#### Noble Gases Help Trace the Behavior of Hydrocarbons in the Crust\*

Thomas Darrah<sup>1</sup>, Robert J. Poreda<sup>2</sup>, and Ronald Perkins<sup>3</sup>

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#### **Abstract**

The occurrence, distribution, and composition of hydrocarbons in the Earth's crust result from the complex interplay between the tectonic and hydrologic cycles. For example, there is complex association between the tectonics of fold-thrust belts, the deformation of foreland basins, and the generation and migration of hydrocarbons and other geologic fluids in the subsurface. Accurately characterizing the relationship between these factors is critical to predicting the economic success of conventional and unconventional energy plays. One technique that is traditionally used in these studies is the analysis of gas geochemistry, specifically stable isotopic compositions (e.g.,  $\delta$ 13C,  $\delta$ 18O, and  $\delta$ 2H) of hydrocarbon gases or CO<sub>2</sub>. The inert noble gases provide a complementary geochemical technique that can be used in concert with hydrocarbon molecular and stable isotope composition to evaluate the source and migrational history of hydrocarbons in conventional and unconventional plays. Additionally, in some cases, noble gases can be used as an external variable to evaluate the timing of closure for hydrocarbon reservoirs, open vs. closed system behavior and to determine and monitor the residual fluids in place during exploration and production.

Herein, we will present noble gas and hydrocarbon molecular and stable isotope data from hydrocarbon plays in the Appalachian Basin (Utica, Trenton-Black River, and Marcellus) and Dallas-Fort Worth (Barnett) basins. Our presentation will focus on insights gained about hydrocarbon stable isotopic roll overs and reversals based on noble gas isotope data. Our preliminary data suggests that producing natural gas wells that exhibit isotopic reversals display distinct noble gas evidence consistent with relatively closed system behavior. Additionally, samples with isotopic reversals retain more than 3x the concentrations of atmospheric (air-saturated water) noble gases suggesting that significantly higher levels of formational waters remain in black shale source rocks that exhibit isotopic reversals.

#### **References Cited**

Ballentine, C.J., and R.K. O'Nions, 1994, The use of He, Ne and Ar isotopes to study hydrocarbon related fluid provenance, migration and mass balance in sedimentary basins: Geofluids: Origin, Migration and Evolution of Fluids in Sedimentary Basins, v. 78, p. 347-361.

<sup>\*</sup>Adapted from oral presentation given at AAPG Annual Convention & Exhibition, Denver, Colorado, May 31-June 3, 2015

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Faill, R.T., 1979, Geology and mineral resources of the Montoursville South and Muncy quadrangles and part of the Hughsville quadrangle, Lycoming, Northumberland and Montour counties, Pennsylvania: Pennsylvania Geological Survey, ser. 4, Atlas 144ab, 114 p.

Hunt, A.G., T.H. Darrah, and R.J. Poreda, 2012, Determining the source and genetic fingerprint of natural gases using noble gas geochemistry: A northern Appalachian Basin case study: AAPG Bulletin, v. 93/10, p. 1785-1811.

# Noble gases help trace the behavior of hydrocarbons in the crust





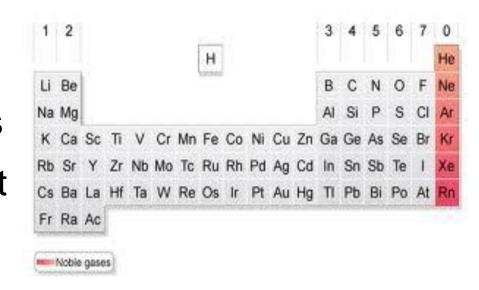
### Tom Darrah, Ron Perkins, Bob Poreda



Need to evaluate the genetic source and migration

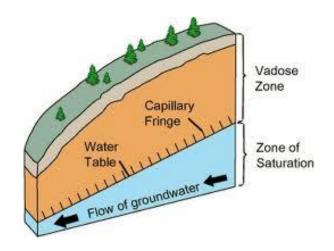
#### Noble gases:

