

Tracing the migration of natural gas in the Marcellus  
Shale using the noble gas geochemistry of silicate mineral  
phases

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## Abstract

Recent improvements in horizontal drilling and hydraulic fracturing technologies have opened numerous unconventional reservoirs such as black shales for hydrocarbon exploration and production globally. Still, the success rate of individual wells remains highly variable and poorly understood. By an investigation of the fundamental properties of fluid flow in low permeability rocks such as the porosity, permeability, thermal maturity, and geological fluid flow, one might improve the extraction of hydrocarbons from unconventional reservoirs. Here, we examined the noble gas and trace element geochemistry of black shale silicate mineral samples collected along the lateral of a production well from the Marcellus Formation located in the northern Appalachian Basin in the northeastern US. We used the trace element data to compare the anticipated versus measured  $^4\text{He}/^{21}\text{Ne}$  ratio throughout the vertical and lateral section of the production well in order to determine how porosity and permeability vary along the well and to determine areas of gas accumulation. The initial data suggests that the majority of radiogenic noble gases are retained in samples from the Marcellus Formation indicating that the migration of hydrocarbons and other crustal fluids is minimal within this formation (i.e., the lateral section of this well acts as a relatively closed system). By comparison, samples from overlying Upper Devonian sequences have experienced loss of more than 90% and 50% of the radiogenic  $^4\text{He}$  and  $^{21}\text{Ne}^*$ , respectively. These results suggest that extensive fluid migration has occurred in the top 0.5km of the crust in comparison to the Marcellus. The preferential loss of  $^4\text{He}$  with respect to  $^{21}\text{Ne}^*$  suggests that fluid migration occurs in lower temperature regimes, possibly following neotectonic fracturing.

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## Table of Contents

Abstract.....	1
Acknowledgements.....	2
Table of Contents.....	3
Introduction.....	4
Noble Gas Background.....	5
Geologic Background of the Study Area.....	8
Methodology.....	10
<i>Sampling Strategy and Collection</i> .....	10
<i>ICPMS Analysis</i> .....	10
<i>Noble Gas MS Analysis</i> .....	11
Results.....	12
Discussion.....	18
Conclusion.....	21
Suggestions for Future Work.....	22
References.....	23

## Introduction

The development of new technologies such as horizontal drilling and hydraulic fracturing has shifted hydrocarbon drilling targets significantly. Instead of focusing on structural or stratigraphic traps and characterizing fluid flow in those reservoirs, horizontal drilling and hydraulic fracturing allows for hydrocarbon exploration in the source (Kerr, 2010; Tour et al., 2010). The use of horizontal drilling and hydraulic fracturing of black shales in particular has dramatically expanded onshore drilling operations throughout the last decade (Kerr, 2010; Tour et al., 2010) in the United States and abroad (Kerr, 2010; Tour et al., 2010). Thus, the successful development of unconventional resources has become very important in the US domestic energy profile. In fact, unconventional production now accounts for more than 35% of the total natural gas production in the US (Vengosh et al., 2014).

Despite the utilization of this new technique, the success rates of individual wells remains highly variable and the reasons for these variations are poorly understood. More importantly, even productive unconventional oil and gas wells recover only 9 to 25% of hydrocarbon fluids-in-place, respectively (Zoback and Gorelick, 2013). By better understanding the fundamental properties of fluid flow in low permeability rocks including the porosity, permeability, thermal maturity, fracture networks, geological fluid flow, and zones of natural gas accumulation, one might improve the extraction of hydrocarbons from unconventional reservoirs (Hunt et al., 2012).

The inert nature and distinct isotopic compositions make noble gases ideal tracers of crustal fluid processes. Thus, noble gas geochemistry provides a promising geochemical approach toward characterizing the fundamental reservoir properties (porosity and permeability)

of black shales, and reconstructing the crustal fluid migration and thermal evolution of unconventional basins, specifically in the Marcellus Shale.

The objectives of this study are to use noble gas and trace element chemistry of rock cuttings from a series of samples along the vertical and lateral leg of a single production well from the Marcellus Formation to investigate the fundamental properties of fluid flow in the Marcellus and to investigate the behavior of noble gases ( $^4\text{He}$  and  $^{21}\text{Ne}$ ) in the Marcellus (Middle Devonian) and Upper Devonian drill cutting samples. Specifically, this study focuses on the radiogenic isotopes of noble gases (helium-4 ( $^4\text{He}$ ), neon-21 ( $^{21}\text{Ne}^*$ ), and argon-40 ( $^{40}\text{Ar}^*$ )) to determine the history of fluid flow in the region and to identify areas of gas accumulation that can be targeted as “sweet spots” for drilling. One important goal is to evaluate how fluids have moved and how much fluid has been lost from various formations over geological time.

### *Noble Gas Background*

Noble gases, specifically  $^4\text{He}$ , can be used to evaluate the fundamental properties of hydrocarbon gas migration in the Marcellus Formation and other black shales globally. Radiogenic  $^4\text{He}$  is produced by the radioactive decay of U and Th, with a fixed production ratio of  $^4\text{He}/^{21}\text{Ne}^*$  of  $2.2 \times 10^7$  (Hunt et al., 2012). As a result, the initial  $^4\text{He}/^{21}\text{Ne}^*$  of each grain of shale is fixed. After radiogenic production,  $^4\text{He}$  and  $^{21}\text{Ne}^*$  in grains equilibrate with the shale matrix as a function of temperature, porosity, and the volume and rate of fluid flow (Hunt et al., 2012; Darrah and Poreda, 2013; Darrah et al., 2014). Thus, the migration of large volumes of methane or crustal brine will efficiently remove  $^4\text{He}$  and decrease the  $^4\text{He}/^{21}\text{Ne}^*$  in the residual shale grain, while the migrated fluid will be enriched in  $^4\text{He}/^{21}\text{Ne}^*$ .

