Assessing Compositional Variability and Migration of Natural Gas in Antrim Shale in the Michigan Basin Using Noble Gas Geochemistry*

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Abstract

Recent studies in the Michigan Basin looked at the atmospheric and terrigenic noble gas signatures of deep brines to place constraints on the past thermal history of the basin and to assess the extent of vertical transport processes within this sedimentary system. In this contribution, we present noble gas data of shale gas samples from the Antrim Shale Formation in the Michigan Basin. The Antrim Shale was one of the first economic shale-gas plays in the U.S. and has been actively developed since the 1980's. This study pioneers the use of noble gases in subsurface shale gas in the Michigan Basin to clarify the nature of vertical transport processes within the sedimentary sequence and to assess potential variability of noble gas signatures in shales. Antrim Shale gas samples were analyzed for all stable noble gases (He, Ne, Ar, Kr, Xe) from samples collected at depths between 300 and 500 m. Preliminary results show R/Ra values (where R and Ra are the measured and atmospheric 3He/4He ratios, respectively) varying from 0.022 to 0.21. Although most samples fall within typical crustal R/Ra range values (~0.02-0.05), a few samples point to the presence of a mantle He component with higher R/Ra ratios. Samples with higher R/Ra values also display higher 20Ne/22Ne ratios, up to 10.4, and further point to the presence of mantle 20Ne. The presence of crustally produced nucleogenic 21Ne and radiogenic 40Ar is also apparent with 21Ne/22Ne ratios up to 0.033 and 40Ar/36Ar ratios up to 312. The presence of crustally produced 4He, 21Ne and 40Ar is not spatially homogeneous within the Antrim shale. Areas of higher crustal 4He production appear distinct to those of crustally produced 21Ne and 40Ar and are possibly related the presence of different production levels within the shale with varying concentrations of parent elements.

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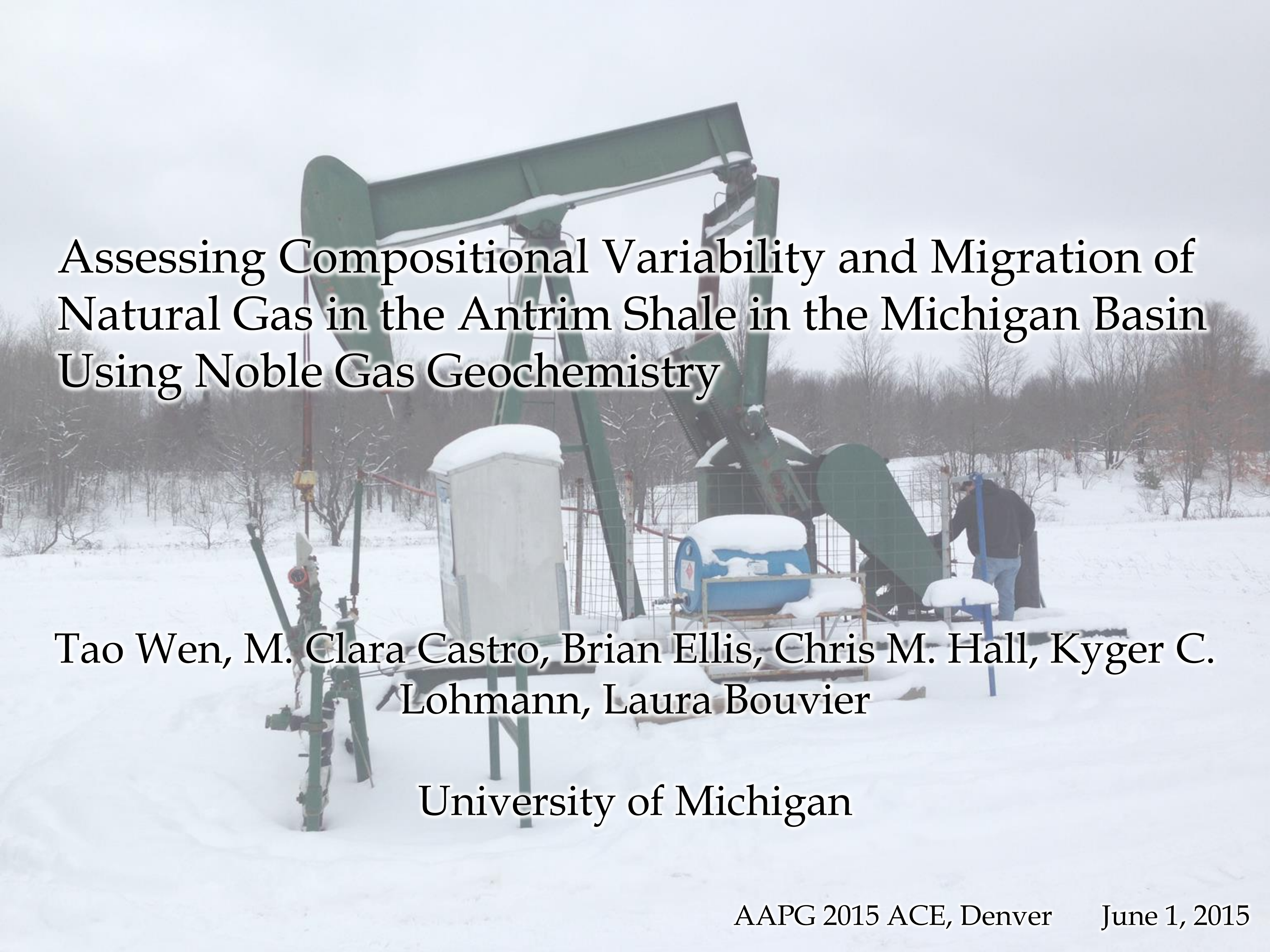

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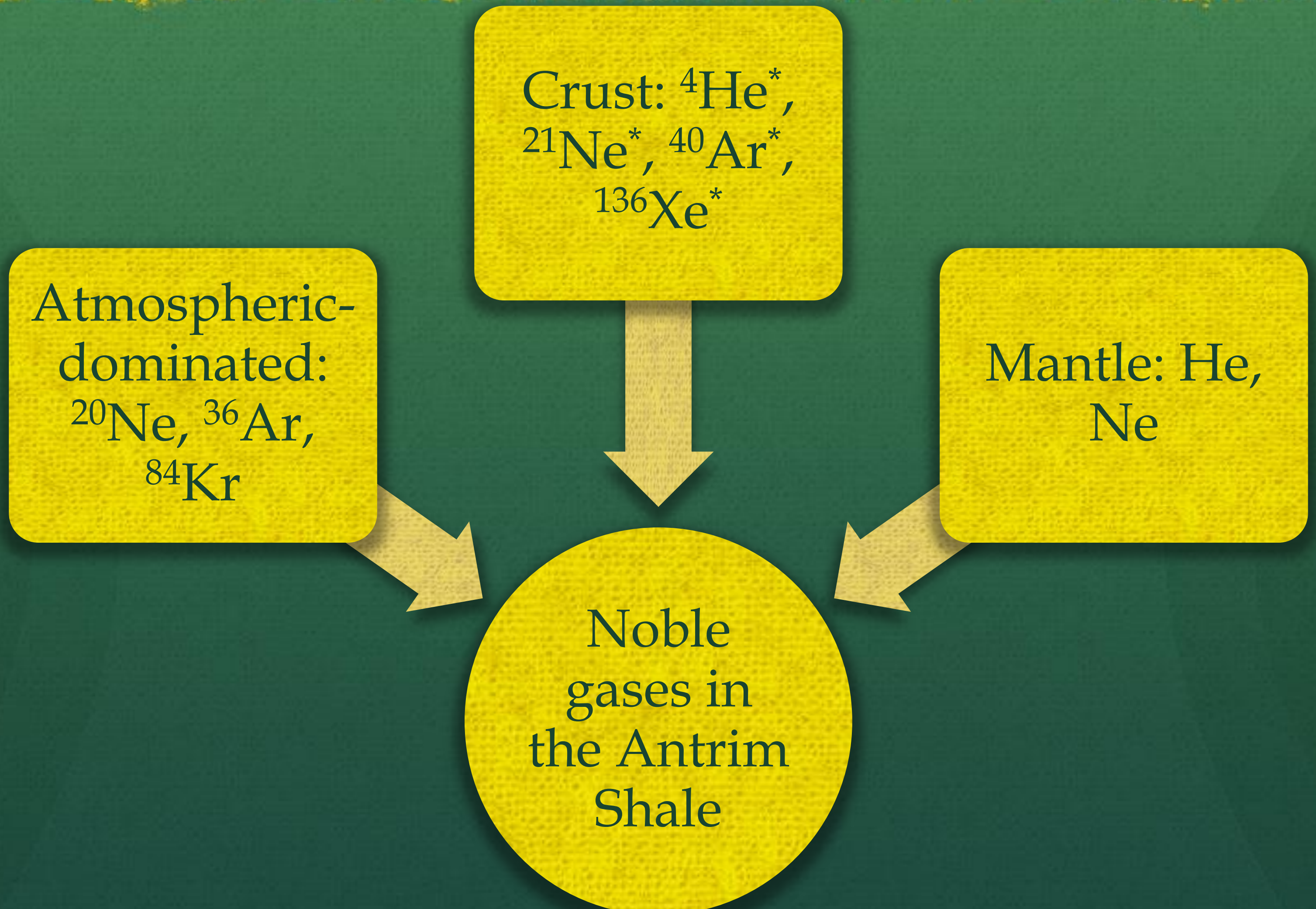
Outline

- Introduction
  - Noble gas systematics in subsurface fluids (SF)
  - Geologic setting of Antrim Shale
- Goals of Study
- Noble Gas Signatures (He, Ne, Ar, Kr and Xe) in the Antrim Shale
  - Compositional variability
  - Water/gas migration and mixing

Noble gases are inert and stable

- Affected almost exclusively by physical processes when dissolved in groundwater
- Solubility of noble gases is temperature dependent

Noble gas systematics in subsurface fluids (SF)



Each source has distinct noble gas isotopic ratios:

1. Atmosphere (ASW)

R=$^{3}He/^{4}He$ and Ra is the atmospheric $^{3}He/^{4}He$ ratio (Ra = 1.384 * 10^{-6}).

