Using Noble Gas and Hydrocarbon Gas Geochemistry to Source the Origin of Fluids in the Eagle Ford Shale of Texas, USA*

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Abstract

The Eagle Ford Shale in south Texas has become one of the most prolific shale plays in the United States in recent years. While production data suggests that oil and natural gas can be produced across a vast area of the field, the source of H_2S and hydrocarbons, and the extent to which fluids have migrated into and out of the Eagle Ford, have yet to be determined. This study uses noble gas isotopes, gas composition, and stable isotopes to evaluate the source gases, to characterize the fluids-in-place, and to characterize the extent of fluid migration from the Eagle Ford Shale. The inert nature and distinct isotopic compositions make noble gases ideal tracers of crustal fluid processes. In most shales, the noble gas isotopic composition reflects a binary mixture of: (1) air-saturated water (ASW), containing 20Ne, 36Ar, and 84Kr derived from solubility equilibrium with the atmosphere during groundwater recharge, and (2) radiogenic noble gases such as 4He*, 21Ne*, and 40Ar* sourced from the decay of U, Th, and K.

Once noble gases incorporate into crustal fluids, they fractionate only by well-constrained physical mechanisms (e.g., diffusion, phase-partitioning). For example, although the decay of U and Th, produces a fixed ratio of 4He/21Ne (2.2×107) and the initial 4He/21Ne of minerals in shale are fixed, 4He will be preferentially released with respect to 21Ne at hydrocarbon-producing temperatures. Over time, the isotopic ratios vary as fluids equilibrate with the shale matrix. Variations occur as a function of temperature, porosity, and the volume of fluid flow. Thus, the isotopic values can be used to reconstruct the history of fluid flow in specific formations. Our data from the Eagle Ford show that mantle-derived gases (elevated 3He/4He= 0.15–0.25Ra and

20Ne/22Ne=10.2–11.1) and radiogenic gases (4He, 21Ne, 40Ar) dominate the overall gas composition. We anticipate that volcanism during Cretaceous/Cenozoic rifting activity caused the observed mantle-gas contributions. Interestingly, higher mantle contributions appear to correlate with elevated H_2S in the production wells from this study suggesting thermal sulfate reduction induced by magmatic activity. Additionally, ASW and radiogenic noble gases can be used to model the relative volume of residual fluids-in-place for this Eagle Ford play. Initial data suggests that there has been minimal fractionation of noble gases, implying minimal loss of the initial hydrocarbon fluids.

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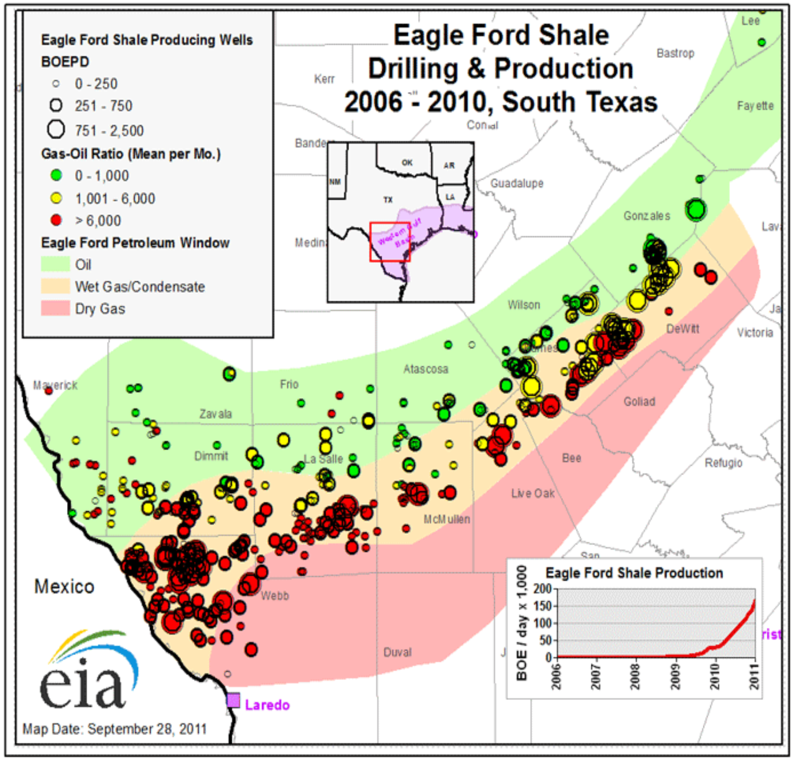
Overview

- Introduction
- Background
- Objectives
- Methods
- Results and Discussion
- Conclusions
- Future Work

Introduction – Eagle Ford Shale

- Hydraulically fractured black shale for oil and natural gas production
- Spans across the entirety of south Texas and into Mexico
- >1.5MMbbls/day of oil
- >7000MMcf/day of gas
- ~150 rigs operating



