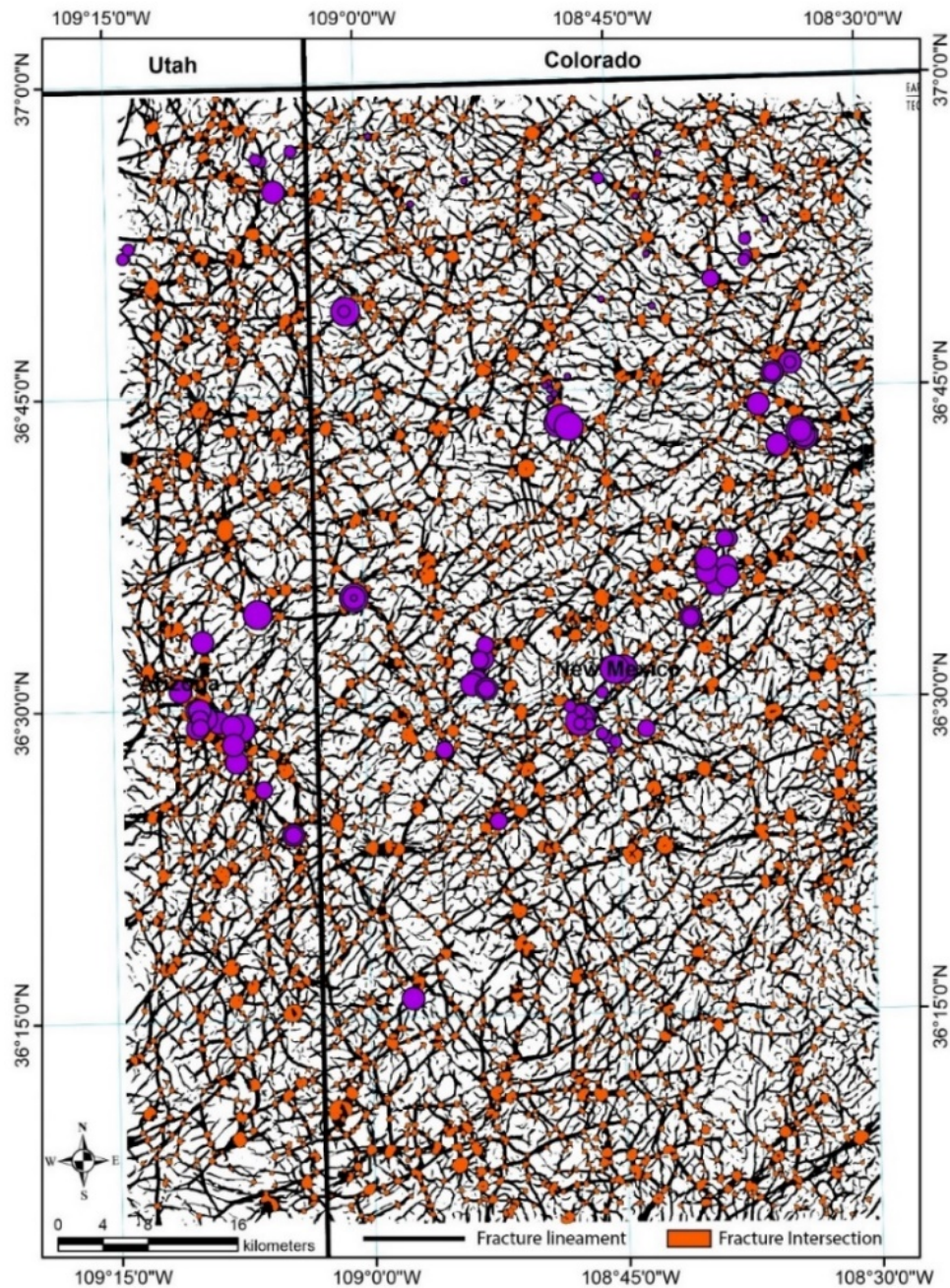


Figure 5.A.3: Interpreted fracture network map and intersections (orange polygons) with He well data (purple circles, Brennan et al., 2021) showing a complex network of predicted fracturing.

5.A.3 Complete Soil Gas Data

Table 5.A.1: Complete raw He soil gas values (He ppb) and air corrected (He_c ppb) values for the 7 fields of interest along with latitude and longitude. A = Akah Nez (n = 202); B = Beautiful Mountain (n = 644); P = Porcupine Dome (n = 262); R = Rattlesnake (n = 290); T = Tom (n = 221); TW = Tohache Wash (n = 88); and W = White Rock (n = 267).

ID	Latitude	Longitude	He ppb	He, ppb
A1	36.23110	-108.95201	5373	43
A2	36.22890	-108.95280	5433	103
A3	36.22740	-108.95201	5346	16
A4	36.22549	-108.95199	5433	103
A5	36.22380	-108.95200	5377	47
A6	36.22200	-108.95200	5368	38
A7	36.22035	-108.95193	5408	78
A8	36.21831	-108.95200	5416	86
A9	36.21638	-108.95135	5382	52
A10	36.21471	-108.95192	5368	38
A11	36.21830	-108.95201	5435	105
A12	36.21109	-108.95193	5416	86
A13	36.20929	-108.95198	5378	48
A14	36.20755	-108.95192	5400	70
A15	36.20569	-108.95192	5395	65
A16	36.20566	-108.94997	5359	29
A17	36.20755	-108.94991	5407	77
A18	36.20938	-108.94999	5391	61
A20	36.21300	-108.94992	5415	85
A21	36.21461	-108.95000	5300	-30
A22	36.21648	-108.95000	5385	55
A23	36.21814	-108.94993	5375	45
A24	36.22015	-108.95002	5418	88
A26	36.22379	-108.95000	5415	85
A27	36.22550	-108.94998	5379	49
A28	36.22730	-108.95000	5413	83
A29	36.22879	-108.95000	5424	94
A30	36.23100	-108.95000	5374	44
A31	36.23110	-108.94799	5448	118
A32	36.22889	-108.94801	5358	28
A33	36.22731	-108.94798	5448	118
A34	36.22552	-108.94799	5401	71
A35	36.22379	-108.94800	5403	73
A36	36.22200	-108.94801	5402	72
A37	36.22020	-108.94700	5367	37
A38	36.21797	-108.94802	5374	44
A39	36.21640	-108.94800	5376	46
A40	36.21460	-108.94801	5372	42
A41	36.21296	-108.94772	5397	67
A42	36.21110	-108.94797	5417	87
A43	36.20928	-108.94801	5466	136
A44	36.20761	-108.94800	5426	96
A46	36.20540	-108.94515	5415	85
A47	36.20751	-108.94500	5465	135
A48	36.20930	-108.94601	5430	100
A49	36.21113	-108.94603	5516	186
A50	36.21299	-108.94555	5340	10
A51	36.21481	-108.94597	5408	78
A52	36.21627	-108.94602	5369	39
A53	36.21794	-108.94595	5270	-60
A54	36.22022	-108.94592	5385	55
A55	36.22190	-108.94602	5411	81
A56	36.22349	-108.94594	5409	79
A57	36.22549	-108.94600	5428	98
A58	36.22741	-108.94598	5378	48
A59	36.22940	-108.94601	5396	66
A60	36.23099	-108.94597	5317	-13
A61	36.23080	-108.94301	5420	90
A62	36.22911	-108.94300	5441	111
A64	36.22568	-108.94302	5386	56
A65	36.22350	-108.94402	5377	47
A66	36.22188	-108.94402	5359	29
A67	36.22019	-108.94398	5337	7
A68	36.21825	-108.94392	5409	79
A69	36.21607	-108.94402	5384	54
A70	36.21481	-108.94398	5360	30
A71	36.21308	-108.94300	5376	46
A72	36.21128	-108.94398	5376	46
A73	36.20923	-108.94300	5296	-34
A74	36.20737	-108.94303	5377	47
A75	36.20571	-108.94302	5370	40
A76	36.20571	-108.94100	5337	7
A77	36.20782	-108.94100	5380	50
A78	36.20929	-108.94099	5403	73
A79	36.21152	-108.94099	5405	75
A80	36.21317	-108.94101	5330	0
A81	36.21504	-108.94098	5411	81
A83	36.21869	-108.94102	5418	88
A84	36.22020	-108.94102	5401	71
A85	36.22210	-108.94100	5377	47
A86	36.22363	-108.94098	5409	79
A87	36.22580	-108.94099	5423	93
A88	36.22811	-108.94103	5417	87
A89	36.22931	-108.94102	5457	127
A90	36.23099	-108.94099	5440	110
A92	36.23291	-108.93801	5468	138
A93	36.22729	-108.93800	5326	-4
A94	36.22550	-108.93800	5383	53
A95	36.22373	-108.93900	5426	96
A96	36.22220	-108.93901	5426	96
A97	36.22022	-108.93900	5425	95
A98	36.21883	-108.93901	5356	26
A99	36.21682	-108.93899	5337	7
A100	36.21511	-108.93901	5350	20
A101	36.21292	-108.93903	5322	-8
A102	36.21113	-108.93901	5338	8
A103	36.20911	-108.93900	5424	94
A104	36.20742	-108.93903	5421	91
A105	36.20569	-108.93899	5469	139
A106	36.20568	-108.93601	5338	8
A107	36.20732	-108.93632	5372	42
A108	36.20940	-108.93600	5330	0
A109	36.21094	-108.93601	5374	44
A110	36.21330	-108.93599	5373	43
A111	36.21510	-108.93700	5405	75
A112	36.21681	-108.93600	5332	2
A113	36.21798	-108.93710	5427	97
A114	36.22011	-108.93594	5439	109
A117	36.22558	-108.93598	5486	156
A118	36.22762	-108.93699	5366	36
A119	36.22910	-108.93600	5449	119
A120	36.23101	-108.93608	5391	61
A121	36.23109	-108.93399	5423	93
A122	36.22942	-108.93417	5416	86
A123	36.22744	-108.93415	5304	-26
A127	36.22023	-108.93398	5375	45
A128	36.21830	-108.93401	5439	109
A129	36.21661	-108.93400	5365	35
A130	36.21470	-108.93398	5372	42
A131	36.21289	-108.93401	5414	84
A132	36.21101	-108.93397	5420	90
A133	36.20930	-108.93401	5378	48
A134	36.20708	-108.93399	5287	-43
A135	36.20570	-108.93401	5375	45
A136	36.20570	-108.93200	5395	65
A137	36.20710	-108.93200	5418	88
A139	36.21109	-108.93199	5336	6
A140	36.21285	-108.93180	5395	65
A141	36.21480	-108.93199	5440	110
A142	36.21660	-108.93201	5439	109
A143	36.21811	-108.93201	5464	134
A144	36.22007	-108.93201	5409	79
A148	36.22743	-108.93213	5398	68
A151	36.23077	-108.92970	5426	96
A152	36.22896	-108.92965	5380	50
A153	36.22747	-108.92979	5463	133
A154	36.22535	-108.92940	5426	96
A155	36.22348	-108.93024	5367	37
A156	36.22228	-108.92967	5430	100
A157	36.22016	-108.92954	5426	96
A159	36.21648	-108.92975	5450	120
A160	36.21481	-108.92999	5456	126
A161	36.21299	-108.92900	5469	139
A162	36.21090	-108.92900	5476	146
A163	36.20889	-108.92896	5504	174
A164	36.20710	-108.93000	5447	117
A165	36.20570	-108.92999	5477	147
A166	36.20570	-108.92800	5441	111
A167	36.20710	-108.92801	5360	30
A169	36.21112	-108.92799	5466	136
A170	36.21320	-108.92800	5411	81
A171	36.21492	-108.92699	5368	38
A172	36.21687	-108.92797	5430	100
A174	36.22052	-108.92673	5416	86
A175	36.22214	-108.92804	5343	13
A176	36.22369	-108.92798	5425	95
A177	36.22571	-108.92699	5403	73
A178	36.22729	-108.92802	5424	94
A179	36.22945	-108.92796	5383	53
A180	36.23100	-108.92789	5387	57
A181	36.23131	-108.92500	5408	78
A182	36.22940	-108.92500	5386	56
A183	36.22750	-108.92500	5404	74
A184	36.22585	-108.92507	5395	65
A185	36.22369	-108.92503	5478	148
A186	36.22210	-108.92500	5369	39
A187	36.22033	-108.92490	5459	129
A188	36.21889	-108.92474	5372	42
A189	36.21682	-108.92493	5419	89
A190	36.21492	-108.92504	5388	58
A191	36.21353	-108.92483	5385	55
A194	36.20741	-108.92501	5434	104
A195	36.20570	-108.92499	5547	217
A197	36.20736	-108.92314	5491	161
A198	36.20911	-108.92309	5389	59
A199	36.21148	-108.92282	5383	53
A200	36.21340	-108.92300	5363	33
A201	36.21486	-108.92284	5378	48
A202	36.21701	-108.92297	5397	67
A203	36.21857	-108.92300	5351	21
A204	36.22016	-108.92300	5443	113
A205	36.22158	-108.92301	5395	65
A206	36.22342	-108.92303	5406	76
A207	36.22551	-108.92300	5341	11
A208	36.22790	-108.92300	5404	74
A209	36.22940	-108.92299	5437	107
A210	36.23130	-108.92299	5432	102
A211	36.23120	-108.92002	5326	-4
A212	36.22965	-108.91997	5355	25
A213	36.22741	-108.92000	5359	29
A215	36.22340	-108.92100	5435	105
A216	36.22202	-108.92099	5402	72
A217	36.22020	-108.92128	5284	-46
A218	36.21870	-108.92100	5385	55
A219	36.21700	-108.92098	5400	70
A220	36.21518	-108.92097	5390	60
A221	36.21313	-108.92094	5387	57
A222	36.21100	-108.92100	5389	59
A223	36.20906	-108.92107	5377	47
A224	36.20752	-108.92091	5403	73
A225	36.20599	-108.92015	5421	91
A19B	36.21120	-108.95000	5400	70
B1	36.56791	-108.90800	5291	-39
B2	36.56610	-108.90800	5402	72
B3	36.56430	-108.90800	5347	17
B4	36.56249	-108.90800	5373	43
B5	36.56091	-108.90800	5405	75
B6	36.55890	-108.90799	5412	82
B7	36.55669	-108.90800	5360	30
B8	36.55510	-108.90800	5379	49
B9	36.55340	-108.90800	5417	87
B10	36.55151	-108.90800	5428	98
B11	36.54990	-108.90800	5292	-38
B12	36.54778	-108.90766	5338	8
B13	36.54602	-108.90753	5335	5
B14	36.54445	-108.90753	5443	113
B15	36.54228	-108.90773	5303	-27
B16	36.54060	-108.90753	5290	-40
B17	36.53880	-108.90799	5326	-4
B18	36.53721	-108.90800	5341	11
B19	36.53550	-108.90800	5304	-26