R/Ra= 1 $^{21}Ne/^{22}Ne$= 0.029 $^{20}Ne/^{22}Ne$= 9.8 $^{40}Ar/^{36}Ar$ = 295.5

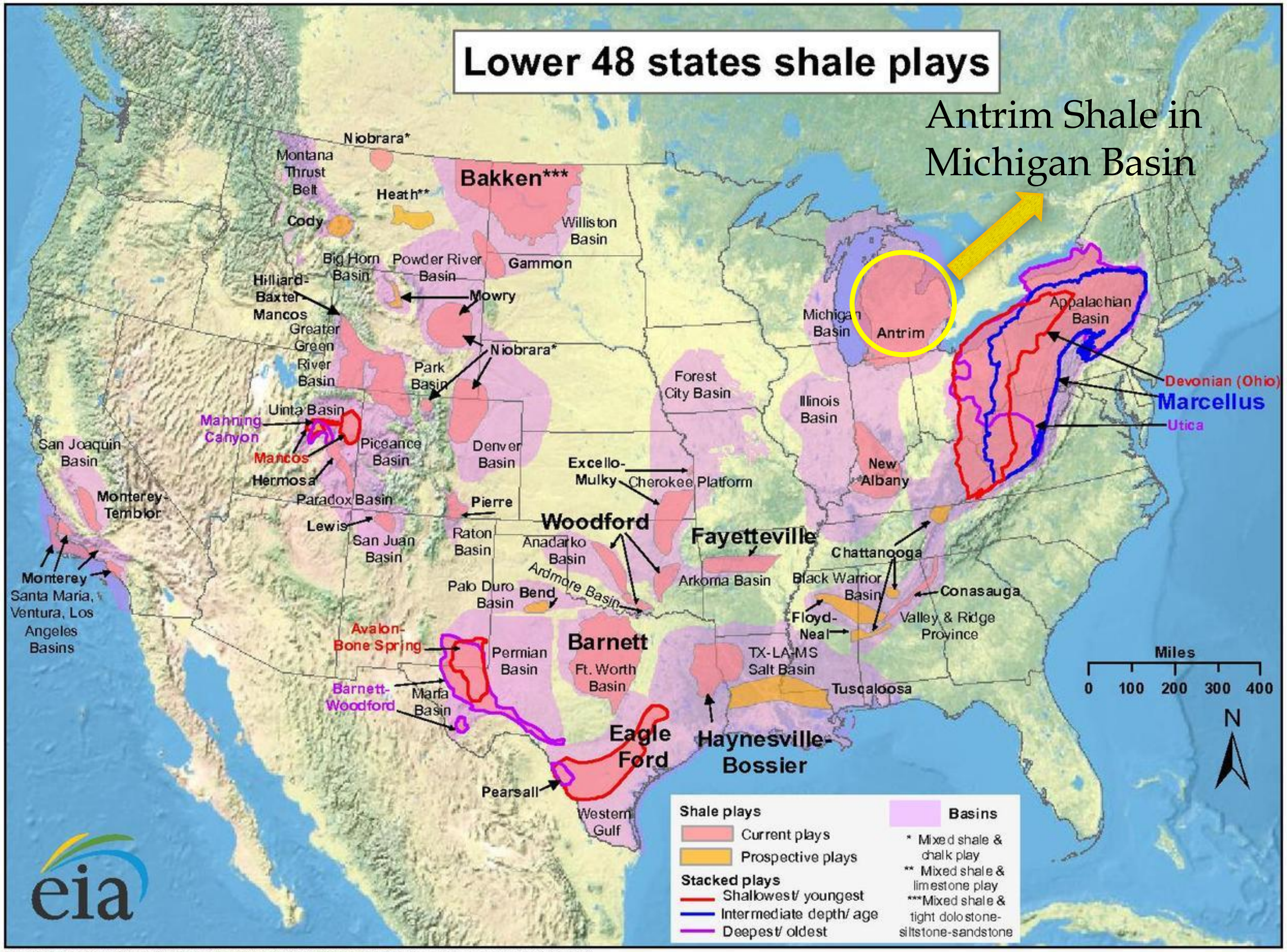
2. Crustal (radiogenic/nucleogenic component)