EIA, 2011

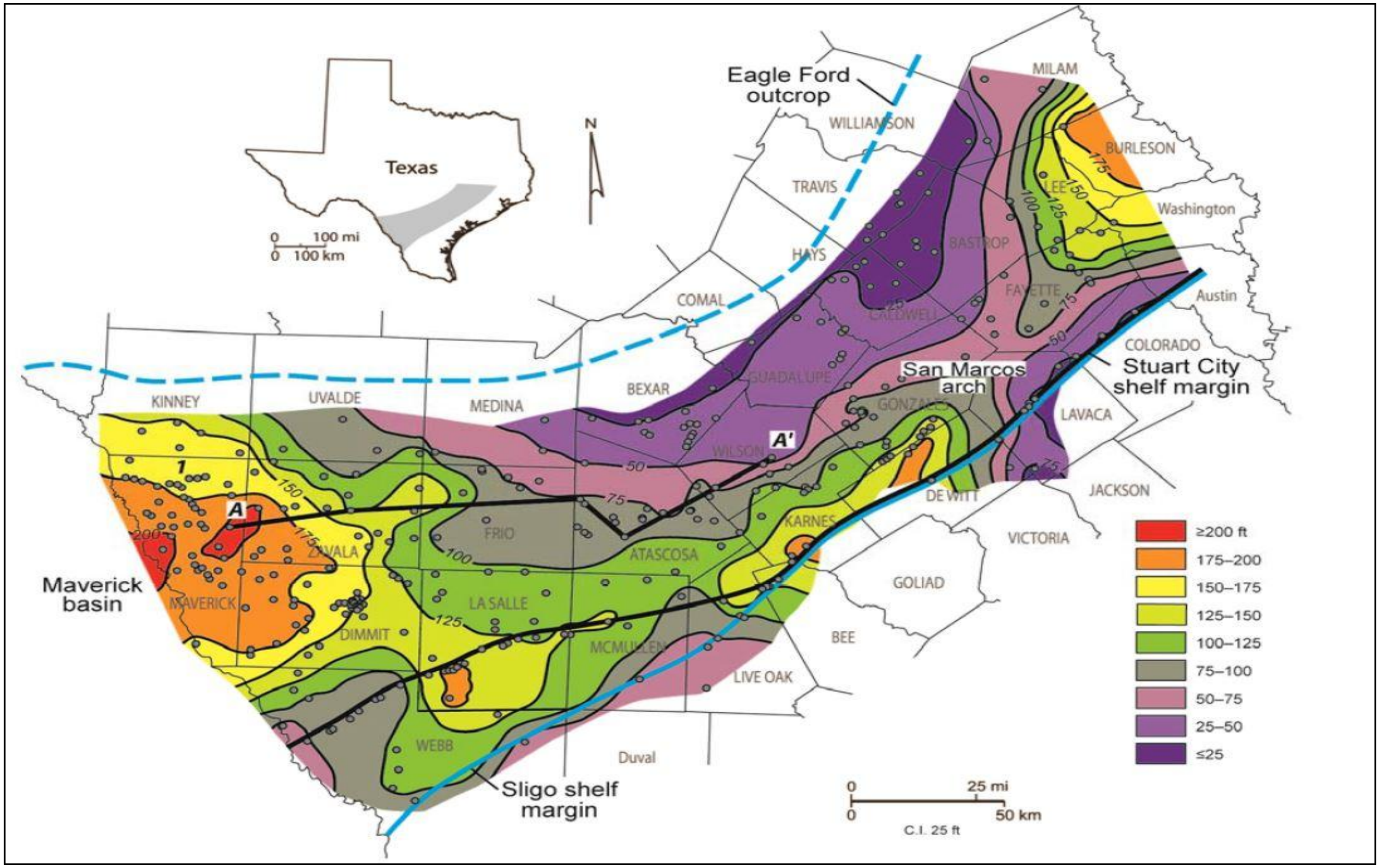
Scientific Motivation

- Tectonically complex region
- Near intersection of paleo-suture zones and rifting
- Fluid migration in unconventional petroleum systems, including the Eagle Ford, are still understudied
- Application for noble gas geochemistry
- Need to understand the factors that controls high H_2S levels in wells across the fields

Background: Geology

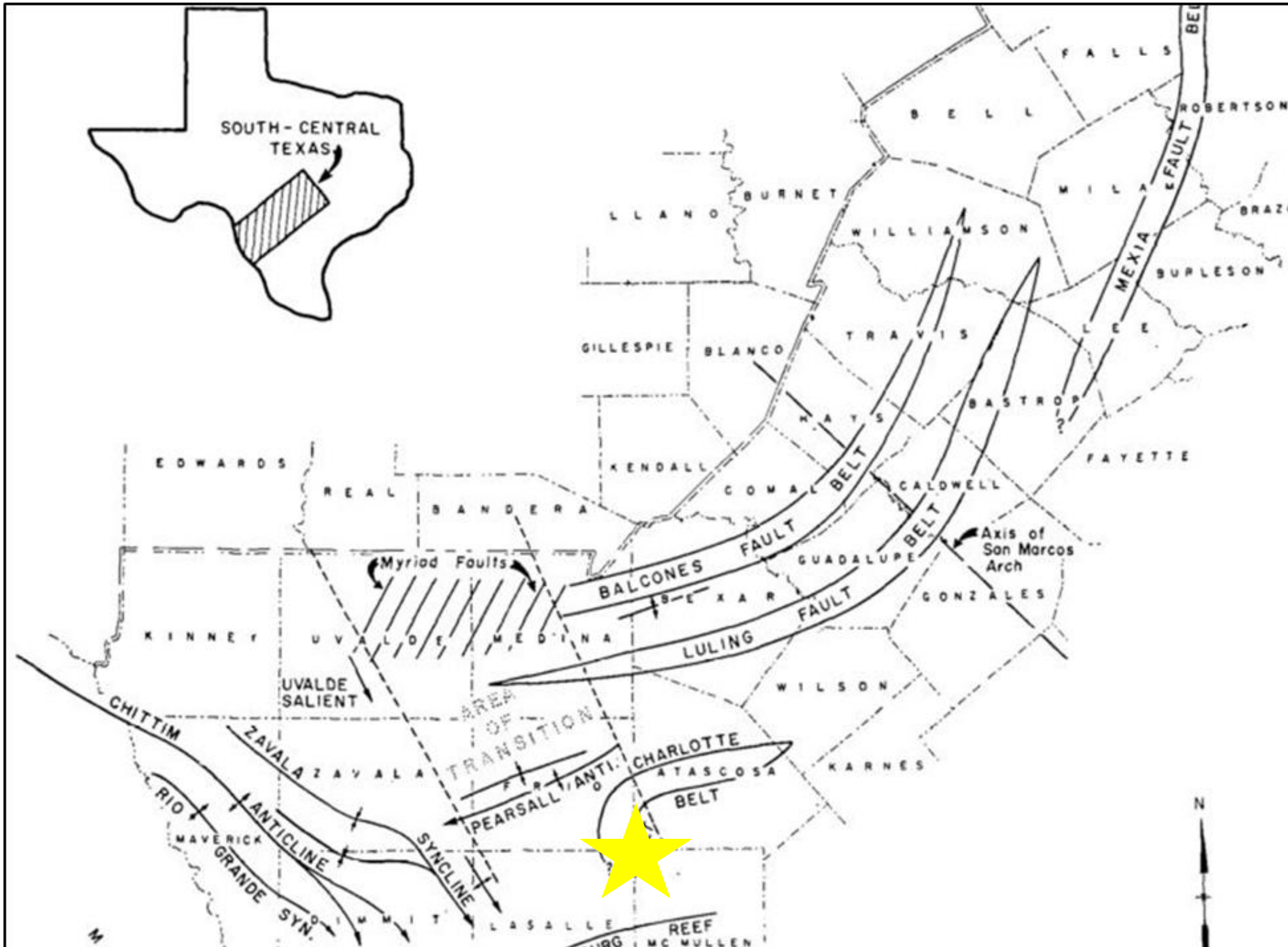
Regional paleogeography map during Eagle Ford time (Blakey, 2014).

Background: Geology



Isopach map of the Eagle Ford Shale in south Texas with major, regional structural features (Hentz et al, 2014)

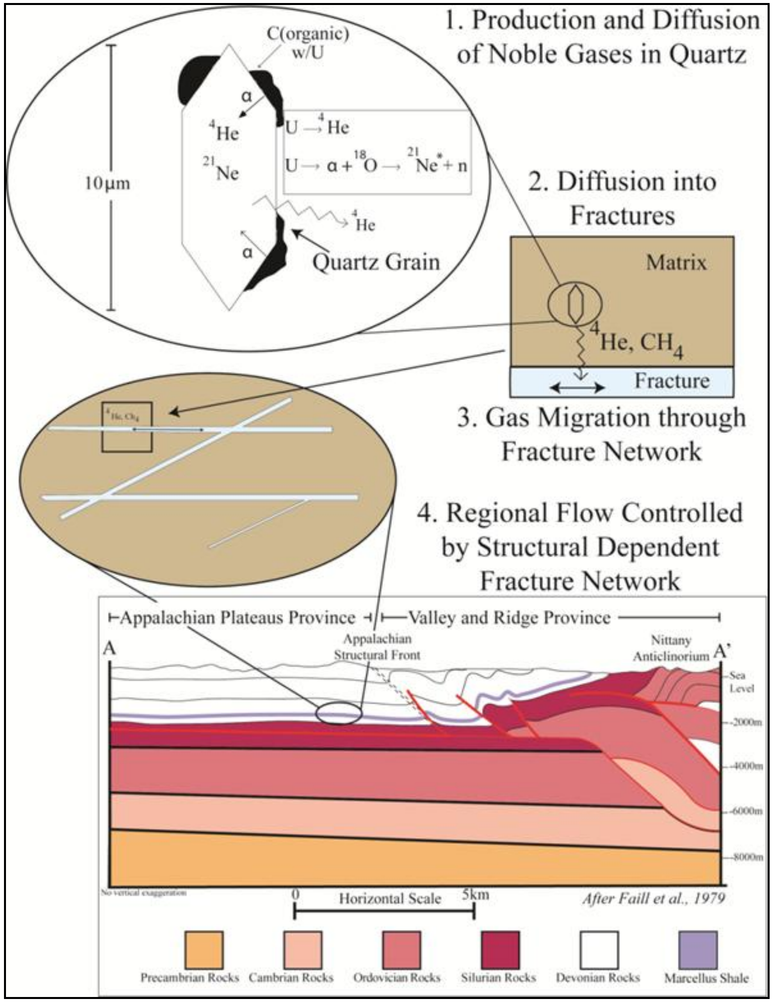
Background: Geology



Map of tectonic features in south Texas. Notice the three parallel fault belts within and north of the study area (Fowler, 1956).