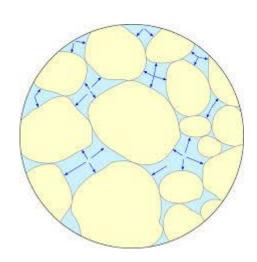
- are inert
- externally defined tracers
- can be used to fingerprint thermogenic sources (e.g., Hunt, Darrah, Poreda, 2012)
- provide information about fluid migration processes



# What makes up a noble gas composition?

- Atmospheric Gases (e.g., <sup>20</sup>Ne, <sup>22</sup>Ne <sup>36</sup>Ar, <sup>84</sup>Kr, <sup>132</sup>Xe)
- Incorporated as a function of Henry's Law solubility

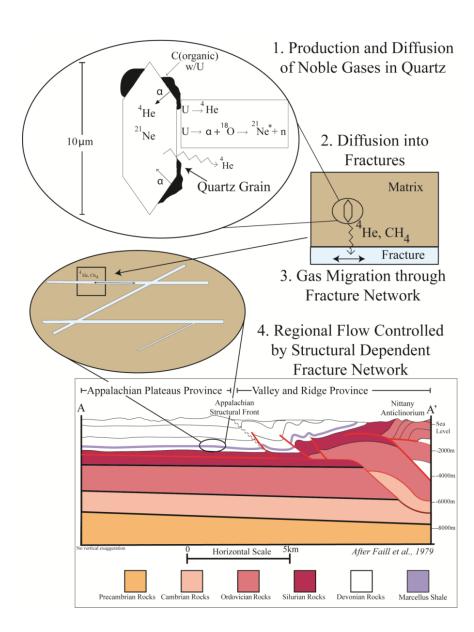




What makes up a noble gas composition?

- Radiogenic Gases (e.g., <sup>4</sup>He\*, <sup>21</sup>Ne\*, <sup>40</sup>Ar\*)
- U, Th (<sup>4</sup>He\*, <sup>21</sup>Ne\*)
- K decay (<sup>40</sup>Ar\*)

Temperature-controlled release from crustal minerals into gas-phase (Ballentine, 1994; Hunt et al, 2012)



What makes up a noble gas composition?

- Atmospheric Gases (<sup>20</sup>Ne, <sup>22</sup>Ne <sup>36</sup>Ar, <sup>84</sup>Kr, <sup>132</sup>Xe)
- Radiogenic Gases (<sup>4</sup>He, <sup>21</sup>Ne\*, <sup>40</sup>Ar)
- Mantle Gases (<sup>3</sup>He)

Not present in the Appalachian Basin (Hunt, Darrah, Poreda, 2012)



## The Northern Appalachian Basin

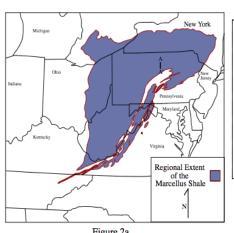
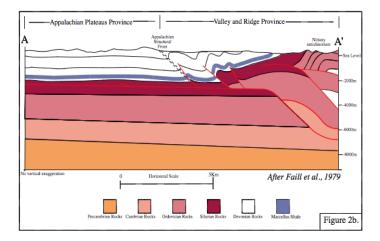
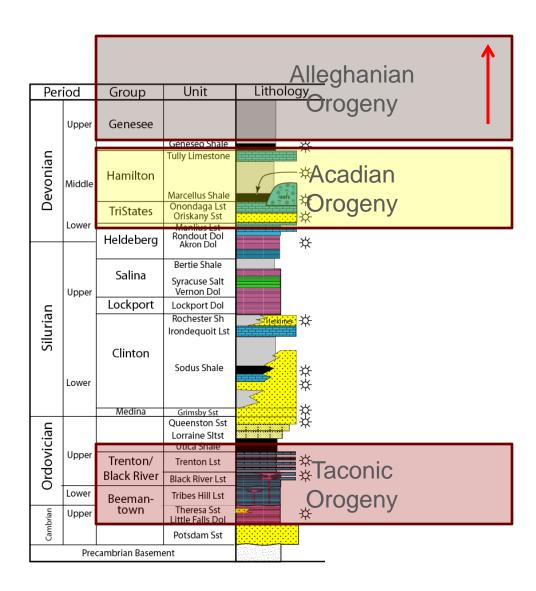


