Noble gases in conventional and unconventional petroleum systems

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Abstract

Petroleum systems represent complex multi-phase subsurface environments. The properties of the noble gases as conservative physical tracers allow them to be used to gain insight into the physical behaviour occurring within hydrocarbon systems. This can be used to better understand the mechanisms of hydrocarbon migration, residence time of fluids, and measurement of the scale of the subsurface fluid system involved in the transport and trapping of the hydrocarbon phase. The noble gases in the subsurface derive from different sources with distinct isotopic compositions, allowing them to be resolved in any crustal fluid. We discuss the processes within petroleum systems that incorporate the noble gases from each of these sources into hydrocarbon accumulations. The dominant mechanism controlling the introduction of air-derived noble gases into petroleum systems is via subsurface groundwater, and this records key information about the interaction of the petroleum system with the hydrogeological regime. Radiogenic noble gases accumulate over time, recording information about the age and relative timing of processes within the petroleum system. We review the conceptual framework and quantitative models describing these processes using examples from previous studies, and discuss both their current limitations and the potential for their application to unconventional hydrocarbon systems.

1. Introduction

1.1 Overview

The study of the origin and post-generation history of hydrocarbons in sedimentary basins has been the subject of thousands of investigations worldwide, both by the academic and industrial communities. Many studies have tried to better understand or characterize the elements or processes that occur within a given hydrocarbon system (e.g. Waples, 1994; Hindle, 1997). In a frontier basin, initial studies may focus on predicting whether a particular package of Earth's crust has the necessary elements of sufficient quality and distribution to generate and store hydrocarbons over geological timescales (e.g. Blanc and Connan, 1994; Whiticar, 1994). In better studied basins, efforts are likely to focus on defining the robustness of critical hydrocarbon play elements. The application of geochemical techniques has been at the forefront of many of these studies by: (i) providing time and temperature constraints on basin evolution (Sweeney & Burnham, 1990; Crowhurst et al., 2002 ;Stolper et al., 2014), (ii) determining the depositional environment, age, thermal maturity and type of organic matter of key source rock intervals (Hughes et al., 1995), and (iii) linking hydrocarbons in reservoirs to the source rock responsible for their generation (Dow, 1974; Stahl, 1978; Philp, 1993). However, the physical histories of accumulated hydrocarbons have proven to be more difficult to understand.

The noble gases have found strong application as physical tracers in a wide range of geochemical fields (Porcelli et al., 2002; Ozima and Podosek 2002; Burnard 2013). Thanks to their chemical inertness, they are unaffected by biological activity, chemical alteration, or redox reactions that complicate many other tracer systems. This means that only physical processes, such as mixing, dissolution, phase partitioning, and diffusion are recorded by the noble gases. This, coupled with the fact that the different components of the Earth's noble gas inventory (atmosphere, crust and mantle) are isotopically distinct and well-constrained, means that the inputs into and the processes occurring within any given system can be accurately deduced. Given these properties, noble gas geochemistry has the theoretical potential to help constrain physical processes and timescales associated with hydrocarbon fluid generation, migration and storage in petroleum systems.

In a typical noble gas investigation of a petroleum system, samples are taken from the produced hydrocarbon and measured for their noble gas composition. From here a range of different models can be applied to investigate different characteristics of the system, from gas, oil, and water interactions to the timing of migration and accumulation. The development of these quantitative noble gas models has happened alongside improvements in analytical technology, allowing measurement of more noble gas isotopes with greater accuracy and precision, and from this an increased understanding of the processes affecting the noble gases within the subsurface.

Consequently noble gases now provide a powerful tool that can reveal information about the subsurface inaccessible by other analytical techniques. For complementary information we refer readers to comprehensive reviews by Ballentine and Burnard (2002), and Holland and Gilfillan (2013) for detailed discussion.

1.2 Definitions

We use the term 'petroleum system' in the sense defined by Magoon & Dow (1994), and provide a schematic representation in figure 1. It is considered to encompass a unit of active source rock, all related hydrocarbon accumulations, and the geological features and processes that are necessary for the hydrocarbon accumulations to exist. This comprises a series of elements and processes; elements include the source rock, migration pathway, reservoir, and trap, whereas processes include hydrocarbon generation, migration, and the geological processes affecting the system. As such, the petroleum system can cover a large geographic, stratigraphic, and temporal range and significant differences may exist between different systems.

We discuss both conventional and unconventional hydrocarbon systems. Conventional hydrocarbon systems comprise of (i) a source rock of sufficient quality and distribution that is buried to temperatures and pressures necessary to result in the generation of and expulsion of hydrocarbons from the source rock, (ii) secondary migration of hydrocarbons along carrier beds to a reservoir rock in a configuration that traps hydrocarbons either stratigraphically or structurally, and (iii) an overlying low permeability seal rock that results in the accumulation of hydrocarbons within the reservoir rock. Whilst the term 'unconventional' has been applied to petroleum exploitation environments ranging from tar sands to ultra-deep water production, we use the term here in a stricter sense to apply to source rock reservoirs such as gas-shales (Curiale & Curtis, 2016). These are traditionally unconventional in that they produce directly from the source rocks that generate the petroleum, with very little secondary migration. The low porosity and permeability of these rocks means that they typically require advanced production techniques such as hydraulic fracturing or directional drilling to produce economically. A schematic representation of conventional and unconventional production is shown in figure 1.

Noble gas isotope ratio measurements are typically reported simply as raw ratios, unlike most other geochemical isotope ratios, which use permil (‰) notation (Hoefs, 1997). Using the raw ratios is more convenient when relatively large isotopic variations are common (Porcelli et al., 2002). Although using raw ratios eliminates the requirement for a universal standard, samples in natural systems are often compared to air, which is well mixed and defined (table 1). In subsurface fluid systems it is also common to use air-saturated water (ASW) as a standard, which is well defined over a range of temperatures and salinities (table 3). Helium isotope ratios ($^3He/^4He$) are usually reported relative to the air ratio (R_a). Quantities of noble gases are typically reported in cm^3 standard temperature and pressure (cm^3STP or ccSTP), due to the small amounts of noble gases usually present in geochemical systems. The cm^{3}STP unit can be directly converted to moles using the molar gas volume (22400cm^3 at STP) (Burnard et al., 2013).

2. Origin of terrestrial noble gases

2.1 Primordial noble gases

Primordial elements are those indigenous to Earth, incorporated during planetary formation. The noble gases are highly volatile, and thus difficult to entrain during planetary accretion (Pepin, 1991). This results in a bulk Earth that is depleted in noble gases by several orders of magnitude compared to the proto-solar nebula from which the planet was formed (Wieler, 2002; Grimberg et al., 2006). Some of the noble gas isotopes (e.g. ^{20}Ne, ^{36}Ar, ^{84}Kr, ^{130}Xe) are not produced on Earth in significant quantities, and thus their provenance in terrestrial reservoirs is assumed to be 100% primordial (Burnard et al., 1997; Moreira et al., 1998). The isotopic composition of possible accretionary precursors such as the protosolar nebula and carbonaceous chondrites have been compared with the terrestrial inventory of the primordial gases to reconstruct the origin and processes responsible for delivery of volatiles to Earth on its formation (e.g. Ballentine et al., 2005; Ballentine and Holland 2008; Holland et al., 2009; Marty, 2012; Halliday, 2013). These models of planetary noble gas acquisition successfully explain the modern terrestrial inventory for all of the primordial noble gases except Xe, whose apparent depletion in the Earth is still the subject of much debate (Sanloup et al., 2005; Lee & Steinle-Neumann, 2006, Pepin & Porcelli, 2006, Pujol et al., 2011).

2.2 Production of noble gases

Noble gases are produced both directly and indirectly from radioactive processes occurring within the Earth. The partitioning of different radioactive elements into chemically and physically distinct parts of the planet is the cause of much of the heterogeneity in the terrestrial noble gas reservoirs. The most productive radioactive elements in terms of abundance and decay rate (U, Th, K) are highly incompatible in the Earth's mantle, meaning that the crust is typically associated with much higher levels of noble gas production (Ballentine & Burnard, 2002).

Noble gas production proceeds by 3 mechanisms: radiogenic, nucleogenic, and fissiogenic. The laws governing the pathways and rates of radioactive decay are well understood, allowing theoretical production rates to be accurately calculated in any system if the parent isotope concentration and half-life (decay constant) is known (Rutherford, 1906; Pierce et al., 1964). This is the basis of a number of successful dating tools such as Ar-Ar dating and ^{4}He dating (Merrihue & Turner, 1966; Farley, 2002; Renne et al., 2010).

2.2.1 Radiogenic production

Radiogenically produced isotopes are those produced as direct daughter products of radioactive decay. For the modern Earth, the most significant radioactive decay pathway is the U, Th series. The initial decay of ^{235}U, ^{238}U and ^{232}Th is by α-decay, significant in terms of noble gas production because an α-particle is equivalent to a ^{4}He nucleus. The vast majority of α-particles ionise the surrounding material upon ejection, collecting electrons to form a ^{4}He atom. Elevated U, Th concentrations are therefore associated with helium that is isotopically enriched in ^{4}He. The incompatibility of both U, Th in the mantle means that they, and consequently ^{4}He, are highly enriched in continental crust.

Similarly, high crustal concentrations of ^{40}K lead to elevated ^{40}Ar when ^{40}K decays by electron capture. The subsequent release of radiogenic ^{40}Ar into the atmosphere has drastically altered the isotopic composition of atmospheric argon over Earth history. Whilst the majority of primordial argon is ^{36}Ar (the proto-solar nebula has a ^{40}Ar/^{36}Ar ~3.0 x 10^{-4}), the atmospheric ^{40}Ar/^{36}Ar ratio in the modern atmosphere is ~298.6 because of radiogenic ^{40}Ar enrichment (Göbel et al., 1978; Anders & Grevasse, 1989; Lee et al., 2006).

2.2.2 Nucleogenic production

In addition to α-particles the emission of neutrons is also a direct result of radioactivity. Nucleogenic production is the interaction of both these particles with the nuclei of nearby atoms, leading to the formation of new elements in Wetherill reactions (Wetherill, 1954).