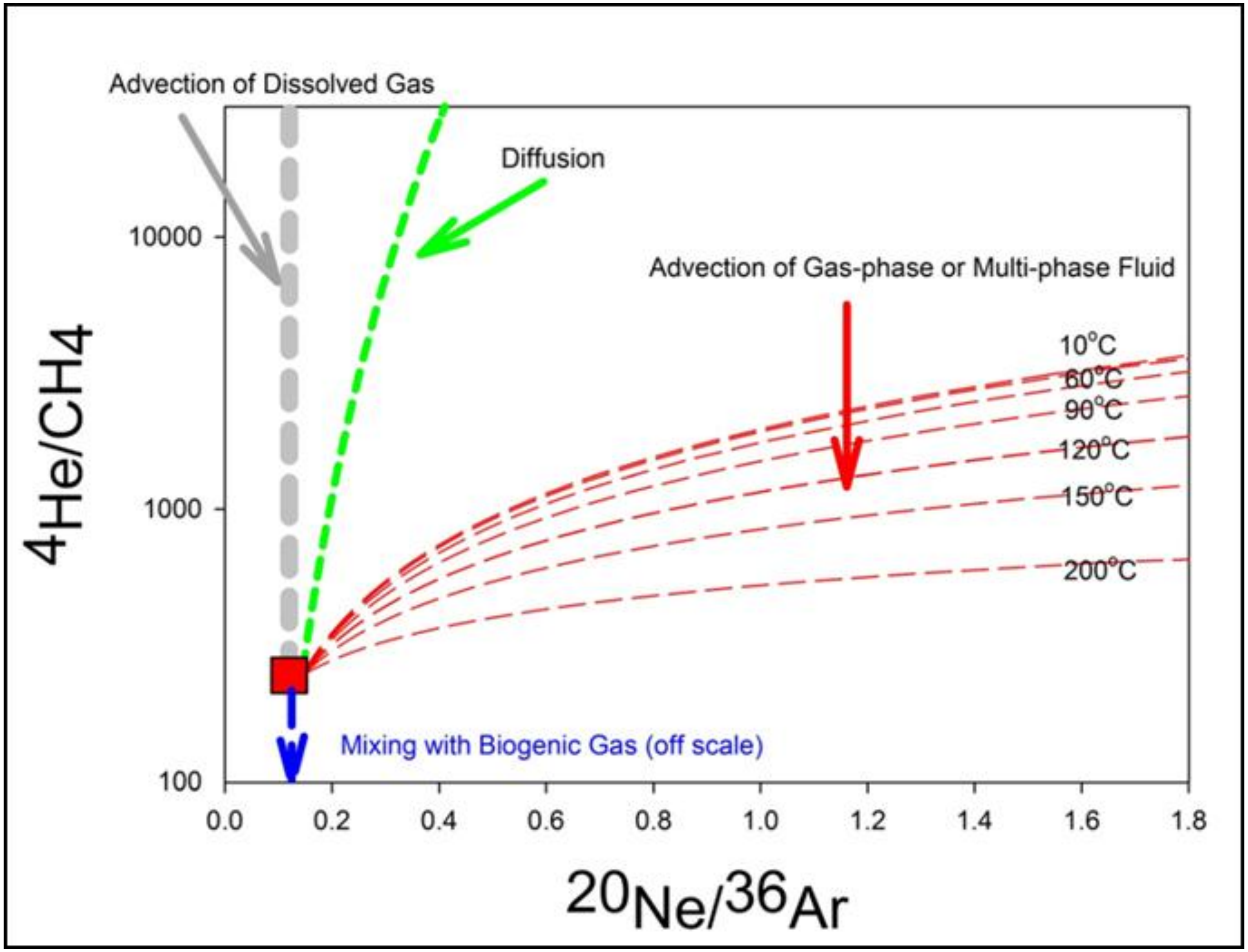
Background: Noble Gases

- Inert
- Low natural abundance
- Well-characterized isotopic composition
- Predictable behavior in fluids