As a result of being inert, noble gases do not react with other chemicals and are not affected by oxidation, reduction or microbial activity. The primary factor that affects noble gases is the physical mechanism of fluid transport [e.g., diffusion, and 2-phase advection (bubble formation)] (Darrah et al., 2014) There are three potential sources of noble gases: 1) atmospheric gases or air-saturated water (ASW); 2) radiogenic isotopes produced in the crust; and 3) primordial gases derived from the mantle.

Atmospheric gases are incorporated into the ground or ocean water by Henry's Law of dissolution (Weiss, 1971a;b). Levels of each atmospheric gas are initially set according to temperature, partial pressure of the gas, and salinity (Weiss, 1971a;b). The main atmospheric gases are  $^{20}\text{Ne}$ ,  $^{36}\text{Ar}$ , and  $^{84}\text{Kr}$ . Once incorporated into the system, only diffusion or the process of making a free gas-phase (i.e., bubble) will fractionate these gases (Ballentine et al., 2002; Ballentine and Burnard, 2002).

Radiogenic noble gases, sometimes called crustal gases, are incorporated into crustal fluids by the decay of U and Th, which produce  $^4\text{He}$  and  $^{21}\text{Ne}^*$ , and K, which then produces  $^{40}\text{Ar}^*$  (Ballentine et al., 2002; Ballentine and Burnard, 2002). Both  $^4\text{He}$  and  $^{21}\text{Ne}^*$  are formed simultaneously by the decay of U and Th (in alpha-neutron reactions), with a fixed production ratio of  $^4\text{He}/^{21}\text{Ne}^* = 22 \times 10^6$  in the crust. As a result, in most crustal grains, we know that for every  $^{21}\text{Ne}^*$  there are 22,000,000  $^4\text{He}$  atoms produced.

Although the initial production ratio of  $^4\text{He}/^{21}\text{Ne}^*$  is fixed, these isotopes can fractionate during diffusional release from mineral grains into crustal fluids (Hunt et al., 2012). The key factor that dictates the release of radiogenic gases is the temperature of the formation. Once the temperatures increase above the closure temperature, gases within mineral grains can freely exchange with gases in the surrounding fluids. Gases can also exchange by diffusion at lower

temperatures. While temperature determines the relative rate of diffusion for  $^4\text{He}$ ,  $^{21}\text{Ne}^*$ , and  $^{40}\text{Ar}^*$  in the crust, the relative rate of diffusion decreases within increasing mass.

Because of this, helium (i.e.,  $^4\text{He}$ ) can diffuse freely out of the quartz grains into fluid-filled pore spaces in rocks on geologically relevant time scales ( $<10,000$  years at  $\sim 15^\circ\text{C}$ ) (Hunt, 2000), while the rates can be much faster at the ambient temperatures of increased burial depths. The best estimates for closure temperatures of helium are below  $\sim 15^\circ\text{C}$  (Hunt, 2000). For this reason, the primary controls on helium concentrations are porosity (i.e., the space around mineral grains into which helium can migrate) and the migration of fluids (i.e., fluid migration carries helium away from source rocks).

By comparison,  $^{21}\text{Ne}^*$  has a significantly higher closure temperature ( $\sim 80^\circ\text{C}$ ). This property indicates that higher temperatures in excess of  $\sim 80^\circ\text{C}$  are necessary before the efficient release of radiogenic neon. This temperature range is important because it reflects temperatures of early catagenesis (i.e., the onset of oil generation). Still,  $^{21}\text{Ne}^*$  can diffuse out of quartz grains in the crust at lower temperatures, but diffusion is approximately 15 times slower than  $^4\text{He}$  (Hunt, 2000).

The third component of noble gases that commonly occurs in some crustal settings is the primordial noble gases that are associated with mantle-derived rocks and fluids (Craig and Lupton, 1975; Ballentine et al., 2002; Ballentine and Burnard, 2002). Because mantle components have not been previously found in the northern Appalachian Basin, they are omitted for brevity.

Once incorporated into crustal fluids, isotopic fractionation of noble gases from any of these sources occurs during some aspect of fluid migration (e.g., 2-phase (gas plus brine) advection, diffusion). Fractionation by 2-phase advection will fractionate gases according to their



