Elucidating water contamination by fracturing fluids and formation waters from gas wells: integrating isotopic and geochemical tracers

EPA workshop on
fracturing fluid composition,
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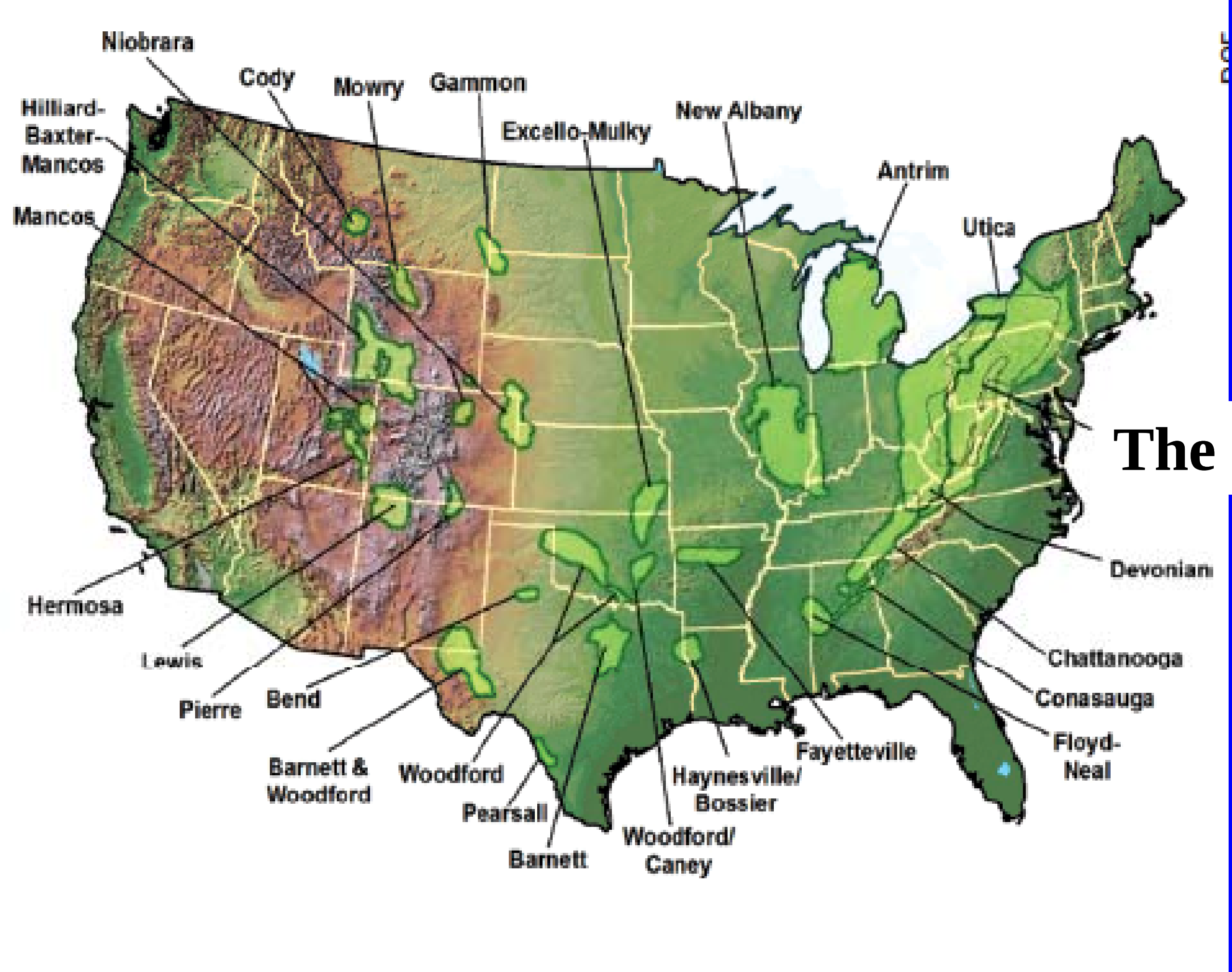
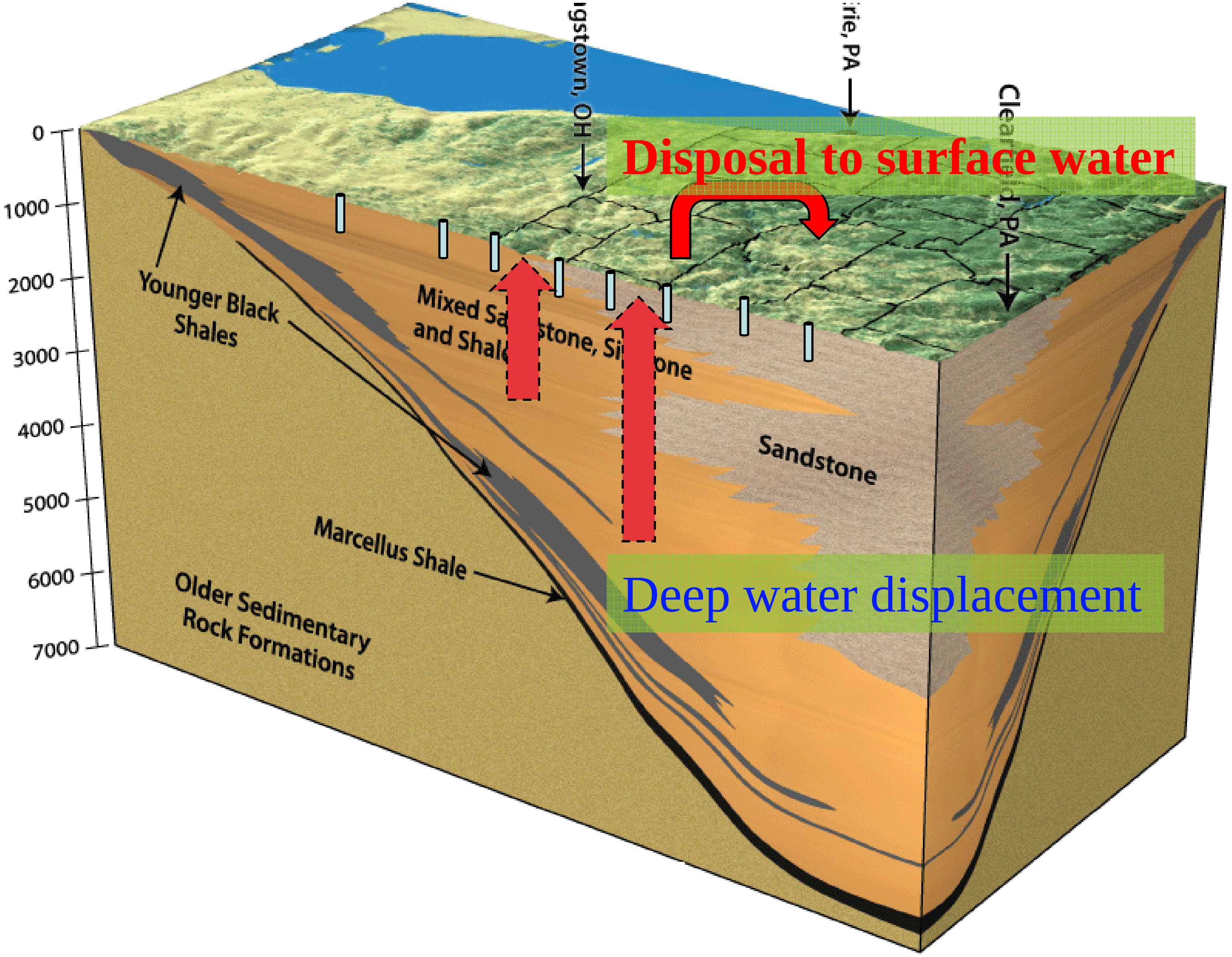
Shale basins in the USA



The Marcellus shale

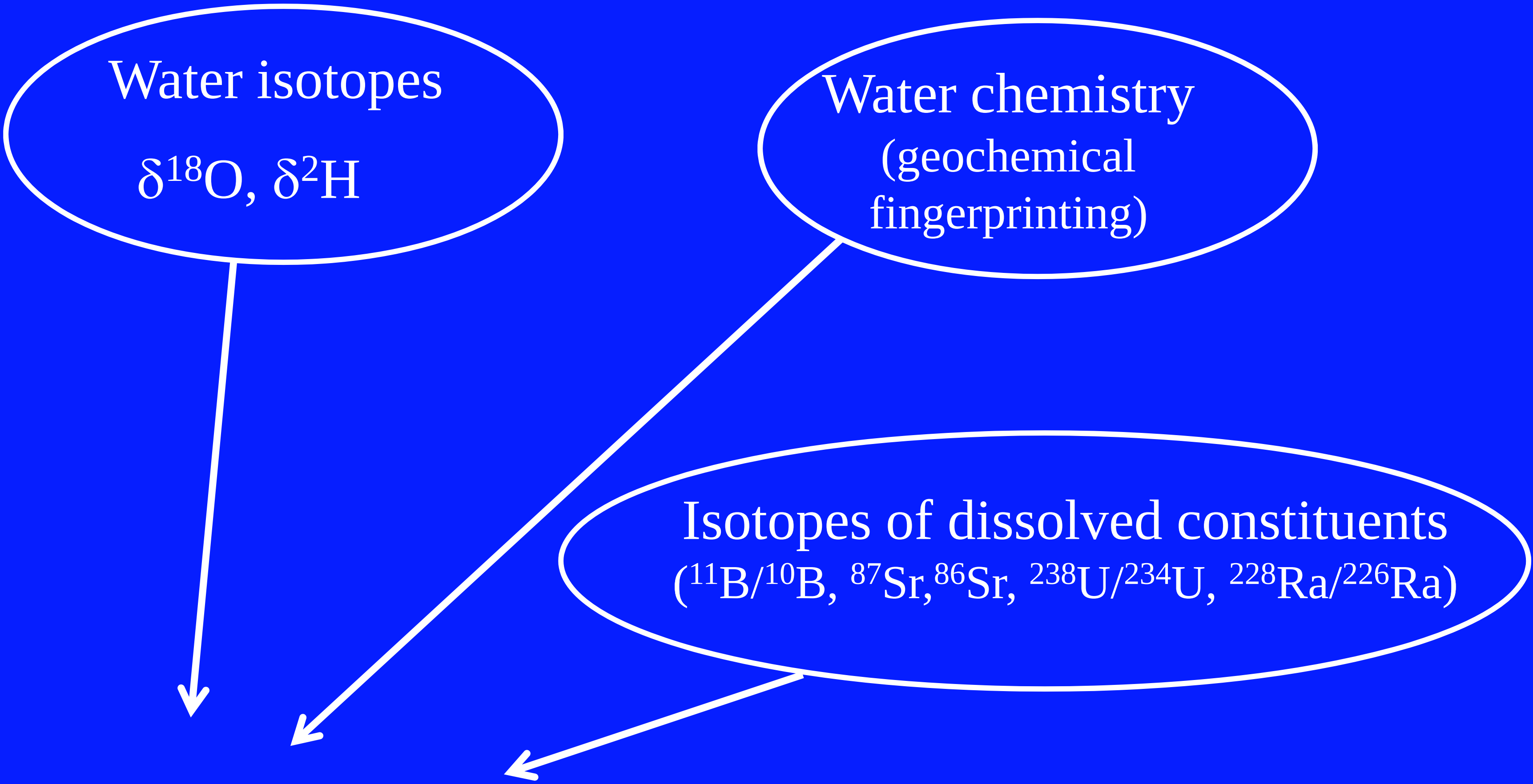
Tracing fracturing fluids and co-produced formation waters