Most commonly the impact of an α-particle into a nucleus is followed by the emission of a neutron in an (α,n) reaction, effectively adding 2 protons and 1 neutron to the nucleus of the affected atom. Noble gases formed in measurable quantities in this fashion include ^{21}Ne, which is derived from the (α,n) reaction of ^{18}O, (^{18}O(α,n)^{21}Ne) as well as ^{22}Ne, which is formed indirectly via the β^{+} decay of the short-lived ^{22}Na produced by (α,n) reaction with ^{19}F (^{19}F(α,n)^{22}Na(β^{+})^{22}Ne).

Alternatively, an incident neutron can cause a nucleus to emit an α-particle, effectively removing 2 protons and 1 neutron in a (n,α) reaction. This pathway provides a further source of ^{21}Ne, produced by the ^{24}Mg(α,n)^{21}Ne reaction, as well as a small contribution to ^{3}He, produced by the ^{6}Li(α,n)^{3}He reaction.

As nucleogenic reactions require a source of α-particles and neutrons, their production rates are tightly coupled with nearby radioactivity, primarily U, Th. Both α-particles and neutrons have a limited range in typical crustal rock after being ejected from the parent nucleus, with typical ranges of 15-45μm and 10-100cm respectively (Martel, 1990; Ziegler 1977). As such, heterogeneities on the mineral-scale can have measurable effects on the relative production of different isotopes. Notably, observed radiogenic ^{21}Ne/^{22}Ne values from the modern crust are incompatible with those predicted from average crust ^{18}O and ^{19}F concentrations. This has led to the inference that the O/F concentration in the modern crust is systematically lower in phases associated with high U, Th concentrations (Kennedy et al., 1990; Hiyagon & Kennedy, 1992).

2.2.3 Fissiogenic production

A further source of noble gas production is as a result of the fission of heavy, unstable nuclei. The systematics of this process are more complex than simple radioactive decay, but the production rates of different isotopes can still be relatively well-constrained (Wieler & Eikenberg, 1999). The dominant fission process in noble gas production is the spontaneous fission of ^{238}U, which produces $^{129, 131, 132, 134, 136}$Xe, as well as smaller amounts of $^{83, 84, 86}$Kr. The spontaneous fission of ^{232}Th, and the neutron-induced fission of ^{238}U, ^{235}U, and ^{232}Th also make minor contributions to the production of these fissiogenic Xe and Kr isotopes (Ballentine & Burnard, 2002).

The production rates of fissiogenic isotopes are much lower than those of radiogenic or nucleogenic isotopes (table 4). As such, fissiogenic Xe excesses are only observed in samples that have been isolated for significant periods of time (Reynolds, 1963; Holland et al., 2013).

3. Physical chemistry of noble gases in fluids

3.1 Henry's law

The dissolution of noble gases into fluids (water, oil, and gas) has been reviewed by Ballentine et al., 2002. Dissolution follows Henry's law, which states that the concentration of a gas in solution is directly proportional to the partial pressure of that gas in the gas phase. This can be formulated for any noble gas i, assuming ideal gas behaviour in both the gas and fluid phases (eq 5.1).

$$p_i = K_i x_i \tag{5.1}$$

Where p_i is the partial pressure, x_i is the mole fraction in solution, and K_i is the Henry's constant. Henry's constants are specific to the solute, and are temperature and salinity dependent; their units depend on the units used to measure the partial pressure and concentration in the fluid phase.

The Henry's constants of noble gases in water have been determined empirically over a temperature range from the freezing point to the critical point of water (Crovetto et al., 1982; Smith, 1985), and equations have been formulated using a compilation of empirical data that allow the calculation of Henry's constants at any temperature (Fernández-Prini et al., 2003). Determination of the Henry's constant for oil faces the further complexity of the natural variation in oil composition. This work is limited to just one study of two oils with API gravities of 25° and 31° (Kharaka & Specht, 1988). The solubility of the noble gases was shown to be affected by the API gravity, but it is likely that the solubility is also controlled by properties other than bulk density (e.g., concentration of polar compounds, trace element concentrations). Hence the Henry's constant for oils remains a key uncertainty in models that apply these constraints.

3.2 Non-ideality

Henry's law can be modified to account for non-ideal behaviour in the gas and fluid phases by taking into account both the gas phase fugacity coefficient, and the liquid phase activity coefficient (eq 5.2).

$$\Phi_i p_i = \gamma_i K_i x_i \tag{5.2}$$

Where Φ_i is the fugacity coefficient, and γ_i is the activity coefficient; a deviation of either of these from unity represents non-ideal behaviour. Fugacity is pressure and temperature dependent, and can be calculated from empirical measurements of real molar volume (Dymond & Smith, 1980). Activity is dependent on temperature and salinity, with the relationship formulated in the Setschenow equation (eq 5.3).

$$\gamma_i = e^{Ck_i(T)} \tag{5.3}$$

Where C is the concentration of salt in the solution, and k_i is the temperature dependent Setschenow coefficient. The response of Ar to changes in salinity is independent of the electrolyte species, and this relationship is assumed to be true for the other noble gases (Ben-Naim & Egel-Thal, 1965). The Setschenow coefficients have been determined empirically for the noble gases over a range of temperatures from 270-340K (Smith & Kennedy, 1983). Unfortunately, the temperatures encountered in subsurface environments often greatly exceed this range, with the onset of oil formation occurring at temperatures of approximately 350K, and secondary cracking to gas being above 420K (Waples, 1980). As such, the extrapolation of curves fitted to the empirical data must be used to account for salinity effects on noble gas solubility in the range of interest of most hydrocarbon systems, and represents a potential source of error in any derivative product. Recent work on noble gas partitioning in CO_2-water systems show measurable deviations from predicted behaviours in high-pressure environments (Warr, 2015). In most petroleum system investigations these deviations from ideality are unlikely to affect the general outcomes of any models, but care must be taken when considering the precision with which they can be applied. Further work involving a combination of empirical and model data will be crucial to refine these models in the future.

4 Terrestrial noble gas inventories

4.1 The atmosphere

Although small in size compared to the solid Earth, the majority of the Earth's primordial noble gases are held in the atmosphere (Porcelli & Ballentine, 2002). The creation and evolution of the atmosphere is complex, and not yet fully understood. Whilst it is likely that terrestrial bodies such as the Earth are able to gravitationally capture volatiles from the proto-solar nebula during formation (Pepin, 2006), the atmosphere is clearly distinct from a solar composition (Brown 1949; Porcelli & Ballentine, 2002). Alternative proposed methods of acquiring noble gases include adsorption onto accumulating dust (Marrocchi et al., 2005), or the implantation by solar wind (Podosek et al., 2000). A contribution of volatile-rich cometary material brought in during the late heavy bombardment has also been suggested as a source of atmospheric noble gases (Owen et al., 1992; Dauphas, 2003; Holland et al., 2009).

The reasons for the atmosphere's distinct noble gas composition are likely due to the atmospheric losses experienced by the Earth during its early history. Whether this occurred by aggregate catastrophic loss, or gradual escape of volatiles, is still debated (Pepin, 2006; Pepin & Porcelli, 2006; Tucker & Mukhopadhyay, 2014). However, the atmospheric composition of noble gases has been remarkably constant over geological timescales. Whilst degassing of the solid Earth at volcanoes and mid-ocean ridges releases mantle noble gases into the atmosphere, it is in such small quantities as to be insignificant even over billions of years. However, exceptions to this include isotopes with high radiogenic production such as ^{40}Ar, which are produced within the Earth to such an extent that solid Earth degassing can influence atmospheric concentrations (Allégre et al., 1996; Ballentine & Burnard, 2002). Helium is gravitationally unbound in the atmosphere. However, the loss into space is balanced by a volcanic degassing flux from mid-ocean ridge, ocean-island, and subduction-related volcanism, resulting in an assumed steady-state helium concentration in the atmosphere (Torgersen, 1989; Lupton & Evans, 2013). When considering most fluids in the crust, and groundwater in particular, it is reasonable to assume that the atmospheric noble gas composition has been constant over the timescale of their introduction into the subsurface.

4.2 Water

When in direct contact with the atmosphere, water will rapidly equilibrate with air according to the processes detailed in the previous section. The solubilities of the noble gases vary by element, meaning that at equilibrium the elemental composition of the water is not air-like (Kipfer et al., 2002). However, isotopic ratios of the individual noble gases are not significantly affected by equilibrium partitioning. As the rules governing this partitioning and the variation with respect to temperature, pressure, and salinity are well known, it is possible to calculate the air-saturated water composition in any given environment. This composition is crucial for noble gas analysis of hydrocarbon reservoirs, as a common assumption in modeling and analysis is that all atmospherically derived noble gases in the subsurface will be delivered in known quantities dissolved as air-saturated water (ASW) through hydrocarbon-water interaction and noble gas partitioning.

One complication to this arises from empirical measurements of atmosphere-derived noble gas concentrations in meteoric groundwater that have often been found to be higher than the values predicted by Henry's law equilibration. This phenomenon is commonly referred to as 'excess air'

(Heaton & Vogel, 1981; Herzberg & Mazor, 1979). The behaviour of this excess air component is generally consistent, with neon being the most strongly affected, and the heavier noble gases proportionally less so (Heaton & Vogel, 1981). Theoretical models describing processes by which this can occur have been developed, and refined over time to more closely match observations (Stute et al., 1995; Ballentine and Hall 1999; Aeschbach-Hertig et al., 2000). Whilst these models differ slightly, they are based on the principle that excess air is introduced into groundwater by the entrapment of air bubbles during fluctuations of the water table. A close fit to experimental observations is found by modeling a closed-system equilibration of these bubbles (Aeschbach-Hertig et al., 2008). Within petroleum systems deposited under marine conditions, the groundwater is likely to have a marine noble gas composition (Kipfer et al., 2002) and excess air within these systems are not expected.