Figure 2a. Map showing the regional extent of the Marcellus shale. The cross section below is represented by A to A'.

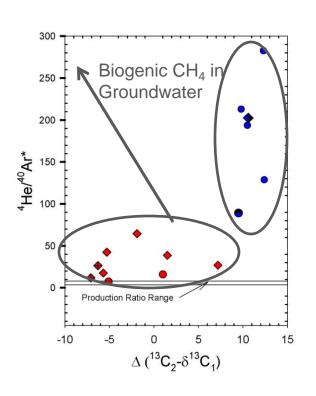
Figure 2b. Cross section of the Appalachian mountains showing the transition from the Valley and Ridge province to the Appalachian Plateaus Province. Please note the change in deformation from the highly deformed Valley and Ridge to the broad open folds of the Appalachian Plateau at the Appalachian Structural Front.

Figure 2a.

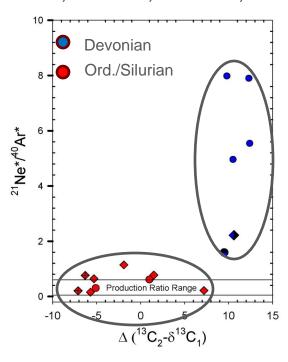




# **Genetic Fingerprint**



Hunt, Darrah, Poreda, AAPG 2012



Noble gases and carbon isotopes clearly distinguish genetic groupings

### What is the next frontier for noble gases?

#### **Using noble gases to:**

- -Understand a history of fluid migration
- -Characterize processes associated with isotope reversals ( $\delta^{13}$ C-CH<sub>4</sub> >  $\delta^{13}$ C-C<sub>2</sub>H<sub>6</sub>)
- -Quantify residual fluids-in-place and potential hydrocarbon production

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Rely on understanding how fluids migrate in the crust

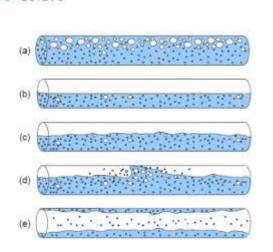
#### **Noble Gas Fractionation**

Noble gases are fractionated by well-defined physical mechanisms

Diffusion

1) Diffusion:

2) Multi-phase advectionfractionates as a function of:-partition coefficients

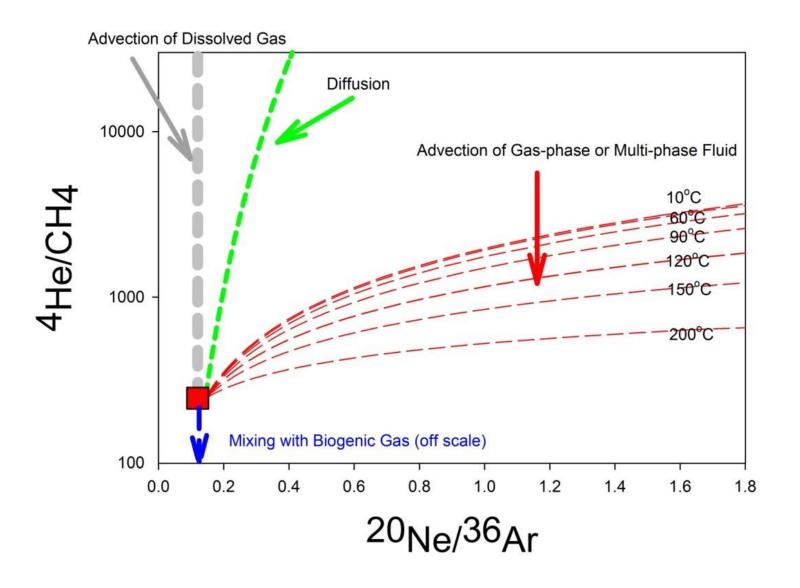


solute

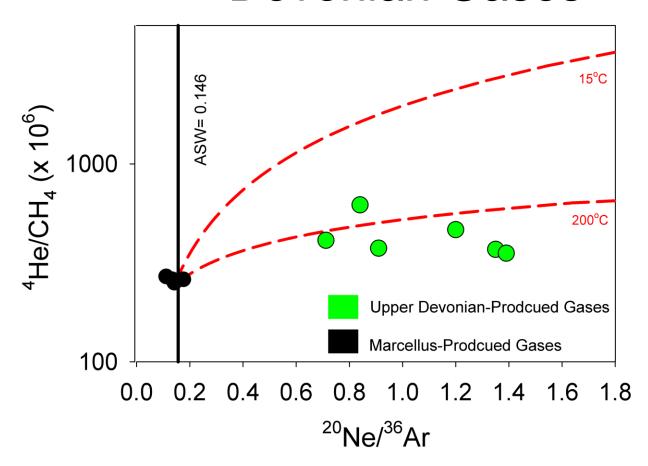
low concentration

Single-phase advection should not significantly fractionate atmospheric noble gases

## **Mechanism of Migration?**

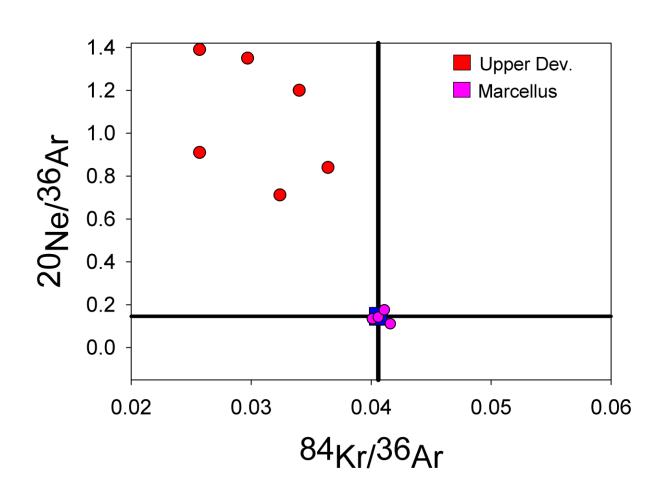


# Northern Appalachian Basin Devonian Gases

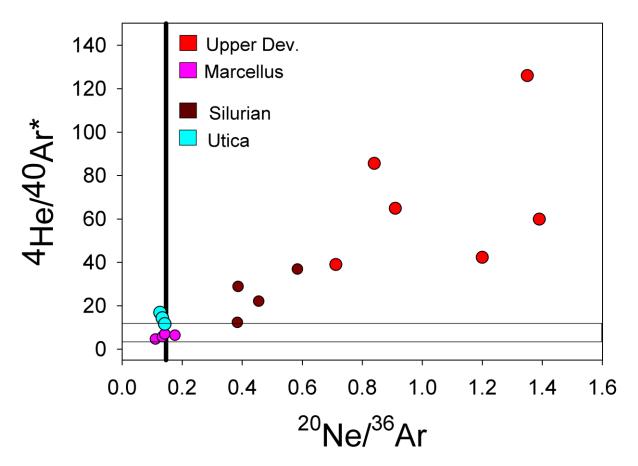


- UD gases migrate by advection
- Marcellus production gases are not migrated!