Disposal to surface water

Deep water displacement

Nature of geochemical and isotopic tracers



Water isotopes

$\delta^{18}\mathrm{O}$, $\delta^{2}\mathrm{H}$

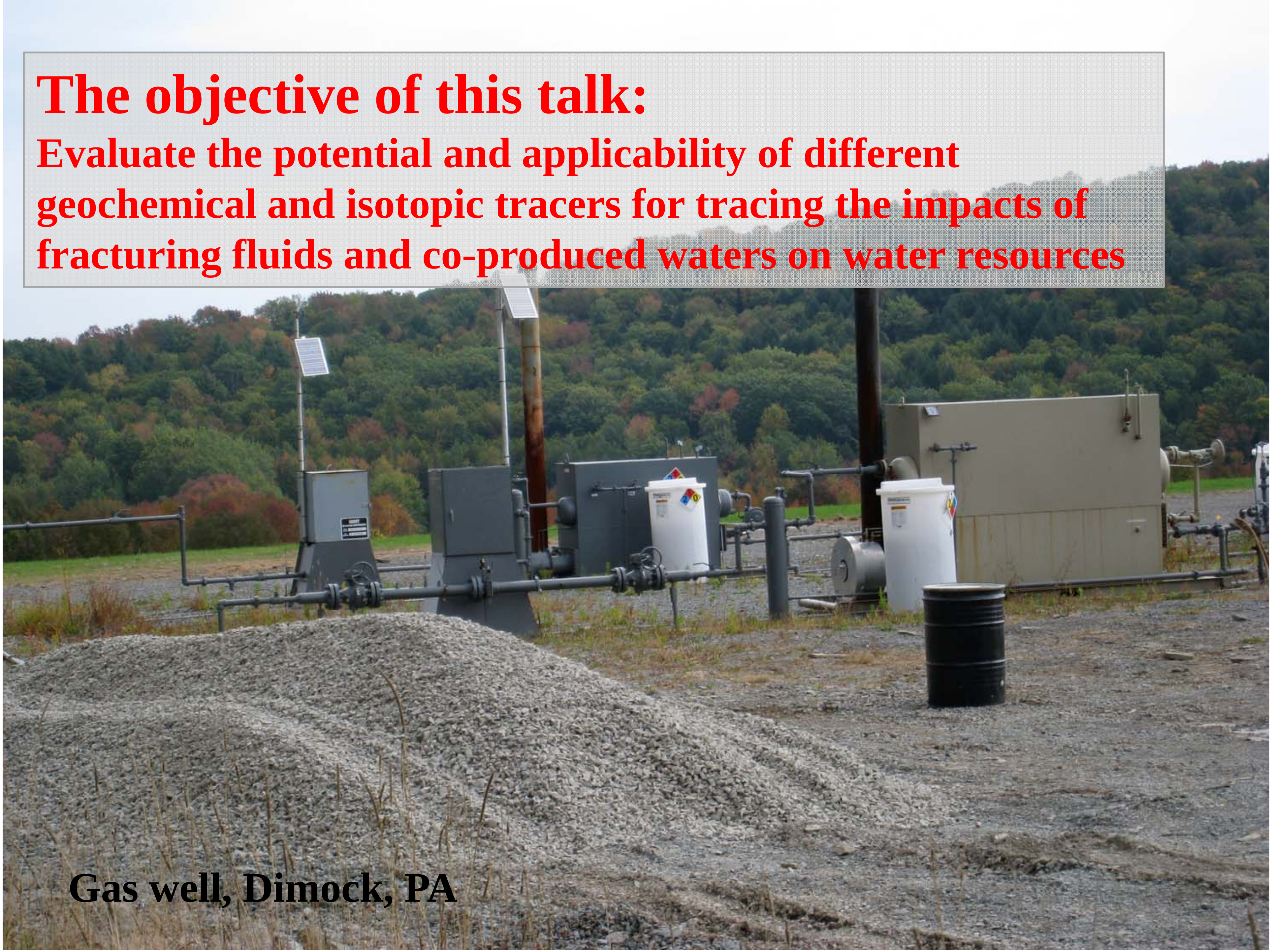
Water chemistry
(geochemical
fingerprinting)

Isotopes of dissolved constituents
($^{11}\mathrm{B}/^{10}\mathrm{B}$, $^{87}\mathrm{Sr},^{86}\mathrm{Sr}$, $^{238}\mathrm{U}/^{234}\mathrm{U}$, $^{228}\mathrm{Ra}/^{226}\mathrm{Ra}$)

1. Conservative versus non-conservative tracers
2. Sensitivity to mixing, dilution effects

The objective of this talk:

Evaluate the potential and applicability of different geochemical and isotopic tracers for tracing the impacts of fracturing fluids and co-produced waters on water resources

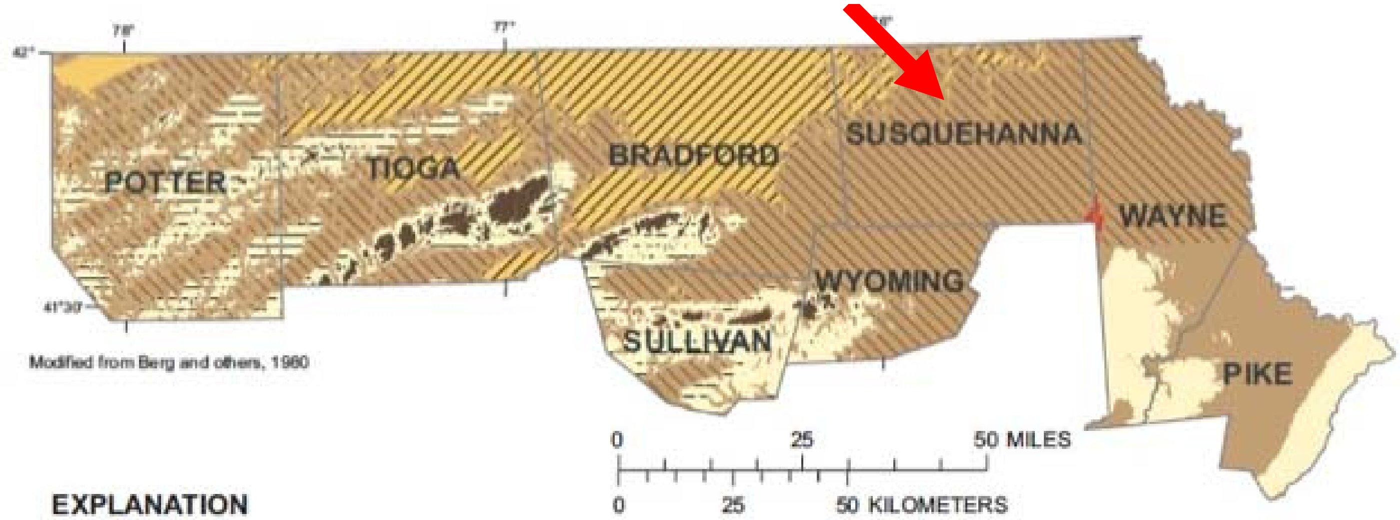


Gas well, Dimock, PA

The research methods:

Duke Research activities (updated February 2011):

1. Sampling ~70 shallow private wells in eastern PA, NY;
2. Sampling 2 producing wells from PA and NY;
3. Analysis of brines from the Marcellus Shale;
4. Analysis of flowback effluents from a Marcellus gas well (provided by USGS);
3. Chemical (major and trace elements) and isotopic ($^{87}Sr/^{86}Sr$, $\delta^{11}B$, $\delta^{18}O$, $\delta^{2}H$) measurements.



EXPLANATION

Bedrock Geolo

▨ Red sed

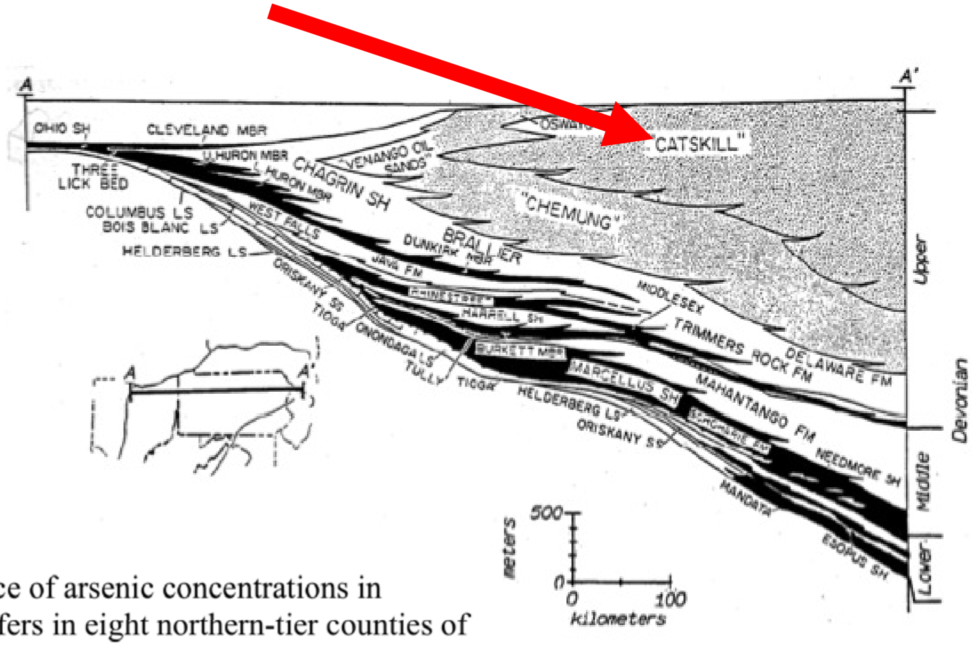
▨ Catsk

▨ Shale

▨ Lock H

Figure 2. The generali

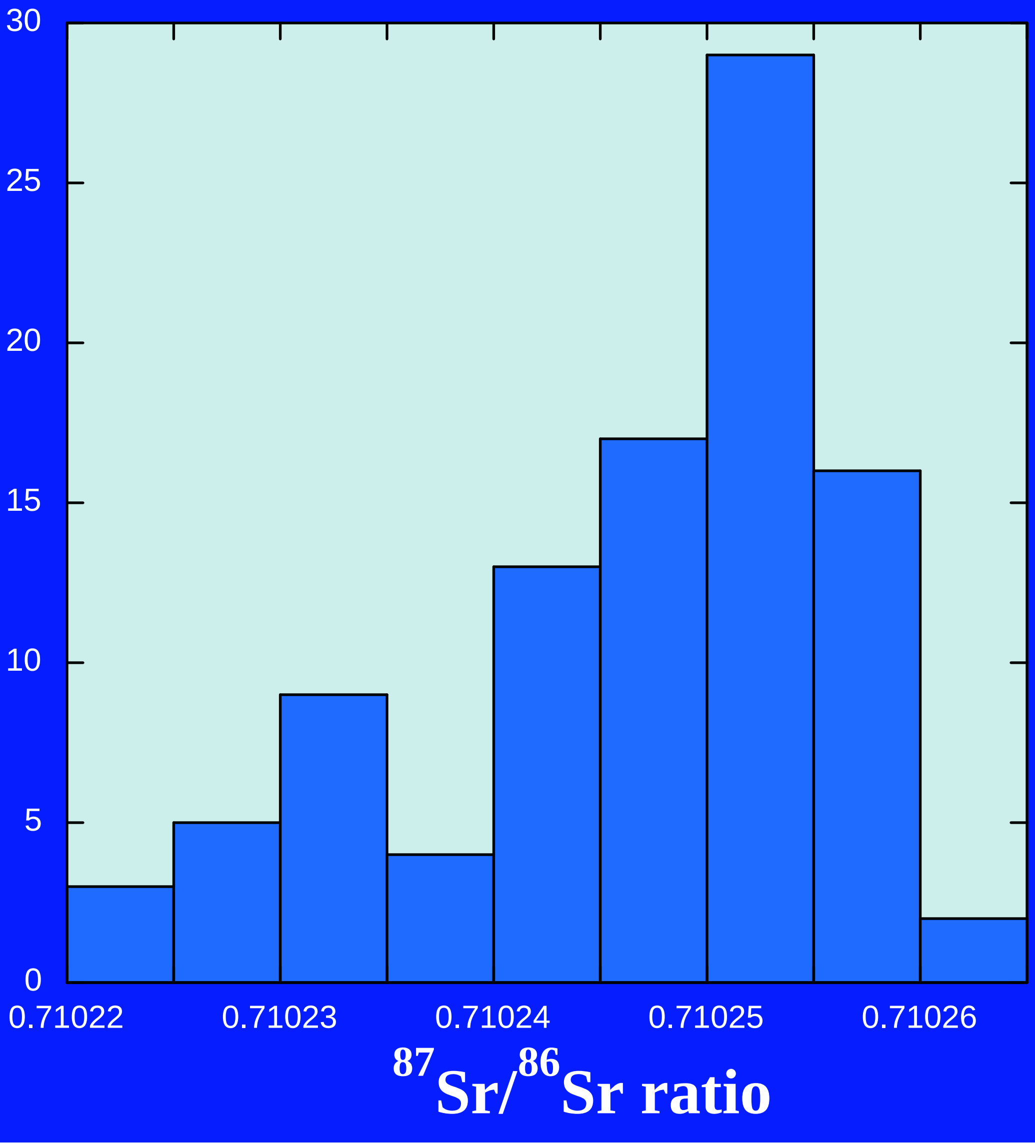
Upper Devonian Catskill



Low, D.J., and Galeone, D.G., (2007) Reconnaissance of arsenic concentrations in ground water from bedrock and unconsolidated aquifers in eight northern-tier counties of Pennsylvania: U.S. Geological Survey Open-File Report 2006-1376, 35 p.