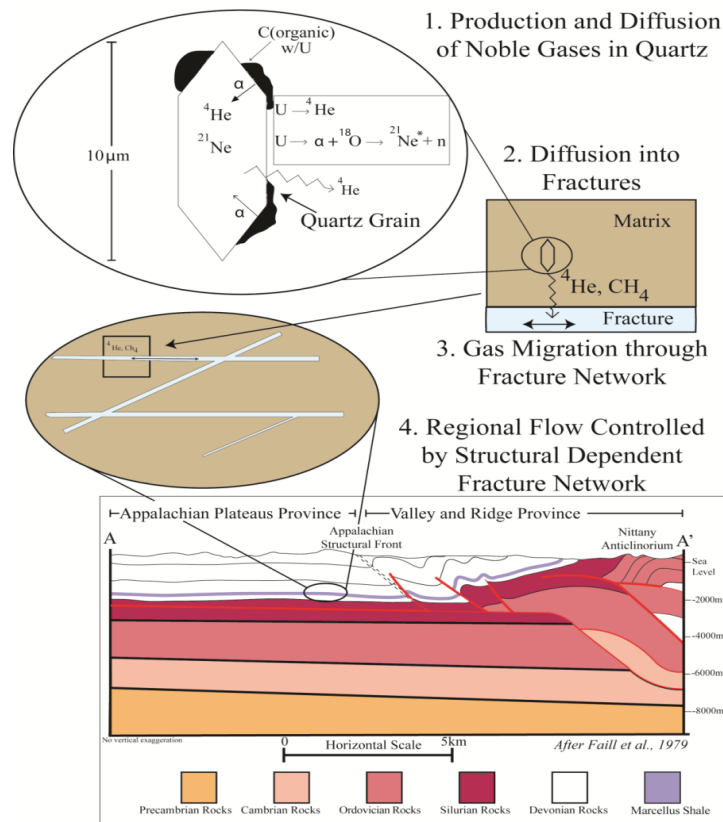
relative solubility, while diffusion will fractionate gases according to the relative square root of their masses (Darrah et al., 2014).

### *Geological Background of the Study Area*

While the Marcellus Formation is located across Pennsylvania, New York, West Virginia, Virginia, Maryland, and Ohio, our study area is located in Cameron County, Pennsylvania in the Appalachian Plateau physiographic province. Our samples are sourced from drilling cuttings in the vertical section and lateral legs of a production well drilled into the Marcellus Formation.

The Marcellus Formation (Figure 1) is an organic-rich Middle Devonian black shale located in the northern Appalachian Basin (Lash and Engelder, 2009; Faill, 1997a;b). The Marcellus was deposited during the Acadian Orogeny approximately 385 Mya (Lash and Engelder, 2009). As shown in Figure 1, there are two black shale subunits (the Union Springs and Oatka Creek Members) that are intersected by the Cherry Valley Limestone in the Marcellus (Lash and Engelder, 2009).

Although the Appalachian structural front contains intense folding, faulting and is heavily deformed, the Appalachian Plateau geographic provenance is significantly less deformed (Rast, 1989). The Appalachian Plateau contains only low angle folds as well as layer parallel shortening (Rast, 1989). One of the dominant deformation features in the plateau is natural joint sets, which are observable as semi-vertical fractures (Evans, 1995; Lash and Engelder, 2009).



**Figure 1. Schematic diagram of the production and release of radiogenic noble gases from minerals (e.g., diffusion) in the Earth's crust. It shows the potential for diffusion of the gases based on fluid interaction via joint sets in the crust. The approximate location of our samples is shown in the context of the northern Appalachian Basin plateau region. Notice that radiogenic noble gases, produced in mineral phases in the crust, can diffuse out of the shale grains into the natural fracture network where they can be transported with regional fluids (sourced from Darrah and Poreda, 2013).**

## Methodology

### *Sampling Strategy and Collection*

The samples used in this study include drill cuttings from a commercial natural gas well located in the Marcellus Shale. The commercial well was drilled in Cameron County, Pennsylvania. The drill cuttings were collected in 10 meter intervals throughout the vertical string and lateral leg of the gas well; the approximate depth of the lateral leg was ~1.2km below land surface.

From these samples, we analyzed the drill cutting samples at intervals of every 30 meters (or every third sample) in the lateral stage of the well; samples were taken every 100 meters in the vertical section of the well. In total, 40 samples were analyzed for trace elements by an Inductively Coupled Plasma Mass spectrometer (ICPMS) and noble gases by the Noble Gas Mass Spectrometer.

#### *ICPMS Analysis of Trace Elements*

Approximately 20 milligrams of each sample were weighed out on an analytical balance and placed into trace metal-free Teflon™ containers. For the first round, 1 milliliter of 12N hydrofluoric acid and 3 milliliters of 16N nitric acid were pipetted into each container with the sample. After the caps were placed back on the containers they were placed on a hot plate which was set to 140 degrees Celsius for ~24 hours. After ~24 hours the hot plate was turned up to 176 degrees Celsius and the caps of the containers were taken off. The samples were then dried down to a pea-sized ball. For the second round, the same process was repeated but instead 1 milliliter of hydrogen peroxide and 3 milliliters of nitric acid were added to the sample. The final drying process was repeated with 3 milliliters of nitric acid and 0.5 milliliters of nitric acid were added to the sample. The mixture was then poured into a 50 milliliter test tube and filled with distilled water to the 50 milliliter mark.

Before ICPMS analysis took place, standards were made by adding 0.25 mL of Indium (In), 0.25 mL of Bismuth (Bi) and 40.5 grams of distilled water to a test tube. The end result equaled a 5ppm standard solution. Samples were then analyzed using a Perkin Elmer DRC II ICP-MS following USEPA method number 200.8 and summarized in Darrah et al. (2009) and Cuoco et al. (2013).