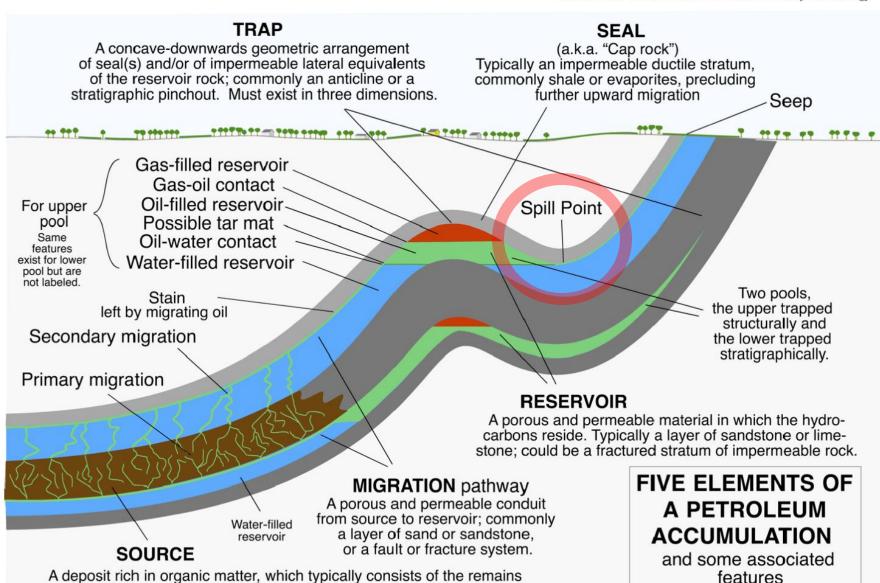
# Northern Appalachian Basin Devonian Gases



# Northern Appalachian Basin Natural Gases



Consistent with Hunt, Darrah, and Poreda 2012, shalesourced gases behave like a closed system



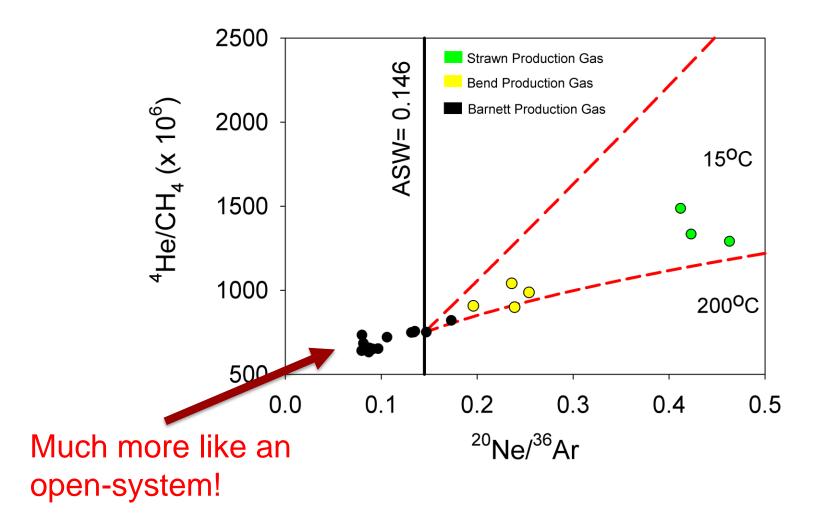
of phytoplankton; typically a fine-grained marine or lacustrine sediment

(e.g. an organic-rich shale). It must have been buried to a depth at which it was subjected to considerable temperature for considerable time.

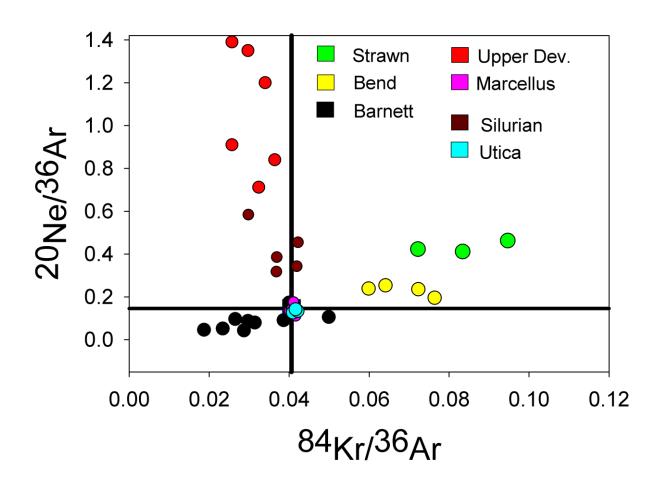
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in an absurdly simple example