$0.02 \leq R/Ra \leq 0.05$ $^{21}Ne/^{22}Ne > 0.0290$ $^{40}Ar/^{36}Ar > 295.5$

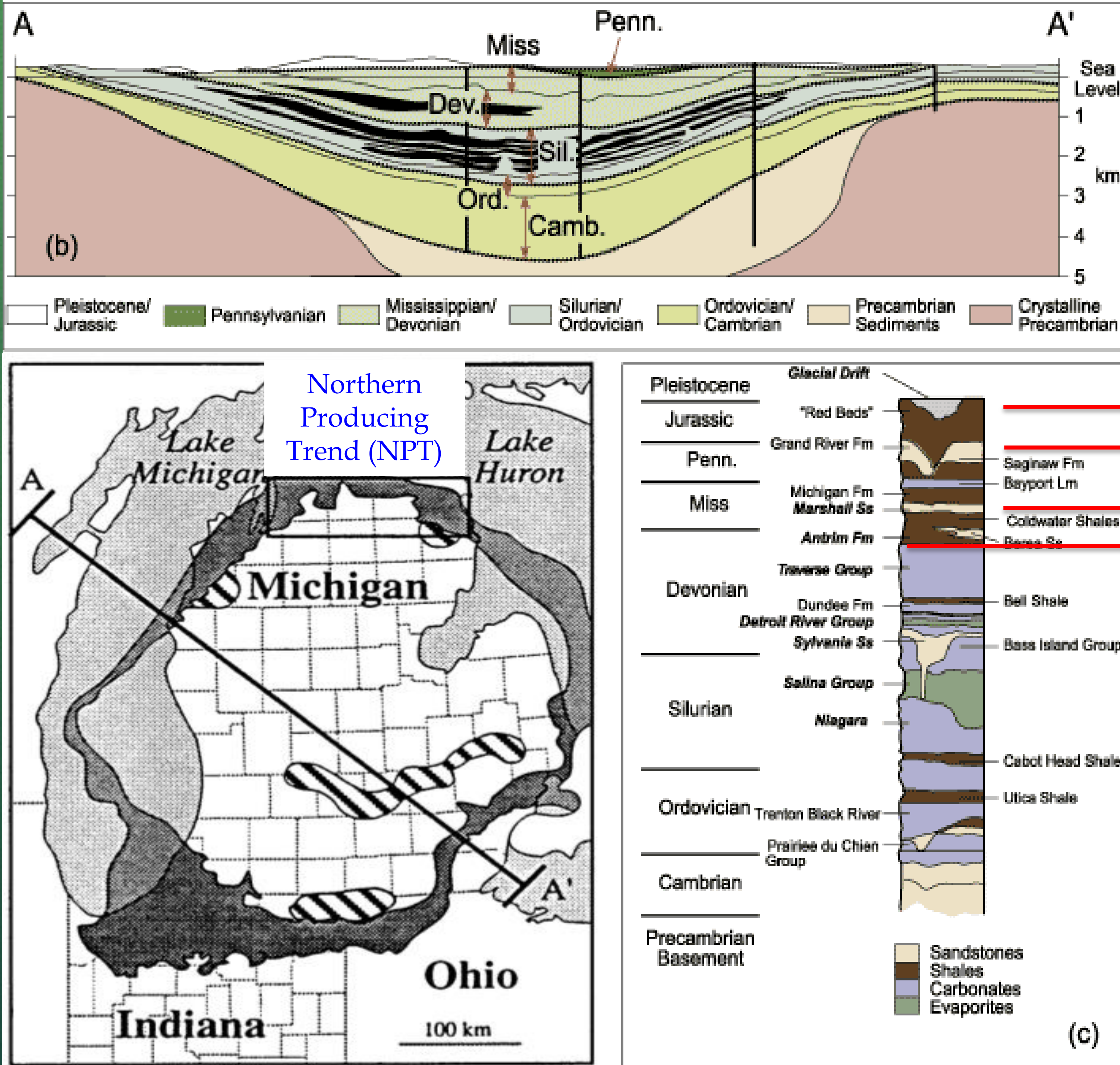
3. Mantle

$\sim 8 \leq R/Ra \leq \sim 50$ $9.8 < {}^{20}Ne/^{22}Ne \leq 13.8$

US Active Shale Gas Plays

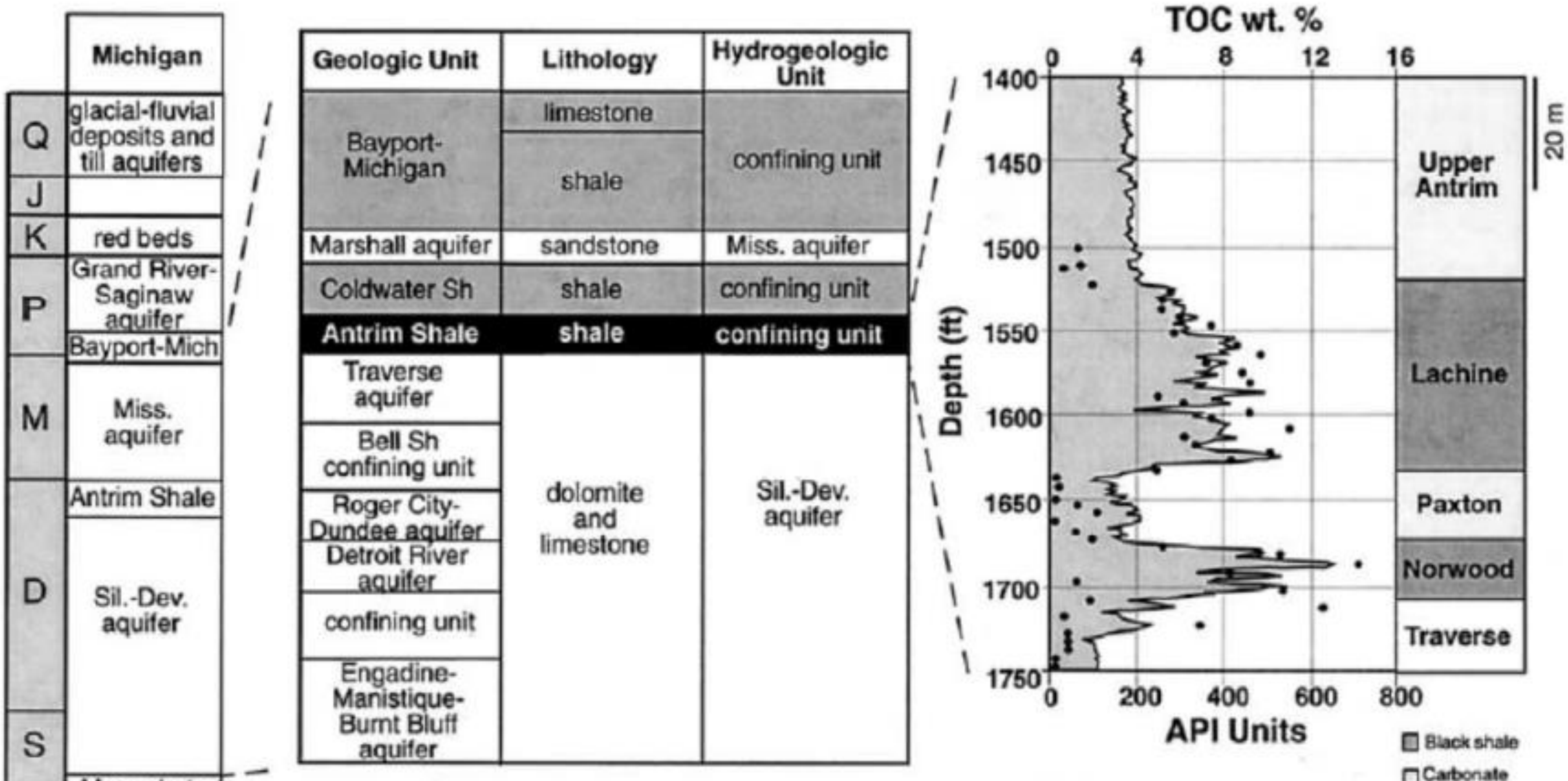


Source: Energy Information Administration based on data from various published studies.
Updated: May 9, 2011



(adapted from Martini *et al.*, 1998 Ma et *al.*, 2005)

Antrim Shale in the Michigan Basin



(McIntosh *et al.*, 2002; Curtis, 2002)

The Antrim Shale is unlike most other shale gas plays in the US

- Highly naturally fractured shale (higher than usual permeability thickness: 1-5000 md-ft)
- Highly variable TOC (also variable U conc.)
- Very shallow formation (180m – 730m)
- It contains both thermogenic and biogenic methane

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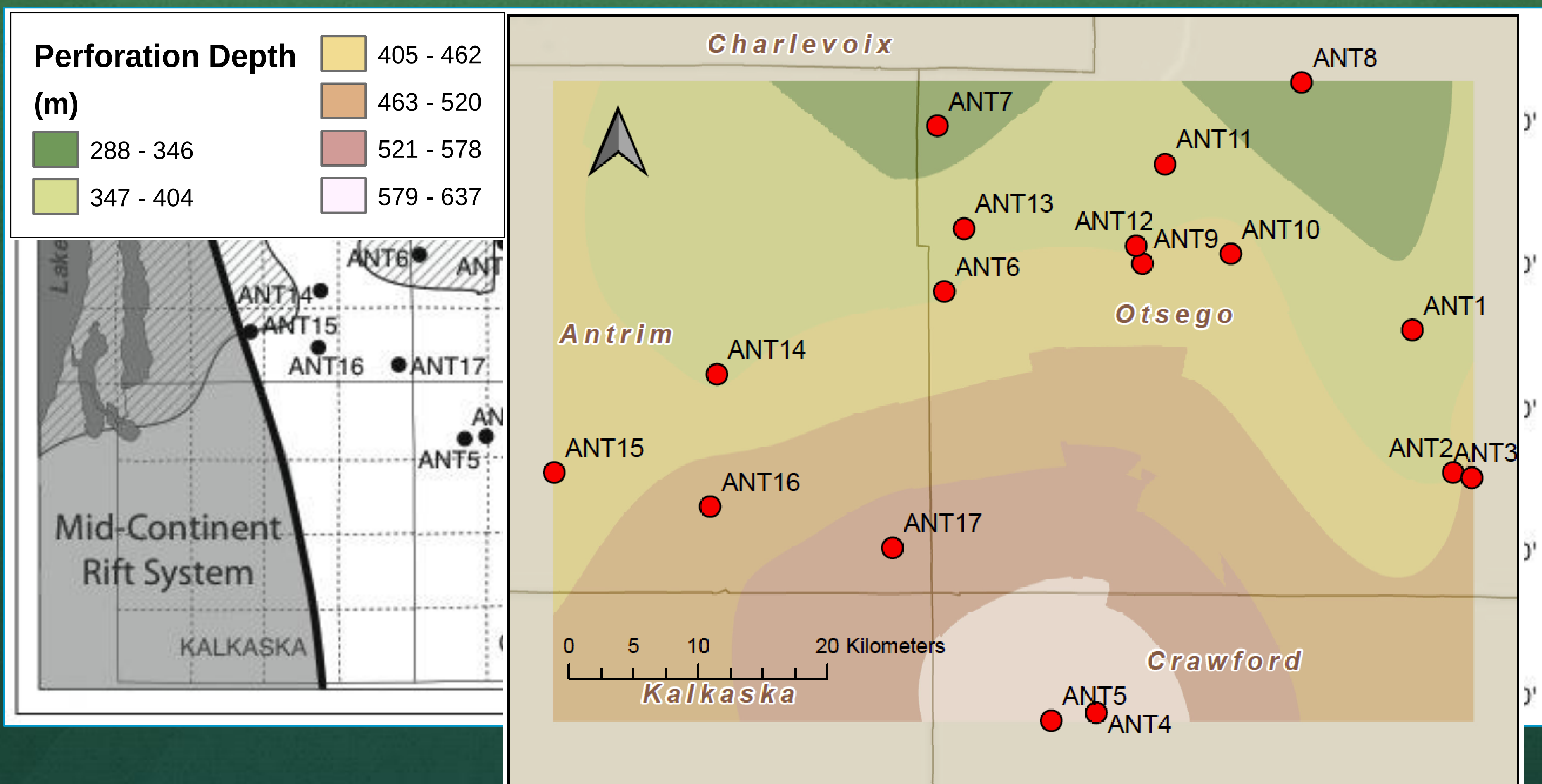
Questions being addressed in our study

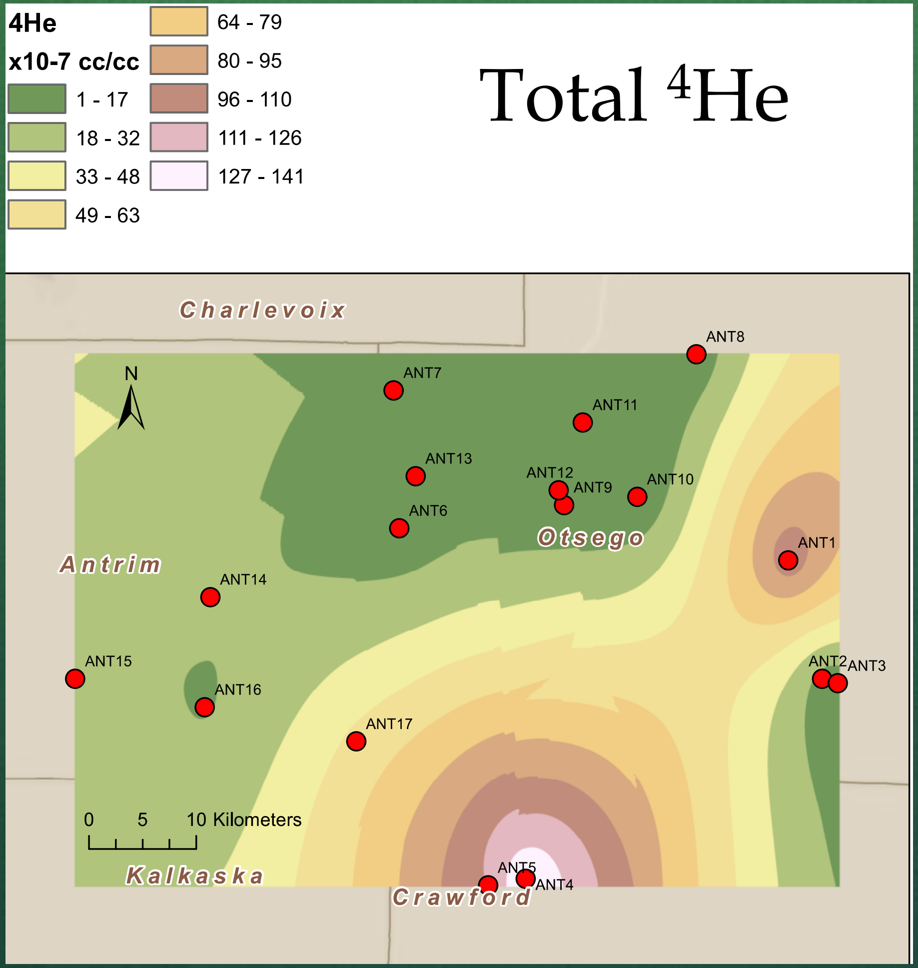
- To assess the compositional variability of crustal noble gases, which in turn, would point to variations in U, Th and K in the Antrim Shale
  - To explore potential vertical transport processes and the extent of water-gas interactions and mixing
- To investigate the potential of noble gases at distinguishing between thermogenic and biogenic methane in the Northern Producing Trend (NPT) of the Antrim Shale