Triton@Duke

NIST SRM 987 Sr standard



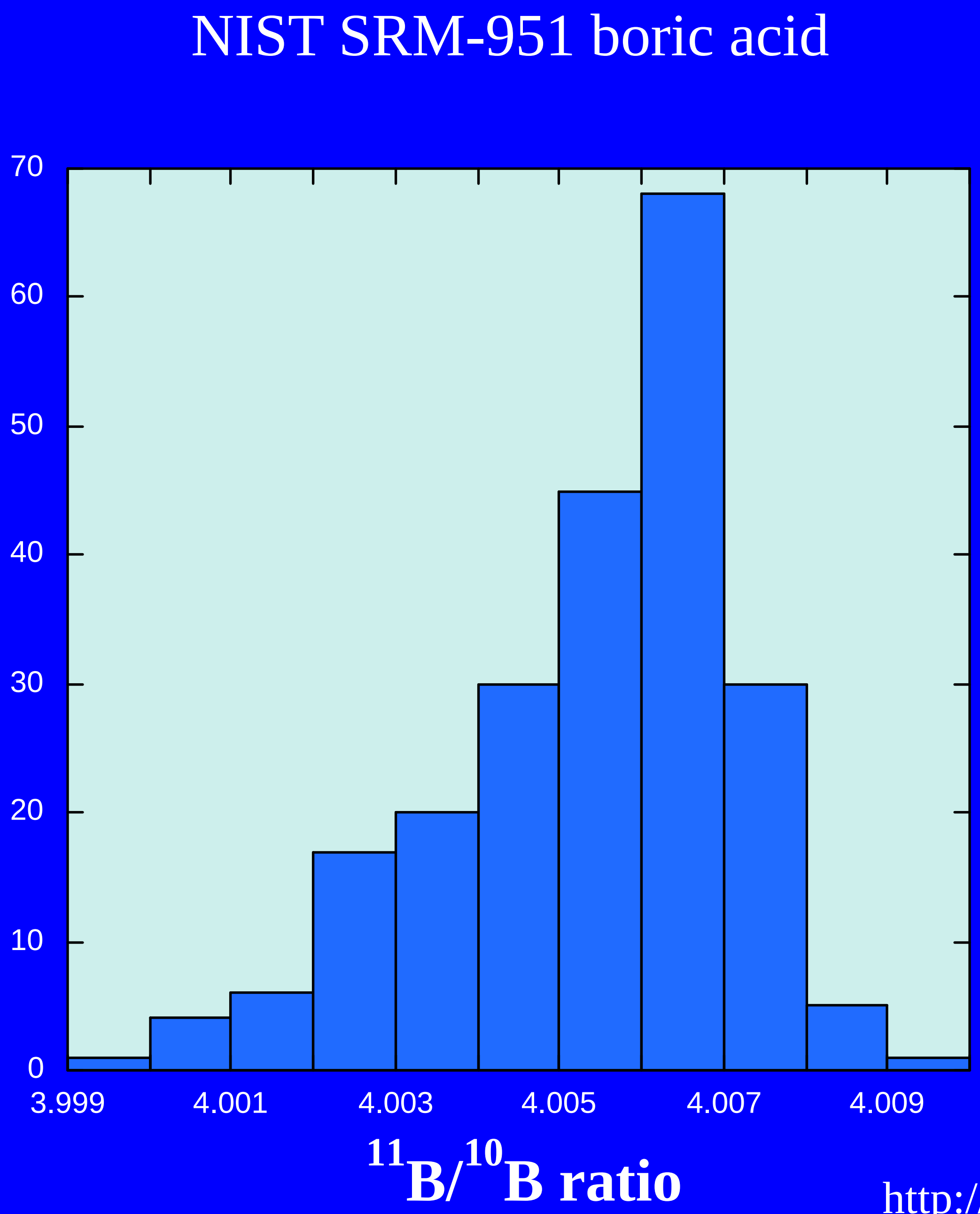
Mean = 0.710246

ST= 9.31×10^{-6} (0.01 per-mil)

n=98

http://www.nicholas.duke.edu/tims/

Triton@Duke



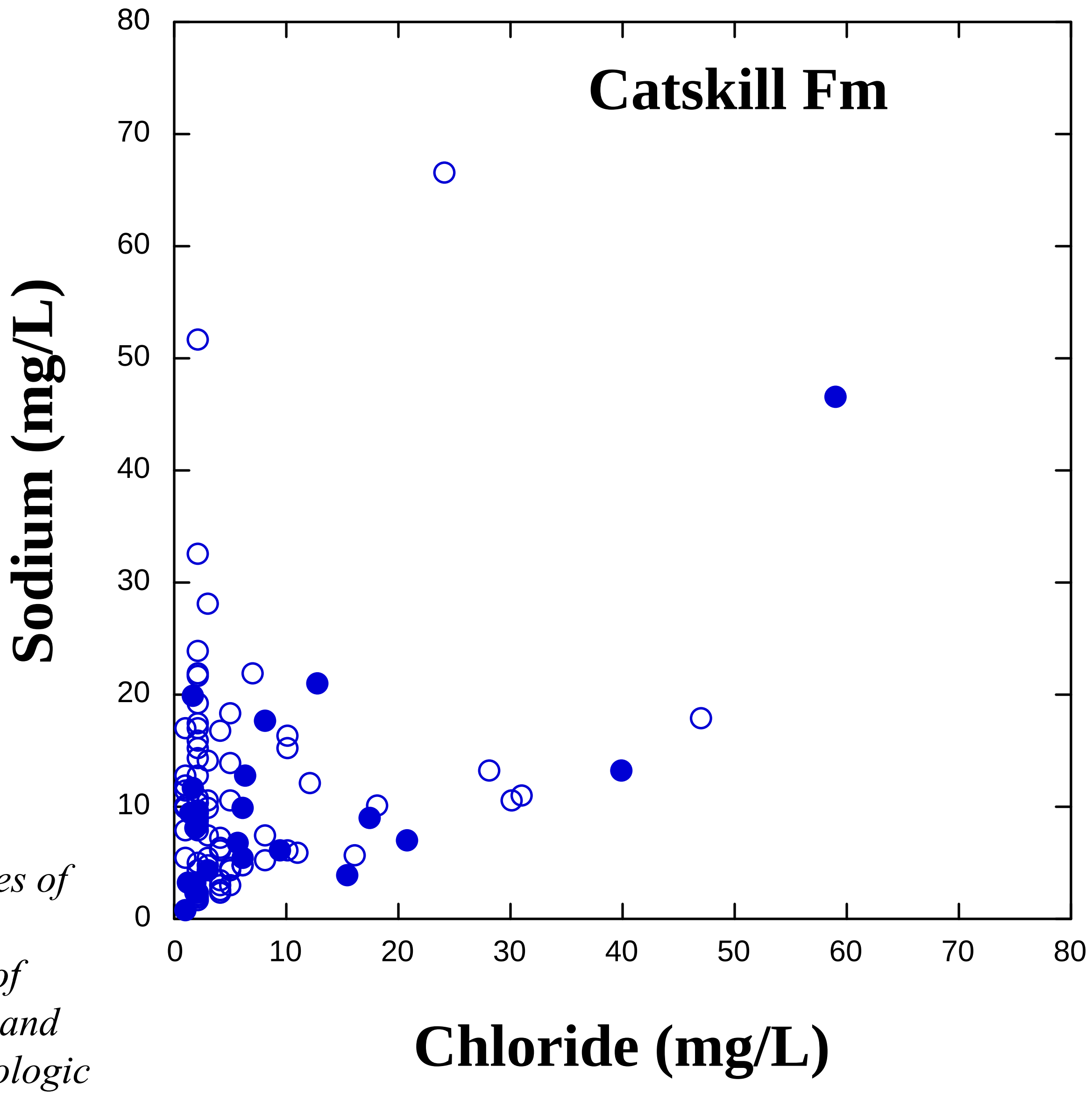
Mean = 4.0051
ST= 0.0026 (0.6 per-mil)
n=238