### *Noble Gas MS Analysis*

All mineral phase samples analyzed for noble gas abundance and isotopic composition were crushed by mortar and pestle. Approximately 50 mg of sample was placed in a vacuum oven and allowed to dry at room temperature (21°C) for ~24 hours.

All samples were separated into individual mineral phases through a series of acid digestions. First, the sample and ~1mL of hydrochloric acid were placed in an SCP Science DigiTube overnight to remove all calcite and dolomite from samples. Next, the residual mineral phases were sonicated in distilled water for ~5 minutes to remove residual debris. Later, the organic matter was removed by adding ~1mL of hydrogen peroxide and waiting ~24 hours. The quartz grains were then extracted manually and identification confirmed by optical microscopy.

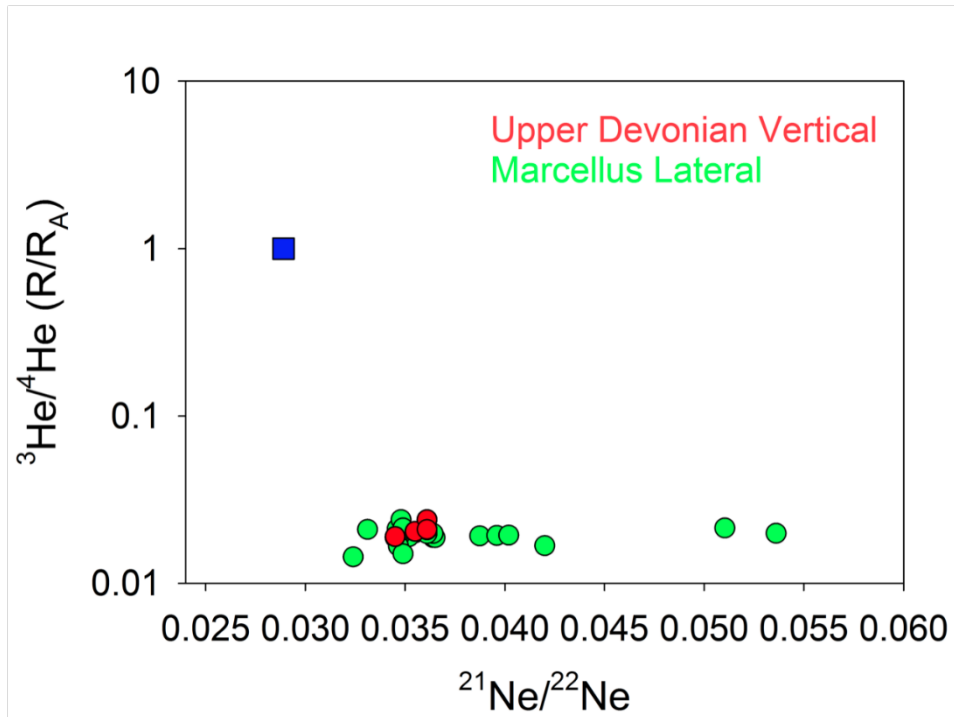
After sample preparation was complete, samples were placed under vacuum in an online stainless steel tube and heated to 650°C for 90 minutes (starting when temperatures equilibrated above 650°C) using an external resistive heater, while the temperature was monitored continuously with an external thermocouple.

All samples were measured, in triplicate, for He and Ne concentrations and isotope measurements using a Thermo Fisher Helix SFT MS at the Ohio State University Rare Gas Facility following the methods of Darrah et al. (2014). Before introduction to the noble gas MS, samples were sequentially purified using a Zr-Al getter heated to ~350°C (to remove N<sub>2</sub>, CO<sub>2</sub>, and hydrocarbons), a SAES 707A chemical sorbance getter (to remove H<sub>2</sub> and residual hydrocarbons), a charcoal finger chilled to -95°C (to separate He and Ne from Ar, Kr, Xe and any remaining gas-phase impurities), and a ARS liquid helium cold head at ~17K to physically separate He from Ne. After purification was complete, samples were introduced to the Thermo Fisher Helix SFT noble gas mass spectrometer for analysis.

Standard analytical errors were all less than  $\pm 2.41\%$  for noble gas concentrations with daily values reported in parentheses ( $[^4\text{He}]$  (0.7%),  $[^{22}\text{Ne}]$  (1.2%), and  $[^{40}\text{Ar}]$  (0.18%) as determined by measuring referenced and cross-validated laboratory standards including a) an established atmospheric standard (Rochester Air) and b) a synthetic natural gas obtained from Praxair including known and validated concentrations of  $\text{C}_1$  to  $\text{C}_5$  hydrocarbon,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ , Ar, and each of the noble gases. Noble gas isotopic errors were approximately  $\pm 0.01$  times the ratio of air (or  $1.4 \times 10^{-8}$ ) for  $^3\text{He}/^4\text{He}$  ratio,  $<\pm 0.47\%$  and  $<\pm 0.89\%$  for  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$ , respectively,  $<\pm 0.93\%$  for  $^{38}\text{Ar}/^{36}\text{Ar}$  and  $^{40}\text{Ar}/^{36}\text{Ar}$ , respectively (higher than typical because of interferences from  $\text{C}_3\text{H}_8$  on mass=36 and 38).