B20	36.53350	-108.90800		

B45	36.50120	-108.90500	5505	175	B107	36.52440	-108.90300	5348	18	B169	36.56060	-108.89899	5352	22	B231	36.54041	-108.89600	5335	5
B46	36.50300	-108.90500	5314	-16	B108	36.52260	-108.90300	5412	82	B170	36.55890	-108.89900	5369	39	B232	36.54240	-108.89700	5354	24
B47	36.50460	-108.90500	5413	83	B109	36.52070	-108.90300	5429	99	B171	36.55700	-108.89901	5359	29	B233	36.54419	-108.89674	5301	-29
B48	36.50660	-108.90500	5350	20	B110	36.51890	-108.90300	5364	34	B172	36.55509	-108.89900	5421	91	B234	36.54608	-108.89695	5324	-6
B49	36.50830	-108.90500	5366	36	B111	36.51720	-108.90300	5321	-9	B173	36.55341	-108.89900	5357	27	B235	36.54787	-108.89677	5318	-12
B50	36.50990	-108.90601	5364	34	B112	36.51511	-108.90300	5345	15	B174	36.55170	-108.89899	5322	-8	B236	36.54990	-108.89700	5444	114
B51	36.51160	-108.90500	5276	-54	B113	36.51350	-108.90300	5237	-93	B175	36.54979	-108.89900	5344	14	B237	36.55171	-108.89702	5317	-13
B52	36.51350	-108.90500	5410	80	B114	36.51160	-108.90300	5282	-48	B176	36.54790	-108.89901	5323	-7	B238	36.55340	-108.89701	5369	39
B53	36.51510	-108.90501	5391	61	B115	36.50990	-108.90300	5311	-19	B177	36.54610	-108.89899	5343	13	B239	36.55520	-108.89700	5298	-32
B54	36.51720	-108.90499	5352	22	B116	36.50840	-108.90300	5376	46	B178	36.54430	-108.89900	5354	24	B240	36.55700	-108.89700	5357	27
B55	36.51910	-108.90499	5367	37	B117	36.50670	-108.90300	5449	119	B179	36.54250	-108.89901	5321	-9	B241	36.55880	-108.89700	5320	-10
B56	36.52094	-108.90494	5305	-25	B118	36.50510	-108.90300	5384	54	B180	36.54050	-108.89899	5301	-29	B242	36.56080	-108.89700	5378	48
B57	36.52260	-108.90500	5340	10	B119	36.50300	-108.90300	5472	142	B181	36.53890	-108.89900	5301	-29	B243	36.56251	-108.89700	5346	16
B58	36.52444	-108.90596	5355	25	B120	36.50140	-108.90300	5415	85	B182	36.53740	-108.89900	5351	21	B244	36.56430	-108.89700	5352	22
B59	36.52611	-108.90499	5283	-47	B121	36.49940	-108.90300	5397	67	B183	36.53529	-108.89899	5198	-132	B245	36.56601	-108.89700	5396	66
B60	36.52790	-108.90500	5224	-106	B122	36.49710	-108.90300	5471	141	B184	36.53348	-108.89900	5320	-10	B246	36.56790	-108.89701	5327	-3
B61	36.52979	-108.90501	5374	44	B123	36.49540	-108.90300	5290	-40	B185	36.53160	-108.89899	5221	-109	B247	36.56790	-108.89499	5290	-40
B62	36.53160	-108.90499	5356	26	B124	36.49540	-108.90100	5307	-23	B186	36.52990	-108.89899	5293	-37	B248	36.56630	-108.89500	5370	40
B63	36.53360	-108.90600	5361	31	B125	36.49730	-108.90100	5332	2	B187	36.52800	-108.89901	5364	34	B249	36.56450	-108.89499	5349	19
B64	36.53551	-108.90600	5429	99	B126	36.49920	-108.90100	5490	160	B188	36.52610	-108.89899	5375	45	B250	36.56300	-108.89509	5359	29
B65	36.53729	-108.90600	5352	22	B127	36.50130	-108.90100	5277	-53	B189	36.52440	-108.89900	5380	50	B251	36.56084	-108.89507	5406	76
B66	36.53890	-108.90599	5239	-91	B128	36.50311	-108.90101	5315	-15	B190	36.52259	-108.89899	5398	68	B252	36.55880	-108.89500	5351	21
B67	36.54068	-108.90601	5354	24	B129	36.50501	-108.90100	5347	17	B191	36.52081	-108.89901	5360	30	B253	36.55690	-108.89500	5350	20
B68	36.54230	-108.90501	5324	-6	B130	36.50679	-108.90099	5454	124	B192	36.51890	-108.89899	5273	-57	B254	36.55529	-108.89500	5296	-34
B69	36.54410	-108.90600	5388	58	B131	36.50860	-108.90100	5259	-71	B193	36.51670	-108.89901	5397	67	B255	36.55340	-108.89499	5316	-14
B70	36.54612	-108.90601	5511	181	B132	36.50989	-108.90099	5517	187	B194	36.51530	-108.89900	5374	44	B256	36.55170	-108.89499	5325	-5
B71	36.54790	-108.90599	5551	221	B133	36.51150	-108.90101	5369	39	B195	36.51350	-108.89901	5458	128	B257	36.55030	-108.89500	5315	-15
B72	36.54970	-108.90601	5412	82	B134	36.51360	-108.90100	5272	-58	B196	36.51180	-108.89900	5369	39	B258	36.54799	-108.89499	5310	-20
B73	36.55150	-108.90598	5454	124	B135	36.51530	-108.90099	5471	141	B197	36.50990	-108.89899	5423	93	B259	36.54600	-108.89500	5327	-3
B74	36.55340	-108.90600	5440	110	B136	36.51710	-108.90100	5449	119	B198	36.50851	-108.89899	5419	89	B260	36.54399	-108.89500	5322	-8
B75	36.55500	-108.90600	5429	99	B137	36.51900	-108.90100	5371	41	B199	36.50671	-108.89900	5396	66	B261	36.54240	-108.89400	5303	-27
B76	36.55687	-108.90607	5354	24	B138	36.52090	-108.90100	5398	68	B200	36.50491	-108.89900	5441	111	B262	36.54029	-108.89401	5493	163
B77	36.55890	-108.90600	5386	56	B139	36.52270	-108.90100	5494	164	B201	36.50299	-108.89901	5421	91	B263	36.53889	-108.89399	5284	-46
B78	36.56091	-108.90599	5375	45	B140	36.52440	-108.90100	5399	69	B202	36.50130	-108.89900	5409	79	B264	36.53730	-108.89400	5310	-20
B79	36.56260	-108.90601	5367	37	B141	36.52610	-108.90100	5314	-16	B203	36.49950	-108.89900	5373	43	B265	36.53562	-108.89399	5247	-83
B80	36.56420	-108.90600	5381	51	B142	36.52820	-108.90100	5593	263	B204	36.49740	-108.89900	5393	63	B266	36.53370	-108.89400	5350	20
B81	36.56620	-108.90600	5361	31	B143	36.52990	-108.90100	5303	-27	B205	36.49540	-108.89900	5415	85	B267	36.53170	-108.89400	5316	-14
B82	36.56791	-108.90601	5434	104	B144	36.53170	-108.90100	5351	21	B206	36.49540	-108.89600	5431	101	B268	36.52980	-108.89400	5321	-9
B83	36.56790	-108.90300	5349	19	B145	36.53360	-108.90100	5357	27	B207	36.49740	-108.89700	5413	83	B269	36.52819	-108.89400	5249	-81
B84	36.56620	-108.90299	5377	47	B146	36.53539	-108.90100	5259	-71	B208	36.49940	-108.89699	5402	72	B270	36.52630	-108.89400	5376	46
B85	36.56439	-108.90299	5372	42	B147	36.53721	-108.90104	5387	57	B209	36.50140	-108.89702	5369	39	B271	36.52441	-108.89401	5333	3
B86	36.56269	-108.90300	5402	72	B148	36.53891	-108.90100	5370	40	B210	36.50303	-108.89701	5381	51	B272	36.52268	-108.89399	5269	-61
B87	36.56090	-108.90400	5463	133	B149	36.54050	-108.90100	5294	-36	B211	36.50499	-108.89702	5413	83	B273	36.52100	-108.89398	5231	-99
B88	36.55879	-108.90300	5419	89	B150	36.54230	-108.90100	5313	-17	B212	36.50670	-108.89701	5407	77	B274	36.51891	-108.89400	5435	105
B89	36.55706	-108.90400	5450	120	B151	36.54430	-108.90101	5238	-92	B213	36.50840	-108.89700	5414	84	B275	36.51680	-108.89398	5390	60
B90	36.55520	-108.90399	5425	95	B152	36.54620	-108.90101	5349	19	B214	36.50990	-108.89700	5378	48	B276	36.51500	-108.89400	5305	-25
B91	36.55341	-108.90301	5421	91	B153	36.54800	-108.90101	5305	-25	B215	36.51180	-108.89700	5398	68	B277	36.51340	-108.89401	5395	65
B92	36.55181	-108.90300	5386	56	B154	36.54979	-108.90101	5404	74	B216	36.51360	-108.89701	5377	47	B278	36.51180	-108.89399	5349	19
B93	36.54991	-108.90300	5295	-35	B155	36.55160	-108.90101	5356	26	B217	36.51530	-108.89700	5374	44	B279	36.50990	-108.89500	5322	-8
B94	36.54830	-108.90301	5316	-14	B156	36.55340	-108.90100	5387	57	B218	36.51689	-108.89701	5408	78	B280	36.50840	-108.89500	5466	136
B95	36.54623	-108.90289	5398	68	B157	36.55520	-108.90101	5392	62	B219	36.51899	-108.89700	5356	26	B281	36.50680	-108.89500	5380	50
B96	36.54429	-108.90299	5324	-6	B158	36.55709	-108.90100	5413	83	B220	36.52080	-108.89700	5387	57	B282	36.50502	-108.89497	5342	12
B97	36.54233	-108.90323	5323	-7	B159	36.55889	-108.90100	5412	82	B221	36.52280	-108.89700	5359	29	B283	36.50300	-108.89500	5365	35
B98	36.54069	-108.90334	5297	-33	B160	36.56091	-108.90100	5369	39	B222	36.52440	-108.89700	5309	-21	B284	36.50130	-108.89500	5361	31
B99	36.53889	-108.90299	5357	27	B161	36.56280	-108.90100	5297	-33	B223	36.52630	-108.89700	5367	37	B285	36.49951	-108.89503	5349	19
B100	36.53720	-108.90302	5334	4	B162	36.56450	-108.90100	5322	-8	B224	36.52800	-108.89600	5314	-16	B286	36.49740	-108.89400	5402	72
B101	36.53550	-108.90300	5283	-47	B163	36.56620	-108.90101	5356	26	B225	36.52990	-108.89600	5337	7	B287	36.49540	-108.89400	5409	79
B102	36.53360	-108.90300	5276	-54	B164	36.56790	-108.90101	5336	6	B226	36.53170	-108.89600	5347	17	B288	36.49542	-108.89198	5482	152
B103	36.53190	-108.90300	5291	-39	B165	36.56790	-108.89901	5383	53	B227	36.53370	-108.89600	5347	17	B289	36.49730	-108.89200	5476	146