4.3 The mantle

The Earth's mantle contains a high proportion of primordial noble gases. It is introduced to the surface in CO_2-rich volcanic gases that can permeate through the crust or get released at mid-ocean ridges and volcanoes. The measured compositions of these gases have distinctive high but variable $^3He/^4He$ ratios. For example, the well-mixed asthenospheric upper mantle, as sampled by depleted mid-ocean ridge basalt (MORB) mantle ranges from 7-9 R_a (Graham, 2002), where the sub-continental lithospheric mantle is defined as 6.1 ± 2.1 (Day et al., 2015). In contrast, many mantle plume regions extend as high as ~50 R_a (e.g., Stuart et al., 2003). Likewise, the mantle is marked by high $^{20}Ne/^{22}Ne$ ratios and $^{40}Ar/^{36}Ar$ ratios (Sarda et al., 1988; Staudacher et al 1989; Holland et al., 2009). Addition of mantle noble gases into subsurface hydrocarbon accumulations, while not useful in the context of origin and history of hydrocarbon gases, may be useful for constraining the origin of non-hydrocarbon gases that in some cases accumulate concurrently in the subsurface – particularly CO_2 and N_2 (Ballentine and Sherwood Lollar 2002; Ballentine et al., 2005; Gilfillan et al., 2009).

4.4 The crust

Due to their incompatibility in the mantle, the major radioactive elements involved in noble gas production were partitioned heavily into the Earth's crust during planetary formation. These elements which include U, Th, and K, initiate the decay chains that produce the radiogenic noble gas isotopes, principally ^4He, ^{40}Ar, ^{21}Ne, ^{22}Ne, and to a lesser extent some Xe and Kr isotopes. Whilst the crust is a complex and heterogeneous system with inputs from many sources, crustal fluids are often characterized by high concentrations of these radiogenic isotopes.

These isotopes are produced within the minerals that make up the crust, but can be released into the surrounding fluid systems (Bach et al., 1999). The extent of this release is controlled by a number of factors including grain size, temperature, and mineral alteration (Honda et al., 1982; Brooker et al., 1998; Baxter et al., 2001). Lighter isotopes are more readily released at lower temperatures, and as such the ratios of radiogenic isotopes (e.g. $^4He/^{21}Ne^*$, $^4He/^{40}Ar^*$) can be used to determine temperatures of release (Torgersen et al., 1992; Baxter et al., 2002).

In general, higher concentrations of radiogenically produced noble gas isotopes reflect older systems that have been isolated for longer periods of time. Data from fracture fluids in mines in Precambrian shields show concentrations that would have taken billions of years to accumulate (Holland et al., 2013).

5 Introduction of noble gases into the petroleum system

5.1 Source rock formation

The genesis of the petroleum system begins with the deposition of an organic carbon rich sedimentary rock. Typically >1% total organic carbon (TOC) is considered sufficient for a source rock (Gluyas & Swarbrick, 2013), although this can vary. As organic carbon comes in a variety of forms, each of which has distinct chemical behaviour in a petroleum system, these source rocks are typically classified according to their kerogen composition, as outlined in Table 2. The type of organic matter that makes up source rocks is of particular importance because it is this that ultimately determines how oil or gas prone a source rock is likely to be, as well as the volume of hydrocarbons that can be generated from the source rock on a gram for gram basis (Peters & Cassa, 1994). Laboratory simulation of this naturally occurring process has been extensively investigated in hydrous pyrolysis experiments, in which immature source rock is heated under controlled conditions to simulate the naturally-occurring process of petroleum formation (Peters, 1986; Peters et al., 2015). These and other experimental studies suggest that the presence of water may be required during catagenesis and hydrocarbon generation to produce the compositions that we observe in nature (Lewan, 1993). Noble gases are more soluble in oil than in water, and thus the formation of a liquid petroleum phase within the source rock will cause the partitioning of noble gases between it and the surrounding water phase that remains in the rock (Ballentine et al., 1991). The water in this context is likely to not represent a significant volume given the prior compaction and lithification of the source rock. Given sufficient pressure generated during the generation of hydrocarbons, oil may escape from the source rock and as such noble gases in the escaping fluid will evolve separately (described below) to the noble gas signature of any retained oil. The extent of kerogen decomposition can further affect the partitioning of noble gases, as the solubility of noble gases has been shown to be positively correlated with the API of the oil (Kharaka & Specht, 1988). Given continued burial and increase in temperature, the retained oil itself will begin to crack to gaseous hydrocarbons. The onset of gas generation will further complicate this phase partitioning, as the noble gases have a strong affinity for the gas phase when it is present. Furthermore, it is unclear how the alteration of the source rock composition will affect the noble gases stored within; it is possible that any component adsorbed onto the organic carbon could be released during thermal degradation.

Most noble gas studies to date have focussed on characterizing or modelling the inheritance and evolution of noble gases during migration and accumulation in conventional reservoirs. However, key gaps exist in our understanding of hydrocarbon generation and expulsion from source rocks, and there have been very few studies to date that have studied the evolution of noble gases during hydrocarbon generation. Questions such as the role of water during hydrocarbon generation, the relative volumes of expelled versus retained oil and gas, and the mechanisms of storage within the source rocks (adsorption or as free gas within porosity or fractures), remain elusive.

5.2 Primary migration

Primary migration is the initial expulsion of the generated hydrocarbons out of the source rock and into the surrounding crust. This occurs by thermally activated diffusion of hydrocarbons through the residual organic-matter network (Stainforth & Reindes, 1990). The rate of primary migration is an important control on the total hydrocarbons produced from the source rock, as well as the extent of secondary cracking. The effects of primary migration on the noble gas composition of the hydrocarbon phase are unclear. Although a thermal-diffusive release mechanism may impart a mass-dependent kinetic fractionation signature onto the noble gases, it has not been identified in real-world samples. It is possible that the effect is small compared to that of other subsurface processes. Such processes include the interaction of noble gases co-transported in or with hydrocarbons with other fluids or the mechanisms and timescales associated with the movement of hydrocarbons within the crust.

5.3 Secondary migration

The principal mechanism driving secondary migration is the buoyancy force due to the density difference between petroleum and the surrounding water. This driving force is balanced by the resistance provided from capillary entry pressure, a function of the surrounding pore-size and permeability (Schowalter, 1979). Empirical investigations into this process suggest that secondary migration likely occurs along restricted pathways, often along structural boundaries, and proceeds rapidly on geological timescales (Dembicki & Anderson, 1989). Figure 1 shows the migration of hydrocarbons through a groundwater-saturated reservoir, and the potential inputs of noble gas sources into the same groundwater. Once in contact the noble gases are expected to equilibrate between the two phases quickly relative to geological timescales (Ballentine & Burnard, 2002).

Secondary migration can occur laterally for up to 100’s of kilometres and vertically through kilometres of groundwater-saturated strata (Demaison & Huizinga, 1991) and have profound effects on the noble gases in the system. The migrating hydrocarbons can undergo phase partitioning with this surrounding groundwater, and as the noble gases are more soluble in hydrocarbons than in water, this can strip the groundwater of much of its noble gases (Ballentine et al., 1996). This occurs via well-defined Henry’s-law solubility-dependent partitioning, and forms the basis of a series of models that investigate hydrocarbon migration using the varying solubilities of the noble gases (Zartman et al., 1961; Bosch & Mazor, 1988; Ballentine et al., 1991; Ballentine et al., 1996). While this has yet to be discussed or tested in studies performed to date, the evolution of noble gas signatures in hydrocarbons in conventional systems is therefore likely to be dependent on the mechanism and length scales of migration. In systems where migration occurs short over distances, it is possible that hydrocarbons may encounter relatively limited volumes of water with which to interact and partition noble gases (e.g. Ballentine et al; 1996). In contrast, migration within hydrocarbon systems such as those of the foreland basins of the Western Canadian Sedimentary basin may occur over tens or hundreds of kilometres and as such will encounter significantly greater volumes of water. However, to date there has been no thorough investigation into the effects of secondary migration distance upon noble gas composition – if any such pattern exists it could prove an invaluable tool in retroactively assessing migration distances and pathways.

The general effects of secondary migration on noble gases can be considered by comparing the conventional systems with unconventional systems where no secondary migration takes place. Figure 2 shows an overlapping but distinct grouping of conventional and unconventional systems with respect to [^{4}He] concentrations. Conventional systems tend to have higher [^{4}He] concentrations, which we speculate could be due to interaction with large-scale aquifer systems during secondary migration. Previous studies of conventional systems have shown some to contain concentrations of radiogenic noble gases far higher than that possible by local production, requiring input from regional systems (Ballentine et al., 1991; 1996).

5.4 Accumulation

The final stage in a conventional petroleum system is the migration of the hydrocarbons into a suitable structural or stratigraphic trap, with a low porosity seal allowing an accumulation to form (Downey, 1984). Once in an accumulation, there are still several processes that can allow further alteration of the noble gas composition. The structure and fluid flow pathways that focused the hydrocarbon migration into the trap are likely to allow fluids from other sources to also arrive at the same location. It is therefore not unusual to see mixing and interaction with CO_2 rich mantle-derived fluids, especially in tectonically active areas (Hooker et al., 1985; Gilfillan et al., 2008; 2009). These mantle fluids have a distinct elevated ^{3}He/^{4}He ratio, and so their presence in the hydrocarbon accumulation is often, though not always, easily identified. Continued subsurface flow of and interaction with groundwater can also transport noble gases from other parts of the crust. In many cases this can lead to high concentrations of crustal radiogenic noble gases that require contributions from a large fetch area or catchment (Ballentine et al., 1991; 1996; Ballentine & Sherwood Lollar 2002).

5.5 Tertiary migration

Once in an accumulation, it is possible for the hydrocarbons to leak gradually through the seal, or through mechanical structures such as faults (Downey, 1984; Wiprut & Zoback, 2000). Evidence for this is apparent in the many natural hydrocarbon seeps found both onshore and on the seafloor (Bojesen-Koefoed et al., 1999; Hornafius et al., 1999, Holzner et al., 2008). It is possible to identify this loss of hydrocarbons within the noble gas signature using a mass-balance approach if the input of noble gases into the accumulation is well constrained. This is particularly notable in systems that are filled to structural spill. A recent study by Barry et al., (2016) demonstrated the sensitivity of noble gases to constraining the relative hydrocarbon volumes lost from the Sleipner Vest reservoirs of the Norwegian North Sea through such a process

5.6 Unconventional systems

As the widespread commercial exploitation of unconventional systems is a relatively recent phenomenon, there is a comparatively small compilation of literature describing the geochemical behaviour of these systems (Curtis, 2002). As source rock reservoirs typically have low porosity and hydrocarbons produced from these systems have not undergone any prior migration, we might expect the noble gas signature to be indigenous to the source rock. However, it is clear that these are not perfectly closed systems, as many source rock reservoirs have generated hydrocarbons that have migrated to form conventional systems (Curiale & Curtis, 2016).

