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

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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., δ13C, δ18O, and δ2H) of hydrocarbon gases or CO₂. 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


Noble gases help trace the behavior of hydrocarbons in the crust

Tom Darrah, Ron Perkins, Bob Poreda
Noble Gas Systematics

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
Noble Gas Systematics

What makes up a noble gas composition?

- Atmospheric Gases (e.g., $^{20}$Ne, $^{22}$Ne $^{36}$Ar, $^{84}$Kr, $^{132}$Xe)
- Incorporated as a function of Henry’s Law solubility
Noble Gas Systematics

What makes up a noble gas composition?

- Radiogenic Gases (e.g., $^4\text{He}^*$, $^{21}\text{Ne}^*$, $^{40}\text{Ar}^*$)
- U, Th ($^4\text{He}^*$, $^{21}\text{Ne}^*$)
- K decay ($^{40}\text{Ar}^*$)

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

What makes up a noble gas composition?

- Atmospheric Gases \( (^{20}\text{Ne}, \enspace ^{22}\text{Ne}, \enspace ^{36}\text{Ar}, \enspace ^{84}\text{Kr}, \enspace ^{132}\text{Xe}) \)
- Radiogenic Gases \( (^{4}\text{He}, \enspace ^{21}\text{Ne}^*, \enspace ^{40}\text{Ar}) \)
- Mantle Gases \( (^{3}\text{He}) \)

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.

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Genetic Fingerprint

Noble gases and carbon isotopes clearly distinguish genetic groupings

Hunt, Darrah, Poreda, AAPG 2012
What is the next frontier for noble gases?

Using noble gases to:

- Understand a history of fluid migration
- Characterize processes associated with isotope reversals ($\delta^{13}\text{C-CH}_4 > \delta^{13}\text{C-C}_2\text{H}_6$)
- Quantify residual fluids-in-place and potential hydrocarbon production
What is the next frontier for noble gases?

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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

1) Diffusion:

2) Multi-phase advection
fractionates as a function of:
- partition coefficients
- $V_{\text{gas}}/V_{\text{water}}$

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

![Graph showing the relationship between 20Ne/36Ar and 84Kr/36Ar with data points for Upper Devonian and Marcellus formations.]
Consistent with Hunt, Darrah, and Poreda 2012, shale-sourced gases behave like a closed system.
TRAP
A concave-downwards geometric arrangement of seal(s) and/or of impermeable lateral equivalents of the reservoir rock; commonly an anticline or a stratigraphic pinchout. Must exist in three dimensions.

SEAL
(a.k.a. “Cap rock”)
Typically an impermeable ductile stratum, commonly shale or evaporites, precluding further upward migration.

RESERVOIR
A porous and permeable material in which the hydrocarbons reside. Typically a layer of sandstone or limestone; could be a fractured stratum of impermeable rock.

SOURCE
A deposit rich in organic matter, which typically consists of the remains 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.

MIGRATION pathway
A porous and permeable conduit from source to reservoir; commonly a layer of sand or sandstone, or a fault or fracture system.

FIVE ELEMENTS OF A PETROLEUM ACCUMULATION
and some associated features
in an absurdly simple example
Much more like an open-system!
Dallas-Fort Worth Basin Natural Gases

Open, Liquid-phase migration?
Northern Appalachian Basin Natural Gases

\[ \Delta^{13}C \ (\delta^{13}C-C_2H_6 \ - \ \delta^{13}C-CH_4) \]

- Red: Upper Dev.
- Purple: Marcellus
- Dark Brown: Silurian
- Light Blue: Utica

[Graph showing data points for different geological formations]
Northern Appalachian Basin Natural Gases

\[ \Delta^{13}C \left( \delta^{13}C_{\text{C}_2\text{H}_6} - \delta^{13}C_{\text{CH}_4} \right) \]

- Upper Dev.
- Marcellus
- Silurian
- Utica
Mantle signature?

Probably not mantle-derived abiogenic hydrocarbons!
• 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

Much more like an open-system!
Gas Shows in superior formations

Productive Illinois Basin Wells

Non- economical; rapid decline; low total production; many already off-line
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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