B104	36.52970	-108.90300	5510	180	B166	36.566													

B293	36.50487	-108.89201	5289	-41	B356	36.51890	-108.89000	5353	23	B418	36.55520	-108.88500	5397	67	B489	36.56240	-108.88300	5314	-16
B294	36.50671	-108.89201	5384	54	B357	36.51700	-108.89001	5293	-37	B419	36.55340	-108.88500	5220	-110	B490	36.56419	-108.88297	5345	15
B295	36.50838	-108.89198	5353	23	B358	36.51509	-108.89000	5360	30	B420	36.55170	-108.88500	5462	132	B491	36.56611	-108.88300	5330	0
B296	36.50989	-108.89201	5437	107	B359	36.51351	-108.88999	5381	51	B421	36.55010	-108.88500	5308	-22	B492	36.56791	-108.88301	5343	13
B297	36.51171	-108.89201	5340	10	B360	36.51170	-108.89000	5353	23	B422	36.54800	-108.88499	5366	36	B493	36.56791	-108.88100	5357	27
B298	36.51360	-108.89200	5322	-8	B361	36.50989	-108.88999	5256	-74	B424	36.54411	-108.88501	5300	-30	B494	36.56610	-108.88100	5369	39
B299	36.51520	-108.89201	5363	33	B362	36.50821	-108.89001	5374	44	B426	36.54050	-108.88501	5320	-10	B495	36.56431	-108.88099	5335	5
B300	36.51690	-108.89201	5281	-49	B363	36.50660	-108.89000	5380	50	B428	36.53720	-108.88501	5333	3	B496	36.56251	-108.88099	5343	13
B301	36.51901	-108.89200	5343	13	B364	36.50491	-108.88900	5360	30	B429	36.53539	-108.88500	5431	101	B497	36.56060	-108.88099	5380	50
B302	36.52110	-108.89199	5395	65	B365	36.50320	-108.88900	5483	153	B430	36.53339	-108.88499	5397	67	B498	36.55860	-108.88100	5392	62
B303	36.52280	-108.89201	5268	-62	B366	36.50100	-108.88900	5375	45	B431	36.53170	-108.88500	5417	87	B499	36.55700	-108.88099	5472	142
B304	36.52440	-108.89200	5301	-29	B367	36.49951	-108.89001	5381	51	B432	36.52970	-108.88501	5330	0	B500	36.55511	-108.88099	5351	21
B305	36.52620	-108.89201	5314	-16	B368	36.49749	-108.88996	5465	135	B433	36.52800	-108.88499	5357	27	B501	36.55337	-108.88100	5456	126
B306	36.52809	-108.89201	5344	14	B369	36.49540	-108.88902	5396	66	B434	36.52608	-108.88500	5409	79	B502	36.55160	-108.88100	5385	55
B307	36.52977	-108.89195	5429	99	B370	36.49540	-108.88698	5409	79	B435	36.52440	-108.88500	5422	92	B503	36.55010	-108.88101	5401	71
B308	36.53170	-108.89201	5437	107	B371	36.49749	-108.88699	5641	311	B436	36.52280	-108.88500	5348	18	B504	36.54820	-108.88100	5361	31
B309	36.53369	-108.89201	5456	126	B372	36.49942	-108.88702	5389	59	B437	36.52119	-108.88500	5320	-10	B506	36.54440	-108.88100	5311	-19
B310	36.53540	-108.89201	5338	8	B373	36.50110	-108.88700	5379	49	B438	36.51892	-108.88467	5364	34	B507	36.54219	-108.88100	5317	-13
B311	36.53728	-108.89201	5334	4	B374	36.50330	-108.88699	5367	37	B439	36.51711	-108.88499	5398	68	B508	36.54050	-108.88099	5405	75
B312	36.53888	-108.89198	5344	14	B375	36.50489	-108.88698	5397	67	B440	36.51508	-108.88502	5347	17	B509	36.53891	-108.88100	5484	154
B313	36.54040	-108.89200	5306	-24	B376	36.50651	-108.88699	5386	56	B441	36.51340	-108.88500	5357	27	B510	36.53730	-108.88100	5386	56
B314	36.54229	-108.89199	5346	16	B377	36.50821	-108.88700	5354	24	B442	36.51160	-108.88499	5347	17	B511	36.53559	-108.88099	5736	406
B315	36.54399	-108.89200	5327	-3	B378	36.50990	-108.88804	5357	27	B443	36.50981	-108.88534	5390	60	B512	36.53401	-108.88100	5323	-7
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B317	36.54781	-108.89200	5373	43	B380	36.51350	-108.88699	5417	87	B445	36.50639	-108.88499	5342	12	B514	36.53159	-108.88100	5248	-82
B318	36.54990	-108.89299	5323	-7	B381	36.51509	-108.88699	5374	44	B446	36.50500	-108.88500	5344	14	B515	36.52798	-108.88101	5366	36
B319	36.55160	-108.89300	5363	33	B382	36.51700	-108.88702	5363	33	B447	36.50340	-108.88499	5334	4	B516	36.52609	-108.88100	5309	-21
B320	36.55339	-108.89300	5323	-7	B383	36.51909	-108.88701	5368	38	B448	36.50101	-108.88498	5386	56	B517	36.52439	-108.88100	5328	-2
B321	36.55530	-108.89199	5430	100	B384	36.52111	-108.88702	5332	2	B449	36.49920	-108.88500	5405	75	B518	36.52270	-108.88100	5406	76
B322	36.55701	-108.89201	5357	27	B385	36.52261	-108.88700	5343	13	B450	36.49728	-108.88499	5387	57	B519	36.52120	-108.88100	5393	63
B323	36.55913	-108.89193	5288	-42	B386	36.52440	-108.88700	5351	21	B451	36.49541	-108.88502	5436	106	B520	36.51940	-108.88100	5389	59
B324	36.56091	-108.89200	5302	-28	B387	36.52620	-108.88699	5333	3	B452	36.49540	-108.88305	5427	97	B521	36.51710	-108.88100	5345	15
B325	36.56259	-108.89200	5349	19	B388	36.52800	-108.88701	5388	58	B453	36.49728	-108.88300	5415	85	B522	36.51529	-108.88099	5408	78
B326	36.56440	-108.89301	5341	11	B389	36.52969	-108.88699	5458	128	B454	36.49920	-108.88300	5453	123	B523	36.51320	-108.88100	5366	36
B327	36.56620	-108.89300	5323	-7	B390	36.53150	-108.88699	5313	-17	B455	36.50110	-108.88300	5395	65	B524	36.51160	-108.88100	5344	14
B328	36.56790	-108.89200	5407	77	B391	36.53360	-108.88800	5322	-8	B456	36.50330	-108.88300	5331	1	B525	36.50990	-108.88099	5417	87
B329	36.56791	-108.89001	5372	42	B392	36.53549	-108.88800	5298	-32	B457	36.50491	-108.88300	5333	3	B526	36.50809	-108.88100	5343	13
B331	36.56440	-108.89001	5355	25	B393	36.53720	-108.88799	5281	-49	B458	36.50640	-108.88300	5297	-33	B527	36.50630	-108.88100	5359	29
B332	36.56270	-108.89000	5346	16	B394	36.53887	-108.88799	5398	68	B459	36.50850	-108.88300	5336	6	B528	36.50480	-108.88100	5405	75
B333	36.56090	-108.89001	5341	11	B395	36.54051	-108.88800	5361	31	B460	36.50990	-108.88300	5338	8	B529	36.50300	-108.88099	5430	100
B334	36.55909	-108.89001	5320	-10	B396	36.54232	-108.88799	5306	-24	B461	36.51186	-108.88248	5318	-12	B530	36.50090	-108.88100	5573	243
B335	36.55708	-108.88999	5350	20	B397	36.54440	-108.88800	5301	-29	B462	36.51329	-108.88300	5335	5	B531	36.49900	-108.88100	5386	56
B336	36.55519	-108.89001	5357	27	B398	36.54580	-108.88802	5354	24	B463	36.51520	-108.88296	5359	29	B532	36.49694	-108.88093	5398	68
B337	36.55340	-108.89000	5343	13	B399	36.54790	-108.88749	5390	60	B464	36.51719	-108.88300	5271	-59	B533	36.49539	-108.88103	5395	65
B338	36.55168	-108.89000	5323	-7	B400	36.54990	-108.88700	5327	-3	B466	36.52130	-108.88300	5398	68	B534	36.49540	-108.87900	5359	29
B339	36.55030	-108.88999	5303	-27	B401	36.55170	-108.88800	5386	56	B467	36.52274	-108.88284	5335	5	B535	36.49720	-108.87900	5401	71
B340	36.54797	-108.88978	5368	38	B402	36.55340	-108.88799	5331	1	B468	36.52440	-108.88300	5393	63	B536	36.49910	-108.87800	5382	52
B341	36.54590	-108.89000	5325	-5	B403	36.55490	-108.88800	5334	4	B469	36.52610	-108.88300	5407	77	B537	36.50090	-108.87800	5315	-15
B342	36.54430	-108.89000	5339	9	B404	36.55720	-108.88800	5364	34	B470	36.52800	-108.88300	5367	37	B538	36.50302	-108.87800	5420	90
B343	36.54259	-108.88999	5316	-14	B405	36.55900	-108.88801	5363	33	B471	36.52990	-108.88300	5280	-50	B539	36.50489	-108.87800	5479	149
B344	36.54052	-108.88999	5415	85	B406	36.56080	-108.88800	5366	36	B472	36.53170	-108.88300	5616	286	B540	36.50669	-108.87900	5427	97
B345	36.53891	-108.88999	5320	-10	B407	36.56250	-108.88800	5370	40	B473	36.53370	-108.88301	5352	22	B541	36.50832	-108.87900	5365	35
B346	36.53710	-108.89001	5405	75	B408	36.56440	-108.88799	5375	45	B474	36.53550	-108.88300	5490	160	B542	36.50990	-108.87899	5427	97
B347	36.53549	-108.89000	5357	27	B409	36.56620	-108.88800	5342	12	B479	36.54420	-108.88301	5343	13	B543	36.51140	-108.87900	5331	1
B348	36.53361	-108.88999	5212	-118	B410	36.56820	-108.88794	5327	-3	B481	36.54790	-108.88300	5343	13	B544	36.51340	-108.87800	5372	42
B349	36.53151	-108.88999	5517	187	B411	36.56791	-108.88499	5425	95	B482	36.54998	-108.88300	5322	-8	B545	36.51522	-108.87900	5363	33
B350	36.52981	-108.89000	5363	33	B412	36.56640	-108.88500	5363	33	B483	36.55160	-108.88303	5315	-15	B546	36.51720	-108.87799	5369	39
B351	36.52810	-108.88902	5174	-156	B413	36.56430	-108.88501	5288	-42	B484	36.55340	-108.88299	5387	57	B547	36.51930	-108.87900	5355	25
B352	36.52610	-108.88900	5299	-31	B414	36.56260	-108.88601	5361	31	B485	36.55520	-108.88300	5421	91	B548	36.52130	-108.87800	5402	72