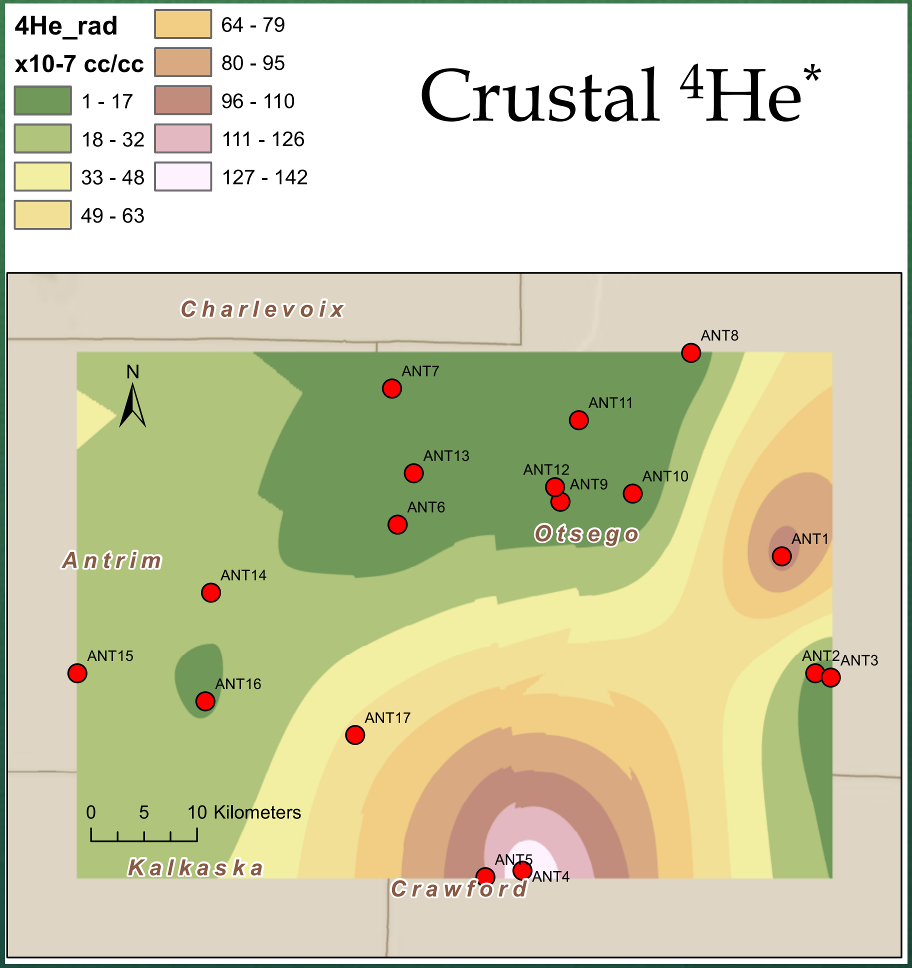
Northern Producing Trend of the Antrim Shale

- 17 shale gas wells were sampled for noble gas analyses

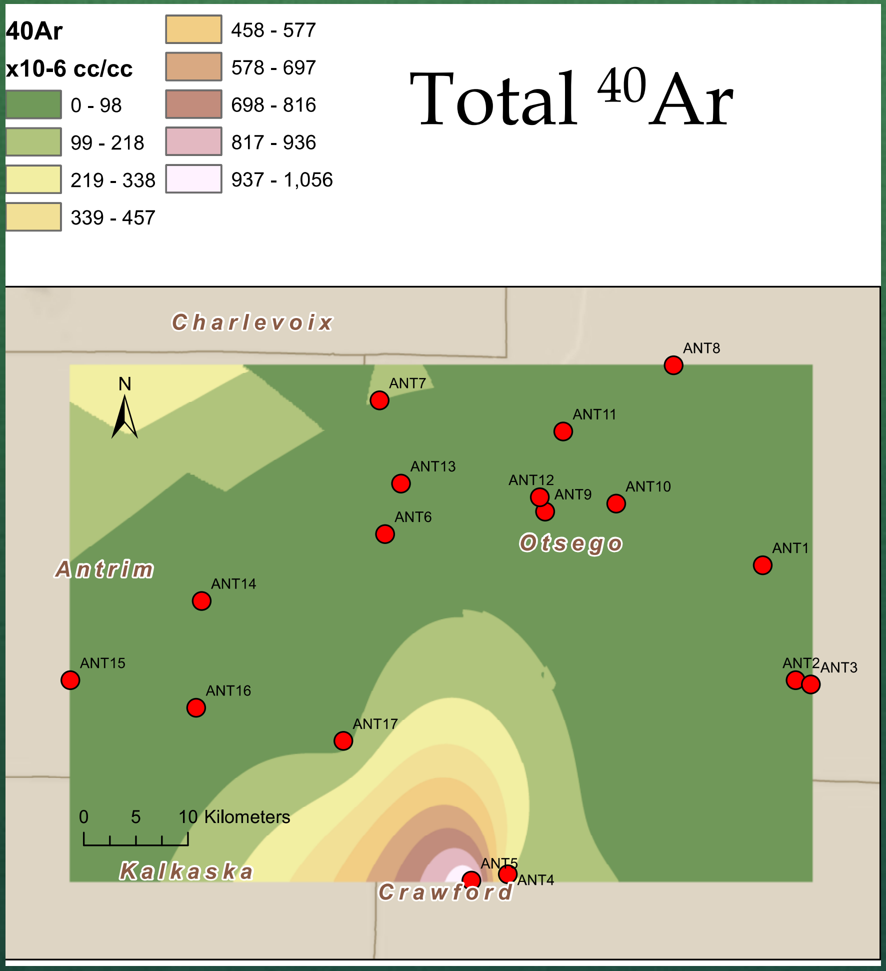


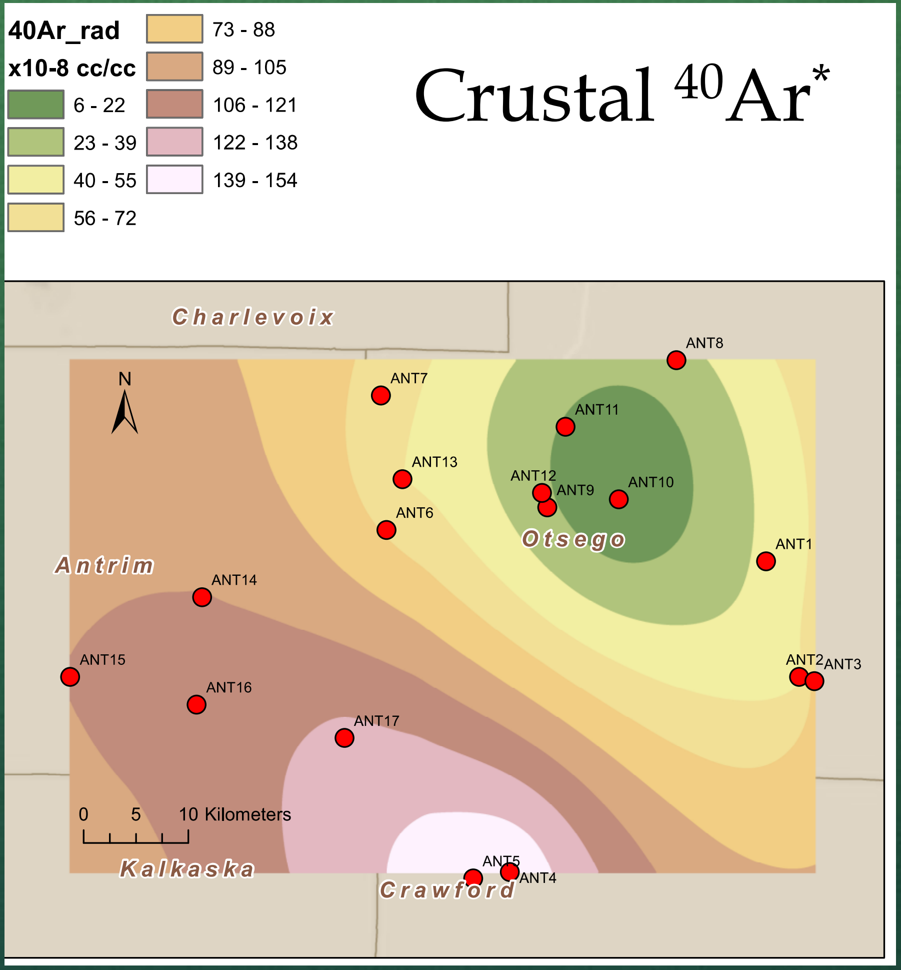
Horizontal: ^{4}He vs. $^{4}He^{*}$
Parent elements: U and Th