Hunt et al, 2012

Background: Noble Gases



Darrah et al, 2014

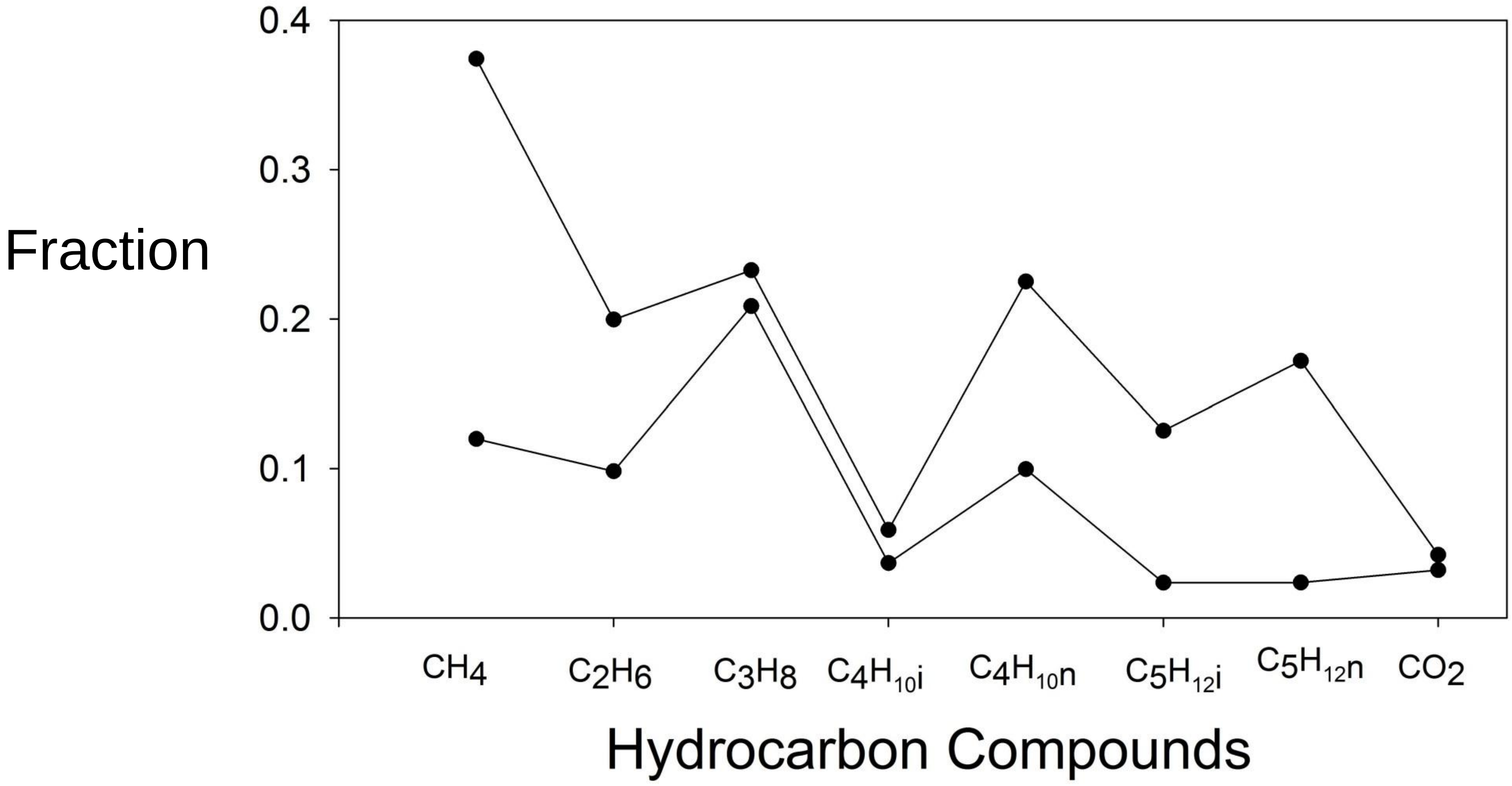
Methods

- 27 samples from horizontally-drilled and hydraulically fractured production wells
- Oil and associated gas collected on site
- Major gas components: SRS quadrupole MS and SRI GC
- Noble gas components: Thermo Fisher Helix SFT MS
- C_1-C_5 and isotopes: Thermo Fisher GC

Hydrocarbon Gas Composition

- Wet, oil-associated gases with C_2+/C_1 from 0.11 to 3.4

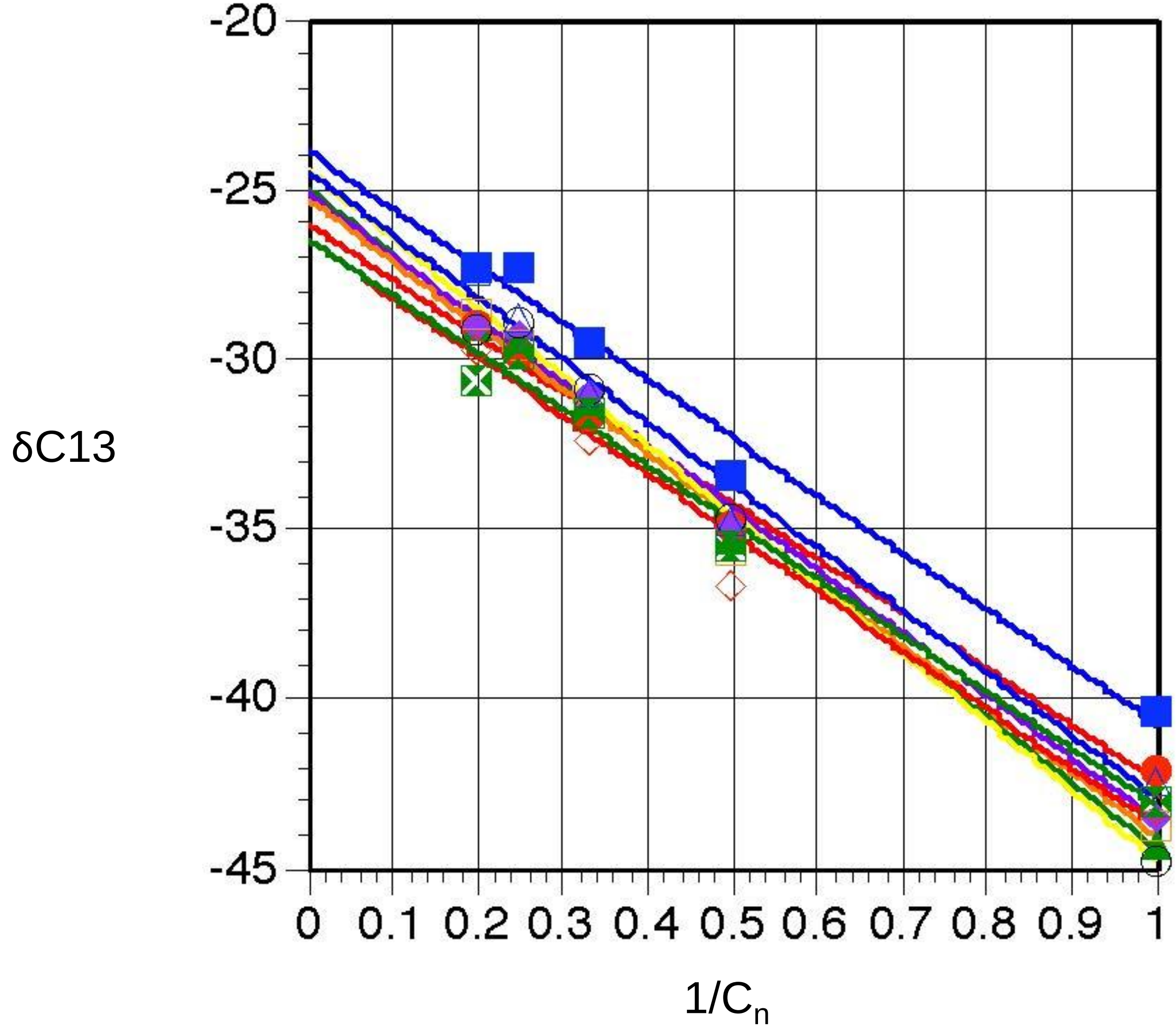
Hydrocarbon Gas Composition



Hydrocarbon Composition

- Wet gases with C_2+/C_1 from 0.11 to 1.4
- $\delta^{13}C\text{-}CH_4$ ranges from -48 to -36 per mil
- "Normal" (not reversed) stable isotopes (i.e., $\delta^{13}C\text{-}C_2H_6$ always heavier than $\delta^{13}C\text{-}CH_4$)

Stable Isotope Composition



After Chung, 1988

Hydrocarbon Composition

- Wet gases with C_2+/C_1 from 0.11 to 1.4
- $\delta^{13}C\text{-}CH_4$ ranges from -48 to -36 per mil
- “Normal” (not reversed) stable isotopes (i.e., $\delta^{13}C\text{-}C_2H_6$ always heavier than $\delta^{13}C\text{-}CH_4$)
- Suggests aliphatic hydrocarbons are formed during early stages of thermogenic maturation

Source of CO_2

Hypotheses:

- Thermal alteration of marine carbonates
- Microbial or inorganic oxidation of petroleum or organic carbon
- Externally sourced from mantle-derived fluids