B353	36.52441	-108.889																	

B552	36.52790	-108.87900	5345	15	B622	36.53729	-108.87399	5328	-2	P22	36.45961	-108.89700	5405	75	P91	36.46161	-108.88800	5390	60
B553	36.52999	-108.87899	5300	-30	B623	36.53888	-108.87402	5446	116	P24	36.46320	-108.89701	5354	24	P92	36.46311	-108.88800	5487	157
B554	36.53170	-108.87901	5358	28	B624	36.54041	-108.87399	5377	47	P25	36.46480	-108.89700	5621	291	P93	36.46471	-108.88799	5433	103
B555	36.53390	-108.87899	5238	-92	B625	36.54254	-108.87402	5424	94	P26	36.46640	-108.89700	5464	134	P94	36.46635	-108.88866	5354	24
B556	36.53550	-108.87898	5408	78	B626	36.54441	-108.87399	5440	110	P27	36.46820	-108.89702	5375	45	P97	36.47191	-108.88801	5391	61
B557	36.53739	-108.87899	5324	-6	B627	36.54610	-108.87399	5396	66	P28	36.46987	-108.89700	5399	69	P98	36.47431	-108.88700	5367	37
B558	36.53889	-108.87900	5332	2	B628	36.54800	-108.87400	5381	51	P29	36.47213	-108.89571	5318	-12	P99	36.47610	-108.88700	5345	15
B559	36.54070	-108.87901	5379	49	B629	36.54979	-108.87399	5320	-10	P30	36.47432	-108.89700	5361	31	P100	36.47791	-108.88701	5368	38
B563	36.54810	-108.87900	5410	80	B630	36.55171	-108.87400	5357	27	P31	36.47641	-108.89700	5294	-36	P101	36.47931	-108.88701	5321	-9
B565	36.55169	-108.87904	5379	49	B631	36.55341	-108.87400	5308	-22	P32	36.47789	-108.89600	5331	1	P102	36.48091	-108.88735	5359	29
B566	36.55341	-108.87794	5321	-9	B632	36.55350	-108.87196	5352	22	P34	36.48089	-108.89701	5304	-26	P103	36.48090	-108.88502	5331	1
B567	36.55338	-108.87599	5333	3	B633	36.55150	-108.87201	5359	29	P35	36.48090	-108.89402	5358	28	P104	36.47950	-108.88500	5292	-38
B568	36.55159	-108.87701	5348	18	B634	36.54991	-108.87199	5348	18	P36	36.47960	-108.89400	5310	-20	P105	36.47799	-108.88502	5313	-17
B569	36.54977	-108.87634	5336	6	B635	36.54800	-108.87199	5377	47	P37	36.47791	-108.89400	5358	28	P106	36.47598	-108.88500	5361	31
B570	36.54820	-108.87601	5406	76	B636	36.54611	-108.87199	5355	25	P38	36.47621	-108.89398	5361	31	P107	36.47401	-108.88501	5334	4
B574	36.54060	-108.87601	5429	99	B637	36.54432	-108.87200	5401	71	P39	36.47410	-108.89400	5366	36	P111	36.46637	-108.88499	5455	125
B575	36.53891	-108.87599	5451	121	B638	36.54240	-108.87199	5370	40	P40	36.47211	-108.89500	5362	32	P112	36.46500	-108.88501	5422	92
B576	36.53740	-108.87599	5331	1	B639	36.54039	-108.87201	5430	100	P41	36.47020	-108.89500	5426	96	P113	36.46350	-108.88500	5510	180
B577	36.53574	-108.87608	5341	11	B640	36.53890	-108.87199	5663	333	P42	36.46850	-108.89499	5426	96	P115	36.45971	-108.88500	5344	14
B578	36.53400	-108.87598	5312	-18	B641	36.53720	-108.87199	5368	38	P43	36.46640	-108.89500	5366	36	P116	36.45780	-108.88501	5385	55
B579	36.53160	-108.87601	5383	53	B642	36.53530	-108.87176	5342	12	P44	36.46486	-108.89502	5431	101	P117	36.45589	-108.88501	5376	46
B580	36.53000	-108.87600	5335	5	B643	36.53367	-108.87202	5419	89	P46	36.46160	-108.89500	5423	93	P118	36.45360	-108.88501	5323	-7
B581	36.52780	-108.87600	5334	4	B644	36.53160	-108.87201	5483	153	P48	36.45789	-108.89500	5348	18	P119	36.45190	-108.88501	5385	55
B582	36.52600	-108.87600	5433	103	B645	36.52950	-108.87199	5381	51	P49	36.45579	-108.89500	5395	65	P120	36.45190	-108.88300	5413	83
B583	36.52438	-108.87600	5370	40	B646	36.52750	-108.87201	5386	56	P50	36.45391	-108.89500	5310	-20	P121	36.45360	-108.88300	5401	71
B584	36.52270	-108.87600	5383	53	B647	36.52580	-108.87200	5350	20	P51	36.45192	-108.89504	5312	-18	P122	36.45560	-108.88300	5391	61
B585	36.52120	-108.87600	5352	22	B648	36.52439	-108.87202	5408	78	P52	36.45190	-108.89299	5284	-46	P123	36.45770	-108.88300	5369	39
B586	36.51930	-108.87600	5375	45	B649	36.52270	-108.87200	5311	-19	P53	36.45370	-108.89193	5362	32	P124	36.45960	-108.88298	5358	28
B587	36.51730	-108.87599	5332	2	B650	36.52090	-108.87200	5370	40	P54	36.45570	-108.89201	5404	74	P126	36.46341	-108.88300	5525	195
B588	36.51520	-108.87600	5386	56	B651	36.51910	-108.87200	5361	31	P55	36.45801	-108.89199	5325	-5	P127	36.46490	-108.88300	5449	119
B589	36.51350	-108.87600	5377	47	B652	36.51701	-108.87199	5358	28	P57	36.46171	-108.89200	5431	101	P128	36.46640	-108.88301	5406	76
B590	36.50990	-108.87601	5437	107	B653	36.51509	-108.87199	5333	3	P58	36.46330	-108.89200	5414	84	P133	36.47601	-108.88300	5353	23
B591	36.50830	-108.87600	5463	133	B654	36.51310	-108.87200	5360	30	P59	36.46473	-108.89200	5384	54	P134	36.47800	-108.88297	5321	-9
B592	36.50671	-108.87601	5521	191	B655	36.51140	-108.87200	5404	74	P60	36.46640	-108.89200	5369	39	P135	36.47920	-108.88300	5328	-2
B593	36.50500	-108.87600	5430	100	B656	36.50990	-108.87200	5336	6	P61	36.46820	-108.89201	5401	71	P136	36.48089	-108.88302	5251	-79
B594	36.50320	-108.87601	5292	-38	B657	36.50840	-108.87200	5341	11	P62	36.47009	-108.89201	5414	84	P137	36.48090	-108.88100	5335	5
B595	36.50100	-108.87700	5401	71	B658	36.50690	-108.87200	5399	69	P64	36.47402	-108.89205	5305	-25	P138	36.47931	-108.88099	5330	0
B596	36.49920	-108.87700	5379	49	B659	36.50500	-108.87200	5405	75	P65	36.47609	-108.89200	5335	5	P139	36.47798	-108.88099	5387	57
B597	36.49730	-108.87600	5388	58	B660	36.50300	-108.87200	5341	11	P66	36.47789	-108.89200	5342	12	P140	36.47601	-108.88100	5320	-10
B598	36.49540	-108.87600	5301	-29	B661	36.50110	-108.87200	5381	51	P67	36.47949	-108.89200	5353	23	P144	36.46818	-108.88081	5404	74
B600	36.49710	-108.87400	5370	40	B662	36.49870	-108.87200	5359	29	P68	36.48090	-108.89201	5394	64	P145	36.46637	-108.88109	5381	51
B601	36.49910	-108.87400	5361	31	B5891	36.51150	-108.87600	5316	-14	P69	36.48088	-108.88986	5358	28	P146	36.46490	-108.88099	5468	138
B602	36.50120	-108.87400	5369	39	P1	36.48088	-108.89899	5330	0	P70	36.47941	-108.89000	5335	5	P147	36.46340	-108.88100	5492	162
B603	36.50330	-108.87400	5325	-5	P2	36.47941	-108.89900	5304	-26	P71	36.47779	-108.89004	5348	18	P148	36.46160	-108.88100	5314	-16
B604	36.50500	-108.87400	5370	40	P3	36.47790	-108.89899	5319	-11	P72	36.47573	-108.88985	5223	-107	P149	36.45980	-108.88099	5394	64
B605	36.50680	-108.87400	5416	86	P4	36.47638	-108.89904	5372	42	P73	36.47408	-108.88975	5385	55	P150	36.45781	-108.88100	5408	78
B606	36.50850	-108.87400	5423	93	P5	36.47506	-108.89906	5362	32	P74	36.47125	-108.89023	5361	31	P151	36.45549	-108.88090	5420	90
B607	36.50990	-108.87400	5519	189	P6	36.47144	-108.89913	5301	-29	P75	36.47018	-108.88999	5469	139	P152	36.45340	-108.88100	5462	132
B608	36.51140	-108.87400	5348	18	P7	36.47009	-108.89899	5312	-18	P77	36.46640	-108.89002	5394	64	P153	36.45190	-108.88100	5438	108
B609	36.51320	-108.87400	5346	16	P8	36.46810	-108.89900	5369	39	P78	36.46479	-108.89000	5413	83	P154	36.45190	-108.87889	5379	49
B610	36.51521	-108.87400	5329	-1	P9	36.46640	-108.89899	5394	64	P79	36.46341	-108.89000	5434	104	P155	36.45364	-108.87894	5362	32
B611	36.51721	-108.87401	5342	12	P10	36.46490	-108.89899	5460	130	P80	36.46171	-108.89001	5401	71	P156	36.45570	-108.87899	5400	70
B612	36.51910	-108.87400	5354	24	P11	36.46320	-108.89899	5396	66	P81	36.45980	-108.89000	5404	74	P157	36.45770	-108.87900	5410	80
B613	36.52110	-108.87400	5370	40	P12	36.46128	-108.89890	5374	44	P82	36.45790	-108.89001	5426	96	P158	36.45961	-108.87800	5377	47
B614	36.52279	-108.87400	5364	34	P14	36.45790	-108.89901	5421	91	P83	36.45600	-108.88999	5378	48	P159	36.46160	-108.87899	5389	59
B615	36.52440	-108.87400	5383	53	P15	36.45550	-108.89900	5341	11	P84	36.45383	-108.88999	5413	83	P160	36.46341	-108.87900	5374	44
B616	36.52588	-108.87396	5366	36	P16	36.45390	-108.89896	5315	-15	P85	36.45206	-108.89063	5307	-23	P161	36.46490	-108.87900	5399	69
B617	36.52770	-108.87397	5392	62	P17	36.45190	-108.89901	5347	17	P86	36.45190	-108.88764	5309	-21	P162	36.46641	-108.87798	5413	83
B618	36.52969	-108.87400	5383	53	P18	36.45192	-108.89702	5333	3	P87	36.45389	-108.88801	5457	127	P163	36.46800	-108.87800	5463	133
B619	36.53165	-108.87393	5417	87	P19	36.45380	-108.89700	5315	-15	P88									