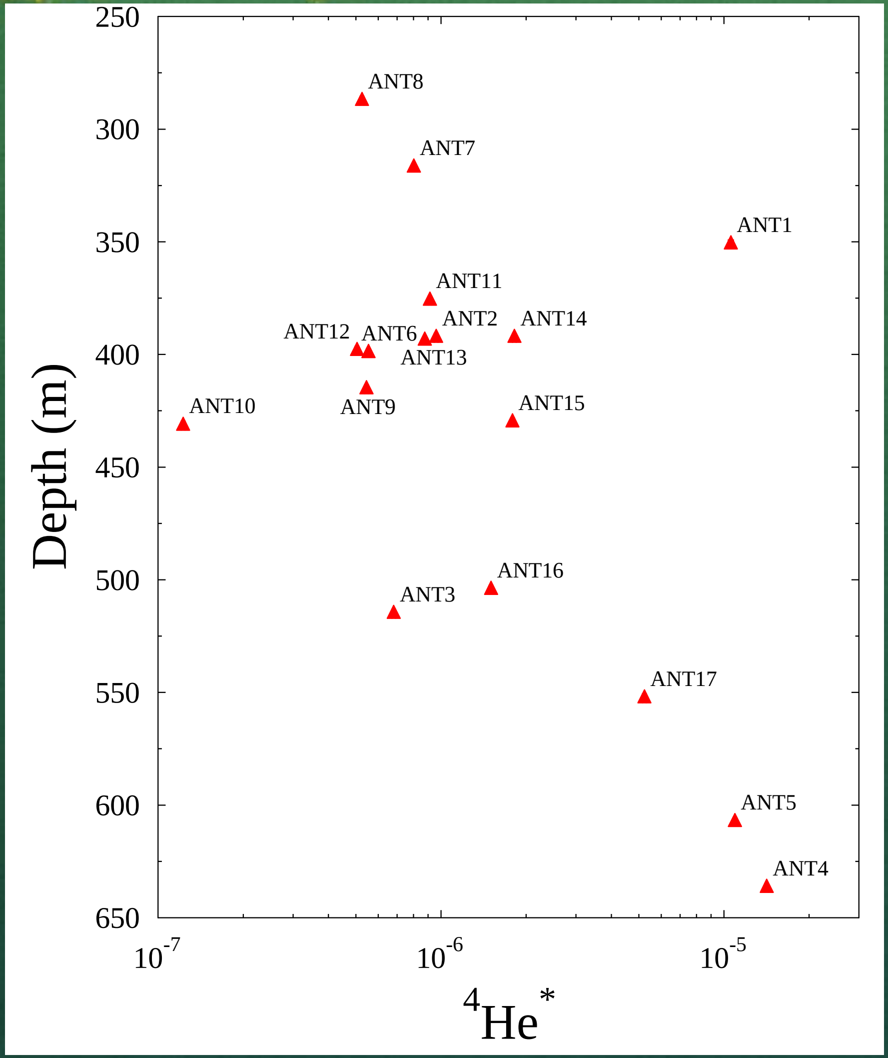


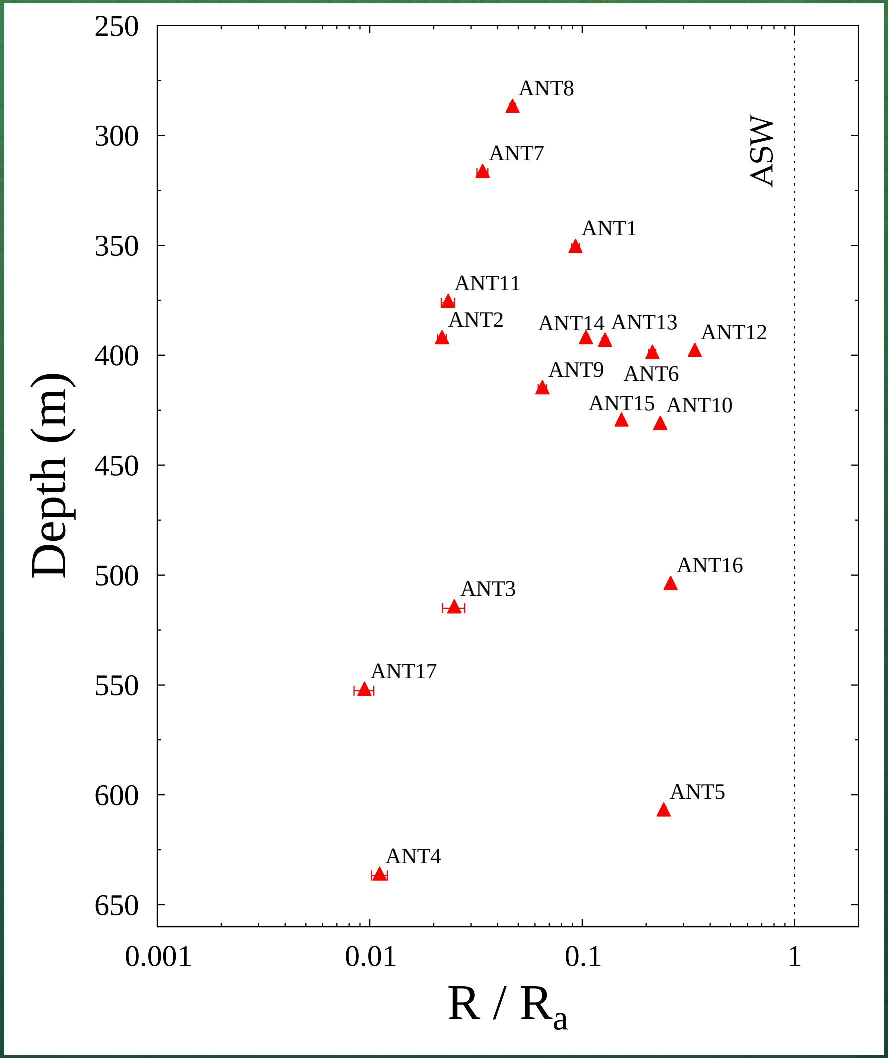
Horizontal: ^{40}Ar vs. ^{40}Ar*
Parent element: ^{40}K