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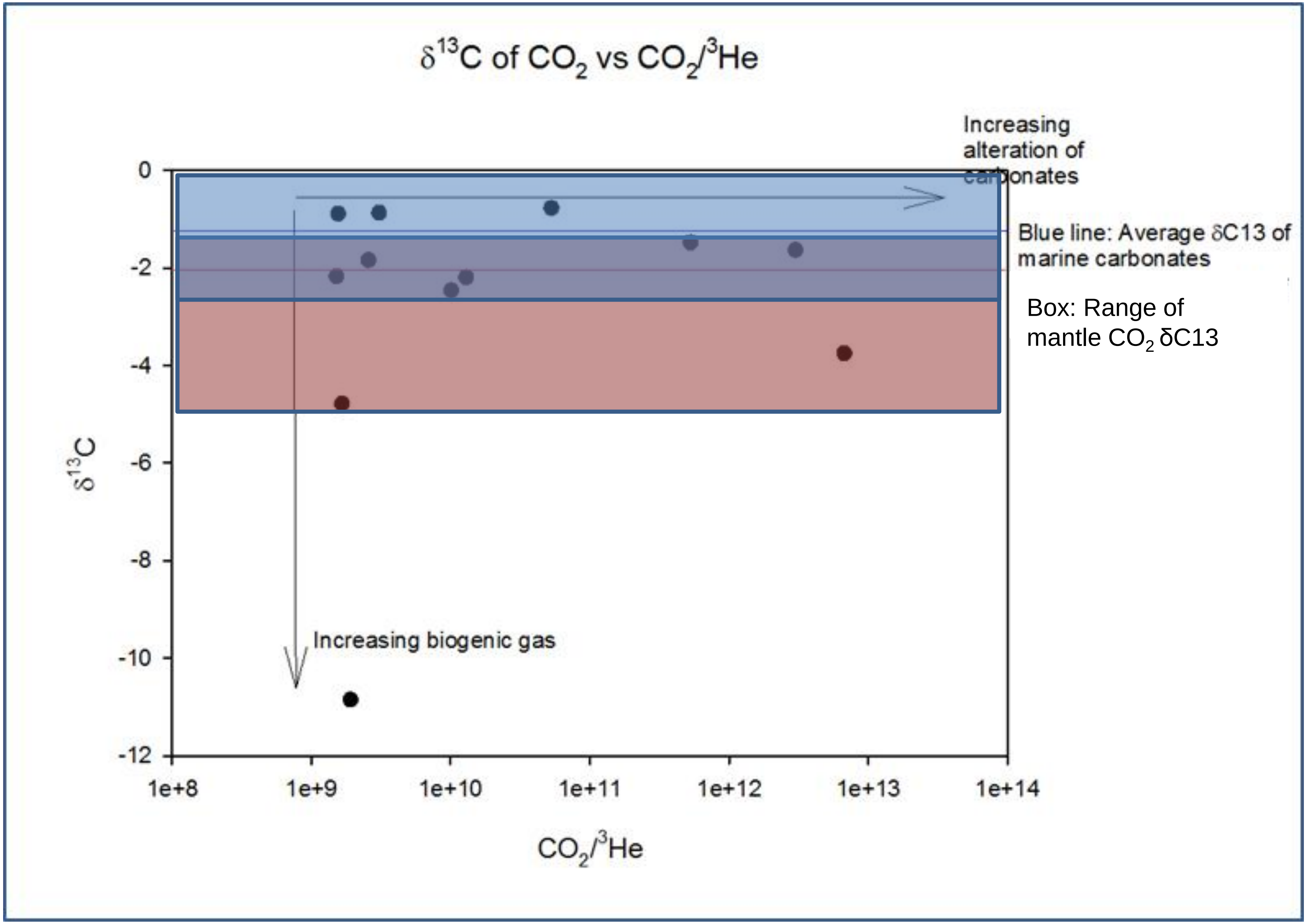