http://www.nicholas.duke.edu/tims/

Chemistry of background groundwater: Catskill aquifer

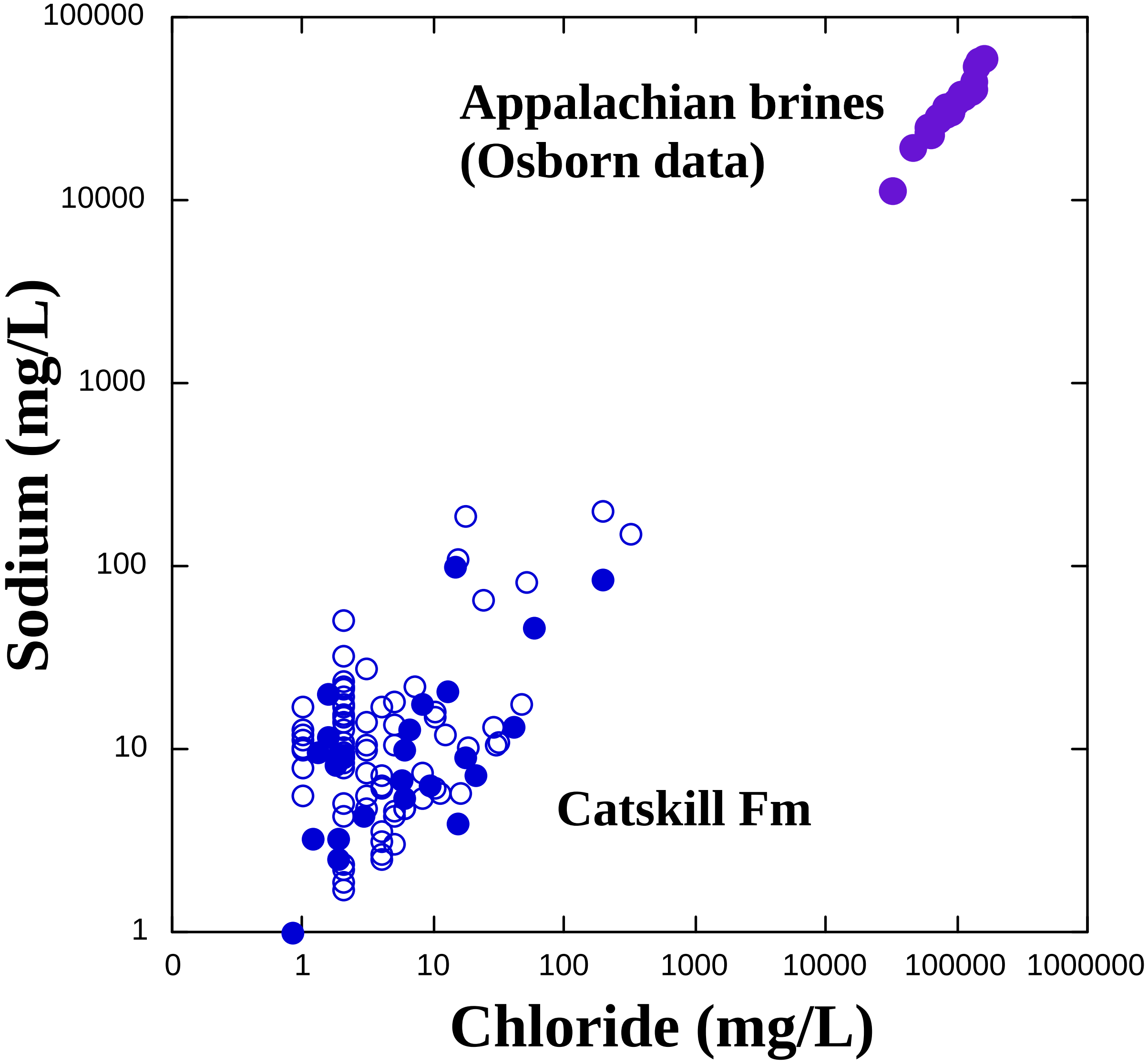
● Duke sampling

○ 1980s data*

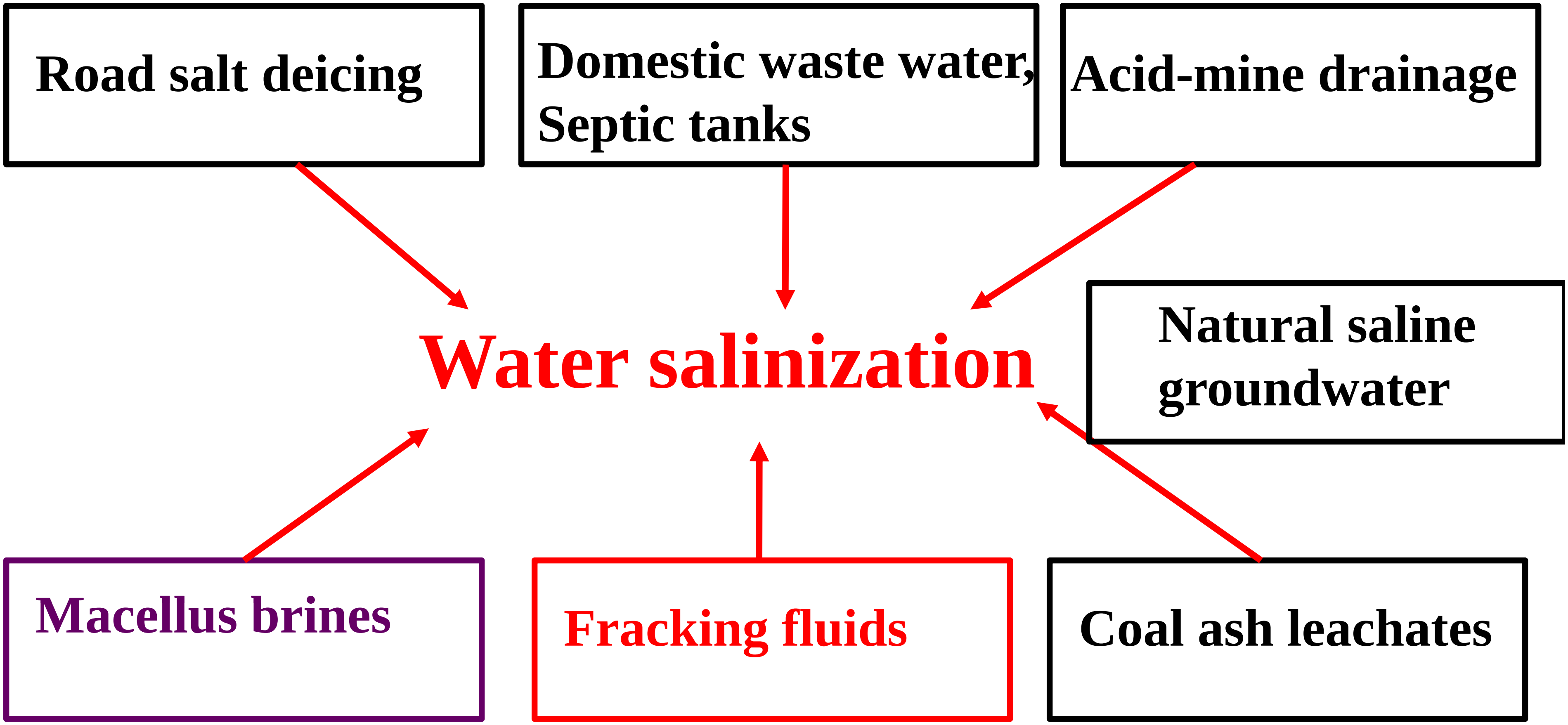


** Taylor LE (1984) Groundwater Resources of the Upper Susquehanna River Basin, Pennsylvania (Pennsylvania Department of Environmental Resources-Office of Parks and Forestry - Bureau of Topographic and Geologic Survey Water Resources Report 58).*

First indication for contamination by fracturing fluids and co-produced formation water: salinity



Multiple salinity sources



Road salt deicing

Domestic waste water, Septic tanks

Acid-mine drainage

Water salinization

Natural saline groundwater

Macellus brines

Fracking fluids

Coal ash leachates

Multiple salinity sources with distinguished chemical compositions

Road salt deicing

Na-Cl water type
Na/Cl=1,
Br/Cl, B/Cl-low

Domestic waste water
Septic tanks

Na-Cl water type
Na/Cl≥1, NO_3*-high*
Br/Cl-low, B/Cl-high

Acid-mine drainage

$Ca\text{-}SO_4$ *water type*
B/Cl-high, low pH

Macellus brines

Ca-Cl water type
Na/Cl<1,
Br/Cl, B/Cl-high

Fracking fluids

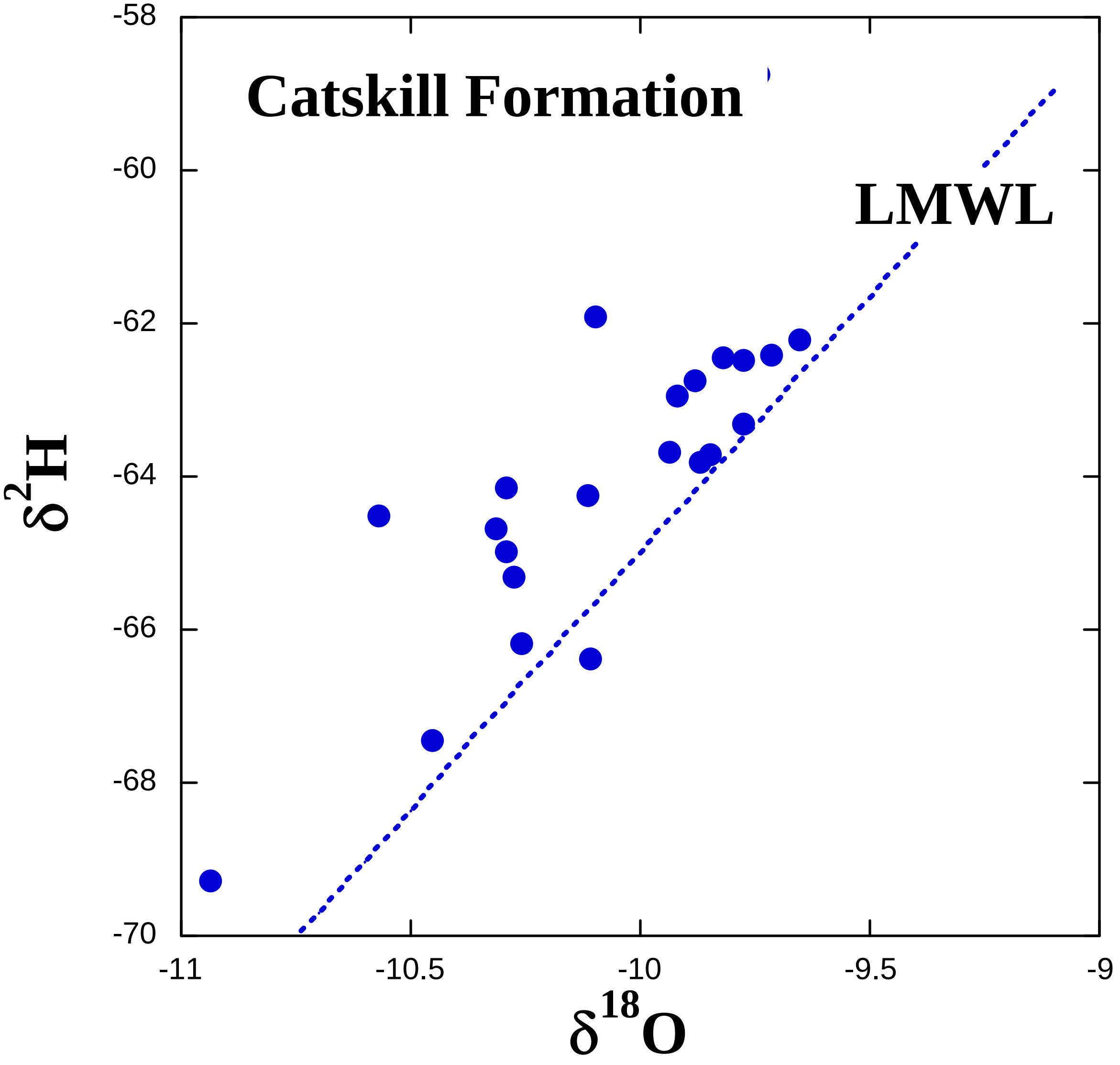
High Ca, Sr, B, Ba

?