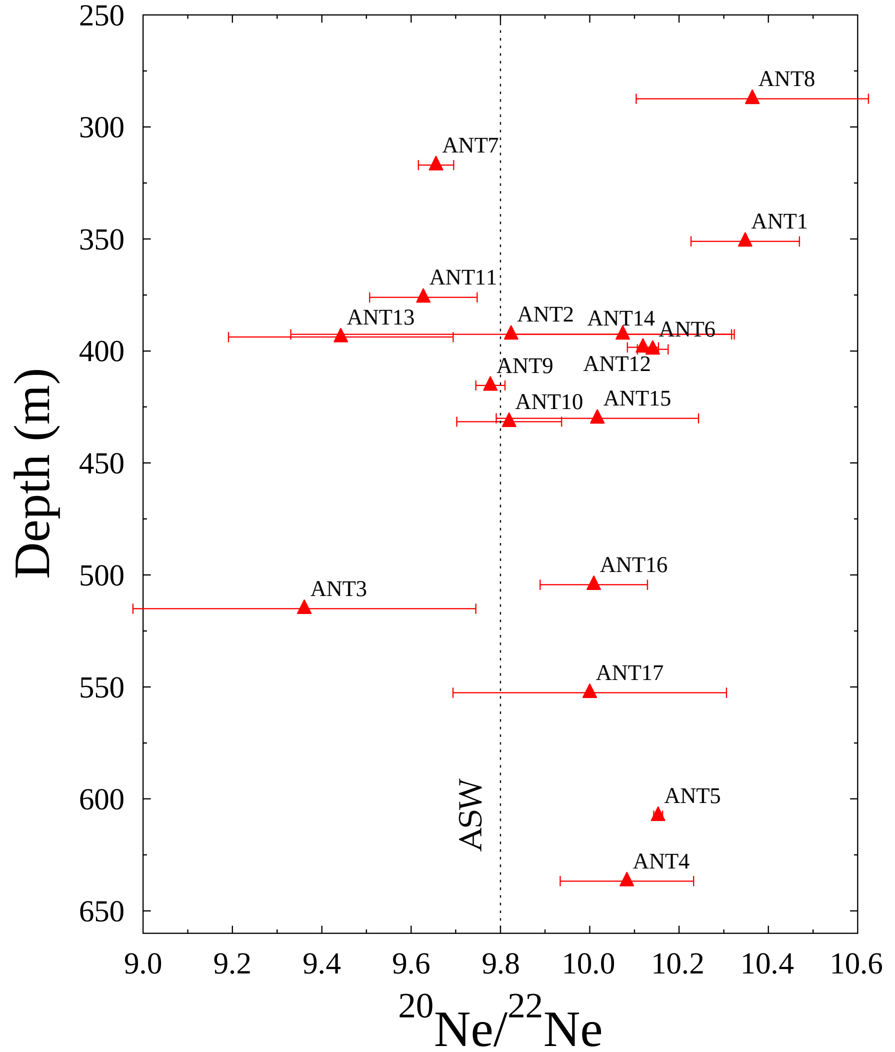


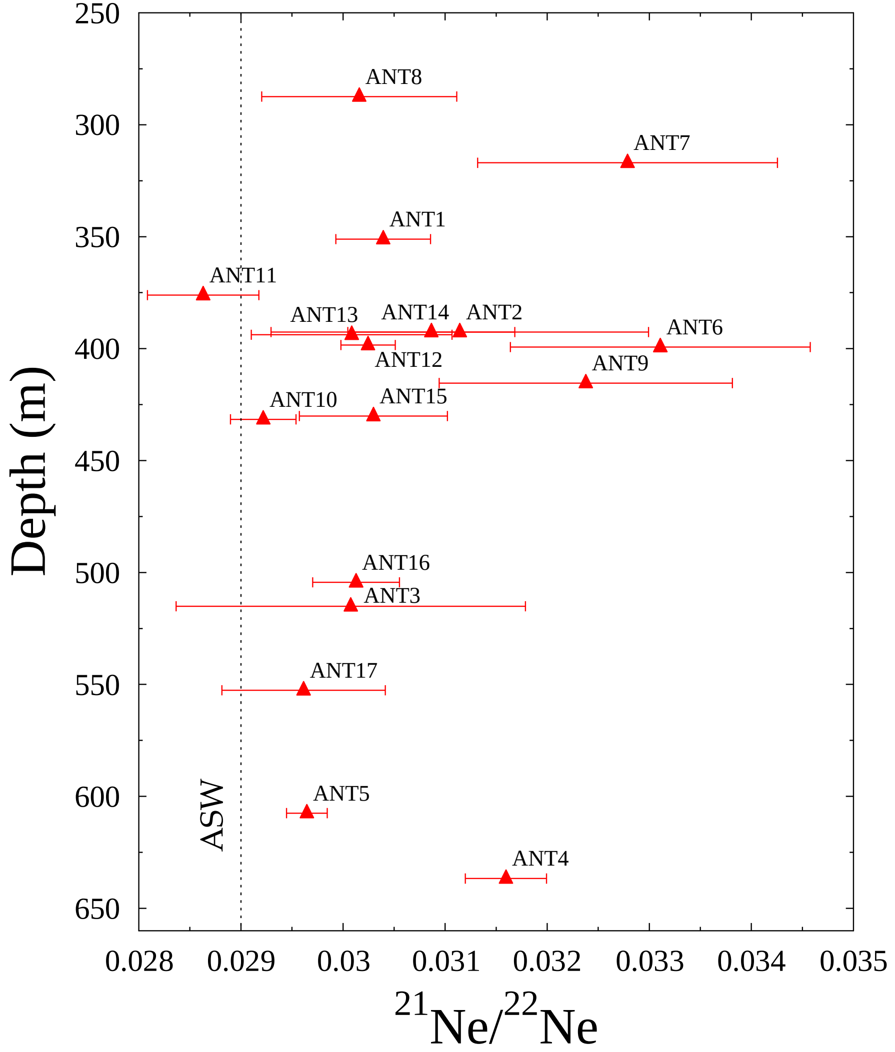
$^4He^*$ and $^3He/^4He$ normalized to R_a (R/R_a) Vertical Profiles