P167	36.47610	-108.87799	5476	146	P231	36.46823	-108.86997	5337	7	R7	36.72331	-108.80898	5294	-36	R70	36.72148	-108.79500	5370	40
P168	36.47801	-108.87798	5423	93	P232	36.47020	-108.86900	5358	28	R8	36.72151	-108.80900	5326	-4	R71	36.71970	-108.79499	5249	-81
P169	36.47950	-108.87801	5382	52	P233	36.47208	-108.86897	5294	-36	R9	36.71971	-108.80900	5267	-63	R72	36.71780	-108.79501	5236	-94
P170	36.48090	-108.87800	5382	52	P234	36.47421	-108.86899	5271	-59	R10	36.71970	-108.80699	5312	-18	R73	36.71619	-108.79498	5307	-23
P171	36.48090	-108.87600	5406	76	P235	36.47589	-108.86900	5358	28	R11	36.72159	-108.80699	5338	8	R74	36.71470	-108.79499	5370	40
P172	36.47940	-108.87601	5344	14	P236	36.47809	-108.86902	5371	41	R12	36.72340	-108.80700	5275	-55	R75	36.71270	-108.79500	5319	-11
P173	36.47790	-108.87601	5352	22	P237	36.47961	-108.86902	5314	-16	R13	36.72509	-108.80700	5264	-66	R76	36.71260	-108.79300	5333	3
P174	36.47617	-108.87599	5325	-5	P238	36.48095	-108.86904	5348	18	R14	36.72680	-108.80698	5345	15	R77	36.71440	-108.79299	5417	87
P175	36.47410	-108.87600	5455	125	P239	36.48093	-108.86697	5356	26	R15	36.72869	-108.80700	5302	-28	R78	36.71611	-108.79301	5274	-56
P176	36.47200	-108.87600	5434	104	P240	36.47950	-108.86700	5388	58	R16	36.73039	-108.80701	5278	-52	R79	36.71881	-108.79300	5298	-32
P177	36.47020	-108.87600	5549	219	P241	36.47800	-108.86697	5404	74	R17	36.73219	-108.80701	5294	-36	R80	36.71970	-108.79300	5213	-117
P178	36.46830	-108.87600	5468	138	P242	36.47588	-108.86700	5392	62	R18	36.73410	-108.80701	5218	-112	R81	36.72131	-108.79300	5216	-114
P179	36.46640	-108.87601	5431	101	P243	36.47380	-108.86699	5377	47	R19	36.73419	-108.80401	5312	-18	R82	36.72320	-108.79310	5254	-76
P180	36.46510	-108.87600	5457	127	P244	36.47200	-108.86698	5409	79	R20	36.73240	-108.80399	5291	-39	R83	36.72510	-108.79292	5300	-30
P182	36.46150	-108.87600	5466	136	P245	36.47010	-108.86699	5365	35	R21	36.73050	-108.80402	5251	-79	R84	36.72701	-108.79300	5352	22
P183	36.45970	-108.87601	5431	101	P246	36.46821	-108.86700	5352	22	R22	36.72850	-108.80401	5335	5	R85	36.72880	-108.79300	5283	-47
P184	36.45770	-108.87700	5475	145	P247	36.46641	-108.86701	5313	-17	R23	36.72679	-108.80400	5242	-88	R86	36.73059	-108.79300	5298	-32
P185	36.45561	-108.87600	5495	165	P248	36.46479	-108.86802	5442	112	R24	36.72497	-108.80395	5332	2	R87	36.73230	-108.79300	5304	-26
P186	36.45360	-108.87600	5460	130	P249	36.46320	-108.86699	5323	-7	R25	36.72350	-108.80402	5282	-48	R88	36.73421	-108.79298	5307	-23
P187	36.45191	-108.87601	5415	85	P252	36.45813	-108.86741	5407	77	R26	36.72150	-108.80400	5304	-26	R89	36.73421	-108.79100	5165	-165
P188	36.45190	-108.87400	5443	113	P253	36.45560	-108.86700	5385	55	R27	36.71970	-108.80401	5283	-47	R90	36.73233	-108.79098	5259	-71
P189	36.45380	-108.87400	5392	62	P254	36.45390	-108.86700	5360	30	R28	36.71971	-108.80201	5298	-32	R91	36.73059	-108.79123	5279	-51
P190	36.45551	-108.87400	5441	111	P255	36.45190	-108.86700	5388	58	R29	36.72141	-108.80203	5344	14	R92	36.72879	-108.79100	5291	-39
P191	36.45741	-108.87399	5488	158	P256	36.45190	-108.86499	5368	38	R30	36.72330	-108.80199	5335	5	R93	36.72689	-108.79100	5448	118
P192	36.45960	-108.87400	5482	152	P257	36.45361	-108.86500	5368	38	R31	36.72500	-108.80201	5293	-37	R94	36.72540	-108.79101	5328	-2
P193	36.46139	-108.87399	5473	143	P258	36.45551	-108.86500	5384	54	R32	36.72690	-108.80199	5304	-26	R95	36.72329	-108.79100	5357	27
P194	36.46341	-108.87400	5508	178	P259	36.45760	-108.86500	5394	64	R33	36.72871	-108.80201	5224	-106	R96	36.72150	-108.79100	5415	85
P195	36.46564	-108.87395	5460	130	P260	36.45941	-108.86501	5425	95	R34	36.73050	-108.80200	5321	-9	R97	36.71970	-108.79099	5160	-170
P196	36.46640	-108.87399	5446	116	P261	36.46128	-108.86501	5359	29	R35	36.73240	-108.80200	5275	-55	R98	36.71751	-108.79100	5287	-43
P198	36.47020	-108.87401	5290	-40	P262	36.46311	-108.86507	5363	33	R36	36.73422	-108.80207	5328	-2	R99	36.71600	-108.79100	5308	-22
P199	36.47210	-108.87400	5363	33	P264	36.46640	-108.86499	5352	22	R37	36.73421	-108.80001	5341	11	R100	36.71410	-108.79100	5395	65
P200	36.47420	-108.87399	5400	70	P265	36.46820	-108.86500	5366	36	R38	36.73230	-108.80001	5313	-17	R101	36.71239	-108.79100	5325	-5
P201	36.47589	-108.87401	5336	6	P266	36.46989	-108.86501	5375	45	R39	36.73071	-108.80000	5242	-88	R102	36.71230	-108.78902	5325	-5
P202	36.47755	-108.87416	5369	39	P267	36.47181	-108.86501	5396	66	R40	36.72870	-108.80001	5327	-3	R103	36.71410	-108.78900	5358	28
P203	36.47920	-108.87400	5329	-1	P268	36.47360	-108.86500	5333	3	R41	36.72681	-108.80000	5324	-6	R104	36.71600	-108.78900	5375	45
P204	36.48089	-108.87400	5352	22	P269	36.47580	-108.86500	5328	-2	R43	36.72310	-108.80000	5231	-99	R105	36.71780	-108.78900	5345	15
P205	36.48092	-108.87200	5290	-40	P270	36.47789	-108.86500	5361	31	R44	36.72139	-108.80002	5296	-34	R106	36.71969	-108.78900	5282	-48
P206	36.47930	-108.87200	5401	71	P271	36.47940	-108.86499	5346	16	R45	36.71969	-108.80000	5328	-2	R107	36.72150	-108.78900	5295	-35
P207	36.47790	-108.87199	5313	-17	P272	36.48089	-108.86499	5353	23	R46	36.71799	-108.80000	5311	-19	R108	36.72350	-108.78901	5290	-40
P208	36.47589	-108.87199	5392	62	P273	36.48090	-108.86301	5318	-12	R47	36.71609	-108.80001	5260	-70	R109	36.72530	-108.78900	5217	-113
P209	36.47421	-108.87200	5390	60	P274	36.47930	-108.86301	5366	36	R48	36.71450	-108.80001	5321	-9	R110	36.72701	-108.78900	5268	-62
P210	36.47208	-108.87204	5373	43	P275	36.47791	-108.86300	5334	4	R49	36.71270	-108.79900	5332	2	R111	36.72701	-108.78700	5200	-130
P211	36.47020	-108.87201	5329	-1	P276	36.47570	-108.86300	5352	22	R50	36.71280	-108.79700	5415	85	R112	36.72520	-108.78700	5305	-25
P212	36.46820	-108.87199	5369	39	P277	36.47360	-108.86300	5318	-12	R51	36.71460	-108.79700	5390	60	R113	36.72330	-108.78700	5232	-98
P213	36.46640	-108.87200	5483	153	P278	36.47171	-108.86300	5363	33	R52	36.71624	-108.79707	5201	-129	R114	36.72160	-108.78701	5270	-60
P214	36.46499	-108.87200	5505	175	P279	36.47000	-108.86300	5365	35	R53	36.71812	-108.79700	5261	-69	R115	36.71970	-108.78600	5251	-79
P215	36.46350	-108.87200	5390	60	P280	36.46821	-108.86299	5366	36	R54	36.71972	-108.79698	5301	-29	R116	36.71780	-108.78600	5278	-52
P216	36.46160	-108.87200	5439	109	P281	36.46637	-108.86298	5351	21	R55	36.72146	-108.79699	5212	-118	R117	36.71578	-108.78601	5296	-34
P217	36.45940	-108.87203	5384	54	P282	36.46431	-108.86300	5353	23	R56	36.72320	-108.79799	5247	-83	R118	36.71400	-108.78600	5275	-55
P218	36.45740	-108.87201	5379	49	P283	36.46279	-108.86300	5365	35	R57	36.72511	-108.79799	5208	-122	R119	36.71239	-108.78601	5331	1
P219	36.45560	-108.87199	5362	32	P284	36.46099	-108.86301	5385	55	R58	36.72691	-108.79799	5293	-37	R120	36.71220	-108.78400	5184	-146
P220	36.45380	-108.87200	5390	60	P285	36.45910	-108.86298	5408	78	R59	36.72858	-108.79800	5214	-116	R121	36.71391	-108.78399	5227	-103
P221	36.45190	-108.87200	5355	25	P286	36.45729	-108.86292	5362	32	R60	36.73080	-108.79798	5218	-112	R122	36.71569	-108.78400	5359	29
P222	36.45190	-108.87000	5380	50	P287	36.45550	-108.86301	5388	58	R61	36.73249	-108.79798	5267	-63	R123	36.71780	-108.78400	5321	-9
P223	36.45379	-108.86900	5335	5	P288	36.45361	-108.86300	5456	126	R62	36.73420	-108.79798	5337	7	R124	36.71971	-108.78400	5310	-20
P224	36.45550	-108.86900	5355	25	P289	36.45190	-108.86300	5393	63	R63	36.73418	-108.79500	5175	-155	R125	36.72120	-108.78400	5332	2
P225	36.45750	-108.86900	5339	9	R1	36.73409	-108.80898	5307	-23	R64	36.73229	-108.79496	5288	-42	R126	36.72330	-108.78400	5298	-32
P226	36.45941	-108.86900	5361	31	R2	36.73230	-108.80961	5326	-4	R65	36.73083	-108.79505	5218	-112	R127	36.72510	-108.78400	5318	-12
P227	36.46140	-108.86900	5373	43	R3	36.73050	-108.80901	5286	-44	R66	36.72891	-108.79499	5252	-78	R128	36.72680	-108.78400	5239	-91