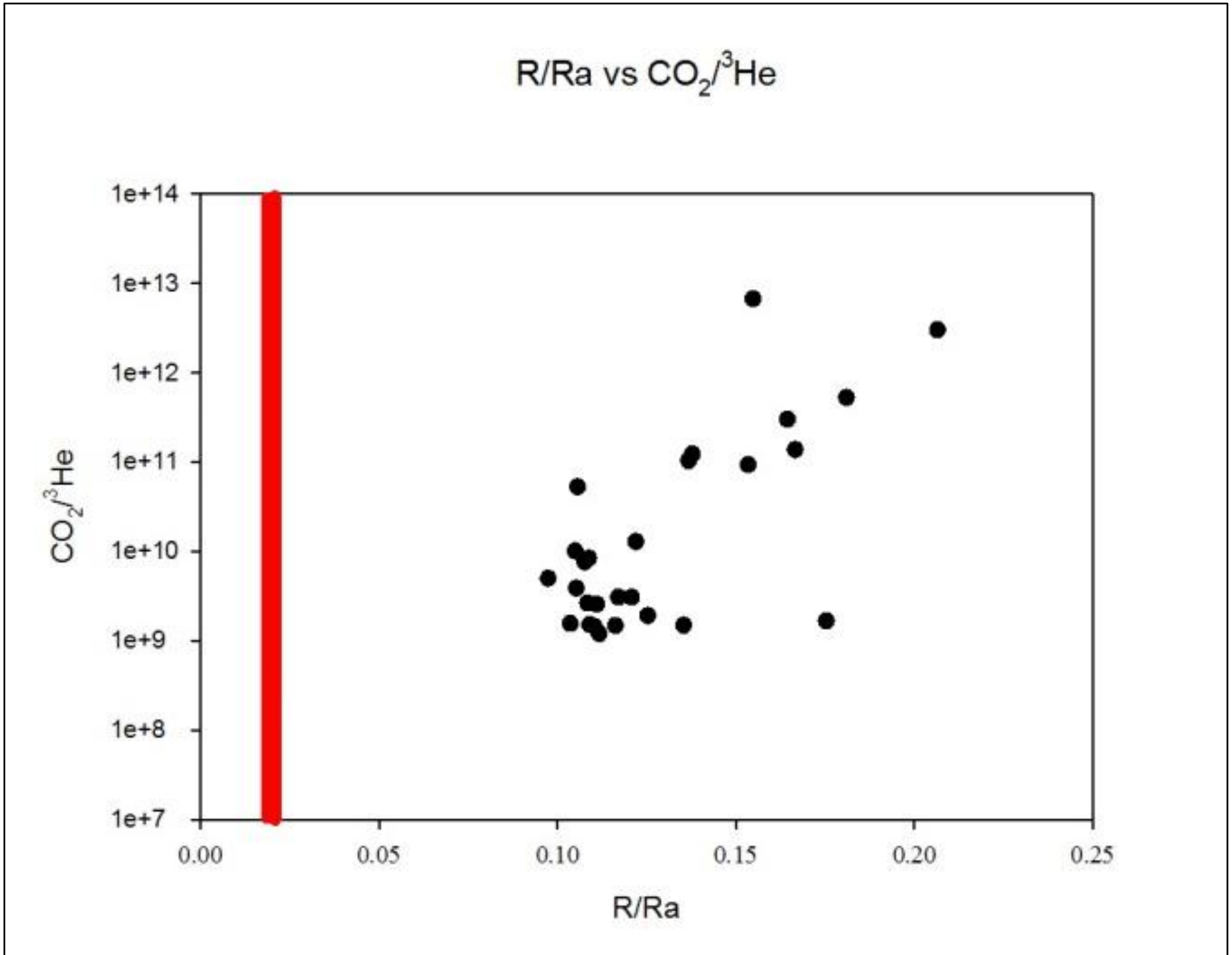
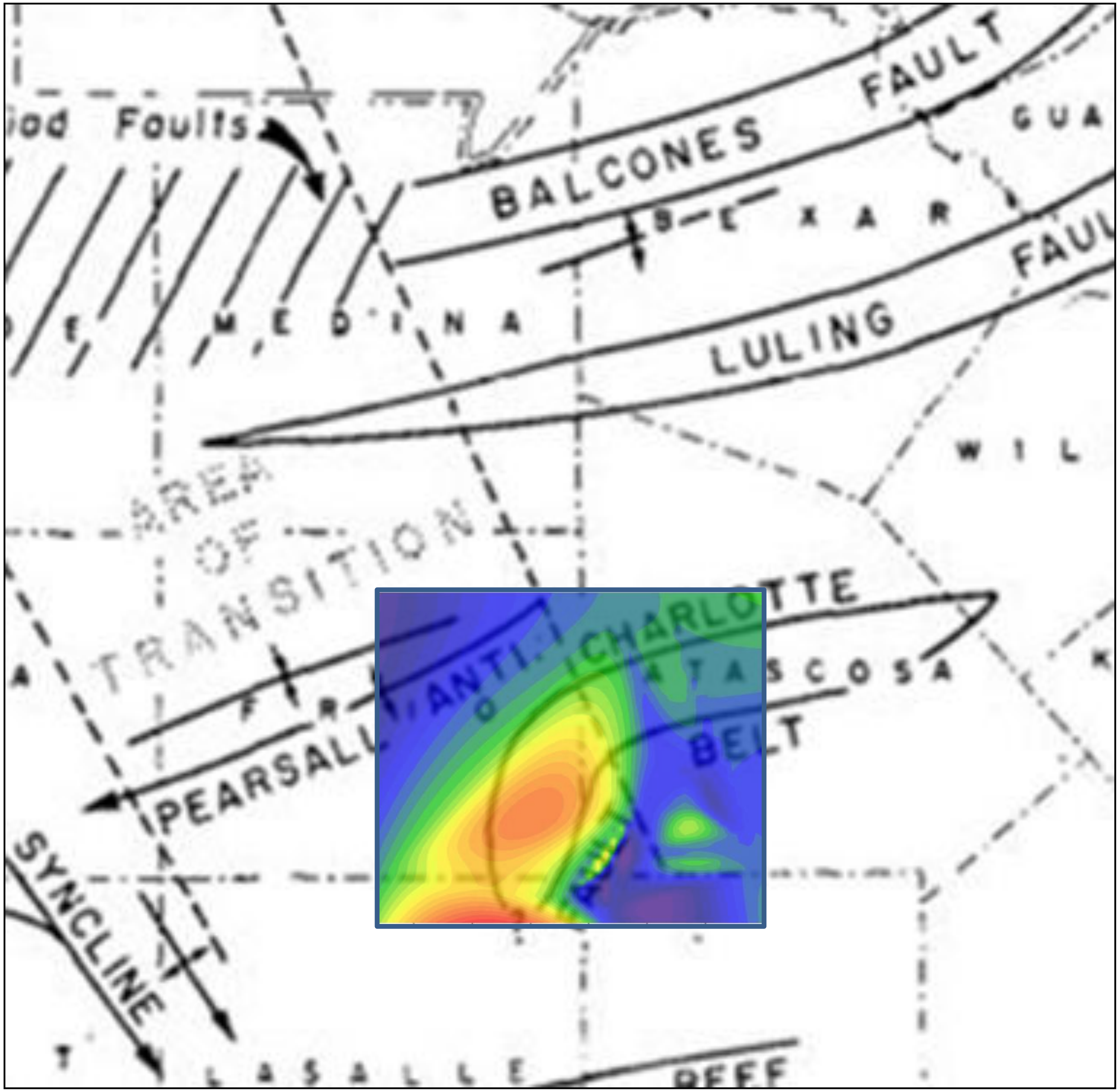
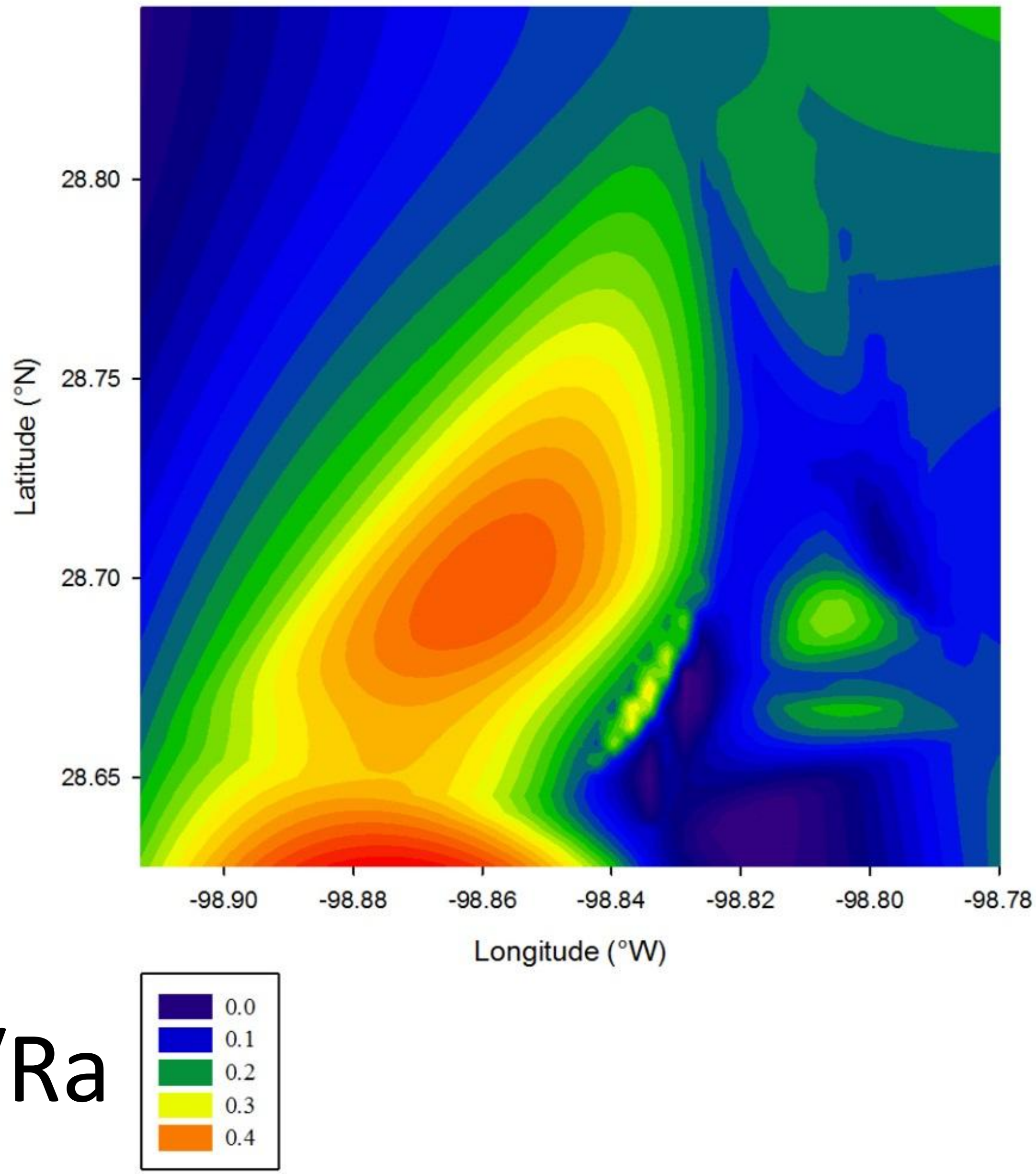