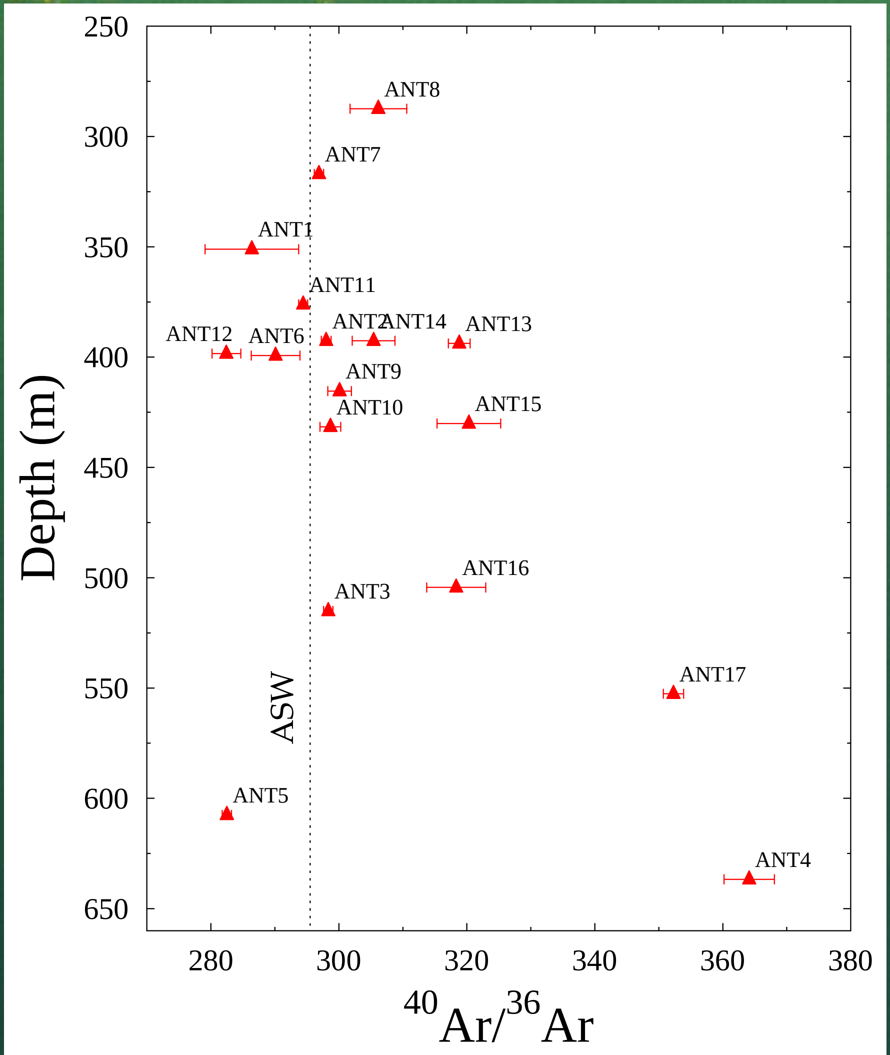


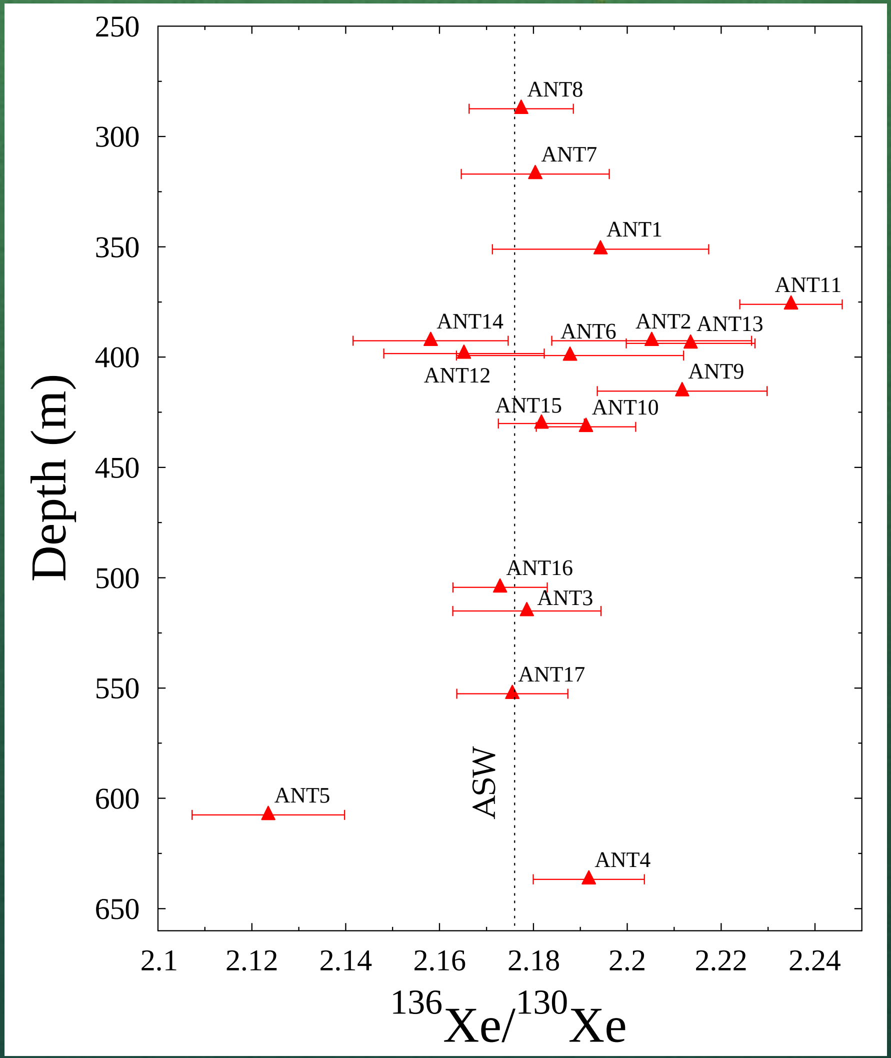
Ne Isotopic Ratios Vertical Profiles





Ar and Xe Isotopic Ratios Vertical Profiles



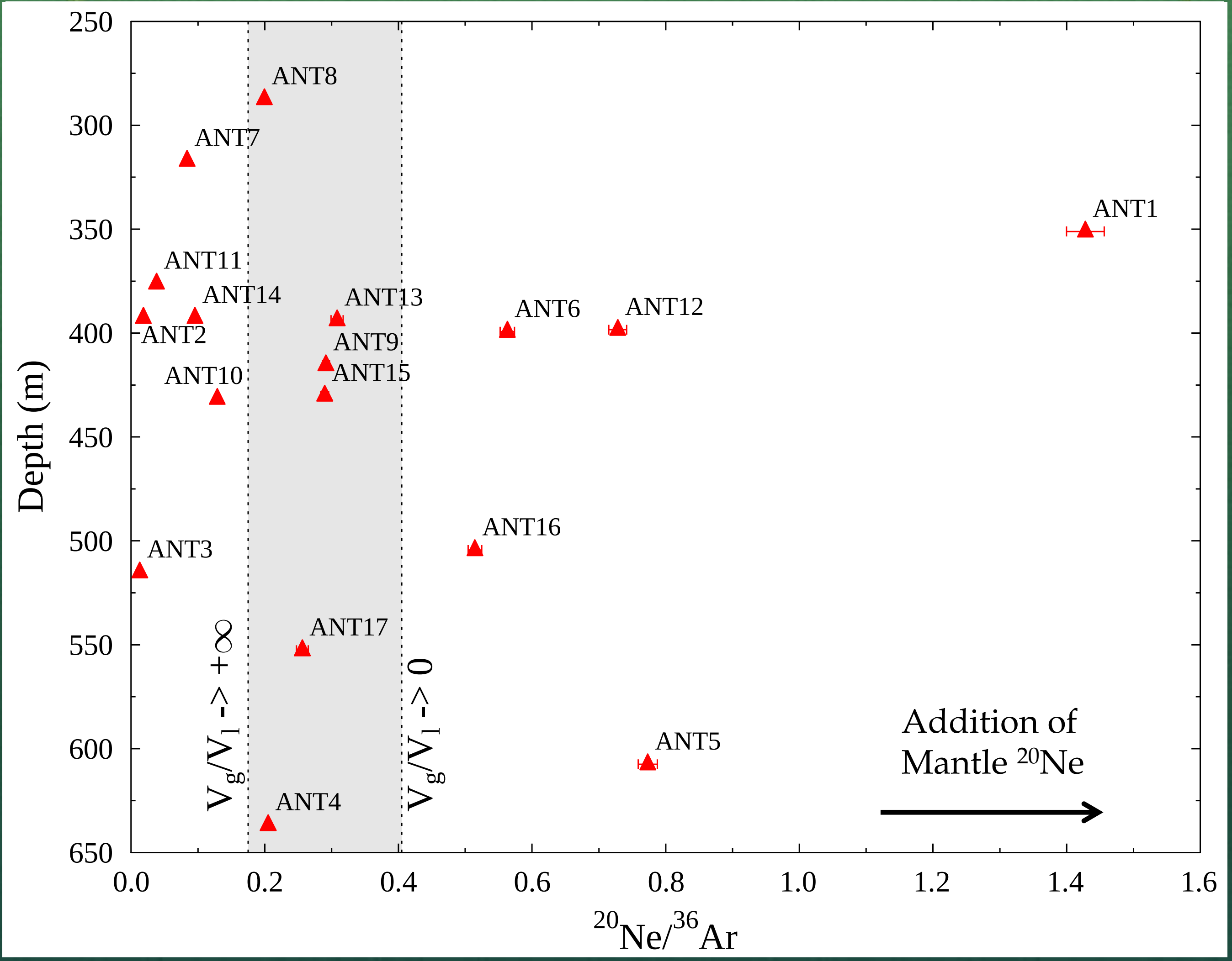


Noble Gas Sources and Spatial Variability in the Antrim Shale
Conclusions

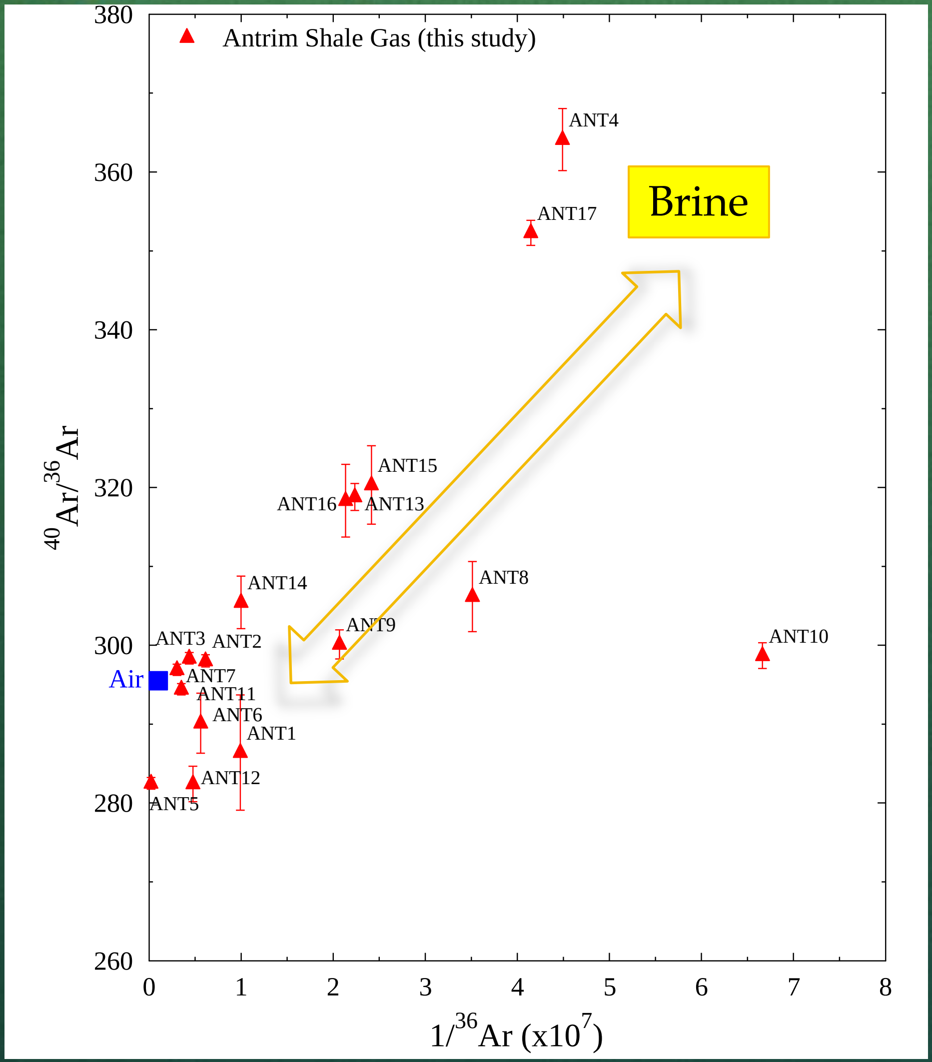
- Multiple sources of noble gases, i.e., crustal ^{4}He, ^{21}Ne, ^{40}Ar and ^{136}Xe in addition to mantle ^{20}Ne
- While ^{4}He is almost entirely of crustal origin, atmospheric ^{21}Ne (not shown), ^{40}Ar and ^{136}Xe largely dominate
- High horizontal and vertical variability in noble gas signatures in the Antrim Shale are observed

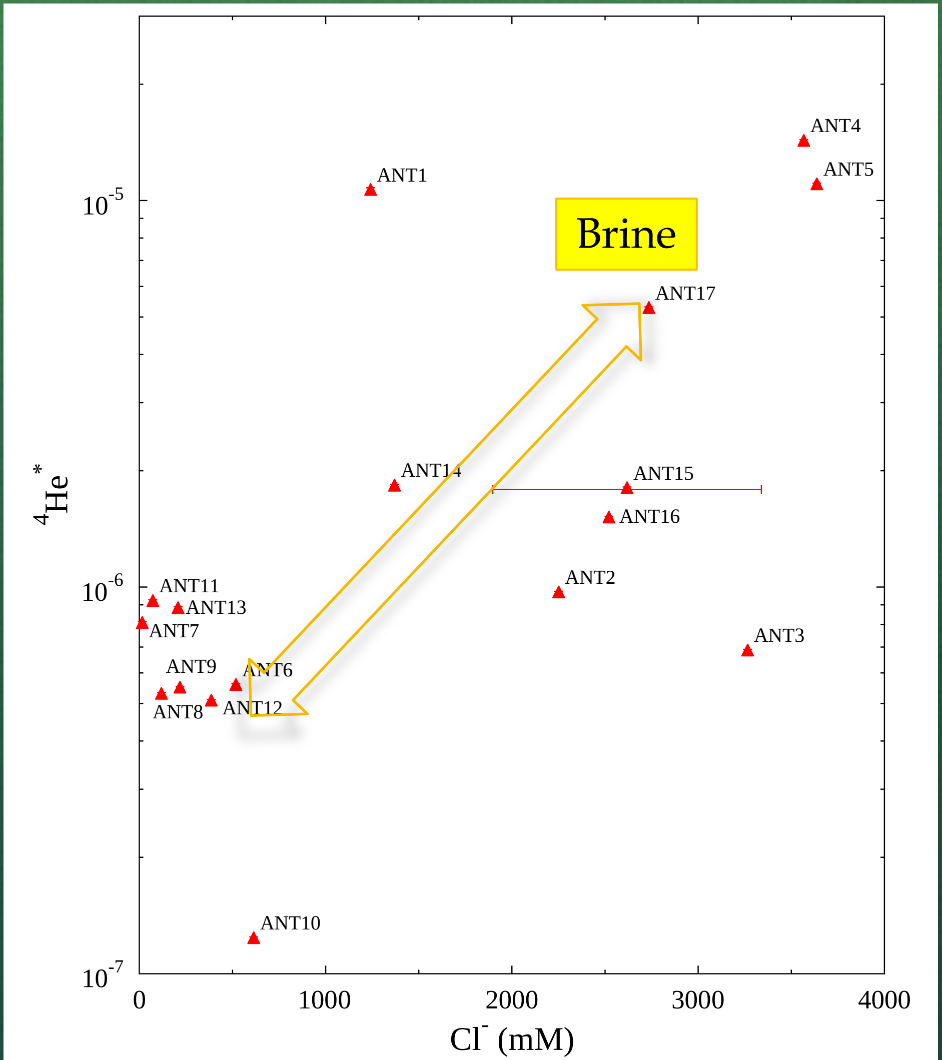
Does this translate into high U, Th and ^{40}K variability within the Antrim Shale ?