## Results

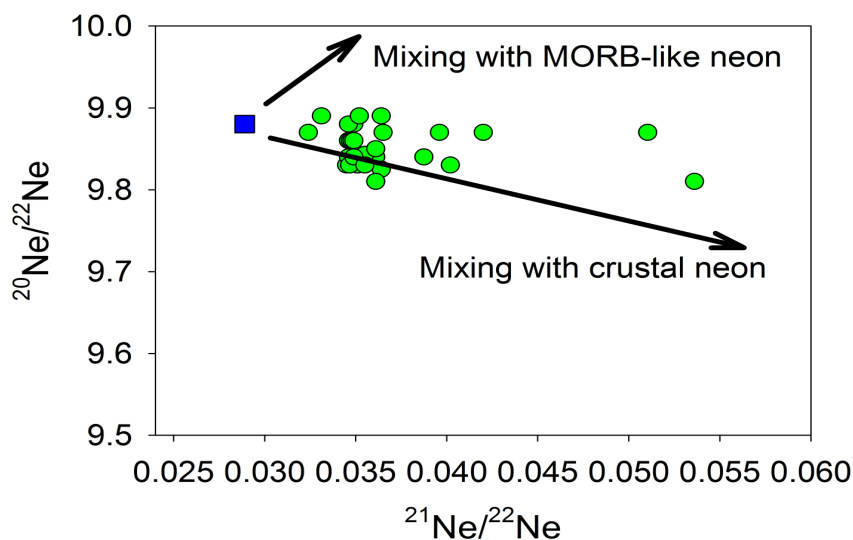
Although previous studies suggest a death of mantle helium in the northern Appalachian Basin, a critical first step in using noble gas data is to constrain dynamic fluid interactions in the Earth's crust is to eliminate the potential for mantle contributions. Two key signatures that often allow one to distinguish mantle-derived signatures are elevated levels of  $[^3\text{He}]$  (i.e., high  $^3\text{He}/^4\text{He}$ ) and  $^{20}\text{Ne}/^{22}\text{Ne}$  values that trend toward the MORB-like or "solar" neon isotopic composition (Poreda and Farley, 1992). Mantle gases have high  $^3\text{He}/^4\text{He}$  values that range from 2 to 8 times atmospheric levels (where the  $^3\text{He}/^4\text{He} = 1.39 \times 10^{-6}$  is termed 1Ra) (Ballentine et al., 2002), while crustal signatures are uniformly 0.02Ra reflecting the addition of radiogenic  $^4\text{He}$ . Many crustal samples have compositions that reflect mixtures of mantle and radiogenic noble gases.



**Figure 2. Plot of the  $^3\text{He}/^4\text{He}$  ratio against the  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio. All samples show crustal  $^3\text{He}/^4\text{He}$  isotopic signatures and an absence of mantle signatures. These data are consistent with samples derived from exclusively crustal sources.**

All samples have helium and neon isotopic compositions consistent with a mixture between crustal and air-saturated water sources (Figures 2 and 3). Mantle contributions, if present, are below detection limits (i.e.,  $< \sim 0.5\%$  of the total He or Ne).

The low  $^3\text{He}/^4\text{He}$  (0.015 to 0.026Ra) values for grains from the Marcellus reflect an exclusively crustal signature (Figure 2). The  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios, which are elevated above ASW values (0.0289), are consistent with the addition of some crustal neon following the release from grains in the Marcellus. Because of the low values for  $^3\text{He}/^4\text{He}$ , these samples reflect exclusively crustal contributions. The two observations allow us to determine that any changes away from the calculated  $^4\text{He}/^{21}\text{Ne}^*$  ratio are most likely due to the fractionation caused by different fluid processes in the crust. Both analyses are consistent with mineral grains in high U black shales.

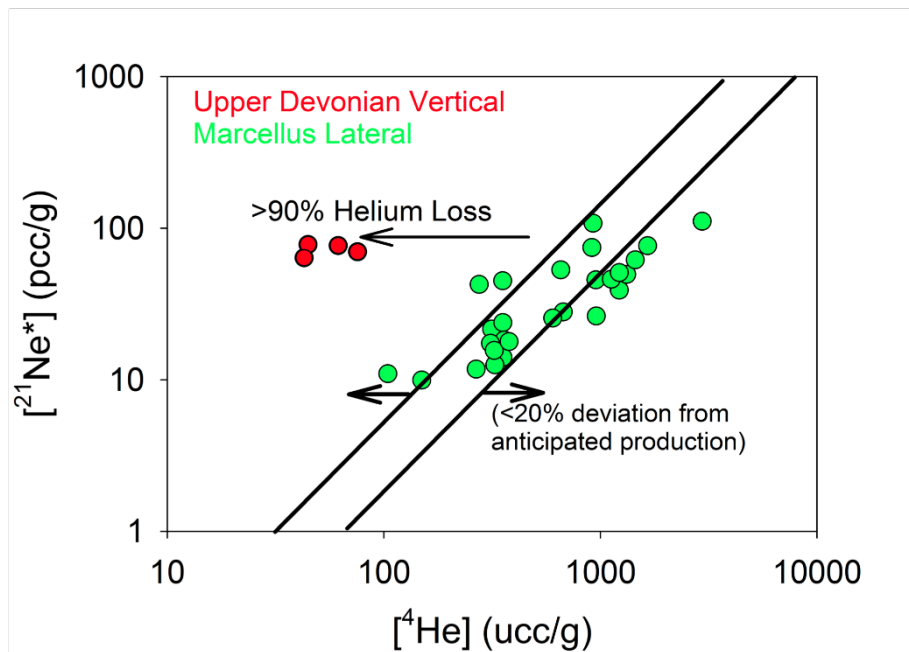


**Figure 3.**  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio plotted against the  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio for Marcellus cuttings; full neon isotope data are not available for the Upper Devonian samples. The neon isotope data reflect exclusively crustal compositions.