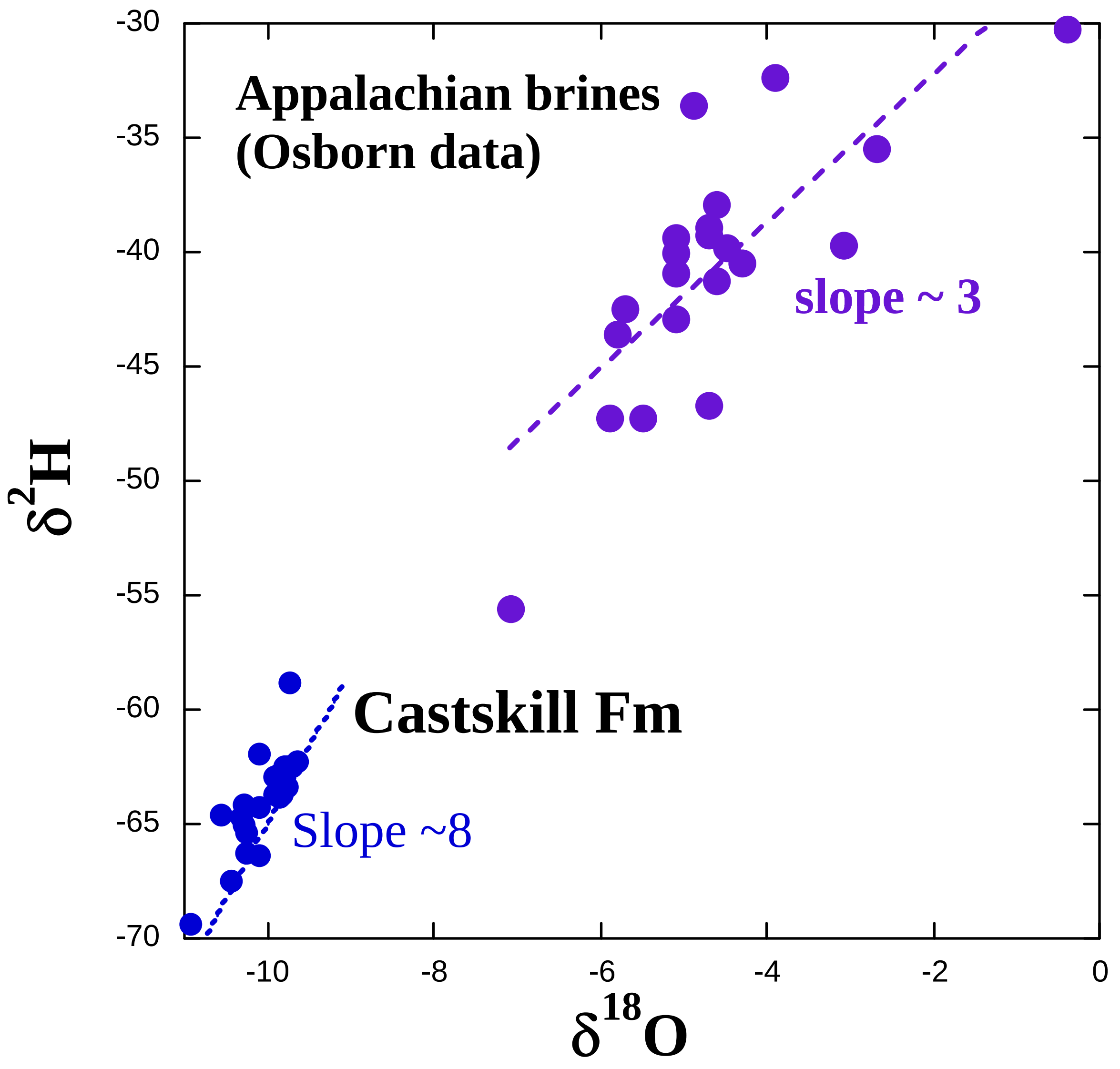
Coal ash leachates

$Ca\text{-}SO_4$ *water type*
High Ca, pH
B/Cl- very high

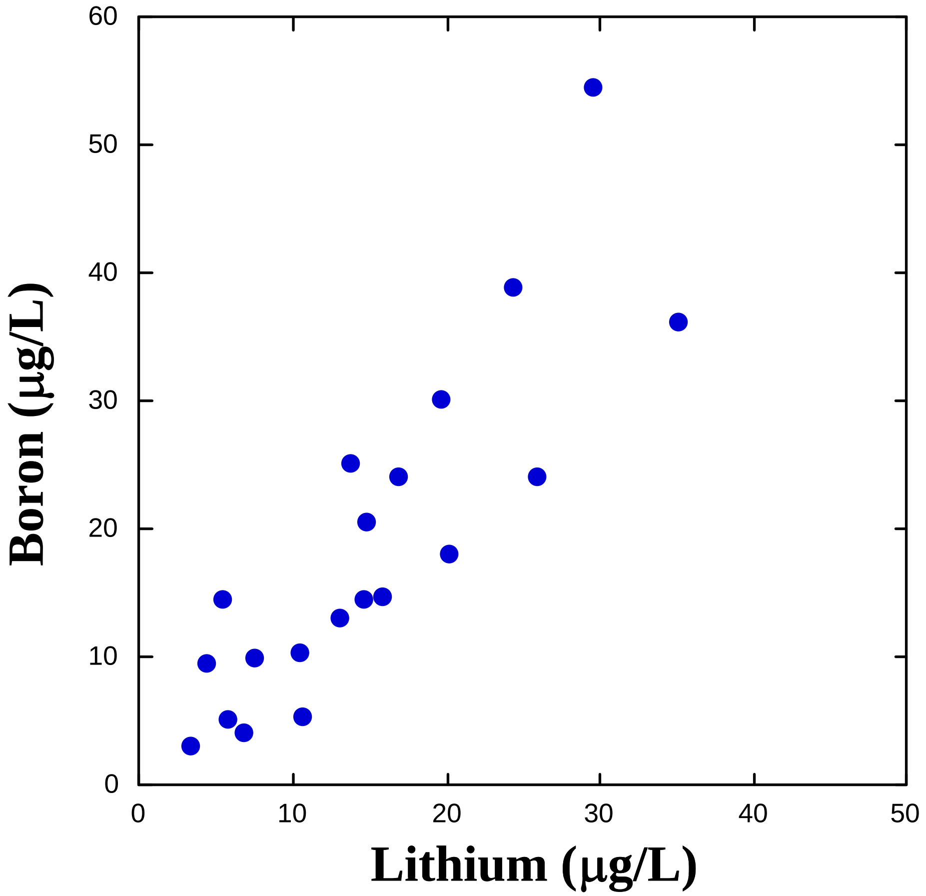
The water isotopes

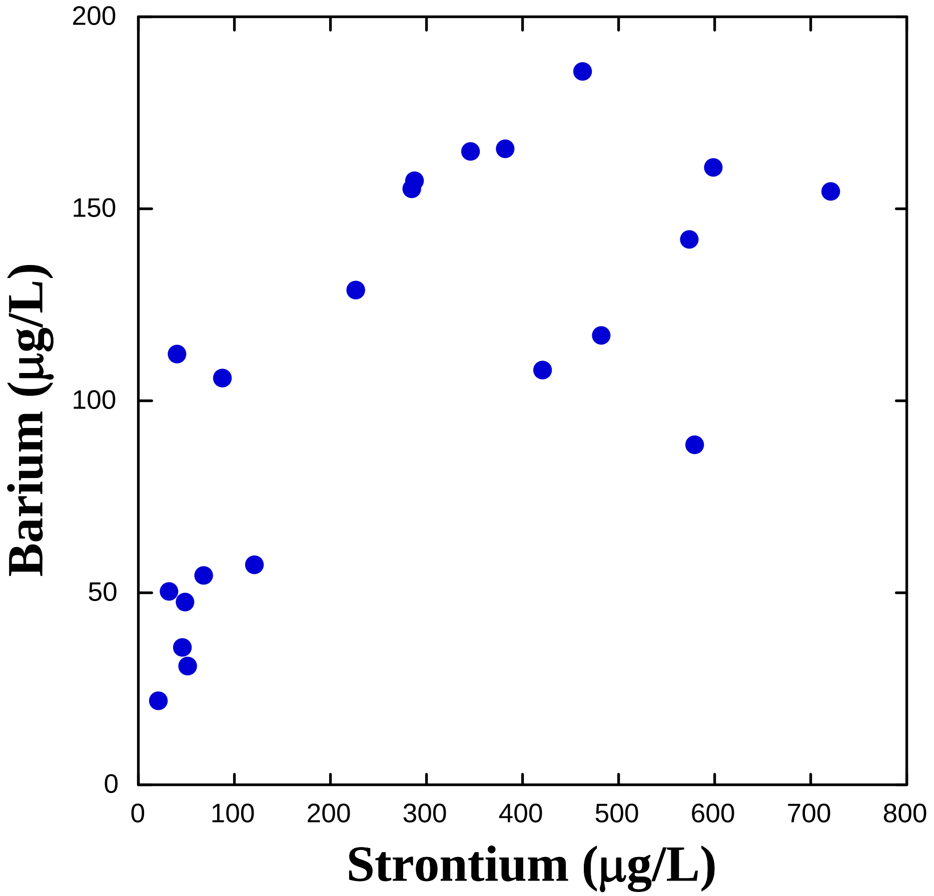


Indication for flowback and formation waters: Enrichment of ^{18}O and ^{2}H, and a lower slope