The behaviour of noble gases within unconventional systems is therefore likely to be similar to that of noble gases within source rocks, barring any drilling or production-related effects. The lack of secondary migration should simplify the factors affecting noble gases composition, as unknowns about the timing and rate of migration can be eliminated.

6. Analysis of the petroleum system using noble gases

6.1 Early noble gas investigations

The presence of significant amounts of Helium in natural gases was first observed over 100 years ago (Cady & McFarland, 1906). The first isotopic measurements of noble gases were made nearly 50 years later, and established using ^{4}He/^{40}Ar ratios that the presence of high concentrations of radiogenic ^{4}He in natural gases was not due to increased local ^{4}He production, but due to fluid migration transporting He from off-structure (Zartman et al., 1961). Wasserburg et al. (1963) also used measurements of natural gases to make early estimates of the terrestrial ^{4}He degassing flux through the crust, and hence residence time in the atmosphere. These pioneering studies highlighted the potential utility of noble gases to study the origin and history of hydrocarbon and non-hydrocarbon fluids in sedimentary basins, and formed the foundations for future studies targeting multiple elements and processes of numerous hydrocarbon systems.

The preparation of samples for noble gas analysis requires specialised equipment and techniques compared to sample collection for traditional hydrocarbon geochemical analyses, mostly to avoid air contamination. Concentrations of noble gas species in air are significantly higher than those of typical crustal samples (especially Ar and Ne), and so even very small air admixtures can have a large impact on measured values even when present only at the ppm level (Barry et al., 2016).

Furthermore, the small size of the noble gas atoms means that they have a much higher propensity to slowly leak across seals that are sufficient to hold hydrocarbon compounds. Valved high-pressure cylinders are not considered to be effective at maintaining the sample integrity required for noble gas analysis over long periods of time. Typically noble gas hydrocarbon samples are collected at low pressure in refrigeration-grade copper tubes that are either crimped or clamped to make a helium-tight seal effective during transport and storage.

6.2 Endmember mixing models

Noble gases are introduced into the petroleum system from several distinct geochemical reservoirs, each with a distinct elemental and isotopic composition. Deconvolving the contribution of different endmember compositions is a key step in beginning to understand the subsurface environment of any petroleum system, and the composition of any accumulations. The detection of mantle-rich fluids can be used to gain insight into the geological history and connectivity of any accumulation. Figure 2 shows that He isotope data reveal a grouping of CO_2-rich petroleum accumulations that are associated with elevated $^3He/^4He$ isotope ratios, in which this CO_2 is postulated to have been derived from magmatic fluids passing through the petroleum system (Gilfillan et al., 2009).

For robust analysis of noble gas provenance by endmember mixing decomposition, it is first crucial that the endmembers themselves are well defined. For some systems, such as the atmosphere, this is certainly the case, however others can be more complicated. The elemental composition of air-saturated groundwater is dependent on temperature and salinity of recharge conditions, and these are often difficult to constrain. However the isotopic composition of each element is unaffected by solubility partitioning, and for He and Ne, their solubilities are similar enough that they can be considered equivalent in certain situations. Radiogenic production ratios are well-known for average crust, although local parent-isotope concentrations can cause significant deviations in some isotope ratios (Ballentine & Burnard, 2002). For the mantle, isotope ratios (e.g., $^3He/^4He$) are reasonably well constrained for different mantle compositions (MORB, OIB) and the fact that these are orders of magnitude different to crustal endmembers makes the uncertainty in them less significant.

Processes that can isotopically or elementally fractionate noble gases, such as those detailed in the following sections, must be identified and taken into account. For this reason, it is preferable to use isotopic ratios of the same element rather than elemental ratios when calculating mixing fractions, as they are less affected by solubility or mass dependent fractionation. As such, mantle contributions to a petroleum system are usually deduced from $^3He/^4He$ ratios (eq 8.1), and radiogenic contributions from $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios.

$$R_{sample} = f_{mantle}R_{mantle} + f_{radiogenic}R_{radiogenic} \tag{8.1}$$

Example equation for deconvolving mantle Helium contributions, where R denotes a $^{3}He/^{4}He$ ratio, and f is the fractional contribution to the measured sample.

A further important use for calculations is the identification of any air contamination in a sample, as even ppm levels of air within a sample can impact measurements. Due to the varying concentrations of the noble gases in typical crustal samples and air, certain isotopes are more sensitive to air contamination. For example, the $^{4}He/^{20}Ne$ ratio is often used to identify atmospheric He contamination, as all of the ^{20}Ne is assumed to be originally atmospheric in origin. A $^{4}He/^{20}Ne$ close to the air value of 0.288 suggests atmospheric contamination, as crustal samples typically have values many orders of magnitude higher (Ballentine et al., 1996). However, as Ar is much more abundant in air than He, it takes a smaller amount of air contamination to affect the $^{40}Ar/^{36}Ar$ ratios.

6.3 Hydrocarbon-water interaction models

Water is a key component in all petroleum systems. It is present in the sediments during burial (known as 'connate' or 'formation water'), however groundwater can also migrate through the system depending on the permeability and structural configuration of reservoir lithologies or carrier beds. Understanding the interactions between hydrocarbon and water phases can help give insight into the history of the formation and migration of the hydrocarbons themselves, as well as their present water contact. The present day water contact may be particularly important in providing pressure support for the production of hydrocarbons at wells, and may have implications for water breakthrough (Toth, 1980).

The noble gases have different solubilities in fluids, with the heavier noble gases typically more soluble. This phenomenon has been demonstrated empirically in noble gas investigations of groundwaters, where Xe and Kr are enriched relative to their atmospheric abundances (Mazor, 1972). Theoretically it should be possible to predict the partitioning behaviour for the noble gases between any fluid phases in the subsurface, such as water and oil or gas. This has led to the development of models describing the partitioning of the noble gases between water and oil/gas phases in the subsurface.

These models make a series of assumptions. Firstly, they assume that the hydrocarbon phase is initially devoid of noble gases and only inherits an atmospheric noble gas inventory through interaction with air-saturated water (ASW) in the subsurface post expulsion from the source rock (i.e. hydrocarbons in source rocks do not contain any noble gases). These models also typically assume that an initial composition of atmosphere-derived noble gases is present in groundwater, which is well constrained over a range of temperatures and salinities (Kipfer, 2002). Isotopes for each gas are chosen which have no significant radiogenic production in the subsurface (^{20}Ne, ^{36}Ar, ^{84}Kr, ^{130}Xe), so that the total amount of each isotope present in the system is constant. These isotopes have previously been used as tracers in the investigation of groundwater circulation patterns (Castro et al., 1998a & b). Helium is typically not considered in these models as ^{4}He is produced radiogenically in large amounts, and atmosphere-derived ^{3}He in the subsurface is negligible. Furthermore, the solubilities of He and Ne are often indistinguishable at crustal pressures and temperatures, meaning that little new information would be gained regardless. In systems with negligible fissiogenic Xe, ^{132}Xe is often used instead of ^{130}Xe, as it is present in higher quantities at atmospheric ratios. The result from these assumptions is that measurement of the atmosphere-derived noble gas isotopes in one phase of the subsurface system allows the volume ratios and partitioning behaviour of the entire system to be reconstructed.

The fundamentals of this approach were originally laid out by Bosch & Mazor (1988), who used the isotope ratios of atmosphere-derived Ne/Ar, Kr/Ar, and Xe/Ar to predict partitioning patterns in water-oil and water-gas systems. Ballentine et al. (1996) used atmosphere-derived ^{20}Ne/^{36}Ar ratios measured in the North Sea Magnus oilfield to quantitatively estimate oil/water volume ratios (V_o/V_w). The technique is similarly applicable to predict gas/water volume ratios (V_g/V_w) in gas-dominated petroleum systems, as shown in the following equation.

$$\frac{V_g}{V_w} = \frac{\left(\frac{^{20}Ne}{^{36}Ar}\right)_{asw}}{\left(\frac{^{20}Ne}{^{36}Ar}\right)_{g}} - \frac{K^{Ar}}{K^{Ne}}$$

Where K^i is the Henry's coefficient of noble gas *i* in water at reservoir conditions, and the subscript *asw* refers to the air-saturated water composition of groundwater recharge. For oil-water systems V_o/V_w is calculated analogously to the above equation, but using the ratio of the Henry's coefficients of oil and water, instead of simply water.

This concept was modified by Zaikowski & Spangler (1990), who used Ne/Ar ratios combined with absolute ^{36}Ar concentrations to predict the evolution of groundwater in contact with varying gas volumes. Using absolute concentrations has the added complexity of uncertainties that arise from the conversion of concentration at STP to reservoir temperature and pressure than using ratios, but can provide an additional constraint on water-gas ratio volumes. Furthermore, at gas/water ratios of over ~0.01, effectively 100% of the noble gases are partitioned into the gas phase, making ratios insensitive to changes in V_g/V_w. Concentrations however will still be diluted by the addition of more hydrocarbons, making them more effective at determining V_g/V_w in these scenarios. The formulation for calculating V_g/V_w using concentrations is as follows.

$$\frac{V_g}{V_w} = \frac{C_{asw}^i}{C_g^i} - \frac{1}{K_i}$$

Where C is the concentration of the noble gas *i* in a particular phase, and K_i is the Henry's coefficient in water at reservoir conditions. Units for Henry's coefficient must be chosen to complement the units used for concentrations in the water and gas phases. For oil-water systems, again the ratio of Henry's coefficients is used.