Neon isotopes are particularly useful for resolving mantle, crustal, and atmospheric sources in the Earth's crust (Ballentine et al., 2002; Ballentine and Burnard, 2002). Consistent with the low  $^3\text{He}/^4\text{He}$ , the neon isotope plot (Figure 3) clearly demonstrates a two-component mixture of air-saturated water neon (consistent with normal meteoric water in the crust) and the addition of crustal  $^{21}\text{Ne}^*$ .

Figure 4 shows that the majority of the samples from the lateral section of the core (green circles) have  $[\text{}^4\text{He}]$  and  $[\text{}^{21}\text{Ne}^*]$  within 90% confidence intervals of the anticipated production lines based on measured  $[\text{U}]$  and  $[\text{Th}]$  (Ballentine et al., 2002; Ballentine and Burnard, 2002), denoted by the black lines. The fact that most samples show a good correlation between  $^4\text{He}$  and  $^{21}\text{Ne}^*$  concentrations suggest that the majority of samples have not experienced preferential loss of helium from high rates of fluid flow or the extensive loss of radiogenic gases over geological time.

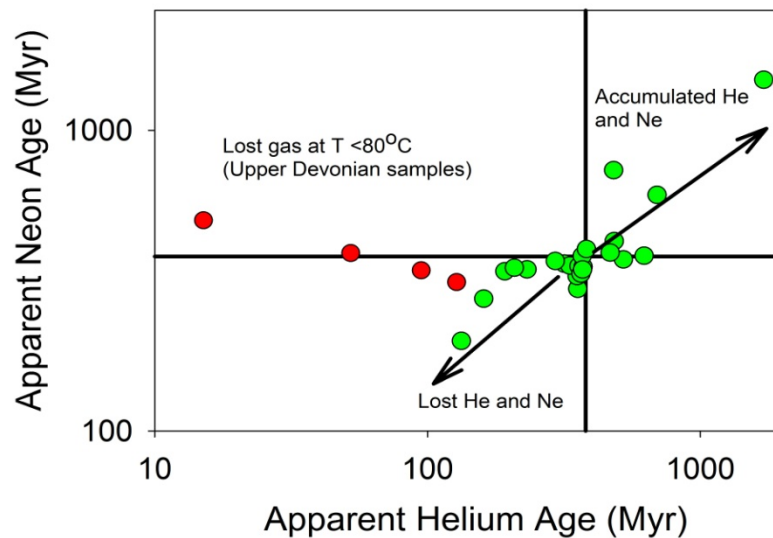
By comparison, Figure 4 also shows an extensive loss of  $^4\text{He}$  in the Upper Devonian samples located in the vertical section of the well. For reference, these Upper Devonian samples appear to have lost greater than 90% of their  $^4\text{He}$ , but less than  $\sim 30\%$  of their  $^{21}\text{Ne}^*$  (discussed more below).



**Figure 4. Plot of  $^{21}\text{Ne}$  against  $^4\text{He}$ . While most of the samples show a trend that is consistent with production values, a subset of samples from vertical section of the well shows extreme loss of He ( $>90\%$ ) relative to Ne. This fractionation suggests that He is lost below the Ne closure temperature ( $80^\circ\text{C}$ ) suggesting that the loss of helium likely occurs following the uplift of Upper Devonian sediments.**

To put these data into perspective, we calculate the apparent age of quartz grains throughout the sampling interval. The ages reflect the ratio of measured  $[\text{}^4\text{He}]$  and  $[\text{}^{21}\text{Ne}^*]$  to the amount of  $^4\text{He}$  and  $^{21}\text{Ne}^*$  that are expected in these grains assuming an age for the Marcellus of  $\sim 380$  million years and the measured  $[\text{U}]$  and  $[\text{Th}]$ . The apparent ages are shown in Figure 5. For the majority of samples (30 of 34) from the lateral leg of the well, the calculated apparent age is within  $\sim 7\%$  of the true age of the Marcellus Formation.