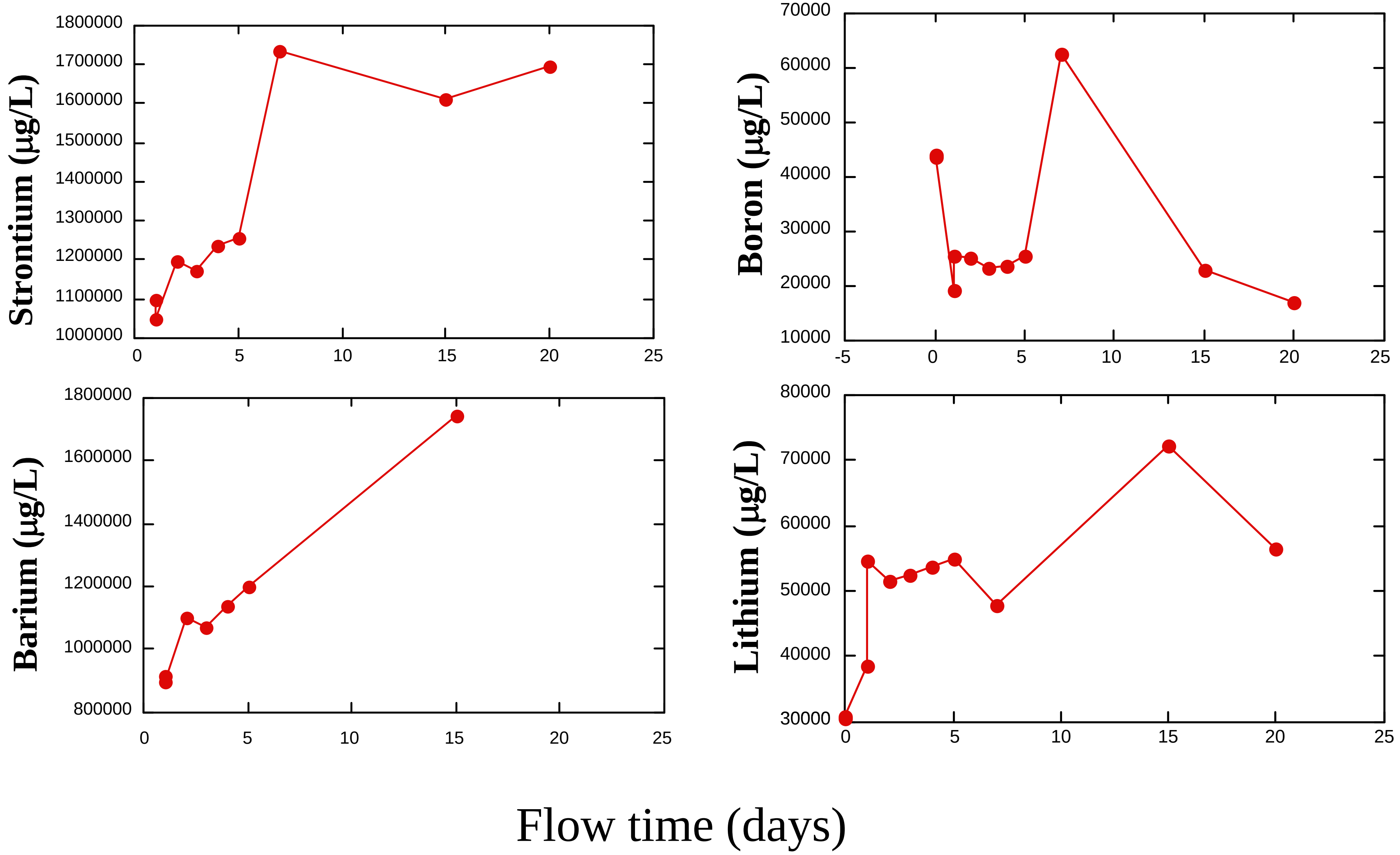


Minor and trace elements

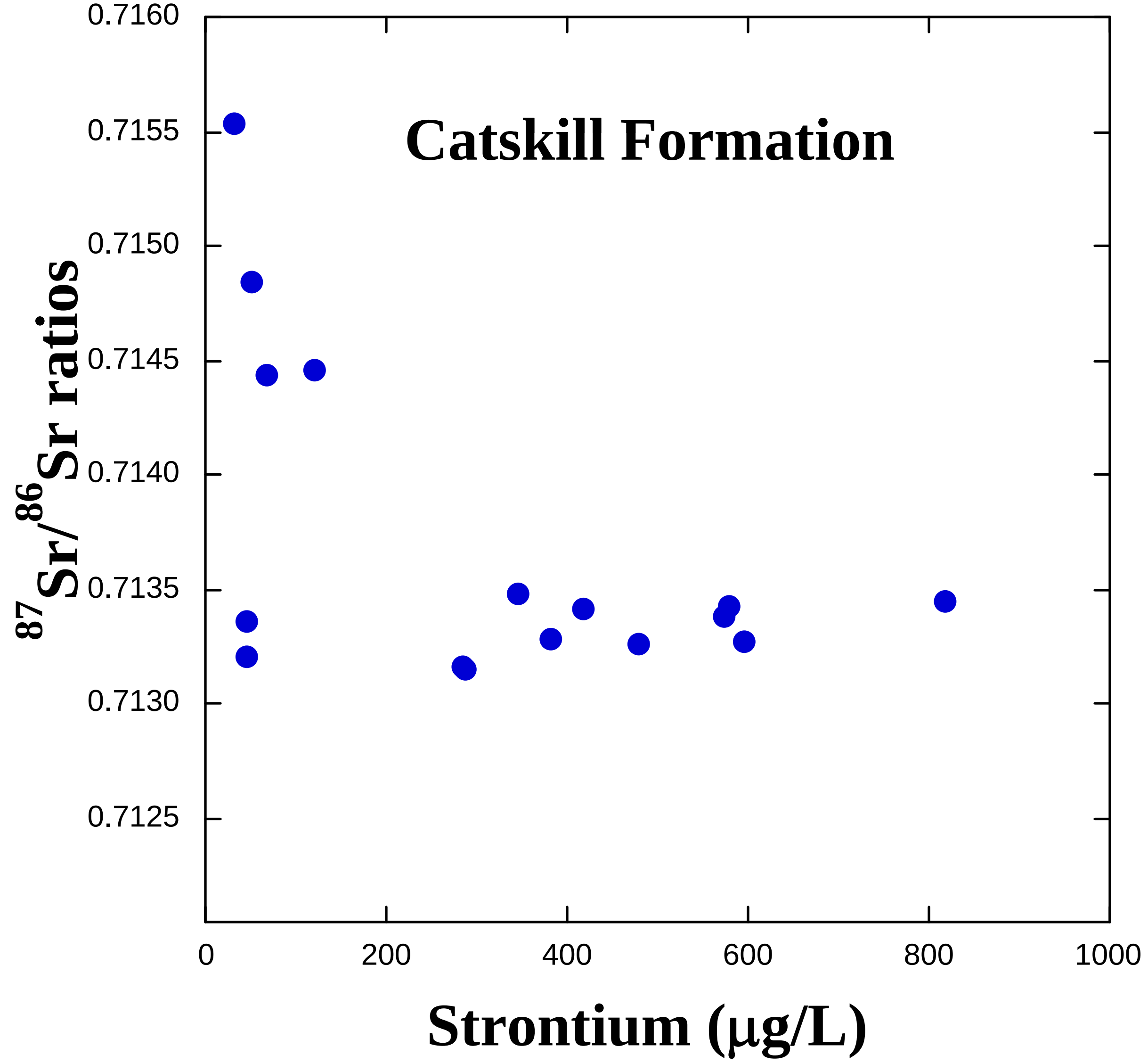




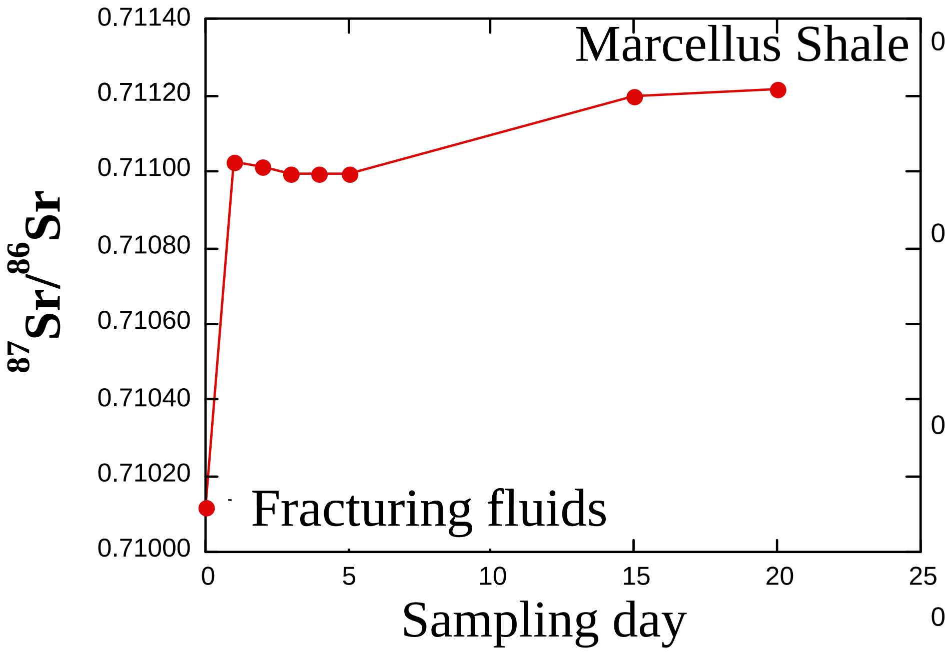
Flowback effluents mixed with Marcellus brines (Meadows #4, DOE/USGS sampling)

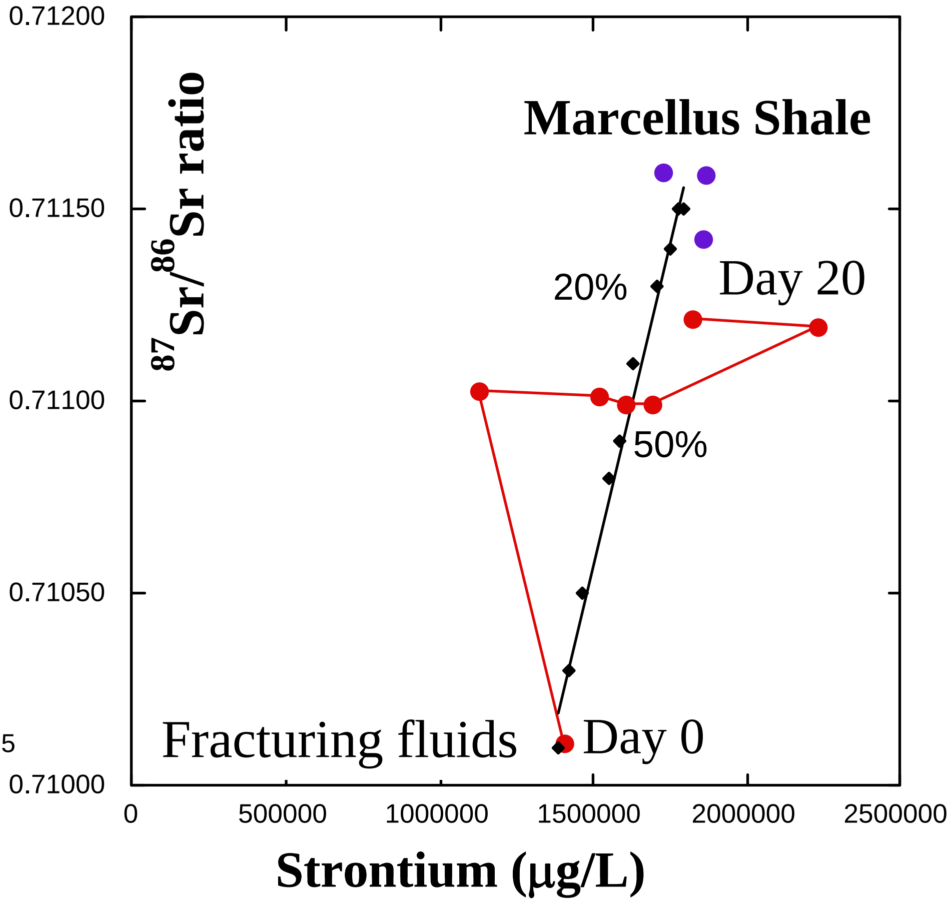


Strontium isotopes

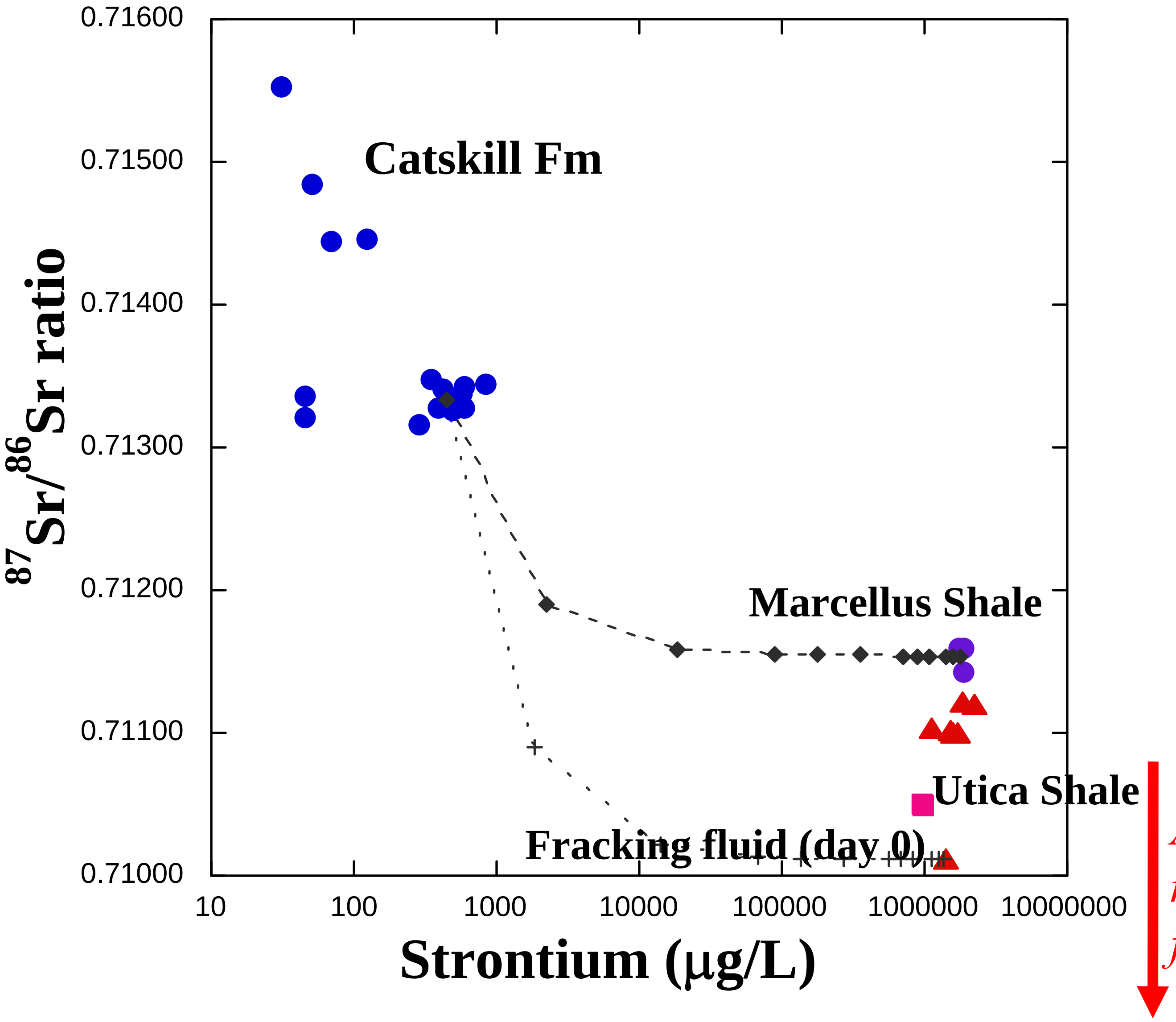


Elucidating between mixed fracturing-formation waters and the Marcellus brines



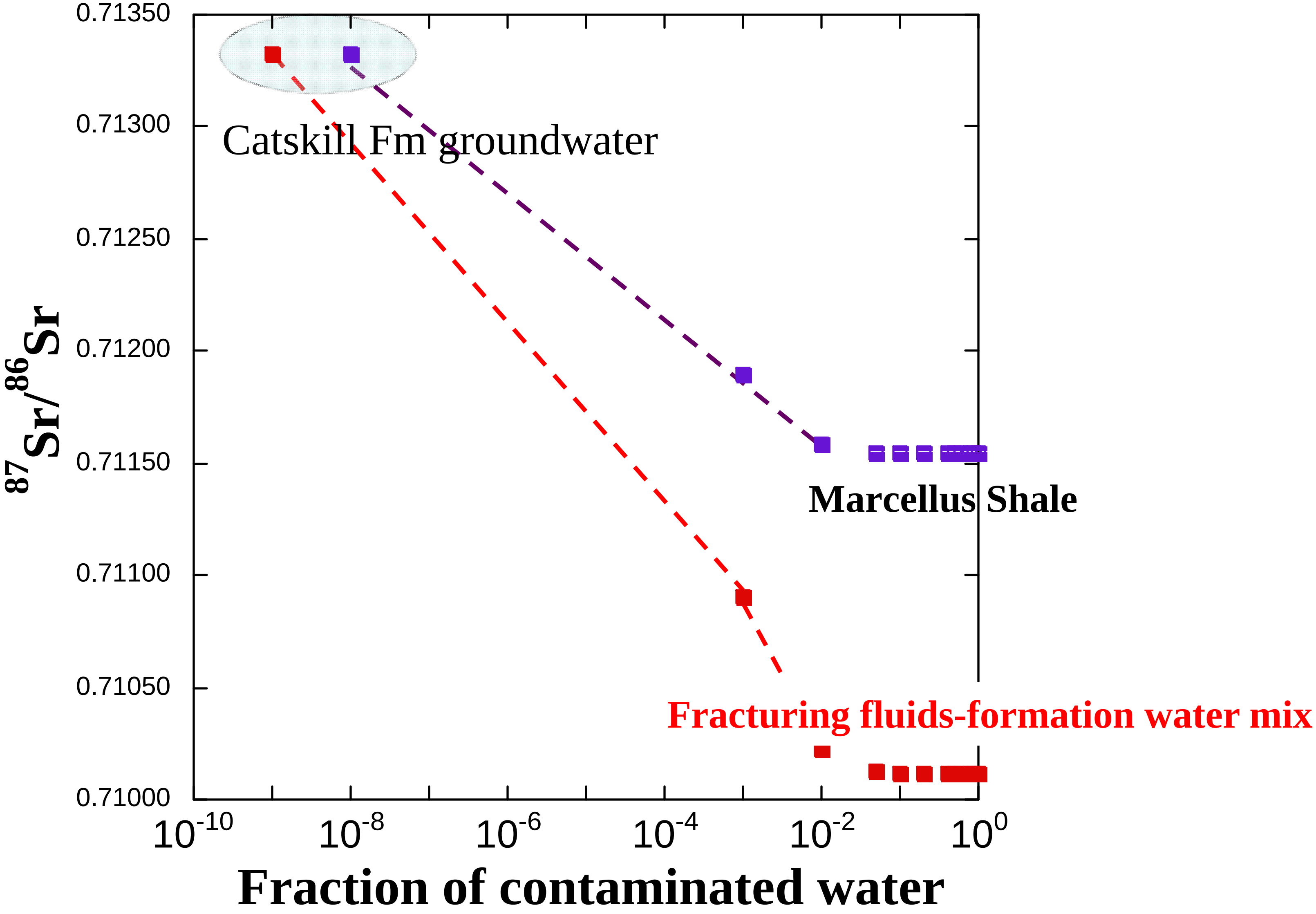


Strontium isotopes: a sensitive tracer for mixing with fracturing fluids/flowback water