The models and equations described thus far are applicable to a simple 2-phase static closed system. In reality, petroleum systems are often more complex, exhibiting open system behaviour in the form of reservoir leakage, gradual noble gas stripping by previous migrating hydrocarbons and dual hydrocarbon phase accumulations (e.g. reservoired oil with a gas cap). These more complex scenarios can be accounted for by using mass-balance for hydrocarbon loss and/or partitioning, or Rayleigh fractionation to describe gradual processes (Zhou et al., 2005). The context of the specific system will dictate which model is most appropriate. For example, Barry et al. (2016) use compound models to describe volume ratio interactions in both open and closed systems from the Sleipner field, North Sea.

A graphical representation of this approach is shown in figure 3, illustrating the different distributions of atmosphere-derived noble gases for both gas-water and oil-water systems. Examples of data from previous studies are shown in figure 4, which shows the observed ranges of ^{20}Ne/^{36}Ar from real world gas and oil systems. It is also clear that whilst the behaviour ^{84}Kr/^{36}Ar and ^{130}Xe/^{36}Ar should follow directly from the measured ^{20}Ne/^{36}Ar, it is frequently observed at elevated levels and therefore usually not considered for quantitative volume ratio calculations.

The practical applications of this approach include measuring the extent of groundwater interaction with a known hydrocarbon phase, which can provide insight into migration patterns and regional subsurface fluid flow regimes (Bosch & Mazor, 1988; Ballentine et al., 1996). The extent of groundwater interaction also has implications for the quality of the hydrocarbons present. The dissolution and removal of soluble hydrocarbons by persistent groundwater flow (also known as 'water-washing') can have a negative impact on the quality of the accumulated oil (Lafargue and Barker, 1988). Furthermore, the movement of groundwater through the system can introduce and maintain microbial communities, which can biodegrade oil, or produce microbial methane (Leahy & Colwell, 1990; Horstad et al., 1992).

The accuracy and precision that arise from the application of this technique is somewhat limited by its input parameters. As detailed in previous sections, the Henry's law solubility of noble gases is dependent on temperature, pressure, salinity (for water), and API gravity (for oil). These relationships are non-linear and must be empirically derived, with some parameters often needing to be extrapolated from empirical data to match reservoir conditions. Additionally, the initial composition of air-saturated groundwater is similarly dependent on temperature and salinity conditions when it is formed at the surface during aquifer recharge. As groundwater associated with hydrocarbon systems can be millions of years old, it can be difficult to predict what these surface conditions would have been, but the generic assumption is made that perturbations in the noble gas composition caused by petroleum system processing is far larger than any uncertainty in initial composition. As the increase in quality data sets from case studies increases, it is interesting to note that data inversion techniques are starting to be used to reconstruct surface conditions and demonstrate that some systems can preserve these signals over many millions of years (Barry et al., 2016).

6.4 Dating by radiogenic ingrowth

The dating of groundwaters using the decay and production of noble gas isotopes is a well-established technique, albeit with many assumptions. Whilst several different methods exist, each appropriate for different timescales or systems, the most widely investigated, and most appropriate for typical basinal fluid timescales, is the accumulation of stable radiogenic ^{4}He and ^{40}Ar (Torgersen & Clarke, 1985; Marty et al., 1993; Tolstikhin et al., 1996; Castro et al., 1998a & b; Mahara et al., 2009). A similar technique using fissiogenic Xe production is possible, but is only applicable in very old samples (>100Ma) due to the slow accumulation rate (Holland et al., 2013). By using the partitioning laws described in the previous section, it is possible to indirectly date the groundwater associated with a petroleum system by measuring the noble gases in the hydrocarbon phase (Zhou & Ballentine, 2006). The importance of groundwater involvement in petroleum systems is detailed in the above section, and constraining the age is a crucial step in resolving the groundwater-hydrocarbon interaction.

The basis for all of these models is to deconvolve the noble gases produced in situ within the system from those present initially in the groundwater, and those brought in from external fluxes. The in situ concentration is then compared with the theoretical production rates (calculated from parent isotope concentrations and decay constants) to give the necessary time for this concentration to accumulate.

$$[^4He]_{total} = [^4He]_{asw} + [^4He]_{in\,situ\,production} + [^4He]_{external\,flux}$$

Where *total* is the total reconstructed concentration in associated groundwater, *asw* is the initial concentration in air-saturated groundwater recharge, *in situ production* is the amount produced in place over the lifetime of the system, and *external flux* denotes the amount brought in from external sources. The age of the system can then be calculated using the following parameterization, after Torgersen, 1980.

$$[^4He]_{in\ situ\ production} = \frac{\rho J \Lambda (1-\varphi)}{\varphi} \times t$$

Where ρ is the density of the rock, J is the in situ production of ^{4}He, Λ is a parameter describing the efficiency of transfer of produced ^{4}He from mineral to surrounding fluid, where $0<\Lambda<1$, and ϕ is porosity. The residence time of the groundwater in the system is t. Λ is thought to be approximately 1 over geological timescales (Ballentine & Burnard, 2002). *J* is calculated as a function of the concentrations of U and Th in the surrounding rocks, after Craig & Lupton, 1976.

$$J = 0.2355 \times 10^{-12} [U] \left\{ 1 + 0.123 \left(\frac{[U]}{[Th]} - 4 \right) \right\}$$

Analogous equations can be formulated for the production of ^{40}Ar, or any other radiogenic isotope.

The principal uncertainty in groundwater dating is the term accounting for external flux of radiogenically produced isotopes. Radiogenic concentrations in excess of those that can be reasonably explained by in situ production are frequently observed in groundwater and hydrocarbon systems (Torgersen et al., 1985; Ballentine et al., 1996; Takahata & Sano, 2000). Several studies suggest that this is due to a universal continental degassing flux from the deep crust, whilst others have suggested a more variable input from old isolated fluid bodies or mineral degassing during alteration (Torgersen & Clarke, 1985; Solomon et al., 1996; Tolstikhin et al., 1996; Patriarche et al., 2004) or due to thermal perturbation of old continental crust (Ballentine et al., 2002; Lowenstern et al., 2014). The exact impacts of these various factors are probably dependent on basin-scale hydrogeological behaviours, and as such knowledge of the basin structure and history are crucial during these calculations and subsequent interpretations.

Zhou & Ballentine, 2006 considered data from 3 previous studies to investigate ^{4}He ages of hydrocarbon associated groundwater In the San Juan basin, biogenic coalbed methane play ^{4}He ages were found to be dependent on distance from recharge at the basin margin. Making an argument that the biogenic degradation of the coal is related to groundwater age enabled a biogenic gas production rate to be calculated, and is in reasonable agreement with biogenic gas production rates estimated using a similar approach in the Antrim Shales, Illinois basin, USA (Schlegel et al., 2011). ^{4}He ages from the North Sea Magnus oilfield gave values of ~2Ma, which when compared with the age of the reservoir (~150Ma) to suggest the influence of formation water has been relatively minor. The He-rich Hugoton-Panhandle gas field in the Southern US yielded slightly older ^{4}He groundwater ages of around 4Ma. This is still relatively young compared to the estimated age of the petroleum system, and is interpreted to be more representative of the ages of groundwaters bringing in the high He concentrations, indicating a relatively recent injection of commercial He.

Dating of groundwaters associated with natural gases in the Piceance basin, Colorado, has also been undertaken by McMahon et al., 2013. They were able to identify a range of groundwater ages using ^{4}He dating in conjunction with ^{14}C dating. This was used to show the compartmentalisation of the field into areas with different ages, with differences in gas composition between the areas. Similarly, the ^{4}He ages determined by Schlegel et al., 2011, in the Illinois basin, showed older groundwater ages associated with thermogenic methane, whilst younger ages were associated with microbially generated methane. This suggests noble gas ages have the potential to constrain the onset and extent of microbial methane generation.

6.5 Unconventional systems

The rapid expansion of unconventional source-rock reservoir hydrocarbon production over the last decade has created an opportunity for the development of new noble gas techniques to advance our understanding of the mechanisms involved in unconventional oil and gas generation, storage, and production (Curiale & Curtis, 2016). As unconventional hydrocarbons are generated and produced in situ, with no secondary migration, the pressure-temperature histories of the systems are better constrained, and the noble gas signatures are likely to be less influenced by basin-scale fluid flow regimes. Furthermore, the retention of hydrocarbons within the source rock allows for the initial noble gas composition of hydrocarbons to be measured directly. This could have important implications for the study of conventional systems, where the initial hydrocarbon noble gas composition is often assumed to be negligible.

Tantalising insights into the potential behaviour of noble gases in source rocks were found in an investigation into biogenic coalbed methane in the San Juan system (Zhou et al., 2005). The produced gases were observed to be highly enriched in atmosphere derived Xe, and to a lesser extent Kr. This effect was suggested to be due to preferential sorption of heavy noble gases onto the organic-carbon rich sediments, a phenomenon that has been observed experimentally in laboratory simulations (Fanale & Cannon, 1971; Podosek et al., 1981) and observed previously in other hydrocarbon systems (Torgersen & Kennedy, 1999). Variable fractionation was also observed in both ^{20}Ne/^{22}Ne and ^{38}Ar/^{36}Ar isotope ratios, consistent with kinetic mass-dependent fractionation. This is proposed to be due to concentration gradients created during gas production imparting a diffusive effect on the produced gas.

An investigation into Marcellus shale gases by Hunt et al. (2012), showed that the gases could be separated into distinct groups with different thermal maturities, based on their radiogenic noble gas contents. The ^{4}He/^{40}Ar* and ^{21}Ne*/^{40}Ar* ratios both showed a distinct grouping that correlated with thermal maturity, suggesting that the temperatures experienced by the source rocks affected the release of radiogenically produced noble gases into the surrounding fluids (e.g. Ballentine et al., 1996). Whilst there are more practical ways of identifying gas maturity, this shows the possibility for using noble gases to track the extent of gas release with temperature, unaffected by chemical or biological effects.