#### Dallas-Fort Worth Basin Natural Gases

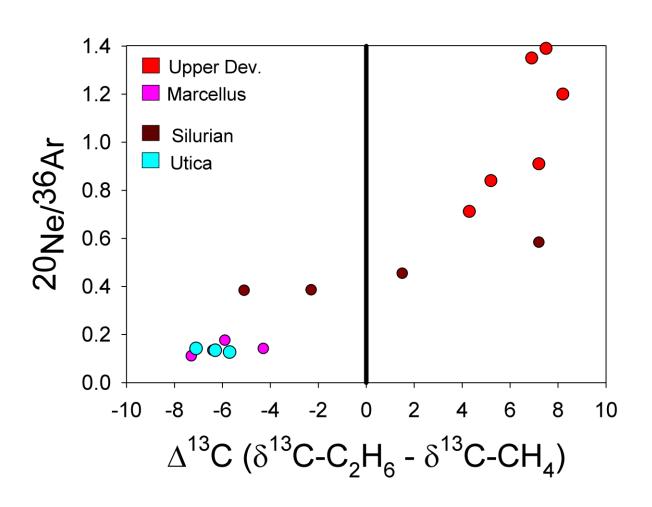


### Dallas-Fort Worth Basin Natural Gases

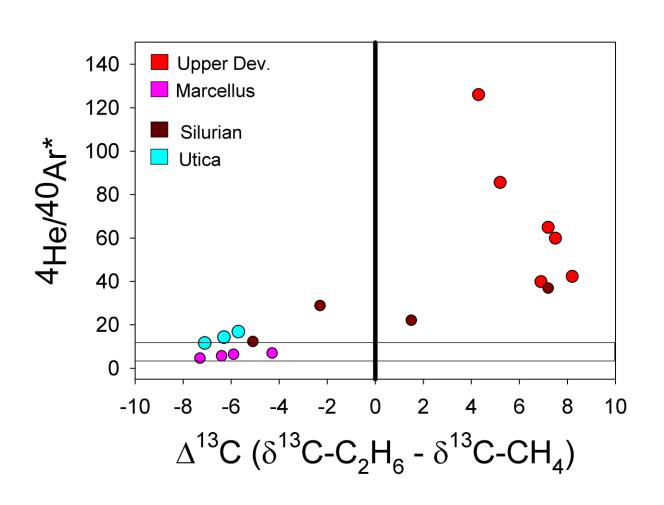


Open, Liquid-phase migration?

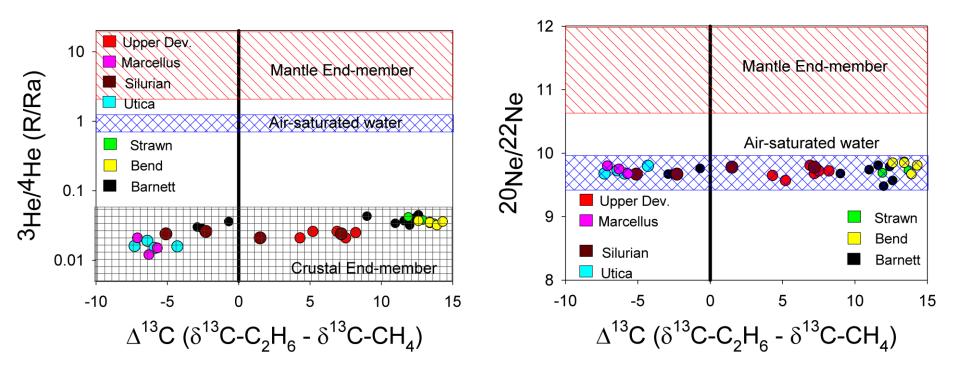
# Northern Appalachian Basin Natural Gases