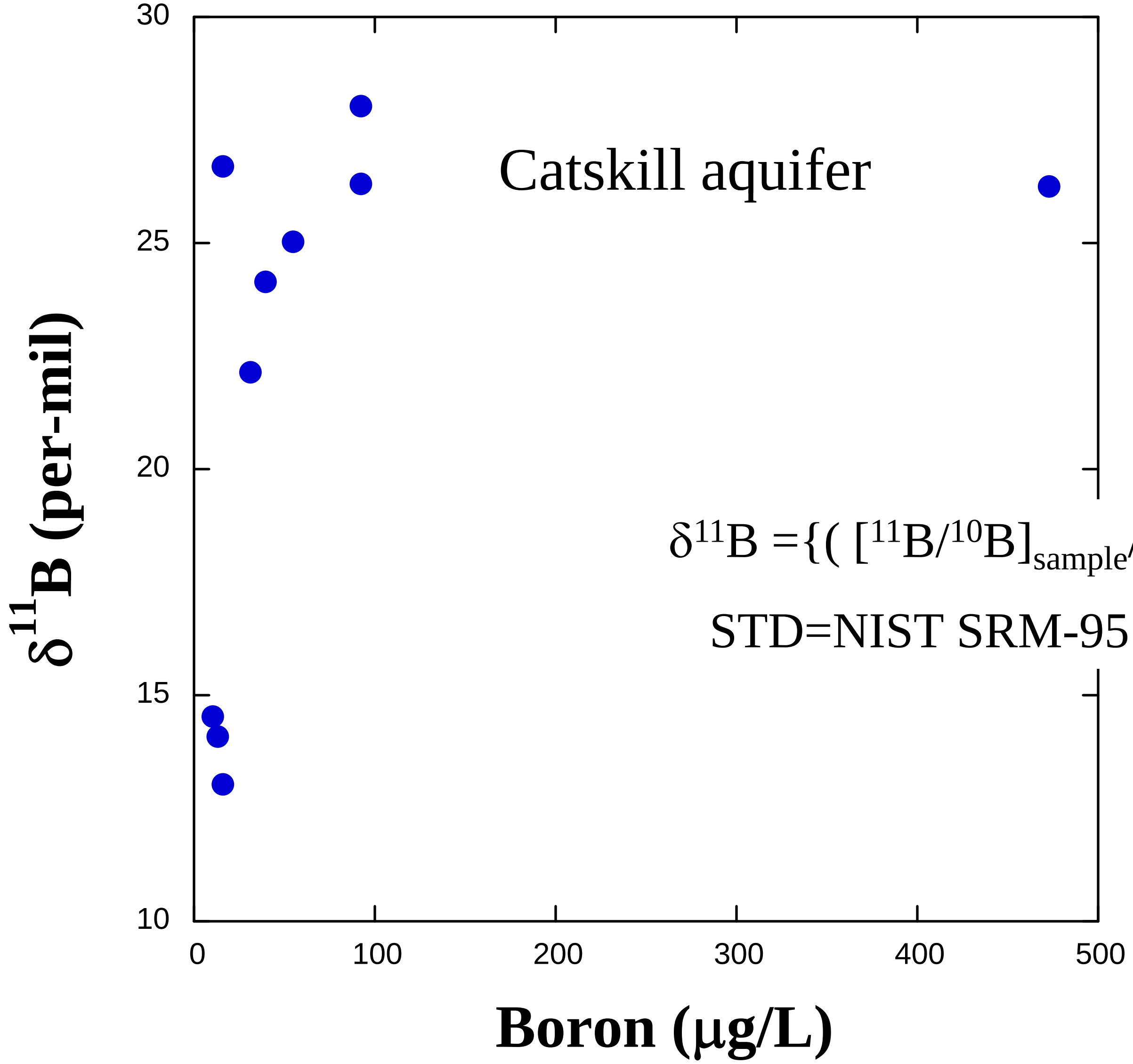


A lower ^{87}Sr/^{87}Sr for non-mixed fracturing fluids

The sensitivity of strontium isotopes to mixing with fracturing fluids and backflow brines



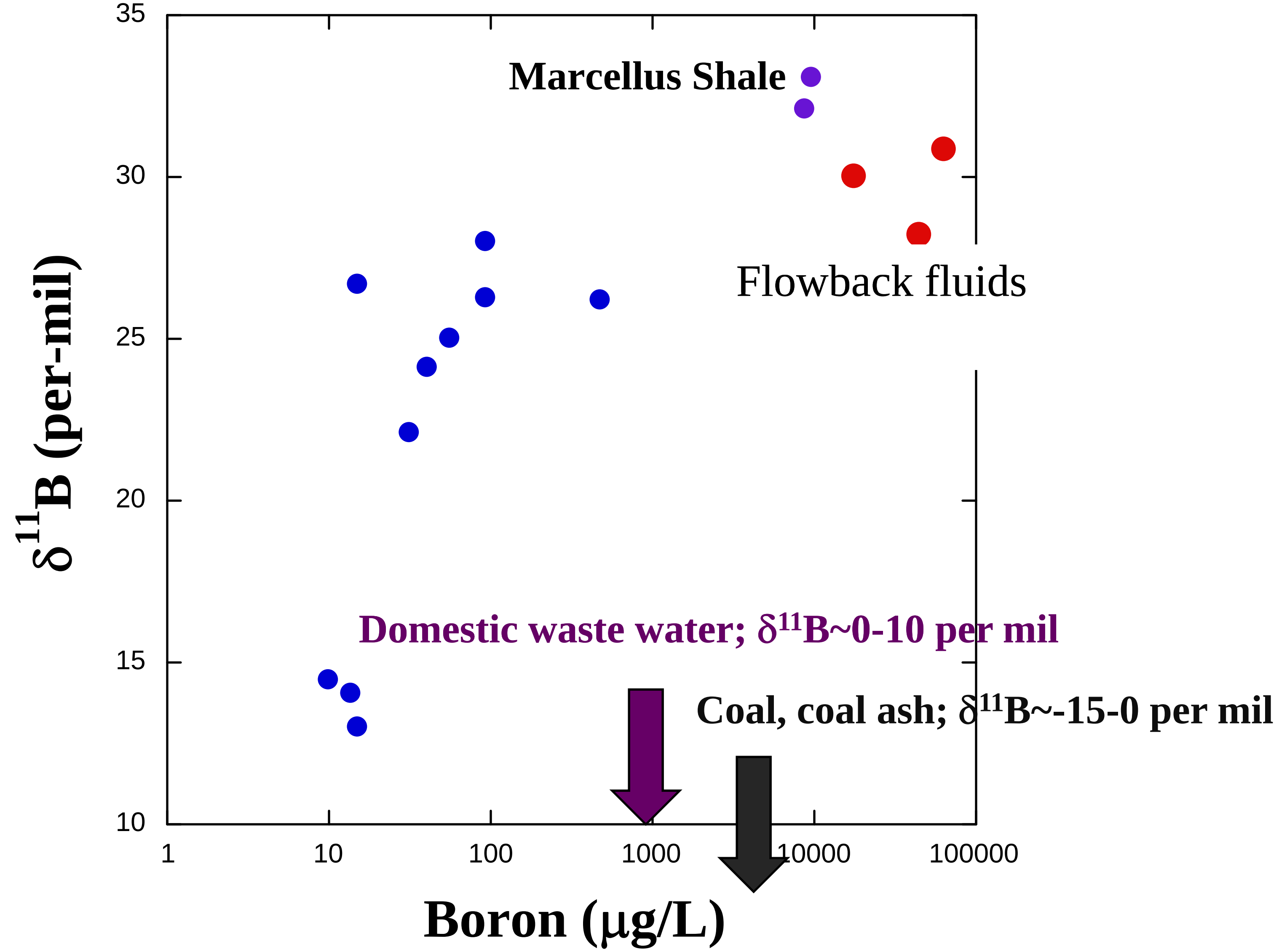
Boron isotopes



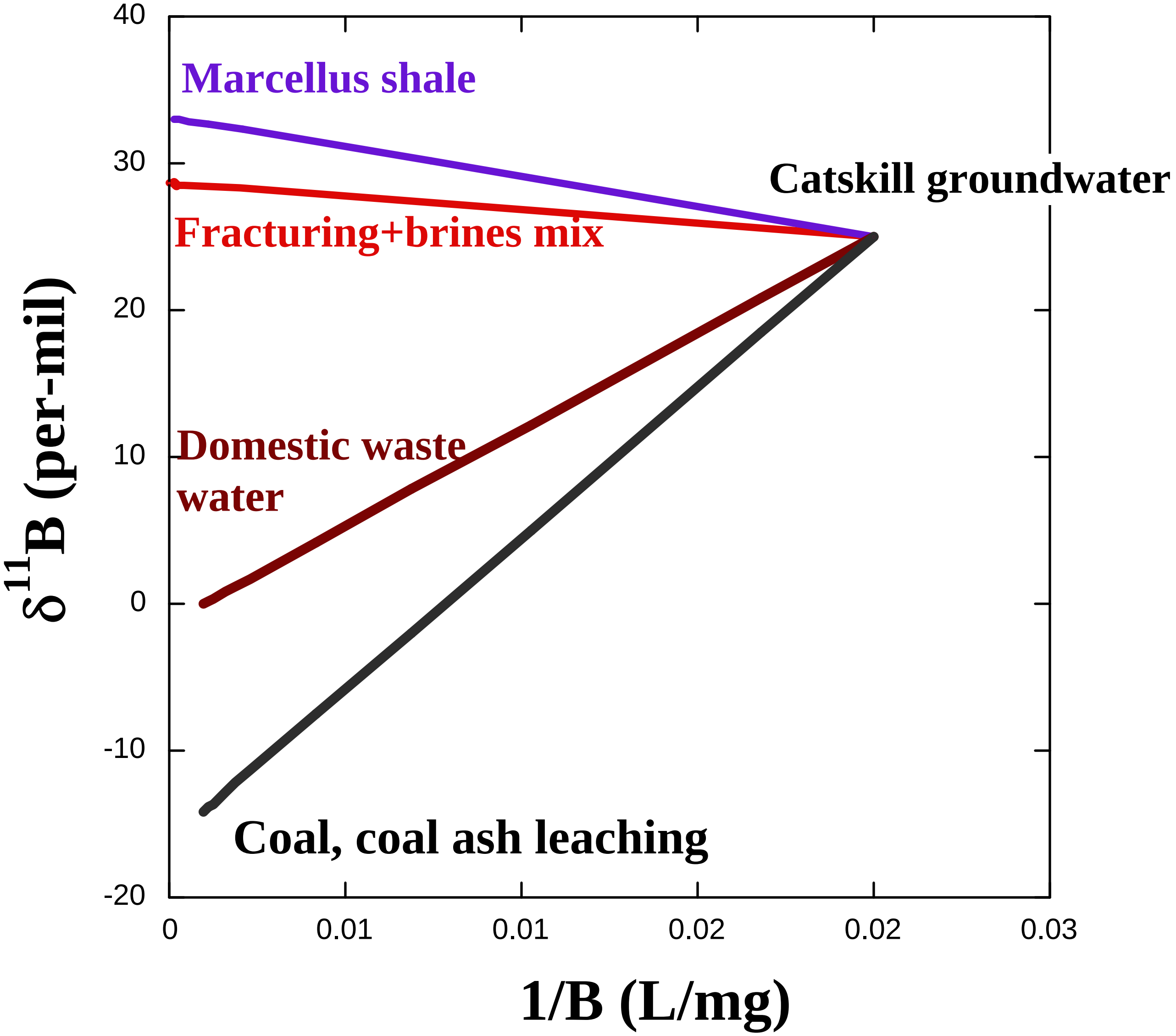
$\delta^{11}B = \{([^{11}B/^{10}B]_{sample}/[^{11}B/^{10}B]_{STD}\} -1\} x1000$