Source of CO_2





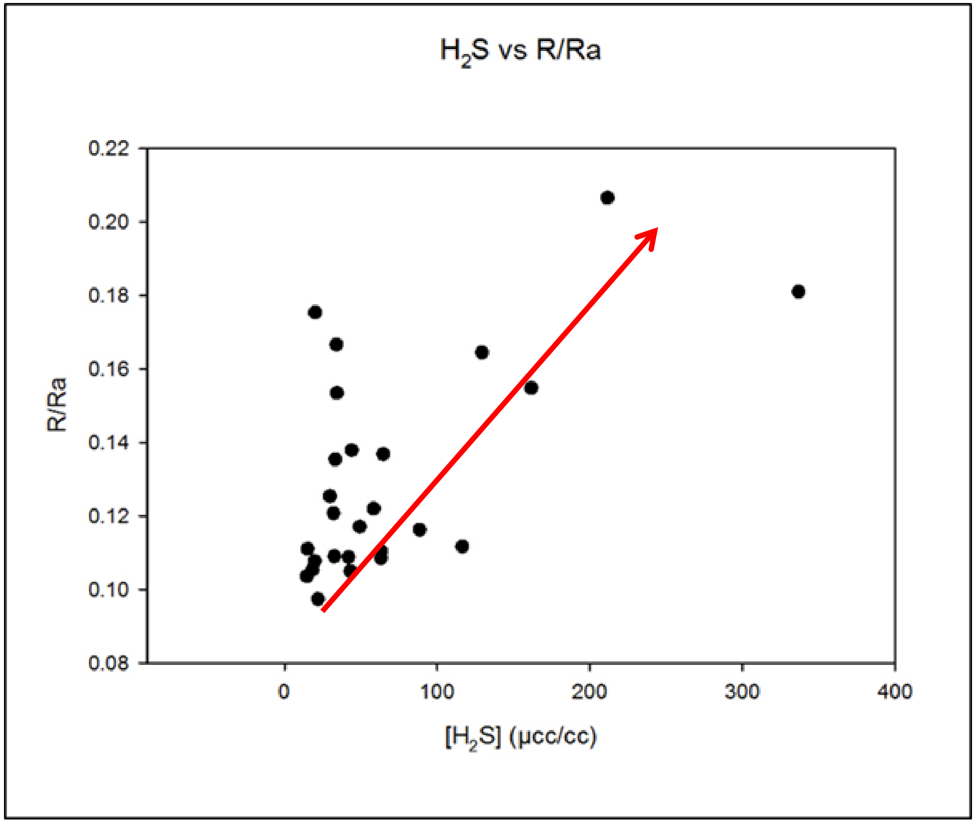
Overlay of R/Ra values in map view with structure map (Fowler, 1956) seen earlier, with red values >0.2 R/Ra


28.80
28.75
28.70
28.65
Latitude (°N)
-98.90
-98.88
-98.86
-98.84
-98.82
-98.80
-98.78
Longitude (°W)
0.0
0.1
0.2
0.3
0.4

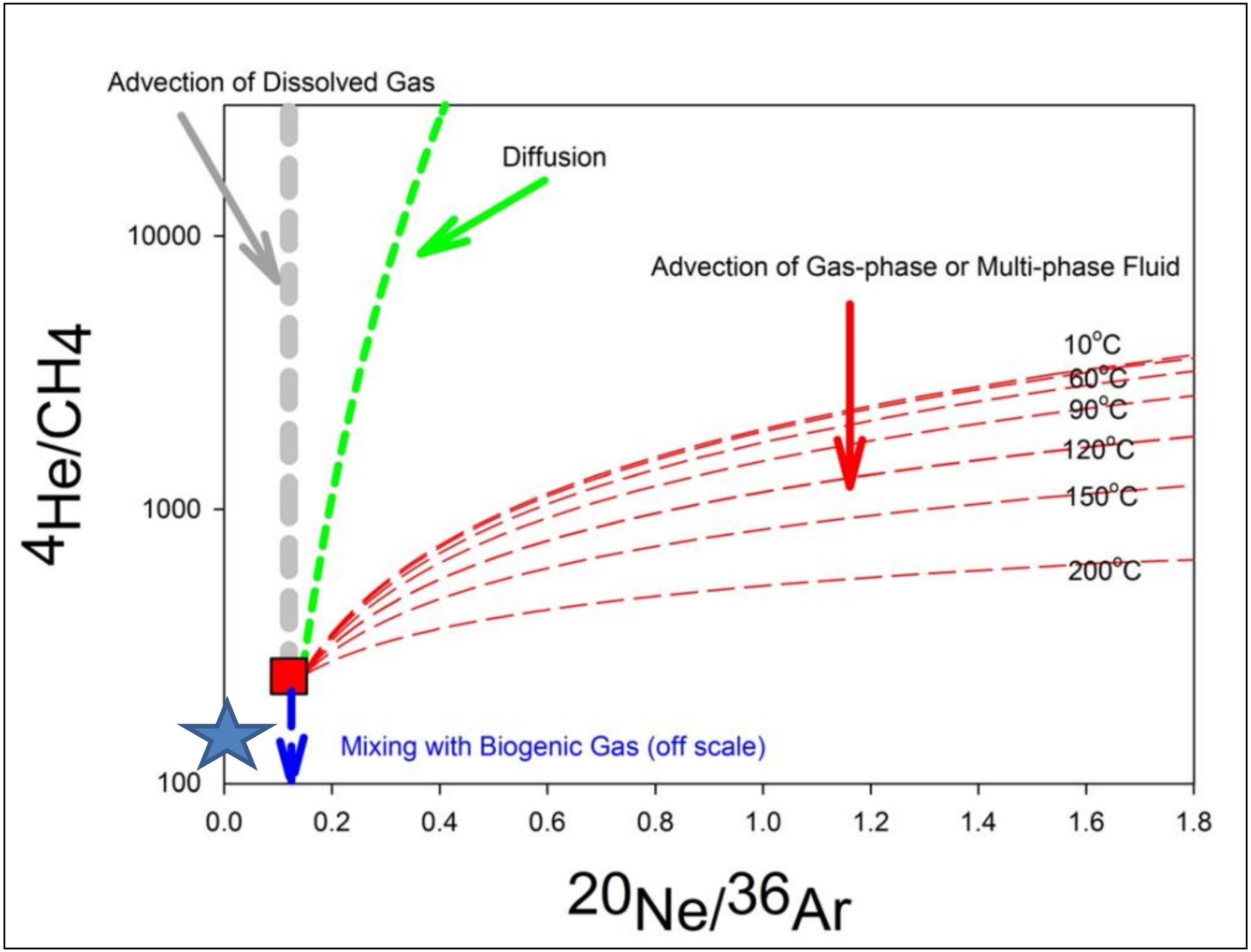
R/Ra

H_2S

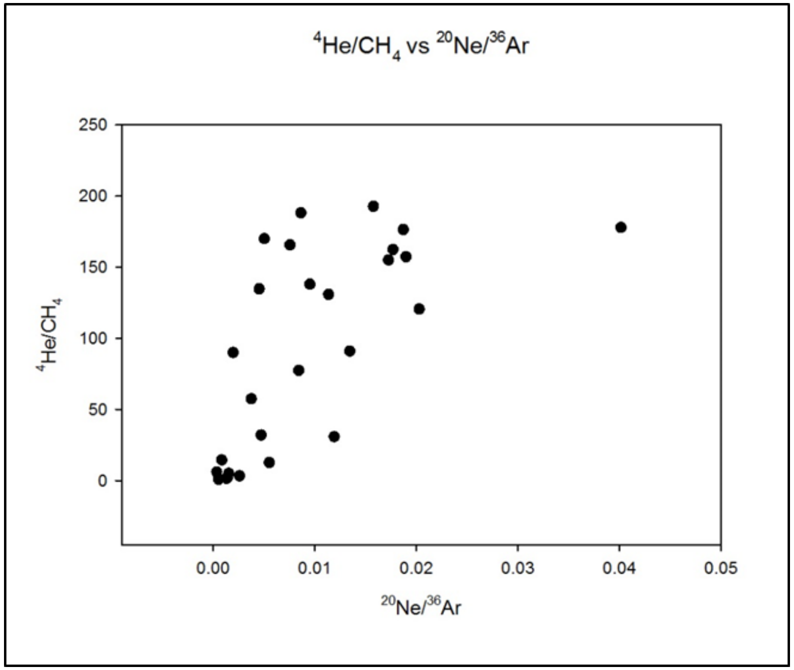
- Elevated H_2S levels associated with increased mantle components
- Suggest thermochemical sulfate reduction
- Can use mantle components to predict future H_2S hazard areas