The Antrim shale-gas play has also been investigated by Wen et al. (2015). Trace amounts of mantle fluids were detected using ^{3}He/^{4}He isotope ratios, and ^{4}He groundwater ages were relatively young (<250ka), coinciding with past glaciations. Both of these findings suggest that despite the low porosity of the rocks, groundwater and other fluids are still able to permeate the system. However, the Antrim shale is naturally fractured to a much greater extent than typical unconventional shale-gas systems, which could artificially increase permeability and hence local fluid flow (Apotria et al., 1994; Ryder, 1996). Further observations from this study include variable Ne isotopes exhibiting scatter in the mass-dependent fractionation directions, similar to the San Juan basin; whether this is a signal common to all unconventional systems is not yet known.

Measured data from unconventional studies are shown alongside those from conventional systems in figures 2, 5, & 6. Helium isotopes show lower ^{4}He concentrations compared to conventional systems, and no significant mantle contributions. Neon isotopes in both datasets show no significant radiogenic contribution but high levels of scatter along mass-dependent fractionation trajectories. ^{40}Ar/^{36}Ar isotopes ratios show little variation in unconventional systems, but large ranges in ^{36}Ar concentration compared to conventional systems. This pattern potentially reflects heterogeneity in production when compared to conventional accumulations, caused by lower permeability and connectivity within the source-rock reservoir. However, more datasets are needed to draw any robust conclusions. It is also important to note that both the San Juan and Antrim shale systems would be considered far from typical for unconventional source-rock reservoir production. The San Juan is a biogenic coalbed methane rather than a more common thermogenic shale gas, and the Antrim system also has a significant biogenic component, and has been highly fractured by recent glaciation events. For a detailed discussion of nomenclature and classification of unconventional systems, see Curiale & Curtis (2016).

Studies of noble gases in produced unconventional hydrocarbons are still relatively sparse (see also Darrah et al., this volume), there have been several noble gas studies of the groundwaters associated with unconventional systems, primarily for assessing environmental impact on aquifers. Of these, Darrah et al., 2014 & 2015 and Jackson et al., 2013, have shown the utility of noble gases in discriminating between anthropogenic hydrocarbon contamination of drinking water aquifers, and natural hydrocarbon migration in subsurface brines.

7. Summary

Despite years of investigation and a number of notable publications in the field, noble gases are still not used as a routine geochemical analytical tool in hydrocarbon systems, in the manner of C or H isotopes. Partly this is due to the expense and difficulty of making the measurements themselves, but it is also due to the complex nature of interpreting noble gas results and the necessity of having proper context to do so. Whilst calculating absolute V_g/V_w ratios and ^{4}He and ^{40}Ar ages represents significant progress towards quantifying fluid exchange and accumulation within a system, it is still not always intuitive what these numbers actually represent. For V_g/V_w and V_o/V_w ratios it is not necessarily the ratio of gas to water in the accumulation itself, but rather the entire history of hydrocarbon-water interaction within the system (e.g., during migration from the source rock to the accumulation). In this way they should be considered not as an alternative to geological observations, but as an additional constraint to complement existing techniques.

A key step in the development of the noble gas toolkit is the continued acquisition and compilation of case studies. Although petroleum systems can be broadly categorized they are all unique, which potentially provides great future utility for identifying the source and history of a hydrocarbon reservoir. Comparison between different systems will allow universal patterns between similar systems to be discerned from local effects particular to that location. This in turn will allow more robust conclusions to be drawn in a more straightforward fashion from new studies.

In the study of unconventional systems, it remains unclear which questions noble gases will be most suited to answer. Will the adaptation and application of existing conventional system tools be appropriate, or will new approaches need to be formulated entirely? The isolation of any Xe-enriched sedimentary component, and the controls on this process should be a preliminary goal. This may lead to insights into the mechanisms controlling gas storage within organic-rich sediment; the importance of adsorption versus free gas stored in porosity could help explain extent of gas generation and recoverability. As previously mentioned, constraining the noble gas characteristics of source rocks could also help refine groundwater models in conventional systems. Indeed, fluid interaction models could also have some utility in unconventional systems themselves. Previous studies have shown that despite their low permeability, groundwater-derived noble gases and mantle fluids are present within produced gases. Unconventional systems are known to expel some generated hydrocarbons, as many simultaneously act as source rocks for conventional accumulations (Robison, 1997). Noble gases could be used to shed light on the mechanisms controlling gas release versus retention within the source rock, effectively helping predict the volumes of hydrocarbons present in a source rock while simultaneously providing constraints on potential volumes in associated conventional petroleum accumulations.

The promise of being able to geochemically decode the physical structure and history of a petroleum system is a tantalising prospect. Although theoretically straightforward, this goal is complicated by the vagaries of any natural system. Completion of further data-rich studies on a wide range of different systems should be aided by improvements in experimental technology. Past investigations were typically focused on a few specific isotopes, it is now possible to routinely measure all naturally occurring noble gas isotopes in a single sample. The acquisition of accurate data for less-studied isotopes such as those of Kr and Xe could lead to development of new investigative techniques as well as the corroboration of existing ideas. Integration of this data will help investigations of individual systems to be generalized into overarching patterns applicable to all petroleum systems, at which point noble gas analysis can become less descriptive, and more predictive.

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Figure Captions

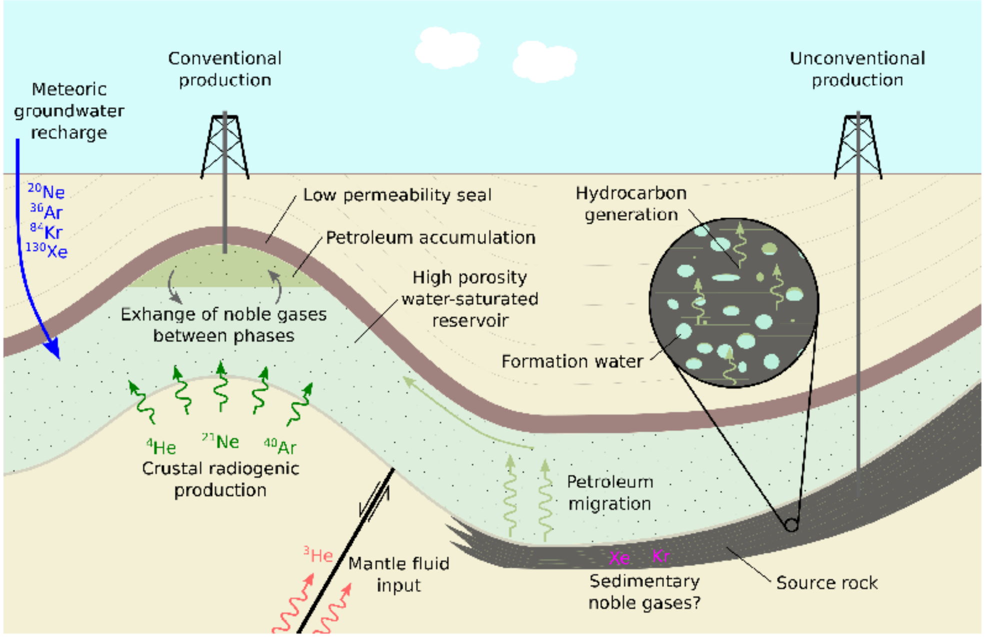

Fig 1. A schematic conceptual model of the sources of noble gases in petroleum systems, modified from Ballentine & O'Nions, 1992. For each input, the major characteristic isotopes are shown, although in reality each source will have varying contributions from a range of isotopes. Groundwater is usually considered to be ubiquitous in the subsurface, although the provenance of the water (meteoric recharge or formation water) and the connectivity of different sources can vary. Meteoric

groundwater recharge has air-saturated water (ASW) composition and air-like isotopic ratios; the isotopes shown have no significant mantle or radiogenic sources, and so are considered characteristic of the subsurface noble gas component. Crustal radiogenic production occurs throughout the crust, though the produced isotopes can be transported via groundwater flow. Phase equilibrium between groundwater and any hydrocarbon accumulation is rapid on a geological timescale, and is the primary conduit for introducing noble gases into the hydrocarbon phase.

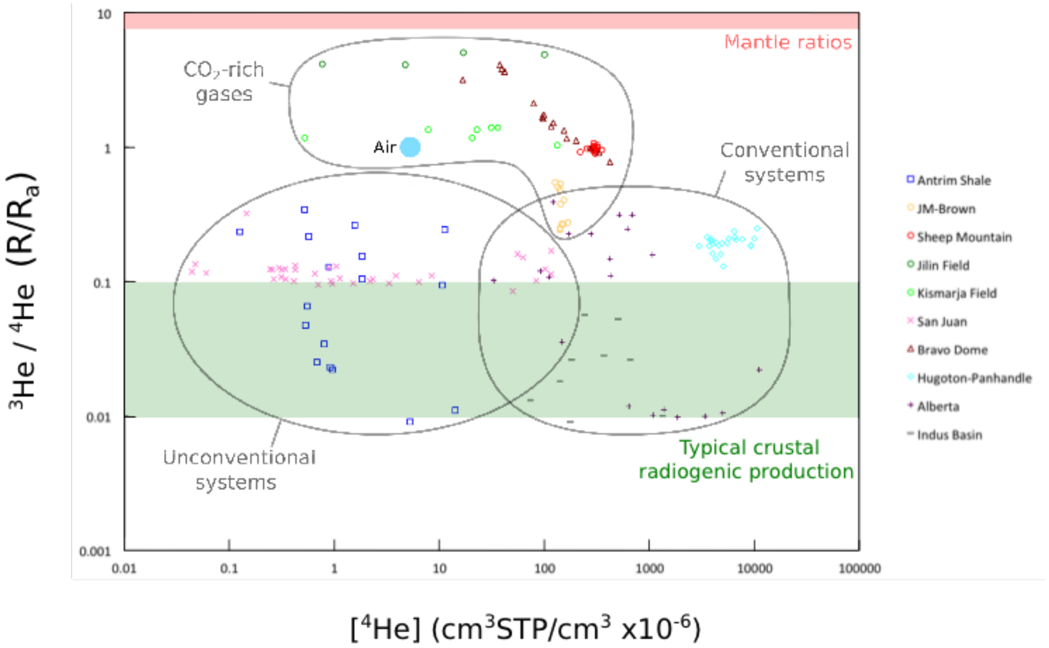

Fig 2. Helium isotope ratio and concentration measurements from selected noble gas studies of petroleum systems. $^3He/^4He$ ratios are reported relative to the atmospheric ratio R_a. The observed range of $^3He/^4He$ ratios and ^4He concentrations is controlled by the regional geology and tectonic regime of the petroleum systems. The $^3He/^4He$ ratio of a system is usually thought to comprise of 2-endmember mixing between crustal fluids with a ratio of 0.01-0.02, and mantle fluids, which have a ratio of >8. Presence of even small contributions of mantle fluids therefore increases $^3He/^4He$ ratios above normal crustal values, and is a feature of extensional tectonic regimes (Marty et al., 1992). Concentrations of ^4He are affected by several factors: radiogenic production of ^4He occurs over time, meaning that older systems will have accumulated more ^4He; the regional hydrogeology can also transport ^4He dissolved in groundwater into the petroleum accumulations; finally, concentrations of all noble gases will be affected by the extent of secondary cracking of hydrocarbons, as this effectively increases the relative volume of hydrocarbon gases in the sample and dilutes the helium concentration. As is evident from the data, different systems show distinct ratios and concentrations, and different amounts of scatter show variations in homogeneity. Mixing lines are apparent in some systems, such as the mantle-CO_2 rich Bravo Dome; others show little or no pattern. Data are broadly clustered according to the type of the system, conventional or unconventional, and CO_2-rich. Data sources: Antrim Shale (Wen et al., 2015); San Juan coalbed methane (Zhou et al., 2005); JM-Brown,