STD=NIST SRM-951 boric acid

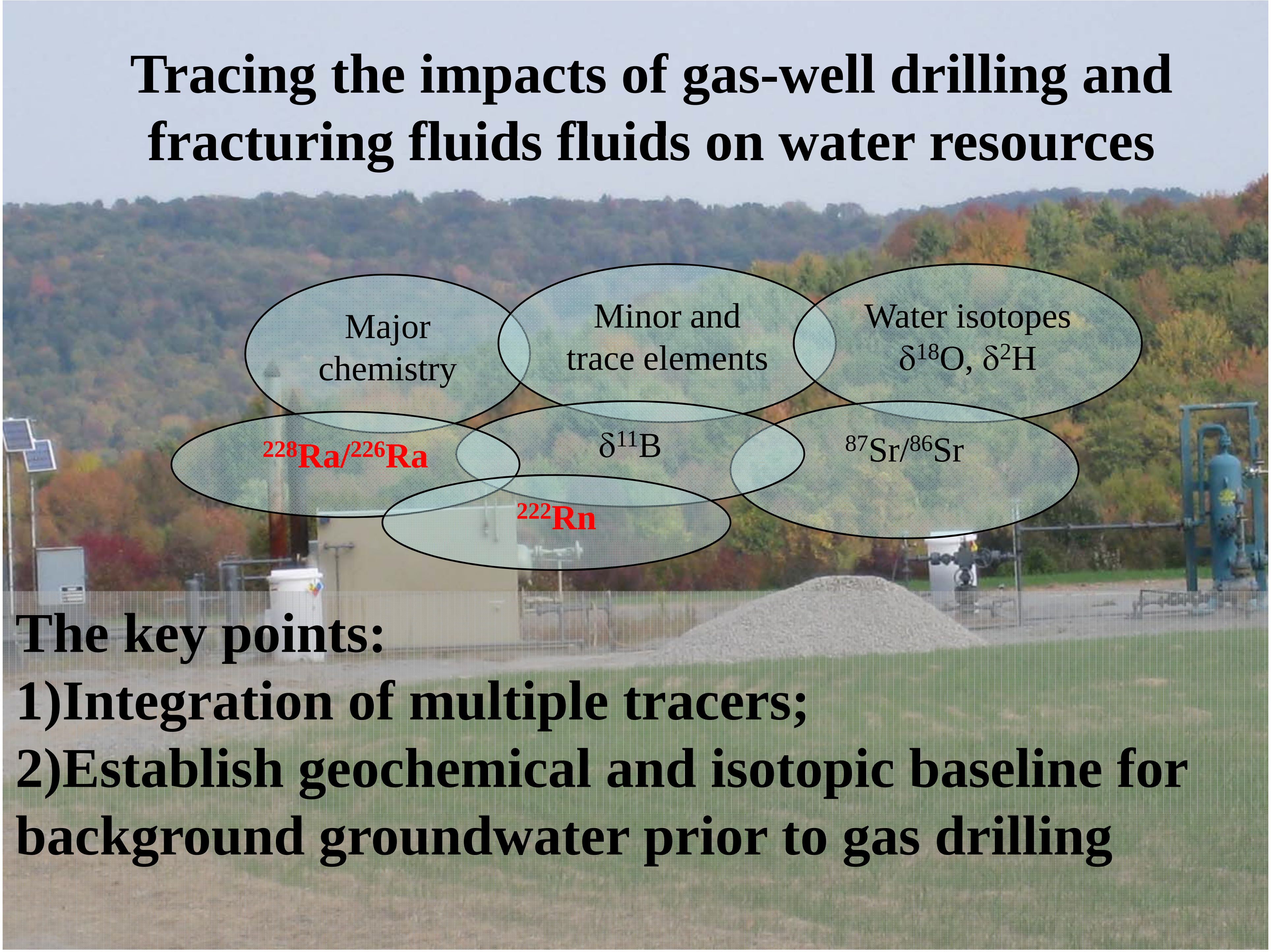
Boron isotopes: differentiation from other contaminant sources



Boron isotopes: differentiation from other contaminant sources



Tracing the impacts of gas-well drilling and fracturing fluids fluids on water resources



Major chemistry

Minor and trace elements

Water isotopes δ^{18}O, δ^{2}H

^{228}Ra/^{226}Ra

δ^{11}B

^{87}Sr/^{86}Sr

^{222}Rn

The key points:

1)Integration of multiple tracers;

2)Establish geochemical and isotopic baseline for background groundwater prior to gas drilling

Elucidating Water Contamination by Fracturing Fluids and Formation Waters from Gas Wells: Integrating Isotopic and Geochemical Tracers

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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

This presentation highlights the use of several isotope-fingerprinting methods coupled with a geochemical evaluation of the possible impacts of fracturing fluids and formation waters on the quality of water resources in gas-drilled affected areas. The presentation is based on preliminary data generated as part of Duke University research on the impact of gas drilling and fracturing fluids on shallow groundwater resources in Pennsylvania and New York. The study presented here is based on (1) systematic sampling of shallow groundwater from private wells from the Catskill aquifer in northeastern Pennsylvania in an attempt to establish baseline water quality data in areas that are expected to be affected by gas drilling and hydro- fracturing; (2) systematic analysis of the chemical and isotopic compositions of brines from the Marcellus Shale, one of the major target formations for unconventional gas exploration in the Appalachian basin; and (3) integration of geochemical (major and trace elements), water isotopes ($\delta^{18}O$, $\delta^{2}H$), and dissolved salt isotopes ($^{11}B/^{10}B$, $^{87}Sr/^{86}Sr$, $^{228}Ra/^{226}Ra$) of co-produced waters from a gas well in Pennsylvania. Boron and strontium isotopes were measured by thermal ionization mass spectrometry (Triton mass spectrometer) at Duke University using advanced methods with analytical reproducibility of 0.6‰ and 0.01‰, respectively (http://www.nicholas.duke.edu/tims/). Radium isotopes were measured at the Laboratory for Environmental Analysis of RadioNuclides at Duke University (http://www.nicholas.duke.edu/learn/). Trace metals were measured by VG PlasmaQuad-3 inductively coupled plasma mass-spectrometer (ICP-MS) at Duke University.

The Upper Devonian Catskill aquifer in northeastern Pennsylvania is the focus of the baseline survey and is composed of various amounts of gray to red shale, siltstone, sandstone, and conglomerate (Low and Galeone, 2007). The bedrock aquifer is underlying glacial deposits, particularly in valleys, and overlying the Lock Haven Formation. Groundwater flow in the Catskill aquifer is mainly through fractures. The investigated private wells had a reported depth range 110 to 430 (median=270) feet.

The chemical data of the Catskill groundwater was evaluated based on preliminary sampling of the Duke team combined with archive water-quality database from Pennsylvania Department of Conservation and Environmental Resources (Taylor, 1984). The data show that the Catskill groundwater has low salinity (TDS<400 mg/L) with a typical Ca-HCO_3 composition. All levels of trace inorganic contaminants were below the EPA Maximum Contaminant level (MCL) drinking water guidelines (e.g, arsenic < 1.4 μg/L, barium< 230 μg/L). Preliminary ^{226}Ra data also show activities of 0.1 to 0.5 pCi/L, significantly lower than the MCL guideline of 5 pCi/L for combined ^{226}Ra and ^{228}Ra activities. The stable oxygen and hydrogen isotope ratios of the Catskill groundwater were found to overlap the local meteoric isotopic composition, with δ^2H - δ^{18}O relationships identical to the Local Meteoric Water Line (Kendall and Coplan, 2001). The strontium isotope ratios show ^{87}Sr/^{86}Sr range of 0.71201 to 0.71553. Boron isotopes (expressed as δ^{11}B values, normalized to SRM951) of the Catskill groundwater have a range of 13.1 to 28.1‰.

In contrast, integration of existing data on the chemical and water isotope compositions of the Marcellus Shale (Osborn and McIntosh, 2010) and new measurements of strontium and boron isotopes of the Marcellus brines and flowback water from a gas well in PA (Meadow #4, provided by the USGS) show that formation/ fracturing fluids waters from gas wells in PA have a significantly different composition relative to the local shallow groundwater in eastern PA. In addition to the large difference in the salinity of the water (TDS of 200-300 to mg/L in shallow groundwater relative to 250,000 mg/L in the Marcellus brines), the shallow groundwater has a Ca-HCO_3 composition relative to a Ca-chloride composition the produced water from the gas well. Given the multiple salinity sources (e.g., sewage and domestic waste water, road salt deicing, coal mining drainage, leachates from coal combustion products), the salinity factor cannot be a sole indicator for the contamination of groundwater by formation/ fracturing waters. Likewise, in spite of the fact that the stable water isotopes of the Marcellus shale are more enriched with ^{18}O and ^{2}H relative to the local groundwater with a significant lower δ^2H-δ^{18}O slope, this parameter cannot be used alone, as other salinity sources, particularly those that involved surface evaporation, would have similar isotopic composition.

A detailed analysis of the geochemical and isotopic variations of the flowback waters samples from Meadows #4 well in PA represents a mixture of fracturing fluids and the original Marcellus Shale brines shows that the concentrations of Ca, Ba, Sr, B, and Li, among others, increase in flowback fluids during the first twenty days sampling following fracturing. Our data also show that ^{87}Sr/^{86}Sr ratios increase from 0.71012 in the initial flow to 0.71122 on 20th flow day, as the isotopic shift occurred already on the first day of flow. Likewise, the δ^{11}B show a slight increase from 28.3‰ in the initial flow to 30.1‰ in the twentieth flow day. The Sr and B isotope ratios of the latest days are similar to those of the Marcellus Shale brines and thus indicating a blending of two end-members (1) fracturing fluids with lower salinity and concentrations of trace elements, lower ^{87}Sr/^{86}Sr ratios (<0.71012) and δ^{11}B (<28‰) values; and (2) the Marcellus Shale end-member with higher ^{87}Sr/^{86}Sr ratios (0.7115) and δ^{11}B values (32-33‰). This flow experiment also demonstrates that under operational conditions of continuous pumping, the composition of the Marcellus brines is expected to predominant the produced waters from gas wells.

Mixing modeling shows that the differences in both strontium concentrations and isotopic ratios between the Marcellus Shale brines and/or the mixed Marcellus-fracturing fluids with the local groundwater in eastern PA could be very useful in delineating even small contribution of formation water. Sensitivity tests show even a very small contribution of formation water (1/100) could be identified in a system that is controlled by mixing of the Marcellus Shale brines ($^{87}Sr/^{86}Sr$ =0.7115) and/or a mixture of the Marcellus Shale and fracturing fluids ($^{87}Sr/^{86}Sr$ <0.71012). Consequently, strontium isotopes could be a very sensitive tracer to track the possible contamination of shallow groundwater and surface water by formation/ fracturing waters from gas wells. While the boron concentrations of the flowback waters (17,000 to 63,000 μg/L) are higher by three orders of magnitude relative to the local groundwater (10 to 400 μg/L), the $\delta^{11}B$ values are only slightly higher (32-33‰ in the Marcellus brines relative to 13-28‰ in the Catskill groundwater). Nonetheless, this isotopic composition is different from other potential salinity sources (e.g., coal ash and acid mine drainage with elevated B concentrations and much lower $\delta^{11}B$ values of -15 to 0‰) and thus should be used, in conjunction with the other tracers as a critical tool to assess the possible interaction of formation/ fracturing waters with shallow groundwater or surface waters.

Overall, our study indicates that a detailed survey of the baseline chemical and isotopic compositions of shallow groundwater is crucial in evaluating possible contamination of flowback fracturing fluids and co-produced formation waters from gas wells. Our preliminary investigation of the Catskill formation groundwater from northeastern PA clearly shows significant chemical and isotopic differences between the shallow groundwater and the Marcellus brines and/or fracturing fluids mixed with the Marcellus brines. The ability to delineate trace levels of formation / fracturing waters in very early stages of water contamination depends on integration of multiple geochemical and isotopic tracers that could provide reliable and sensitive detections of contamination by effluents associated with hydro-fracturing and gas drilling.

References

Low, D.J., and Galeone, D.G., (2007) Reconnaissance of arsenic concentrations in ground water from bedrock and unconsolidated aquifers in eight northern-tier counties of Pennsylvania: U.S. Geological Survey Open-File Report 2006-1376, 35 p.

Osborn S.G., McIntosh, J.C. (2010) Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl Geochem* 25: 456-471.

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Kendall, C. and Coplan, T. B., (2001) Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrological Processes* 15: 1363-1393.