# Northern Appalachian Basin Natural Gases

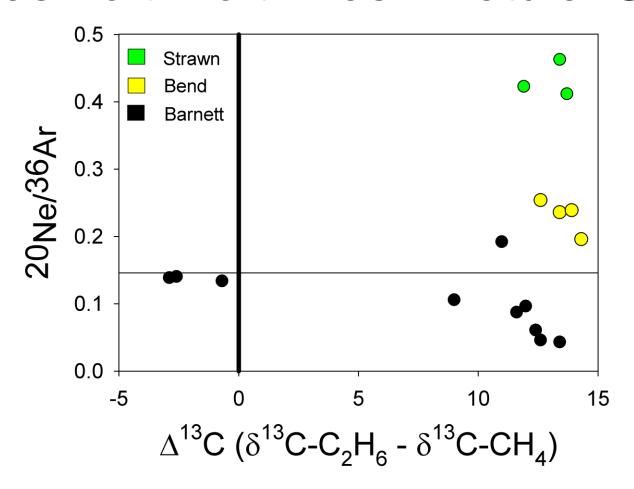


## Mantle signature?



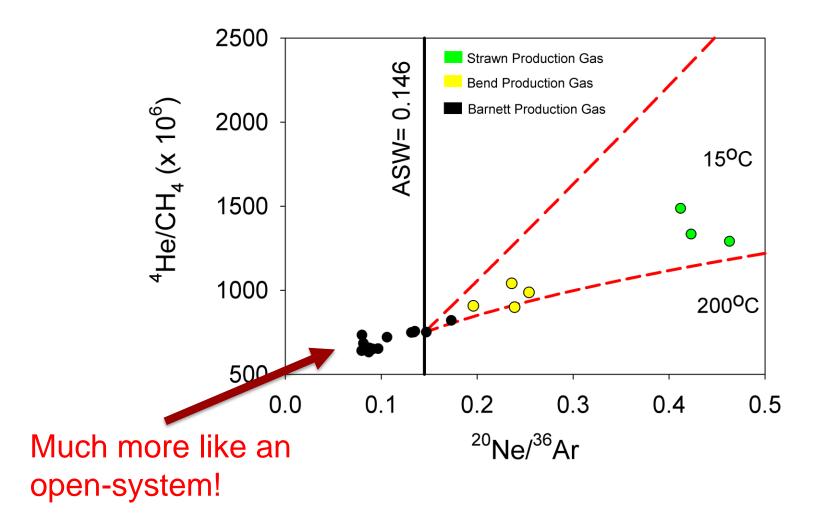
Probably not mantle-derived abiogenic hydrocarbons!