Sheep Mountain, Jilin and Kismarja fields (Gilfillan et al., 2009); Alberta field (Hiyagon & Kennedy, 1992); Indus Basin (Battani et al., 2000); Hugoton-Panhandle field (Ballentine & Sherwood Lollar, 2002); Bravo Dome (Ballentine et al., 2005).

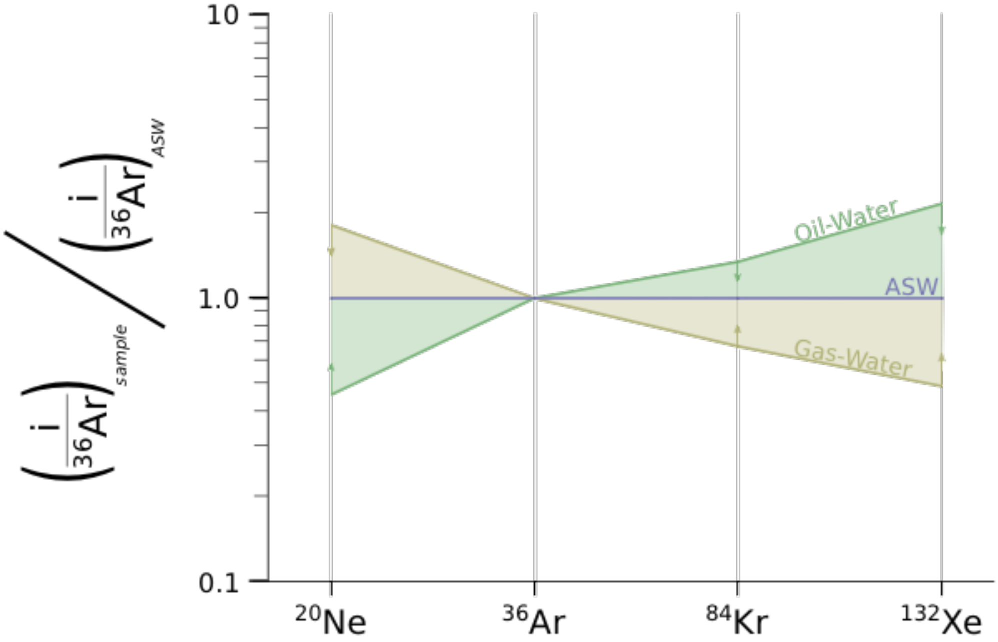

Fig 3. Model for the distribution of atmosphere-derived noble gases (ANG) in subsurface partitioning between water and oil/gas phases, after Bosch & Mazor, 1988. All values are normalized to the air-saturated water (ASW) reference, which is assumed to be the initial composition of groundwater in the subsurface. Upon first interaction with a small gas volume ($V_g/V_w \approx 0$) the different solubilities of the noble gases cause different amounts of exsolution into the gas. The composition of the gas volume at $V_g/V_w = 0$ will be that defined by the gas-water interaction line. As the gas volume, and consequently V_g/V_w increases, the proportion of noble gases in the gas volume increases, and the composition of the gas will evolve back towards the initial ASW values, as shown by the arrows. In a closed system, the gas remains in contact with the water, and as V_g/V_w increases the noble gases will eventually be ≈100% in the gas phase, resulting in the gas phase having the initial ASW composition. In an open system, where gas is able to escape, the remaining water can become highly fractionated, and eventually the noble gases exsolving from this water will evolve to compositions beyond the ASW line. In this way the ANG's can be used to assess to what extent a system is open or closed (i.e. how much gas is potentially escaping from the system). Furthermore, quantitative V_g/V_w ratios can be calculated from this method (see text). In an oil system, the same method applies. The initial gas-water and oil-water interaction lines were calculated for an initial ASW composition of zero salinity at STP (Kipfer et al., 2002), and the phase partitioning occurring at a reservoir temperature of 100°C.

Choosing different initial ASW and reservoir conditions can substantially affect the magnitude of fractionation upon partitioning.

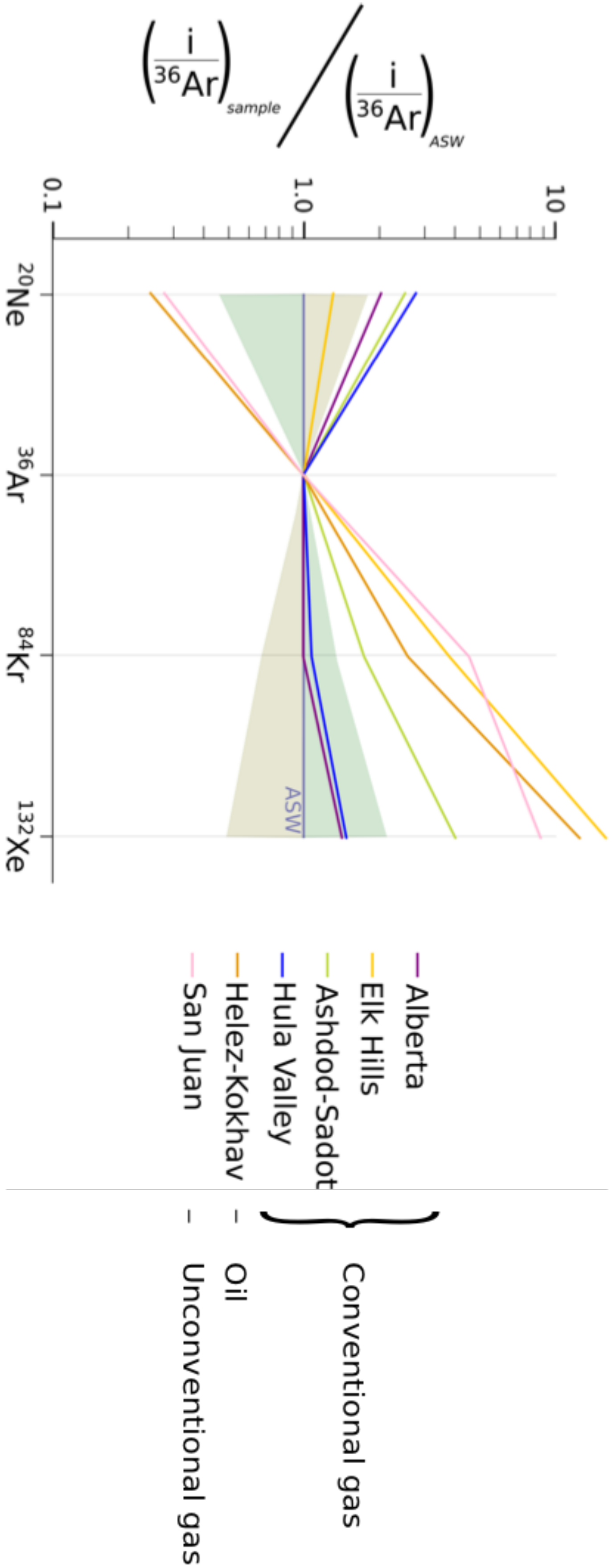
(i / 36Ar)sample / (i / 36Ar)ASW
0.1
1.0
10
20Ne
36Ar
84Kr
132Xe
ASW
Alberta
Elk Hills
Ashdod-Sadot
Hula Valley
Helez-Kokhav
San Juan
Conventional gas
Oil
Unconventional gas

Fig 4. Selected data displayed on the ANG composition chart described in fig 5. Shaded areas correspond to the gas-oil and water-oil partitioning lines described in fig 5, although as these lines are sensitive to temperature, pressure and salinity both in the reservoir and at initial groundwater recharge conditions, the actual partitioning lines will vary for each system. The Hula Valley and Ashdod-Sadot systems (Bosch & Mazor, 1988) show similar elevated $^{20}Ne/^{36}Ar$ ratios suggesting gas-water partitioning with small V_g/V_w, although enrichments in Kr and Xe vary. The Helez-Kokhav oil system (Kennedy et al., 1990) shows partitioning in the direction of the oil-water line, suggesting a low V_o/V_w. The San Juan coalbed methane (Zhou et al., 2005) shows a gas system fractionated strongly away from the gas-water line past the ASW reference. This is potentially indicative of an open system with significant gas loss, or some other mechanism fractionating the noble gases. The Elk Hills system (Torgersen & Kennedy, 1999) shows $^{20}Ne/^{36}Ar$ values expected for a gas system, although the $^{84}Kr/^{36}Ar$ and $^{130}Xe/^{36}Ar$ are highly enriched. The Alberta system (Hiyagon & Kennedy, 1992) is described in the caption to fig 2. A common observation amongst the different systems is an enrichment in atmospheric Kr and Xe compared to the values predicted from the $^{20}Ne/^{36}Ar$ partitioning. The extent of this enrichment is variable, although it is often suggested to derive from an adsorbed component within the source rock.