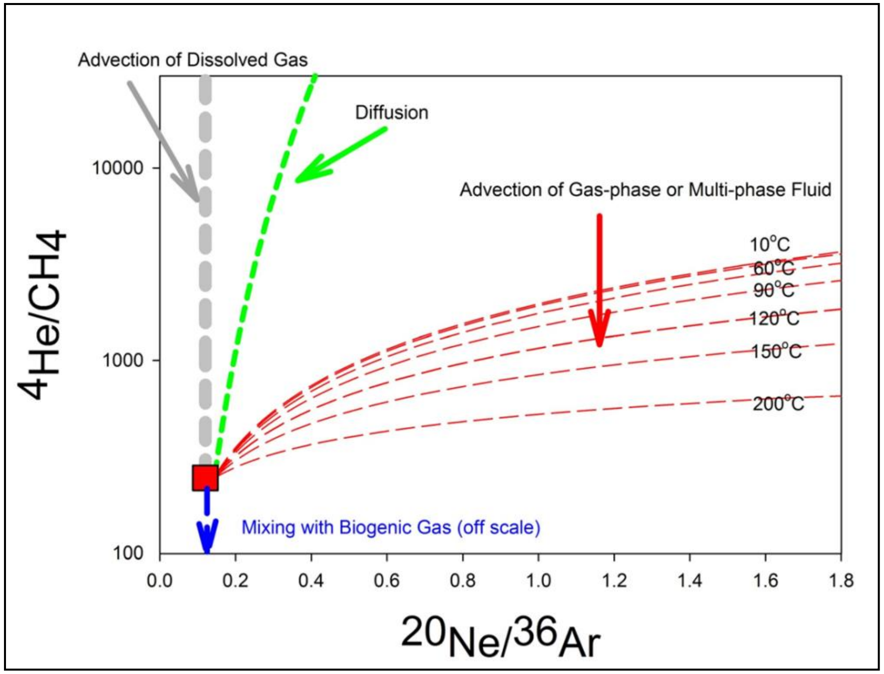


Noble Gases and Production



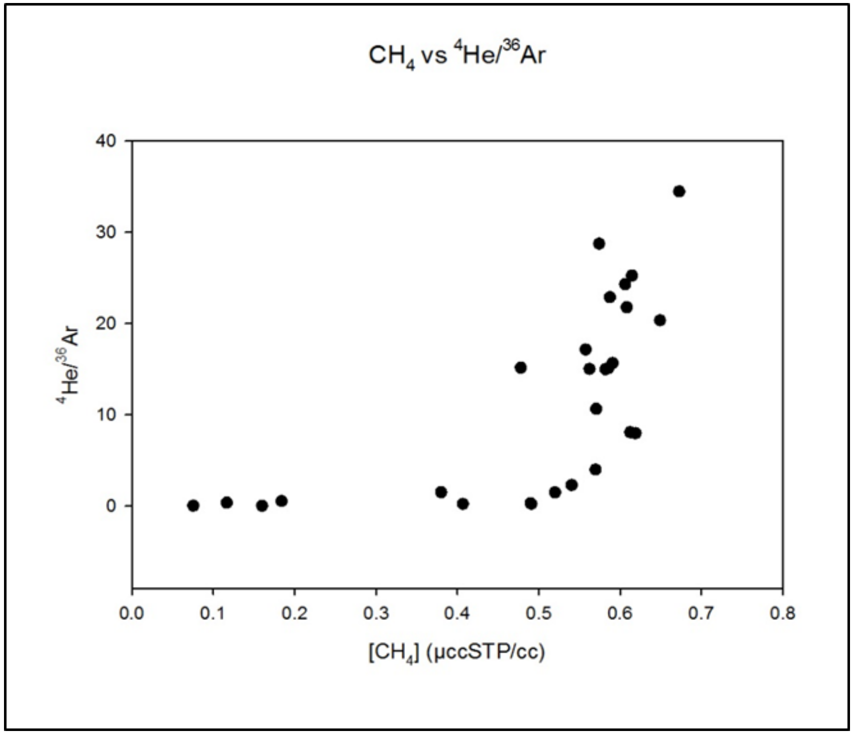
Noble Gases and Production

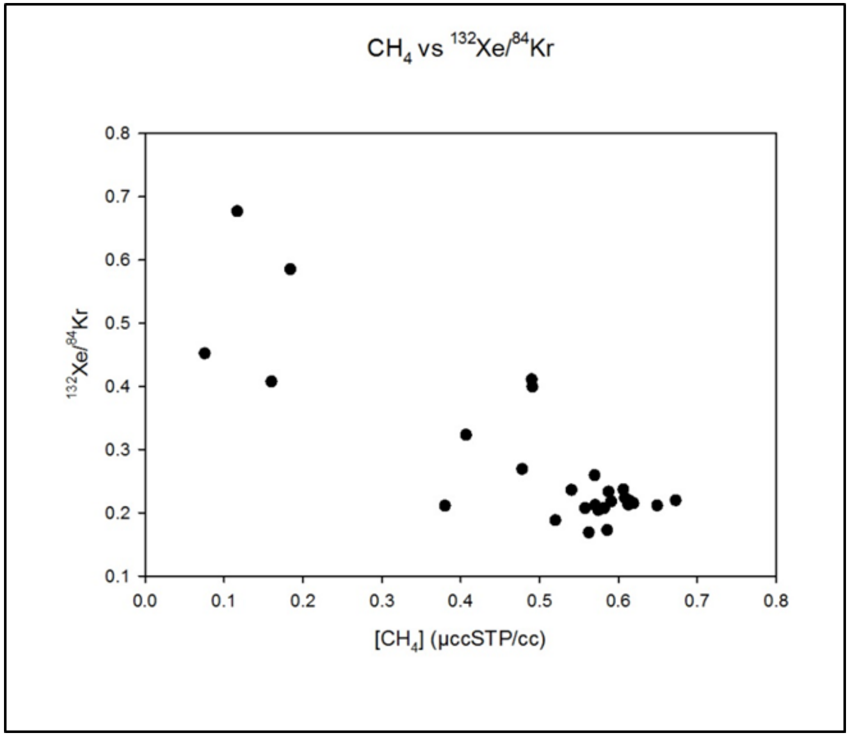




Darrah et al, 2014

Noble Gases and Production





Conclusions

- Eagle Ford fluids contain mantle-derived components
- An ancient rifting environment allowed for the necessary heat to generate excess CO_2 and H_2S by thermal alteration
- Noble gases allow us to determine the relative fluids-in-place within the field

Future Work

- Carefully map suspected areas with elevated H_2S (using R/Ra) to avoid future hazards
- Compare active and failed rift environments to determine mantle contributions and kinematic extent of intrusive bodies or hydrothermal circulation
- Model producible hydrocarbon potential based on noble gas data
- Find future industry collaborators for more robust sample suite

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The Ohio State University

Smart Gas sciences

Cabot Oil & Gas Corporation