P228	36.46299	-108.87002	5386	56	R4	36.72870	-108.80899	5307	-23	R67									

R132	36.72130	-108.78200	5291	-39	R196	36.71391	-108.77999	5395	65	R260	36.73739	-108.81100	5280	-50	T28	36.37040	-108.86717	5340	10
R133	36.71970	-108.78200	5300	-30	R197	36.71609	-108.77700	5276	-54	R261	36.73571	-108.81100	5323	-7	T29	36.36825	-108.86753	5320	-10
R134	36.71761	-108.78200	5247	-83	R198	36.71430	-108.77700	5339	9	R262	36.73200	-108.81302	5376	46	T30	36.36642	-108.86701	5282	-48
R135	36.71600	-108.78199	5301	-29	R199	36.71800	-108.77700	5227	-103	R263	36.73230	-108.81100	5368	38	T31	36.36479	-108.86695	5381	51
R136	36.71400	-108.78201	5368	38	R200	36.71799	-108.77500	5293	-37	R264	36.73061	-108.81100	5293	-37	T32	36.36301	-108.86702	5323	-7
R137	36.71230	-108.78200	5315	-15	R201	36.71590	-108.77500	5205	-125	R265	36.74081	-108.80000	5330	0	T33	36.36139	-108.86704	5291	-39
R138	36.73420	-108.78900	5254	-76	R202	36.71390	-108.77500	5272	-58	R266	36.74089	-108.80401	5278	-52	T34	36.35930	-108.86700	5364	34
R139	36.73220	-108.78900	5326	-4	R203	36.71600	-108.77300	5388	58	R267	36.74080	-108.80700	5234	-96	T35	36.35770	-108.86700	5436	106
R140	36.73059	-108.78886	5238	-92	R204	36.71799	-108.77300	5292	-38	R268	36.74080	-108.80201	5331	1	T36	36.35392	-108.86697	5339	9
R141	36.72870	-108.78901	5271	-59	R205	36.71391	-108.77300	5307	-23	R269	36.73750	-108.80000	5357	27	T37	36.35379	-108.86926	5346	16
R142	36.72860	-108.78701	5239	-91	R206	36.70881	-108.79100	5391	61	R270	36.73930	-108.80000	5262	-68	T38	36.35400	-108.87200	5336	6
R143	36.73050	-108.78700	5317	-13	R207	36.71060	-108.79099	5366	36	R271	36.73589	-108.80002	5308	-22	T40	36.35020	-108.87209	5394	64
R144	36.73230	-108.78700	5246	-84	R208	36.70520	-108.78600	5394	64	R272	36.73759	-108.80399	5344	14	T41	36.35038	-108.86897	5293	-37
R145	36.73429	-108.78700	5302	-28	R209	36.70520	-108.78100	5445	115	R273	36.73930	-108.80399	5342	12	T42	36.35228	-108.86900	5305	-25
R148	36.73230	-108.78503	5222	-108	R210	36.70520	-108.77701	5246	-84	R274	36.73550	-108.80399	5238	-92	T43	36.35220	-108.86700	5416	86
R149	36.73420	-108.78501	5315	-15	R211	36.70520	-108.77300	5353	23	R275	36.73580	-108.80201	5341	11	T44	36.35040	-108.86700	5422	92
R150	36.72860	-108.78201	5267	-63	R212	36.70520	-108.78399	5357	27	R276	36.73750	-108.80200	5282	-48	T45	36.35040	-108.86501	5399	69
R151	36.73051	-108.78201	5317	-13	R213	36.70521	-108.77900	5335	5	R277	36.73930	-108.80200	5333	3	T46	36.35179	-108.86500	5304	-26
R152	36.73230	-108.78300	5239	-91	R215	36.70880	-108.77300	5410	80	R278	36.73570	-108.80698	5244	-86	T47	36.35401	-108.86501	5319	-11
R153	36.73420	-108.78300	5326	-4	R216	36.71080	-108.77301	5444	114	R279	36.73761	-108.80700	5399	69	T48	36.35609	-108.86501	5316	-14
R154	36.73420	-108.77800	5305	-25	R218	36.70881	-108.78100	5392	62	R280	36.73920	-108.80701	5290	-40	T49	36.35756	-108.86456	5379	49
R155	36.73420	-108.78101	5327	-3	R219	36.70700	-108.78201	5355	25	R281	36.71801	-108.80199	5288	-42	T50	36.35922	-108.86490	5357	27
R156	36.73419	-108.77500	5322	-8	R220	36.71060	-108.78200	5386	56	R282	36.71799	-108.80399	5278	-52	T51	36.36121	-108.86501	5302	-28
R157	36.73419	-108.77301	5302	-28	R221	36.70880	-108.78601	5399	69	R283	36.71599	-108.80202	5378	48	T52	36.36309	-108.86501	5241	-89
R158	36.72689	-108.77301	5356	26	R222	36.70880	-108.78800	5355	25	R284	36.71440	-108.80201	5304	-26	T53	36.36491	-108.86497	5400	70
R159	36.73050	-108.77300	5242	-88	R223	36.70873	-108.78376	5459	129	R285	36.71070	-108.79301	5410	80	T54	36.36663	-108.86498	5330	0
R160	36.73249	-108.77298	5246	-84	R224	36.71060	-108.78600	5405	75	R286	36.71609	-108.80402	5398	68	T55	36.36834	-108.86478	5404	74
R161	36.72869	-108.77300	5300	-30	R225	36.71080	-108.78900	5405	75	R287	36.71819	-108.80698	5291	-39	T56	36.37030	-108.86507	5346	16
R162	36.72330	-108.77300	5320	-10	R226	36.71070	-108.78400	5418	88	R288	36.72870	-108.81101	5302	-28	T57	36.37215	-108.86514	5445	115
R163	36.72540	-108.77300	5303	-27	R227	36.70680	-108.78400	5365	35	R289	36.72681	-108.81100	5365	35	T58	36.37409	-108.86500	5382	52
R164	36.72140	-108.77300	5247	-83	R228	36.70670	-108.78601	5405	75	R290	36.73058	-108.81301	5257	-73	T59	36.37590	-108.86500	5434	104
R165	36.71970	-108.77300	5262	-68	R229	36.70881	-108.77701	5405	75	R291	36.73248	-108.81500	5324	-6	T60	36.37770	-108.86499	5324	-6
R166	36.71970	-108.77700	5317	-13	R230	36.71040	-108.77699	5356	26	R292	36.72530	-108.81100	5179	-151	T61	36.37940	-108.86499	5430	100
R167	36.71970	-108.78000	5321	-9	R231	36.70660	-108.77700	5355	25	R293	36.72341	-108.81099	5383	53	T62	36.37940	-108.86300	5488	158
R168	36.71970	-108.77500	5314	-16	R232	36.71060	-108.77900	5375	45	R294	36.73881	-108.81302	5327	-3	T63	36.37780	-108.86299	5463	133
R169	36.72710	-108.77800	5324	-6	R233	36.70860	-108.77900	5460	130	R146A	36.72860	-108.78400	5316	-14	T64	36.37580	-108.86301	5396	66
R170	36.72700	-108.77999	5191	-139	R234	36.70680	-108.78001	5453	123	T2	36.37390	-108.87102	5441	111	T66	36.37210	-108.86299	5285	-45
R171	36.72710	-108.77500	5295	-35	R235	36.70679	-108.77502	5390	60	T3	36.37239	-108.87100	5477	147	T67	36.37005	-108.86302	5264	-66
R172	36.72319	-108.77699	5270	-60	R236	36.70880	-108.77500	5324	-6	T4	36.37040	-108.87101	5408	78	T68	36.36848	-108.86300	5344	14
R173	36.72341	-108.77500	5287	-43	R237	36.71110	-108.77500	5460	130	T5	36.36860	-108.87200	5354	24	T69	36.36660	-108.86300	5357	27
R174	36.72331	-108.78000	5250	-80	R238	36.73410	-108.81700	5309	-21	T6	36.36660	-108.87200	5291	-39	T70	36.36491	-108.86300	5317	-13
R175	36.72129	-108.78000	5275	-55	R239	36.74089	-108.81799	5336	6	T7	36.36491	-108.87179	5387	57	T71	36.36291	-108.86299	5333	3
R176	36.72140	-108.77700	5284	-46	R240	36.74070	-108.80900	5357	27	T8	36.36277	-108.87185	5392	62	T72	36.36129	-108.86299	5406	76
R177	36.72141	-108.77500	5288	-42	R241	36.73740	-108.80901	5183	-147	T9	36.36089	-108.87180	5327	-3	T73	36.35899	-108.86267	5345	15
R178	36.72520	-108.77501	5317	-13	R242	36.73410	-108.81300	5296	-34	T10	36.35920	-108.87199	5343	13	T74	36.35759	-108.86301	5326	-4
R179	36.72520	-108.77800	5292	-38	R243	36.73748	-108.81699	5343	13	T11	36.35962	-108.86916	5436	106	T75	36.35586	-108.86299	5321	-9
R180	36.72520	-108.78000	5312	-18	R244	36.74080	-108.81300	5303	-27	T12	36.36131	-108.86900	5377	47	T76	36.35400	-108.86298	5360	30
R181	36.73030	-108.77801	5295	-35	R245	36.73910	-108.80901	5349	19	T13	36.36333	-108.86900	5378	48	T77	36.35190	-108.86300	5403	73
R182	36.72860	-108.77799	5282	-48	R246	36.73570	-108.80901	5222	-108	T14	36.36491	-108.87000	5324	-6	T78	36.35040	-108.86300	5332	2
R183	36.73240	-108.77800	5231	-99	R247	36.73411	-108.81099	5337	7	T15	36.36639	-108.86896	5345	15	T79	36.35040	-108.86099	5344	14
R184	36.73030	-108.78000	5285	-45	R248	36.73410	-108.81501	5271	-59	T16	36.36840	-108.86901	5421	91	T80	36.35219	-108.86101	5360	30
R185	36.73240	-108.78000	5318	-12	R249	36.73580	-108.81701	5331	1	T17	36.37030	-108.86900	5419	89	T81	36.35410	-108.85999	5348	18
R186	36.72869	-108.78001	5198	-132	R250	36.73940	-108.81702	5382	52	T18	36.37240	-108.86901	5543	213	T82	36.35557	-108.86024	5306	-24
R187	36.72860	-108.77500	5340	10	R251	36.74089	-108.81601	5291	-39	T19	36.37390	-108.86900	5480	150	T83	36.35835	-108.86140	5360	30
R188	36.73050	-108.77500	5349	19	R252	36.74080	-108.81099	5226	-104	T20	36.37600	-108.86900	5512	182	T86	36.36320	-108.86000	5379	49
R189	36.73260	-108.77500	5294	-36	R253	36.73748	-108.81303	5211	-119	T21	36.37791	-108.86901	5445	115	T87	36.36490	-108.86000	5473	143
R190	36.71230	-108.77700	5349	19	R254	36.73573	-108.81302	5346	16	T22	36.37940	-108.86900	5374	44	T88	36.36663	-108.86002	5324	-6
R191	36.71240	-108.77301	5313	-17	R255	36.73571	-108.81499	5361	31	T23	36.37940	-108.86599	5461	131	T89	36.36860	-108.85999	5339	9
R192	36.71259	-108.77499	5331	1	R256	36.73748	-108.81500	5368	38	T24	36.37781	-108.86700	5464	134	T90	36.37021	-108.86099	5390	60