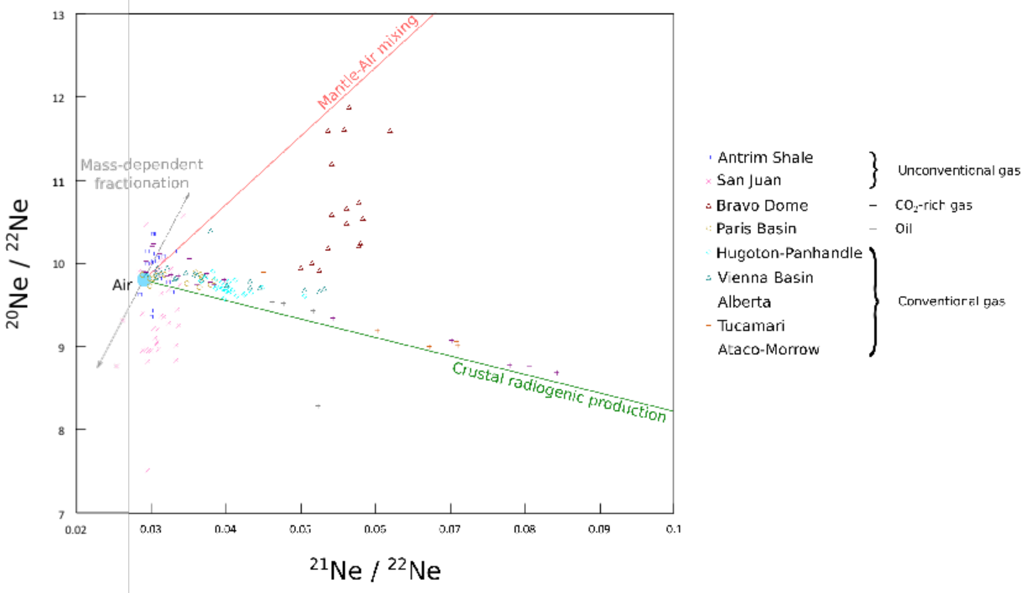

Fig 5. Neon 3-isotope plot for selected noble gas studies of petroleum systems. Neon isotopes are conventionally thought of as a 3-endmember mixing system, with crustal radiogenic production and mantle mixing lines shown. In crustal systems, both ^{21}Ne and ^{22}Ne are produced radiogenically, resulting in alteration of the isotope ratios along the crustal evolution line defined in Kennedy et al., 1990 and Ballentine & Burnard, 2002. The Bravo Dome system shows radiogenic ingrowth in addition to mixing with a mantle Ne endmember (Ballentine et al., 2005). Additionally,

mass-dependent fractionation of the system can cause the isotopes to evolve along the mass-fractionation line in either direction, consistent with data observed in both the Antrim and San Juan systems. Both of these systems are unconventional, the San Juan being a coalbed methane system, and the Antrim a more typical shale gas play. The Bravo Dome system is rich in CO_2 that is interpreted to be sourced from mantle fluids; the Neon isotopes clearly show mixing with a mantle endmember. Data sources: Antrim Shale (Wen et al., 2015); San Juan coalbed methane (Zhou et al., 2005); Bravo Dome (Ballentine et al., 2005); Paris Basin (Pinti & Marty, 1995); Vienna Basin (Ballentine & O'Nions, 1992); Alberta, Tucamari, and Ataco-Morrow (Kennedy et al., 1990).

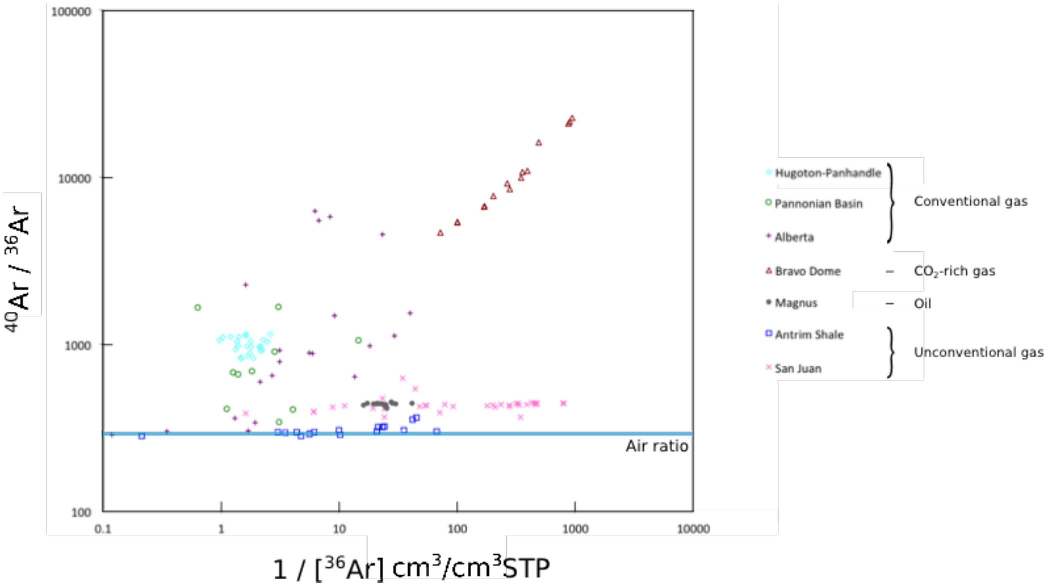

Fig 6. Selected examples of Ar isotope ratio and concentration measurements from previous studies. $^{40}Ar/^{36}Ar$ is plotted against $1/[^{36}Ar]$ so that mixing trajectories are clearly apparent. The Ar isotope system is a mixing system between the air-like ratio of 298.6 (Lee et al., 2006) and addition of radiogenic ^{40}Ar, produced in the crust from ^{40}K decay. As is evident from the data shown, ratios below the air value are not usually observed. Elevated $^{40}Ar/^{36}Ar$ ratios can be caused both by radiogenic production of ^{40}Ar within the crust, as well as mixing with mantle fluids which have high levels of radiogenic ^{40}Ar. The Ar isotope system is also important for the detection of any air contamination in samples; the relatively high concentration of Ar in Air makes even small amounts of contamination drastically affect measured Ar concentrations and isotope ratios. Data sources: Magnus (Ballentine et al., 1995); Pannonian Basin (Ballentine & O'Nions, 1993); Hugoton-Panhandle gas field (Ballentine & Sherwood Lollar, 2002); Alberta field (Hiyagon & Kennedy, 1992); Bravo Dome (Ballentine et al., 2005); Antrim Shale (Wen et al., 2015); San Juan coalbed methane (Zhou et al., 2005).

Table 1. The volume mixing ratios for the noble gases in dry air. Data from Porcelli et al., 2002.

Table 2. The equilibrium concentrations of the noble gases in air-saturated water at atmospheric pressure for selected salinities and temperatures, calculated from Henry's constant equations in Fernández-Prini et al., 2003, and Setschenow coefficient equations in Smith & Kennedy, 1983.

Table 3. The isotopic ratios of noble gases in air. Data from Porcelli et al., 2002; Lee et al., 2006.

Table 4. Present day production rates for the radiogenic noble gases in typical continental crust. Data from Ballentine & Burnard, 2002.

Table 1

Element	**Volume mixing ratio**
He	$5.24(\pm 0.05)\times 10^{-6}$
Ne	$1.818(\pm 0.004)\times 10^{-5}$
Ar	$9.34(\pm 0.01)\times 10^{-3}$
Kr	$1.14(\pm 0.01)\times 10^{-6}$
Xe	$8.7(\pm 0.1)\times 10^{-8}$

Table 2

Element	**Concentration (cm^{3}STPg^{-1})**		
	Freshwater 10°C	Freshwater 20°C	Seawater 10°C
He	4.73×10^{-8}	4.65×10^{-8}	4.04×10^{-8}
Ne	2.06×10^{-7}	1.93×10^{-7}	1.70×10^{-7}
Ar	3.91×10^{-4}	3.23×10^{-4}	3.11×10^{-4}
Kr	9.21×10^{-8}	7.27×10^{-8}	7.26×10^{-8}
Xe	1.34×10^{-8}	9.29×10^{-9}	1.04×10^{-8}

Table 3

Isotope	**Relative abundance**
^{3}He	$1.399(\pm 0.013)\times 10^{-6}$
^{4}He	$\equiv 1$
^{20}Ne	9.80 ± 0.08
^{21}Ne	0.0290 ± 0.0003
^{22}Ne	$\equiv 1$
^{36}Ar	$\equiv 1$
^{38}Ar	0.1885 ± 0.0003
^{40}Ar	298.56 ± 0.31
^{78}Kr	0.6087 ± 0.0020
^{80}Kr	3.9599 ± 0.002
^{82}Kr	20.217 ± 0.004
^{83}Kr	20.136 ± 0.021
^{84}Kr	$\equiv 100$
^{86}Kr	30.524 ± 0.025
^{124}Xe	2.337 ± 0.008
^{126}Xe	2.180 ± 0.011
^{128}Xe	47.15 ± 0.07

^{129}Xe	649.6 ± 0.9
^{130}Xe	$\equiv 100$
^{131}Xe	521.3 ± 0.8
^{132}Xe	660.7 ± 0.5
^{134}Xe	256.3 ± 0.4
^{136}Xe	217.6 ± 0.3

Table 4

Isotope	**Present day production rate cm^{3}STPkg^{-1}yr^{-1}**
^{3}He	2.49×10^{-18}
^{4}He	3.31×10^{-10}
^{20}Ne	1.47×10^{-18}
^{21}Ne	1.51×10^{-17}
^{22}Ne	3.03×10^{-17}
^{36}Ar	2.38×10^{-18}
^{38}Ar	1.09×10^{-18}
^{40}Ar	6.05×10^{-11}
^{83}Kr	5.86×10^{-21}
^{84}Kr	2.12×10^{-20}
^{86}Kr	1.39×10^{-19}
^{131}Xe	7.89×10^{-20}
^{132}Xe	5.24×10^{-19}
^{134}Xe	7.50×10^{-19}
^{136}Xe	9.09×10^{-19}