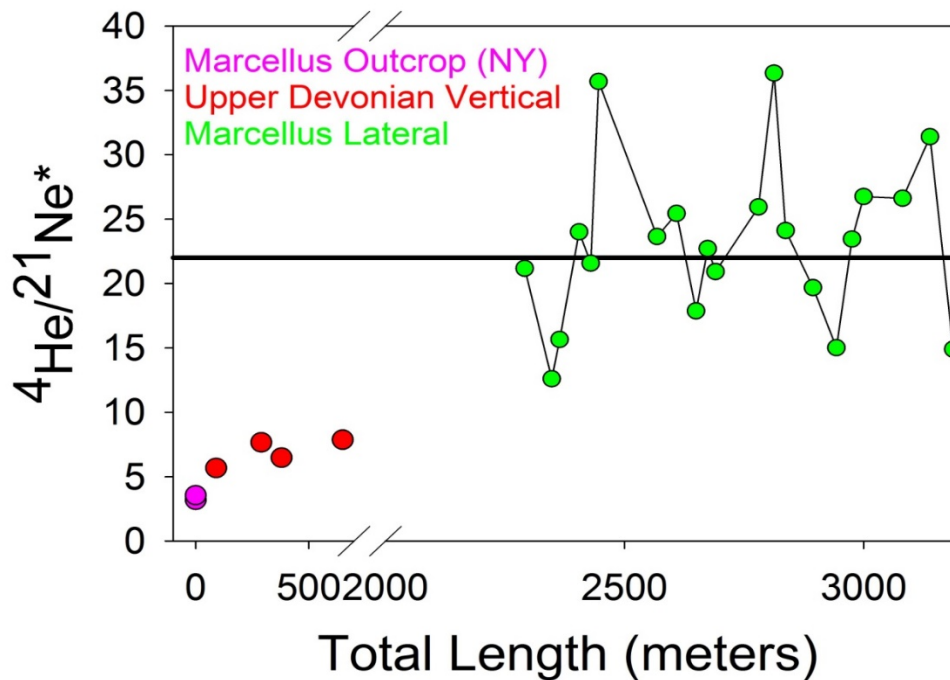




**Figure 5. Plot of the calculated apparent Neon Age vs. the calculated Helium apparent Age of a Marcellus lateral. The calculated ages of He and Ne were based on the measured [U] and [Th], which allow us to determine if samples have a) remained at equilibrium with the radiogenic production; b) been zones of gas loss; or c) been zones of gas accumulation.**

Several samples, 4 of 34, from the lateral leg of the well have either higher or lower apparent ages than the Marcellus for both He and Ne. In fact, two samples (upper right hand corner) have apparent ages that are greater than the age of the Marcellus. These results likely reflect the addition of exogenous  $^4\text{He}$  and  $^{21}\text{Ne}^*$  that dissolve into the samples from external sources. One alternative explanation for the elevated  $^4\text{He}$  and  $^{21}\text{Ne}^*$  is that these excesses represent residual  $^4\text{He}$  and  $^{21}\text{Ne}^*$  from older sedimentary grains that accumulated radiogenic noble gases in the sediment protolith. While this hypothesis is feasible, the detrital grains deposited in the Middle-Devonian Marcellus Formation were sourced from the Acadian orogeny, less than 30 Myr prior to the Marcellus deposition. As a result, even if we assume a model age consistent with the Acadian, it will reflect an exogenous source of  $^4\text{He}$  and  $^{21}\text{Ne}^*$  in the Marcellus. Additionally, previous work from the Appalachian Basin shows that nearly 100% of the accumulated helium is removed from detrital grains by flowing groundwater in less than

10,000 years following sedimentary deposition (Hunt, 2000). Thus, conversely, the samples with lower apparent ages of both  $^4\text{He}$  and  $^{21}\text{Ne}^*$  reflect sample areas that have lost gas over time.



**Figure 6. Plot of  $^4\text{He}/^{21}\text{Ne}^*$  against depth (shown in meters). By measuring variations in the  $^4\text{He}/^{21}\text{Ne}^*$  ratio, we can determine how natural gases have migrated throughout geological time. Extremely low  $^4\text{He}/^{21}\text{Ne}^*$  ratios reflect residual fluids that have lost natural gas and are typically not as productive for hydrocarbon recovery. By comparison, zones of highly elevated  $^4\text{He}/^{21}\text{Ne}^*$  are consistent with the accumulation of natural gas with higher economic potential.**

Consistent with helium values below production, the Upper Devonian samples once again show an extreme loss of helium. The apparent ages for helium in Upper Devonian samples range from 110 to 14Mya.

Figure 6 depicts how the  $^4\text{He}/^{21}\text{Ne}^*$  ratio changes over the length of the lateral leg of the Marcellus well and shows the Upper Devonian samples from the vertical portion of the well along with Marcellus outcrop samples for comparison. While the variations in the  $^4\text{He}/^{21}\text{Ne}^*$  ratio vary by about 50%, overall, the data suggest that most samples in the lateral section of the

well have retained the majority of their noble gases. Samples with  $^4\text{He}/^{21}\text{Ne}^*$  above  $\sim 22 \times 10^6$  display evidence for an exogenous source of  $^4\text{He}$ , while several samples have  $^4\text{He}/^{21}\text{Ne}^*$  below production values reflecting a relative loss of helium. Similar to the other plots, the Upper Devonian and Marcellus outcrop samples show larger depletions of  $^4\text{He}$  with respect to  $^{21}\text{Ne}^*$ . This suggests extensive loss of helium, most likely in lower thermal conditions than the rest of the Marcellus samples. This indicates that the helium loss that is seen is due to the lower temperature conditions and this loss is likely related to the increase connectivity in the hydrological cycle that is caused after uplift, denudation, and neotectonic fracturing occur.

## Discussion

Overall, our data shows two distinct behaviors. The first behavior is found in samples collected from the lateral leg of Marcellus wells; these samples retain a larger portion of their radiogenic gases (>92% of He and Ne) with relatively minor variations associated with what appears to be localized loss of helium or incorporation of exogenous helium. The second observation is that samples from the vertical section of the well in Upper Devonian samples have lost much of their radiogenic gases (ranging up to 90% and 50% of their total  $^4\text{He}$  and  $^{21}\text{Ne}^*$ , respectively).