R193	36.71250	-108.78000	5353	23	R257	36.73940	-108.81600	5343	13	T25									

T94	36.37781	-108.86103	5354	24	T168	36.37074	-108.84879	5386	56	T234	36.34650	-108.85300	5374	44	TW54	36.89410	-109.06900	5252	-78
T95	36.37941	-108.86098	5316	-14	T169	36.36860	-108.84900	5361	31	T235	36.34671	-108.85601	5371	41	TW55	36.89410	-109.06700	5257	-73
T96	36.37966	-108.85803	5281	-49	T170	36.36660	-108.84900	5361	31	T236	36.34670	-108.85800	5337	7	TW56	36.89430	-109.07800	5212	-118
T97	36.37773	-108.85847	5352	22	T171	36.36493	-108.84866	5367	37	T237	36.34681	-108.85990	5383	53	TW57	36.89430	-109.08200	5314	-16
T98	36.37568	-108.85889	5385	55	T174	36.36140	-108.84900	5409	79	T238	36.34680	-108.86201	5208	-122	TW58	36.89440	-109.08500	5356	26
T99	36.37389	-108.85798	5384	54	T177	36.35550	-108.84900	5405	75	T239	36.34691	-108.86401	5457	127	TW59	36.89620	-109.08500	5218	-112
T100	36.37230	-108.85799	5358	28	T178	36.35381	-108.84900	5347	17	T240	36.34670	-108.86700	5387	57	TW60	36.89800	-109.08500	5241	-89
T101	36.37050	-108.85800	5282	-48	T179	36.35210	-108.84900	5401	71	T241	36.34680	-108.86900	5388	58	TW61	36.89980	-109.08500	5267	-63
T102	36.36908	-108.85802	5375	45	T180	36.35040	-108.84900	5430	100	T242	36.34671	-108.87200	5387	57	TW62	36.89970	-109.08200	5168	-162
T103	36.36690	-108.85802	5319	-11	T181	36.35040	-108.84701	5370	40	TW1	36.91420	-109.08237	5594	264	TW63	36.89800	-109.08200	5211	-119
T104	36.36491	-108.85800	5575	245	T182	36.35190	-108.84699	5410	80	TW2	36.91440	-109.08300	5840	510	TW64	36.89620	-109.08200	5242	-88
T106	36.36140	-108.85800	5465	135	T183	36.35350	-108.84700	5453	123	TW3	36.91512	-109.08225	5529	199	TW65	36.89440	-109.08000	5242	-88
T107	36.35950	-108.85800	5428	98	T184	36.35570	-108.84700	5375	45	TW4	36.91428	-109.08414	5401	71	TW66	36.89490	-109.08400	5205	-125
T110	36.35379	-108.85802	5361	31	T185	36.35789	-108.84700	5340	10	TW5	36.91682	-109.08284	5731	401	TW67	36.91570	-109.07400	5245	-85
T111	36.35209	-108.85799	5336	6	T186	36.35950	-108.84701	5392	62	TW6	36.91597	-109.08431	5666	336	TW68	36.90180	-109.09600	5153	-177
T112	36.35041	-108.85799	5392	62	T187	36.36220	-108.84701	5394	64	TW7	36.91449	-109.08597	5604	274	TW69	36.90350	-109.09600	5269	-61
T113	36.35039	-108.85600	5383	53	T188	36.36301	-108.84700	5439	109	TW8	36.91220	-109.08687	5600	270	TW70	36.90180	-109.09800	5302	-28
T114	36.35200	-108.85600	5325	-5	T189	36.36486	-108.84704	5382	52	TW9	36.91212	-109.08176	5358	28	TW71	36.90210	-109.10100	5303	-27
T115	36.35374	-108.85603	5372	42	T190	36.36681	-108.84700	5464	134	TW10	36.91100	-109.07900	5778	448	TW72	36.90370	-109.10200	5167	-163
T116	36.35590	-108.85600	5370	40	T191	36.36850	-108.84700	5484	154	TW11	36.91229	-109.08073	5456	126	TW73	36.90360	-109.10000	5257	-73
T118	36.35982	-108.85605	5385	55	T192	36.37030	-108.84702	5374	44	TW12	36.91069	-109.08238	5461	131	TW74	36.90550	-109.09600	5232	-98
T120	36.36320	-108.85600	5418	88	T193	36.37210	-108.84699	5319	-11	TW13	36.91050	-109.08000	5148	-182	TW75	36.90660	-109.09600	5259	-71
T121	36.36490	-108.85600	5343	13	T194	36.37390	-108.84699	5335	5	TW14	36.90719	-109.08189	5570	240	TW76	36.90720	-109.09800	5276	-54
T122	36.36705	-108.85595	5353	23	T195	36.37590	-108.84701	5297	-33	TW15	36.90848	-109.08295	5496	166	TW77	36.90720	-109.10000	5185	-145
T123	36.36892	-108.85599	5559	229	T196	36.37770	-108.84600	5316	-14	TW16	36.90868	-109.08409	5403	73	TW78	36.90740	-109.10200	5236	-94
T124	36.37078	-108.85599	5382	52	T197	36.37941	-108.84602	5330	0	TW17	36.90712	-109.08430	5605	275	TW79	36.90550	-109.10000	5276	-54
T125	36.37260	-108.85602	5281	-49	T198	36.37935	-108.84504	5298	-32	TW18	36.90898	-109.08624	5465	135	TW80	36.90550	-109.09800	5293	-37
T126	36.37389	-108.85605	5336	6	T199	36.37741	-108.84500	5336	6	TW19	36.91035	-109.08632	5472	142	TW81	36.90570	-109.10200	5270	-60
T127	36.37607	-108.85624	5315	-15	T200	36.37581	-108.84501	5327	-3	TW20	36.90710	-109.08600	5812	482	TW82	36.93200	-109.09900	5323	-7
T128	36.37785	-108.85608	5281	-49	T201	36.37403	-108.84499	5270	-60	TW21	36.90650	-109.08600	5757	427	TW83	36.93090	-109.10100	5237	-93
T129	36.37951	-108.85585	5351	21	T202	36.37212	-108.84500	5342	12	TW22	36.91050	-109.08407	5467	137	TW84	36.93450	-109.06500	5186	-144
T130	36.37939	-108.85397	5341	11	T203	36.37052	-108.84489	5289	-41	TW23	36.91203	-109.08448	5474	144	TW85	36.92730	-109.06500	5274	-56
T131	36.37788	-108.85398	5355	25	T204	36.36851	-108.84499	5381	51	TW24	36.91420	-109.07700	5482	152	TW86	36.93090	-109.06900	5284	-46
T132	36.37588	-108.85394	5365	35	T205	36.36650	-108.84500	5413	83	TW25	36.91420	-109.07900	5296	-34	TW87	36.93450	-109.07400	5196	-134
T133	36.37394	-108.85384	5249	-81	T206	36.36489	-108.84499	5465	135	TW26	36.91290	-109.07800	5267	-63	TW88	36.93130	-109.07800	5266	-64
T134	36.37250	-108.85300	5416	86	T207	36.36290	-108.84499	5444	114	TW27	36.91070	-109.07800	5293	-37	W1	36.59690	-109.02501	5314	-16
T136	36.36910	-108.85400	5430	100	T208	36.36131	-108.84499	5438	108	TW28	36.91050	-109.07500	5247	-83	W2	36.59500	-109.02500	5383	53
T137	36.36700	-108.85400	5489	159	T209	36.35928	-108.84505	5421	91	TW29	36.91230	-109.07500	5032	-298	W4	36.59210	-109.02499	5441	111
T138	36.36485	-108.85415	5470	140	T210	36.35768	-108.84500	5314	-16	TW30	36.91410	-109.07500	5194	-136	W5	36.59031	-109.02499	5309	-21
T139	36.36290	-108.85400	5458	128	T211	36.35510	-108.84499	5424	94	TW31	36.90910	-109.07800	5275	-55	W6	36.58830	-109.02501	5381	51
T140	36.36130	-108.85399	5418	88	T212	36.35321	-108.84500	5425	95	TW32	36.90870	-109.07500	5315	-15	W7	36.58630	-109.02500	5439	109
T141	36.35968	-108.85397	5396	66	T213	36.35190	-108.84500	5403	73	TW33	36.90986	-109.07267	5310	-20	W8	36.58420	-109.02500	5391	61
T142	36.35790	-108.85400	5335	5	T214	36.35040	-108.84500	5403	73	TW34	36.90860	-109.07198	5320	-10	W9	36.58230	-109.02500	5401	71
T144	36.35392	-108.85404	5360	30	T215	36.35760	-108.87201	5406	76	TW35	36.90645	-109.07062	5330	0	W10	36.58046	-109.02451	5391	61
T145	36.35200	-108.85400	5423	93	T216	36.35599	-108.87211	5396	66	TW36	36.90310	-109.06874	5280	-50	W11	36.57891	-109.02401	5299	-31
T146	36.35040	-108.85300	5308	-22	T217	36.34870	-108.87199	5323	-7	TW37	36.90158	-109.06788	5280	-50	W12	36.57709	-109.02400	5388	58
T147	36.35040	-108.85094	5475	145	T218	36.34862	-108.86901	5363	33	TW38	36.89950	-109.06700	5316	-14	W13	36.57560	-109.02400	5338	8
T148	36.35219	-108.85100	5362	32	T219	36.34889	-108.86698	5410	80	TW39	36.89770	-109.06700	5299	-31	W14	36.57351	-109.02400	5461	131
T149	36.35390	-108.85180	5386	56	T220	36.34870	-108.86500	5394	64	TW40	36.89590	-109.06700	5215	-115	W15	36.57131	-109.02399	5445	115
T150	36.35561	-108.85092	5426	96	T221	36.34872	-108.86200	5377	47	TW41	36.89590	-109.06900	5269	-61	W16	36.56954	-109.02446	5308	-22
T152	36.35979	-108.85099	5413	83	T222	36.34863	-108.86102	5330	0	TW42	36.89600	-109.07100	5221	-109	W17	36.56785	-109.02438	5309	-21
T155	36.36489	-108.85093	5372	42	T223	36.34869	-108.85800	5403	73	TW43	36.89760	-109.07100	5244	-86	W18	36.56791	-109.02200	5339	9
T156	36.36684	-108.85104	5370	40	T224	36.34848	-108.85600	5398	68	TW44	36.89960	-109.07100	5244	-86	W19	36.56939	-109.02205	5371	41
T160	36.37442	-108.85101	5232	-98	T225	36.34871	-108.85400	5391	61	TW45	36.89950	-109.06900	5207	-123	W20	36.57183	-109.02299	5416	86
T161	36.37607	-108.85110	5268	-62	T226	36.34840	-108.85101	5422	92	TW46	36.89810	-109.06900	5229	-101	W21	36.57371	-109.02241	5469	139
T162	36.37791	-108.85119	5281	-49	T227	36.34859	-108.84900	5434	104	TW47	36.89970	-109.07800	5266	-64	W22	36.57571	-109.02200	5386	56
T163	36.37941	-108.85101	5381	51	T228	36.34850	-108.84699	5434	104	TW48	36.89970	-109.08000	5266	-64	W23	36.57730	-109.02201	5302	-28
T164	36.37940	-108.84801	5288	-42	T229	36.34860	-108.84401	5470	140	TW49	36.89790	-109.07800	5208	-122	W24	36.57880	-109.02200	5380	50