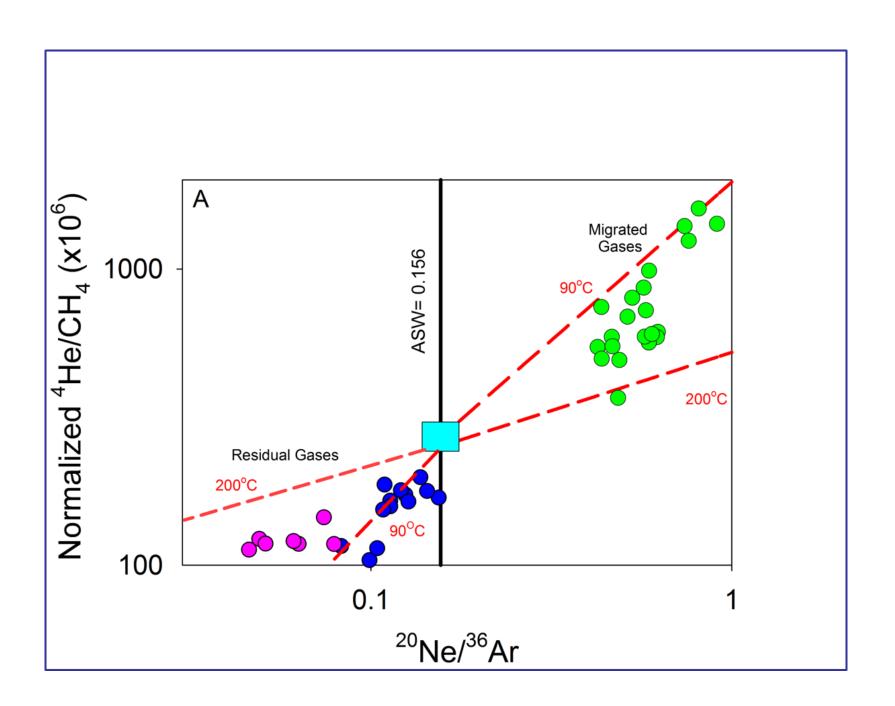
#### Dallas-Fort Worth Basin Natural Gases

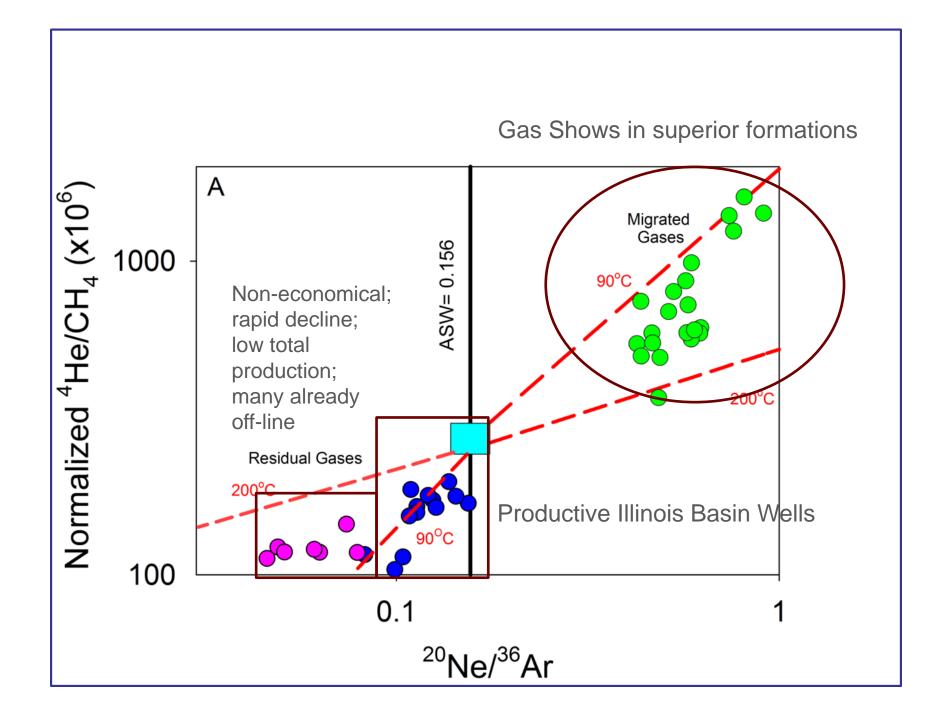


- Only samples with "closed" system behavior show reversals.
- Migrated and residual-phase (after oil migration) gases do not show a reversal.

#### Dallas-Fort Worth Basin Natural Gases







#### Conclusions

- Noble gas partitioning can provide insights into gas- and oil-phase migration
- Noble gases can track open vs. closed system behavior of hydrocarbons in shales
- C and H isotopic reversals are consistent with closed system (even closed to water) behavior
- The Marcellus and Barnett have very different hydrocarbon loss histories

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