The first observation suggests that samples from the Marcellus production intervals have retained their radiogenic gases in a dominantly “closed” system. This interpretation is based on the extremely high residual [ $^4\text{He}$ ]. Diffusion from the quartz grains into the pore spaces will continue until there is no longer a concentration gradient. In systems with active flow systems, migrating gas or groundwater will preferentially remove  $^4\text{He}$  with respect to  $^{21}\text{Ne}^*$ . However, in

a closed system that does not experience active fluid flow, the gases will only diffuse out of the grains up to the point where the low porosities balance the concentration gradient.

By comparison, we know that the upper 0.5km of the crust often experiences neotectonic fracturing after uplift and denudation (basin inversion). When neotectonic fracturing occurs, there is increased permeability and hydrologic communication. This communication allows natural gas or groundwater to remove  $^4\text{He}$  and dramatically reduce the  $^4\text{He}/^{21}\text{Ne}^*$  below production values.

In Figure 4, the two diagonal black lines show a 90% confidence interval for paired production of  $^4\text{He}$  and  $^{21}\text{Ne}^*$ . The ratio is equivalent to 22 Million  $^4\text{He}$  atoms per  $^{21}\text{Ne}^*$  atom. Most of the samples from the Marcellus (green) show relatively good correlation between  $^4\text{He}$  and  $^{21}\text{Ne}^*$ . This suggests that there was little fractionation between  $^4\text{He}$  and  $^{21}\text{Ne}^*$  in the Marcellus. There were also minor variations in the Marcellus lateral reflecting minor accumulation and loss without fractionation. Figure 4 also indicates that these samples retain most of their radiogenic gases and also retain both gases equivalently. This retention is consistent with the low rates of hydraulic conductivity seen here (i.e., a relatively static system without much fluid migration).

The subset of Upper Devonian samples collected from the vertical leg of the well shows substantial losses of  $^4\text{He}$  (>90%). This preferential helium loss suggests that fractionation occurs at relatively low temperatures, possibly following uplift and denudation as neotectonic fractures are formed and the Upper Devonian starts to interact with the hydrological cycle. In this figure the data suggests an “open system” behavior with areas of active hydrologic flow. An important aspect, besides losing the majority of the total gases, is the clear preferential loss of  $^4\text{He}$ . This preferential loss suggests that at lower temperatures, which are below the closure rates for neon,

there is more gas loss occurring for the helium. These results suggest that it is most likely that gases are lost during both uplift and denudation via basin inversion.

An alternative approach to interpreting our data is to consider how much  $^4\text{He}$  and  $^{21}\text{Ne}^*$  is retained in grains compared to what should have been produced by the uranium (U) and thorium (Th) decay throughout the history of the Marcellus. One thing that sticks out in Figure 5 is that most samples have apparent calculated He and Ne ages within  $\sim 7\%$  of the age of the Marcellus Formation. This is very close to the true age which implies that  $>92\%$  of the gas has not left the system in 380Myr (or at minimum 87% if one assume an age consistent with the sediment protolith). These data suggest a remarkably “closed system behavior” for the Marcellus Formation. One interpretation is that the formation became closed within the first  $\sim 15\text{Myr}$  after deposition. Because this suggests a closed system, this formation should hold the majority of its natural gas today. Some samples show strong accumulation of both He and Ne, while others show a fluid loss of both (zones of fluid loss). The data also suggests the fluid migration happened at comparatively higher temperatures. The Upper Devonian samples show significant loss of  $^4\text{He}$  compared to  $^{21}\text{Ne}^*$ . These results reflect a loss at lower temperatures. These results are likely after uplift and denudation.

Similarly, Figure 6 plots the length along the lateral leg of the Marcellus against the  $^4\text{He}/^{21}\text{Ne}^*$  ratio supporting the idea that the Marcellus is a relatively closed system, with high residual fluids-in-place. This is different than the Marcellus outcrop and the Upper Devonian vertical samples, which both show preferential loss of  $^4\text{He}$  at the lower temperature conditions. These higher peaks are representative of zones of gas accumulation in the lateral. These negative peaks are representative of zones of gas loss.

## Conclusions

The radiogenic noble gases record a history of fluid migration in the crust. We see that the expected  $^4\text{He}$  and  $^{21}\text{Ne}^*$  concentrations can be calculated from measured U and Th concentrations, and that by comparing the measured and calculated values one can estimate the relative accumulation or loss of gas due to fluid migration. The  $^4\text{He}/^{21}\text{Ne}^*$  ratio shows variations in gas migration along the well lateral. Based on this ratio we can see that some zones record gas accumulation, while others show gas loss or a quantitative retention of gas (i.e., a “tight gas”). The Upper Devonian formations show significant evidence for helium loss, while the Marcellus appears to be a relatively tight formation.

## Suggestions for further research

In the future we would like to compare this data set to others from different wells in the Marcellus. A few key test cases should include a comparison along: smaller interval sections of the lateral portion of the well; across different physiographic sections of the Appalachian Basin (e.g., near the structural front or in different deformation zones in the Appalachian Plateau); and potentially along laterals oriented in different direction. This will give a better idea of classifying the migration patterns of the formation as a whole and will help support our conclusions of the Marcellus being a tight formation or not. It would also be interesting to compare the data to production data from this well which would help confirm our conclusions.

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