T165	36.37759	-108.84900	5336	6	T230	36.34686	-108.84392	5488	158	TW50	36.89610	-109.07800	5256	-74	W26	36.58229	-109.02200	5532	202

W30	36.59026	-109.02301	5406	76	W98	36.59000	-109.01300	5477	147	W167	36.59191	-109.00398	5351	21	W231	36.58443	-108.99552	5444	114
W31	36.59190	-109.02200	5378	48	W99	36.59180	-109.01299	5451	121	W168	36.59341	-109.00400	5342	12	W232	36.58586	-108.99498	5349	19
W32	36.59350	-109.02200	5393	63	W100	36.59360	-109.01299	5395	65	W169	36.59528	-109.00378	5338	8	W233	36.58788	-108.99508	5380	50
W33	36.59510	-109.02301	5345	15	W101	36.59530	-109.01300	5376	46	W170	36.59687	-109.00403	5339	9	W234	36.58953	-108.99506	5359	29
W34	36.59690	-109.02300	5302	-28	W102	36.59690	-109.01299	5357	27	W171	36.59690	-109.00101	5325	-5	W235	36.59160	-108.99500	5413	83
W35	36.59687	-109.02047	5275	-55	W103	36.59690	-109.01100	5389	59	W172	36.59519	-109.00069	5422	92	W236	36.59339	-108.99500	5415	85
W36	36.59521	-109.02000	5358	28	W105	36.59370	-109.01100	5366	36	W173	36.59342	-109.00101	5381	51	W237	36.59521	-108.99501	5347	17
W37	36.59360	-109.01999	5332	2	W106	36.59190	-109.01100	5445	115	W174	36.59181	-109.00202	5332	2	W238	36.59690	-108.99501	5367	37
W38	36.59200	-109.01999	5341	11	W107	36.59000	-109.01100	5404	74	W175	36.58975	-109.00237	5305	-25	W239	36.59690	-108.99300	5399	69
W39	36.58955	-109.01933	5357	27	W108	36.58820	-109.01100	5420	90	W176	36.58791	-109.00199	5260	-70	W240	36.59520	-108.99300	5362	32
W40	36.58829	-109.02000	5301	-29	W109	36.58610	-109.01099	5473	143	W177	36.58595	-109.00201	5231	-99	W241	36.59339	-108.99298	5405	75
W41	36.58621	-109.02003	5430	100	W110	36.58419	-109.01101	5433	103	W178	36.58413	-109.00162	5387	57	W242	36.59171	-108.99199	5460	130
W42	36.58411	-109.02005	5534	204	W111	36.58230	-109.01101	5384	54	W179	36.58230	-109.00198	5412	82	W243	36.58980	-108.99200	5393	63
W43	36.58230	-109.01999	5546	216	W112	36.58682	-109.01100	5393	63	W180	36.58079	-109.00201	5405	75	W244	36.58804	-108.99204	5414	84
W44	36.58070	-109.02000	5379	49	W113	36.57878	-109.01102	5405	75	W181	36.57900	-109.00199	5467	137	W245	36.58591	-108.99200	5350	20
W45	36.57911	-109.02000	5323	-7	W114	36.57693	-109.01132	5373	43	W182	36.57700	-109.00200	5454	124	W246	36.58411	-108.99198	5335	5
W46	36.57730	-109.02000	5375	45	W115	36.57520	-109.01099	5316	-14	W183	36.57529	-109.00200	5429	99	W247	36.58231	-108.99199	5303	-27
W47	36.57570	-109.02000	5351	21	W116	36.57330	-109.01102	5334	4	W184	36.57309	-109.00201	5384	54	W248	36.58068	-108.99197	5384	54
W48	36.57370	-109.02000	5510	180	W117	36.57139	-109.01099	5344	14	W185	36.57160	-109.00200	5406	76	W249	36.57883	-108.99240	5338	8
W49	36.57160	-109.02000	5398	68	W118	36.56952	-109.01099	5358	28	W186	36.56970	-109.00200	5427	97	W250	36.57687	-108.99231	5366	36
W50	36.56942	-109.02101	5354	24	W119	36.56800	-109.01120	5357	27	W187	36.56791	-109.00199	5396	66	W251	36.57523	-108.99228	5310	-20
W51	36.56790	-109.02000	5348	18	W122	36.57152	-109.00851	5342	12	W188	36.56789	-109.00001	5444	114	W252	36.57320	-108.99200	5424	94
W52	36.56789	-109.01801	5302	-28	W123	36.57359	-109.00874	5354	24	W189	36.56969	-108.99999	5432	102	W254	36.56940	-108.99299	5429	99
W53	36.56930	-109.01804	5294	-36	W124	36.57503	-109.00860	5299	-31	W190	36.57129	-108.99899	5437	107	W255	36.56790	-108.99300	5407	77
W54	36.57180	-109.01800	5365	35	W125	36.57685	-109.00877	5314	-16	W191	36.57320	-108.99900	5525	195	W257	36.56960	-108.99099	5482	152
W55	36.57370	-109.01800	5554	224	W126	36.57890	-109.00802	5390	60	W192	36.57520	-108.99900	5436	106	W259	36.57330	-108.99000	5416	86
W56	36.57560	-109.01798	5370	40	W127	36.58000	-109.00802	5382	52	W193	36.57690	-108.99900	5435	105	W260	36.57526	-108.99029	5334	4
W57	36.57708	-109.01799	5354	24	W128	36.58231	-109.00863	5439	109	W194	36.57898	-108.99938	5396	66	W261	36.57690	-108.99008	5327	-3
W58	36.57911	-109.01800	5437	107	W129	36.58410	-109.00900	5451	121	W196	36.58231	-108.99901	5416	86	W262	36.57874	-108.99014	5388	58
W59	36.58080	-109.01799	5279	-51	W130	36.58610	-109.00900	5464	134	W197	36.58404	-108.99942	5402	72	W263	36.58056	-108.99017	5328	-2
W60	36.58230	-109.01800	5482	152	W131	36.58810	-109.00900	5405	75	W198	36.58601	-108.99899	5388	58	W264	36.58229	-108.98999	5465	135
W62	36.58610	-109.01800	5434	104	W132	36.59000	-109.00901	5424	94	W199	36.58789	-108.99902	5401	71	W265	36.58418	-108.98999	5399	69
W63	36.58831	-109.01792	5440	110	W133	36.59190	-109.00900	5449	119	W200	36.58981	-108.99899	5348	18	W266	36.58642	-108.99091	5376	46
W64	36.59000	-109.01800	5395	65	W134	36.59361	-109.00900	5480	150	W201	36.59170	-108.99899	5352	22	W267	36.58775	-108.98997	5333	3
W65	36.59190	-109.01800	5478	148	W135	36.59541	-109.00900	5362	32	W202	36.59359	-108.99995	5402	72	W268	36.58990	-108.99000	5397	67
W66	36.59360	-109.01800	5457	127	W136	36.59690	-109.00900	5418	88	W203	36.59509	-108.99900	5401	71	W269	36.59159	-108.99000	5432	102
W67	36.59520	-109.01801	5407	77	W138	36.59540	-109.00700	5379	49	W204	36.59691	-108.99899	5446	116	W270	36.59340	-108.98999	5371	41
W69	36.59690	-109.01500	5398	68	W139	36.59361	-109.00700	5406	76	W205	36.59689	-108.99702	5436	106	W271	36.59519	-108.99000	5361	31
W70	36.59530	-109.01500	5411	81	W140	36.59180	-109.00700	5468	138	W206	36.59531	-108.99700	5422	92	W272	36.59690	-108.99099	5434	104
W71	36.59360	-109.01600	5378	48	W141	36.59000	-109.00700	5373	43	W207	36.59329	-108.99700	5422	92	W273	36.59690	-108.98901	5421	91
W72	36.59190	-109.01601	5482	152	W142	36.58790	-109.00700	5429	99	W208	36.59120	-108.99723	5251	-79	W274	36.59501	-108.98900	5388	58
W73	36.59000	-109.01600	5452	122	W143	36.58611	-109.00700	5435	105	W209	36.58978	-108.99698	5342	12	W275	36.59348	-108.98900	5421	91
W74	36.58810	-109.01600	5398	68	W144	36.58410	-109.00700	5420	90	W210	36.58781	-108.99699	5346	16	W276	36.59191	-108.98899	5415	85
W75	36.58600	-109.01599	5408	78	W145	36.58228	-109.00601	5339	9	W211	36.58588	-108.99700	5398	68	W277	36.59021	-108.98906	5421	91
W76	36.58430	-109.01600	5446	116	W146	36.58045	-109.00645	5387	57	W212	36.58463	-108.99689	5361	31	W278	36.58799	-108.98900	5339	9
W77	36.58229	-109.01600	5556	226	W147	36.57867	-109.00648	5393	63	W213	36.58234	-108.99716	5307	-23	W279	36.58596	-108.98851	5390	60
W78	36.58081	-109.01600	5329	-1	W148	36.57690	-109.00600	5431	101	W214	36.58086	-108.99704	5305	-25	W280	36.58421	-108.98901	5372	42
W79	36.57879	-109.01599	5373	43	W149	36.57510	-109.00600	5433	103	W215	36.57899	-108.99700	5364	34	W281	36.58231	-108.98901	5376	46
W80	36.57727	-109.01566	5439	109	W150	36.57299	-109.00600	5469	139	W216	36.57689	-108.99701	5389	59	W282	36.58044	-108.98776	5399	69
W81	36.57531	-109.01500	5402	72	W151	36.57148	-109.00600	5438	108	W217	36.57508	-108.99697	5422	92	W283	36.57923	-108.98804	5384	54
W82	36.57370	-109.01600	5470	140	W152	36.56960	-109.00601	5351	21	W218	36.57320	-108.99699	5470	140	W284	36.57678	-108.98848	5365	35
W83	36.57170	-109.01600	5483	153	W153	36.56790	-109.00599	5443	113	W219	36.57144	-108.99690	5366	36	W285	36.57559	-108.98845	5432	102
W84	36.56939	-109.01600	5355	25	W154	36.56791	-109.00399	5392	62	W220	36.56970	-108.99700	5428	98	W286	36.57301	-108.98800	5454	124
W86	36.56791	-109.01394	5337	7	W155	36.56969	-109.00399	5406	76	W221	36.56791	-108.99699	5425	95	W288	36.56939	-108.98799	5411	81
W87	36.56950	-109.01299	5425	95	W156	36.57169	-109.00401	5410	80	W222	36.56790	-108.99501	5425	95					
W90	36.57529	-109.01301	5376	46	W157	36.57320	-109.00399	5468	138	W224	36.57150	-108.99500	5415	85					
W91	36.57722	-109.01299	5403	73	W158	36.57510	-109.00400	5427	97	W225	36.57320	-108.99500	5450	120					
W92	36.57878	-109.01300	5315	-15	W159	36.57710	-109.00400	5417	87	W226	36.57540	-108.99500	5442	112					
W93	36.58070	-109.01299	5348	18	W160	36.57880	-109.00400	5548	218	W227	36.57708	-108.99472	5363</						

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