Assessing the Extent of Deep Brine Migration into the Antrim Shale

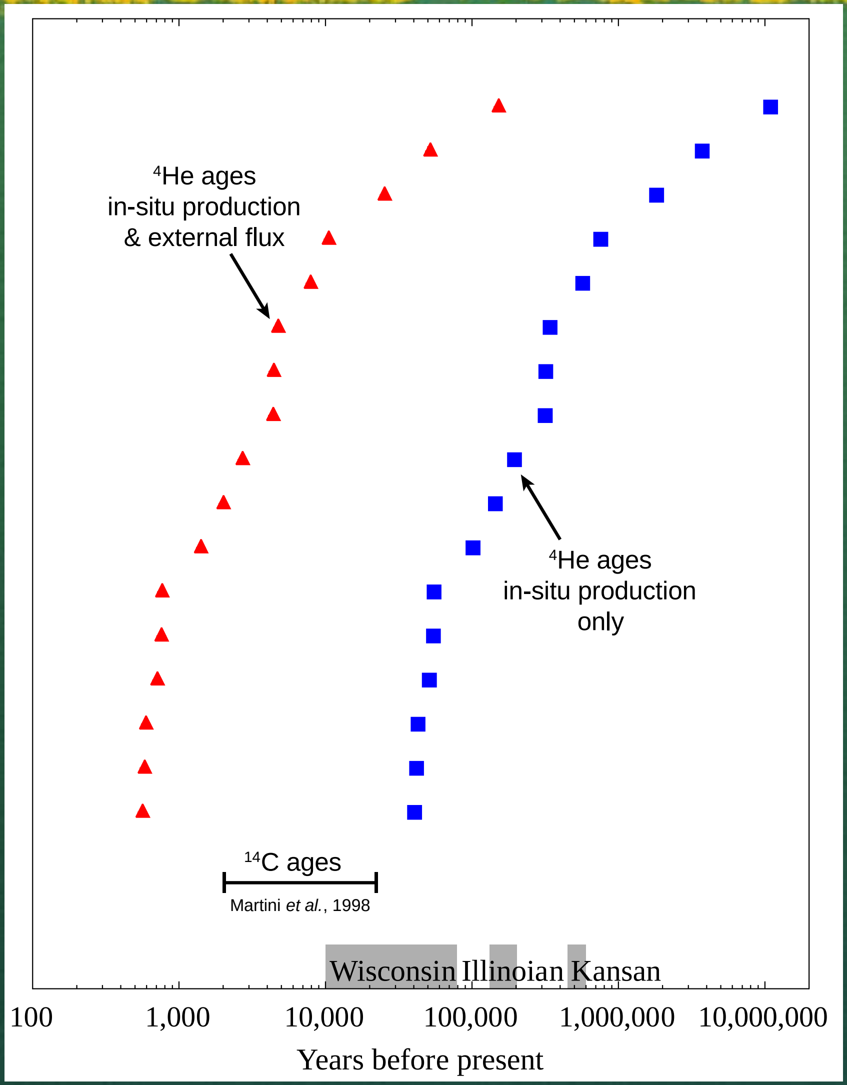


Mixing of Deep Brine with Meteoric Water in the Antrim Shale





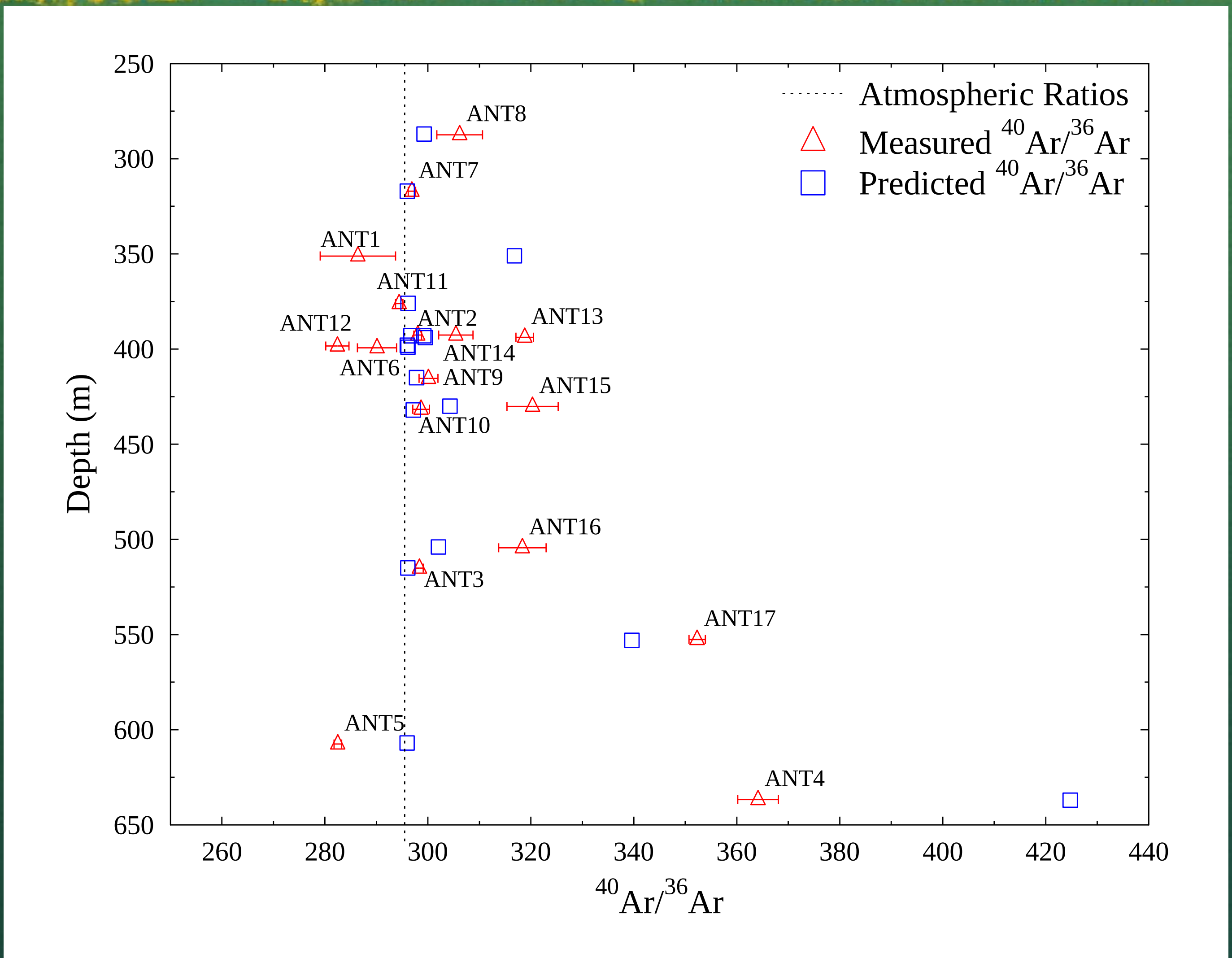
Timing and Origin of Freshwater Recharge in the Antrim Shale



Assumptions for in-situ production and external flux:

1. An average $^4He^*$ in-situ production rate (U-20ppm, Th-11ppm)
2. An average external $^4He^*$ flux into the Antrim Shale (U-2.8ppm, Th-10.7ppm)
3. Minimal fractionation of noble gases with near complete transfer of noble gases in the water to the gas phase

Thermogenic vs. Biogenic
Subsurface Temperature is Critical!



1. Ar release Temperature > 250°C
2. ~~Thermogenic Methane~~ 157°C ~ 221°C

Samples	Predicted / Measured
ANT1	1.11
ANT2	1.00
ANT3	0.99
ANT4	1.17
ANT5	1.05
ANT6	1.02
ANT7	1.00
ANT8	0.98
ANT9	0.99
ANT10	0.99
ANT11	1.01
ANT12	1.05
ANT13	0.94
ANT14	0.98
ANT15	0.95
ANT16	0.95
ANT17	0.96

Lippolt and Weigel, 1988
Stolper *et al.*, 2014

Conclusions

- Brines from deeper formations migrate into the Antrim Shale and mix with freshwater recharge.
- Variable noble gas signatures in the Antrim Shale are mostly due to the variable contributions of deeper brines.
- Atmospheric noble gas (^{20}Ne, ^{36}Ar and ^{84}Kr) are highly depleted in Antrim Shale gas due to the occurrence of a past thermal event.
- Noble gases can be used to investigate the presence of thermogenic methane. In particular, noble gas signatures in the Antrim Shale for most of our samples support the presence of thermogenic methane.

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BREITBURN