New Isotopic Tracers for Shale Gas and Hydraulic Fracturing Fluids

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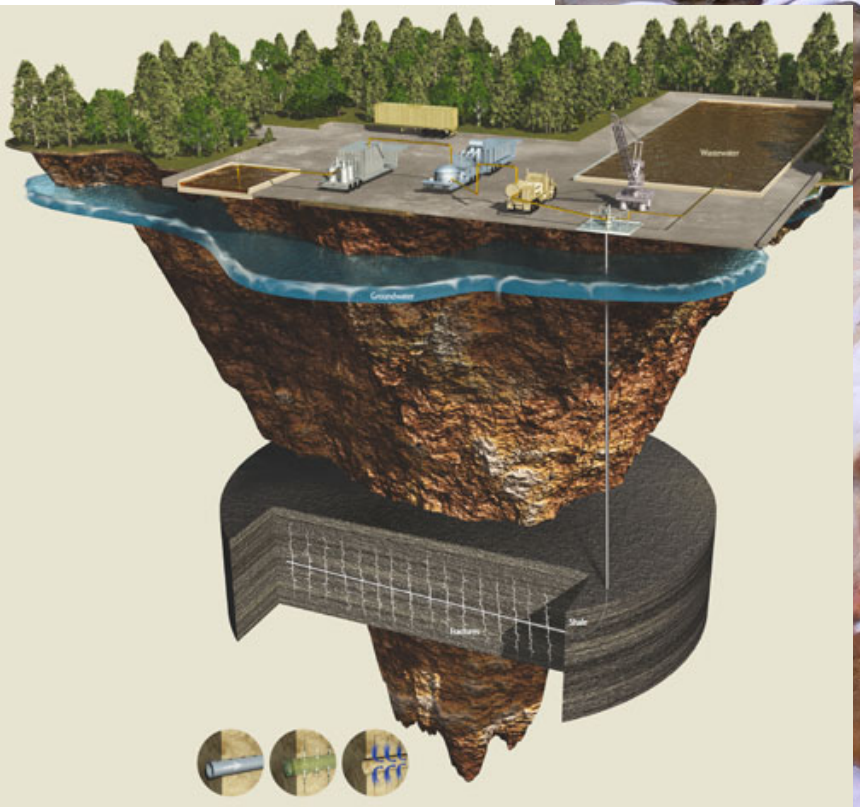
Duke study:

1. Since 2010 sampling over 600 shallow private wells in PA, NY, WV, AK, NC, TX;
2. Sampling produced/flowback waters from the Marcellus Shale and other formations in PA and NY;
3. Sampling over 100 surface waters in PA and river sediments downstream from waste waters disposal sites;
3. Analysis of methane geochemistry in private wells – concentrations, ratios (C_1/C_2), isotopes ($\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$)
4. Analysis of the chemistry (major and trace elements) and isotopes ($^{87}Sr/^{86}Sr$, $\delta^{11}B$, $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$-DIC)
5. Measurements of naturally occurring radium (^{226}Ra, ^{228}Ra) radionuclides;
6. Measurement of noble gas in groundwater

The challenge of tracing fracking and shale gas waste fluids in the environment:

Naturally occurring tracers: $^{87}Sr/^{86}Sr$, $\delta^{11}B$, $\delta^{18}O$, $\delta^{2}H$, $^{228}Ra/^{226}Ra$



Thermal ionization mass spectrometry

Boron isotopes:

Mean $^{11}B/^{10}B$=4.0057

SD-$\delta^{11}B$= 0.4‰

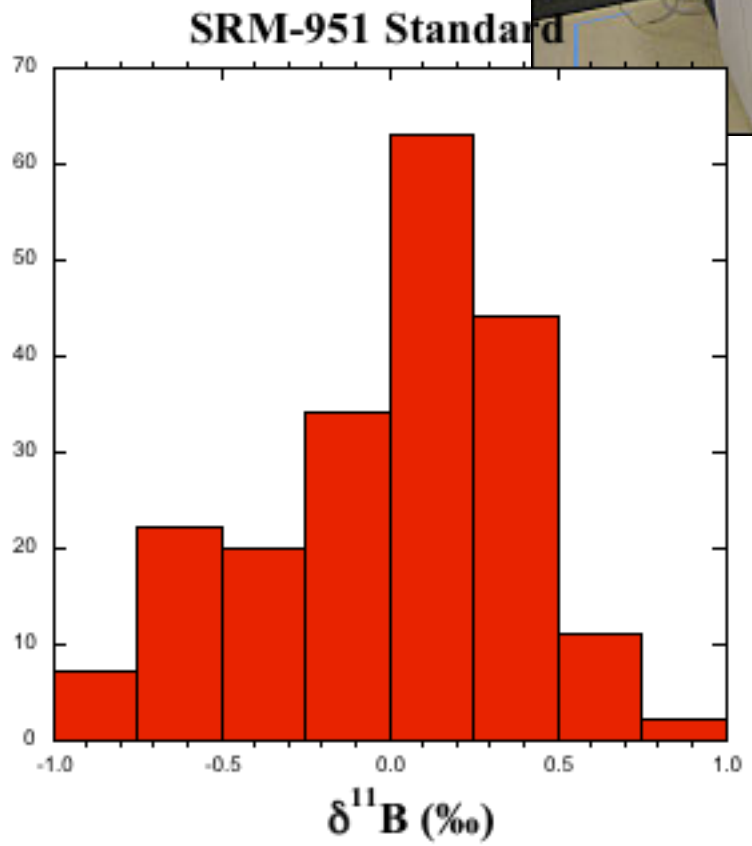
N=210

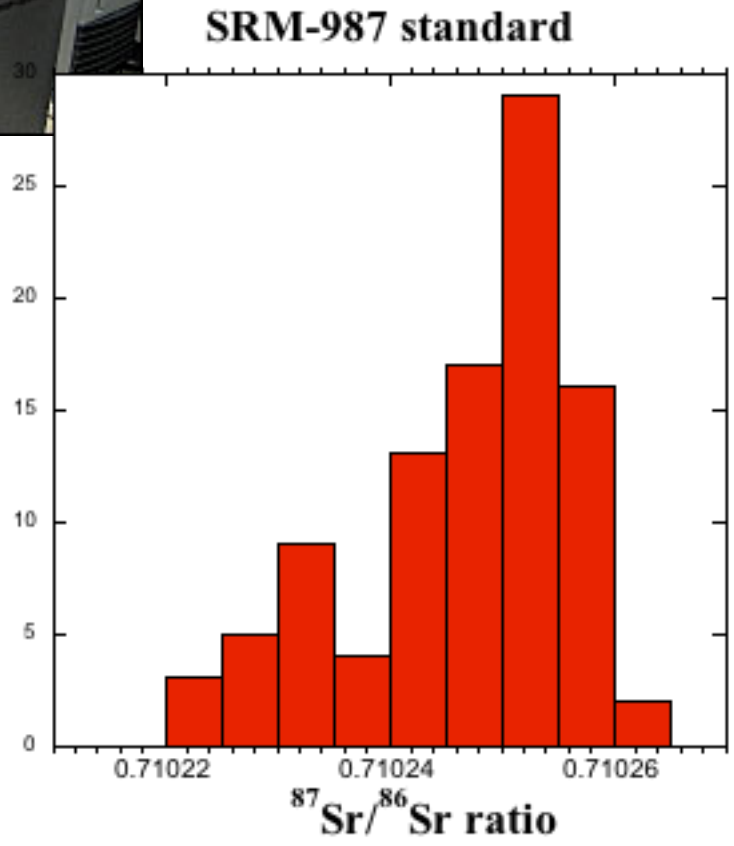
Strontium isotopes:

Mean $^{87}Sr/^{86}Sr$=0.710246

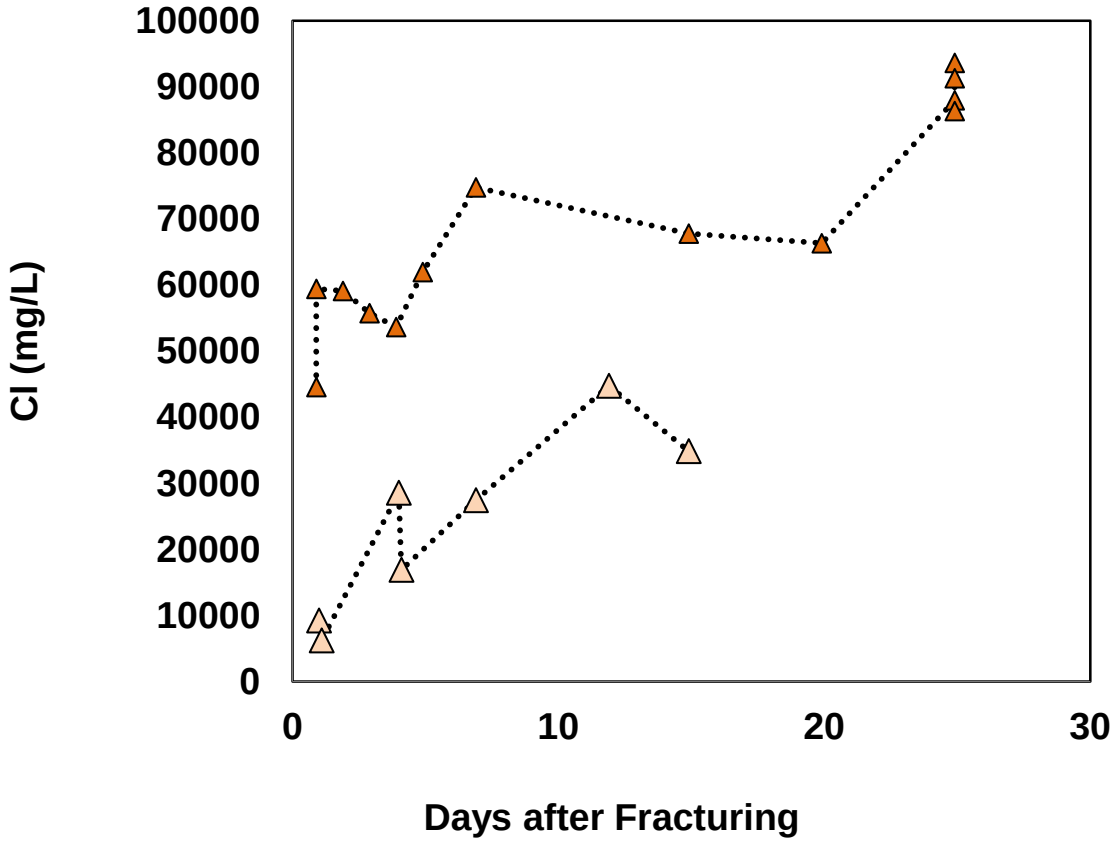
SD= 0.013 ‰

N=98





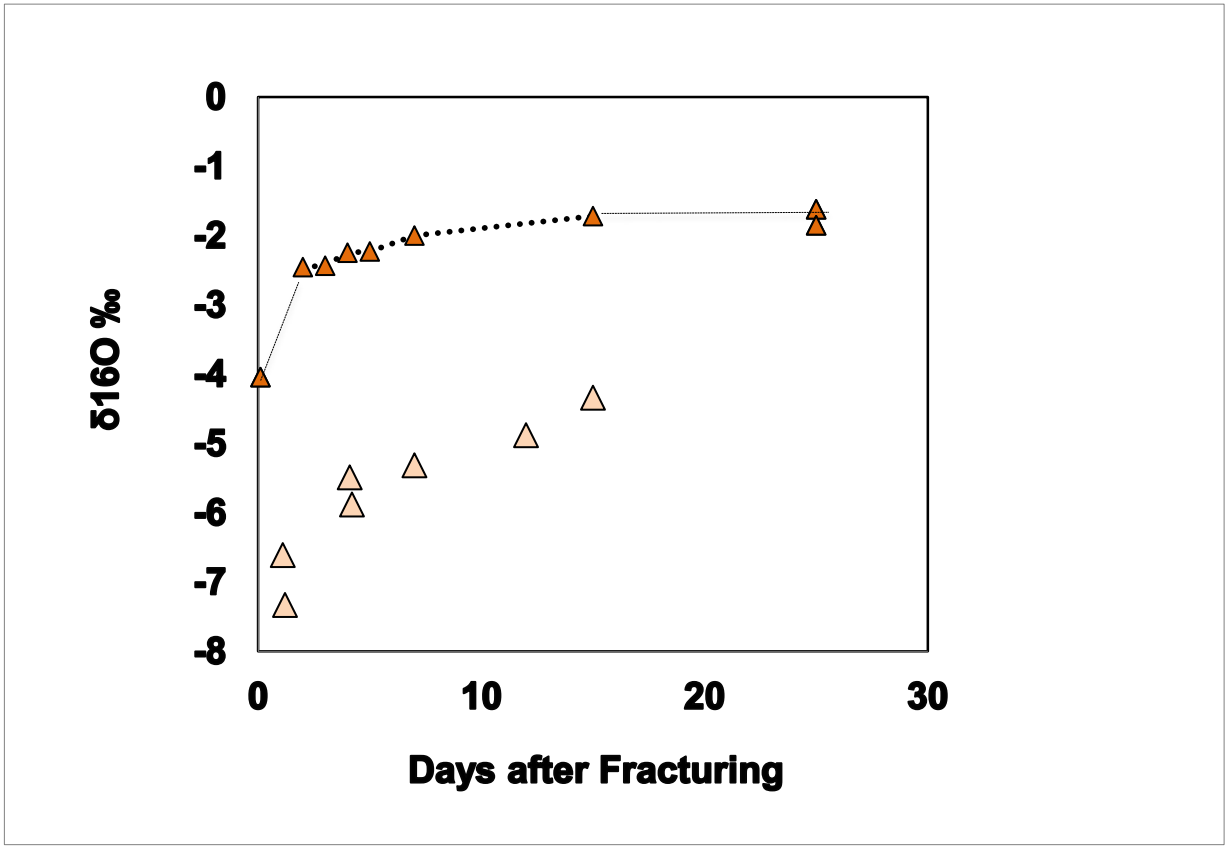
Flowback from the Marcellus gas wells



Two types of flowback waters:

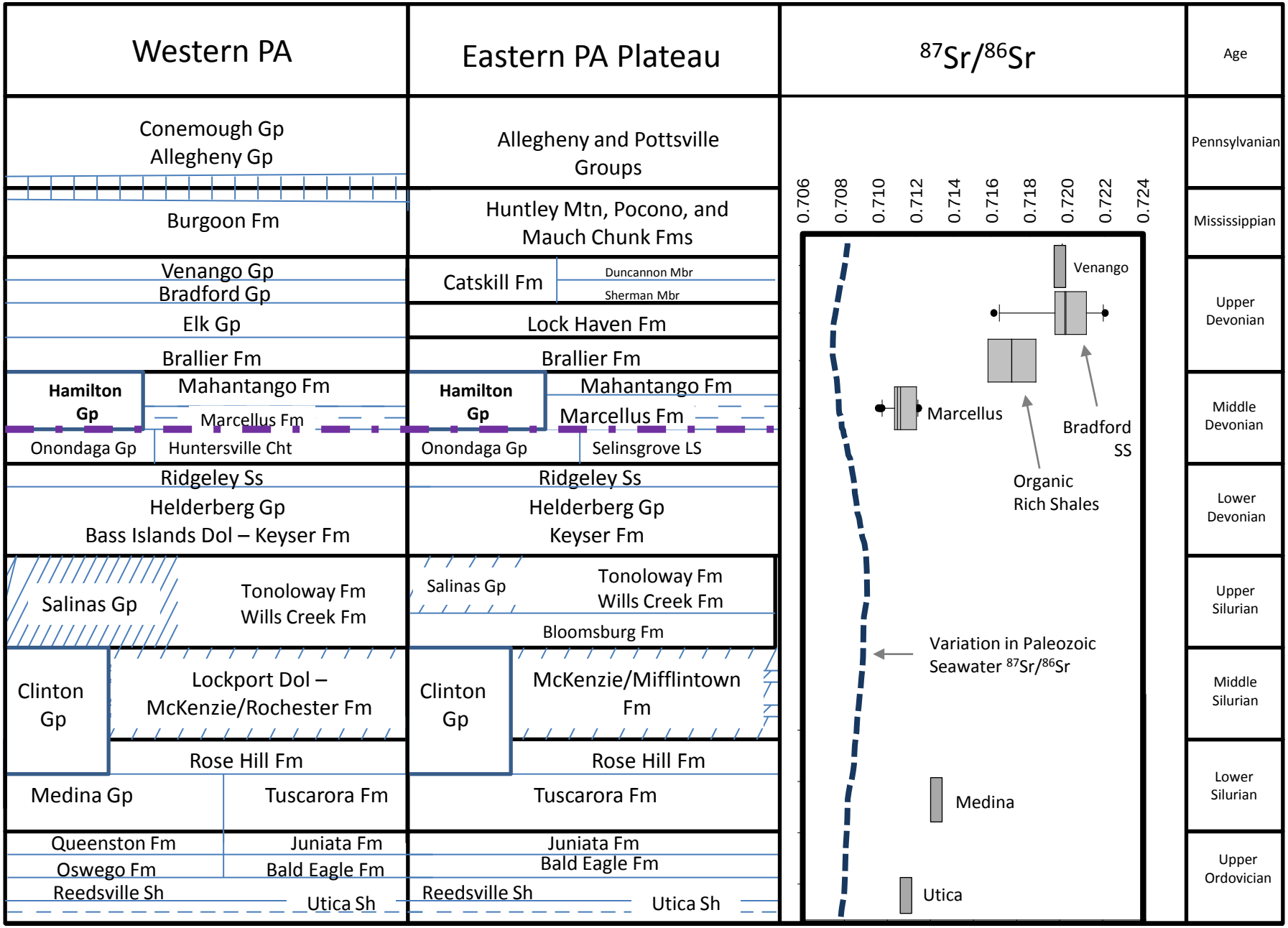
1) Injection water for fracturing was fresh water;
2) Injection water for fracturing was recycled (saline) frack water

Stable isotopes in Flowback waters from the Marcellus gas wells



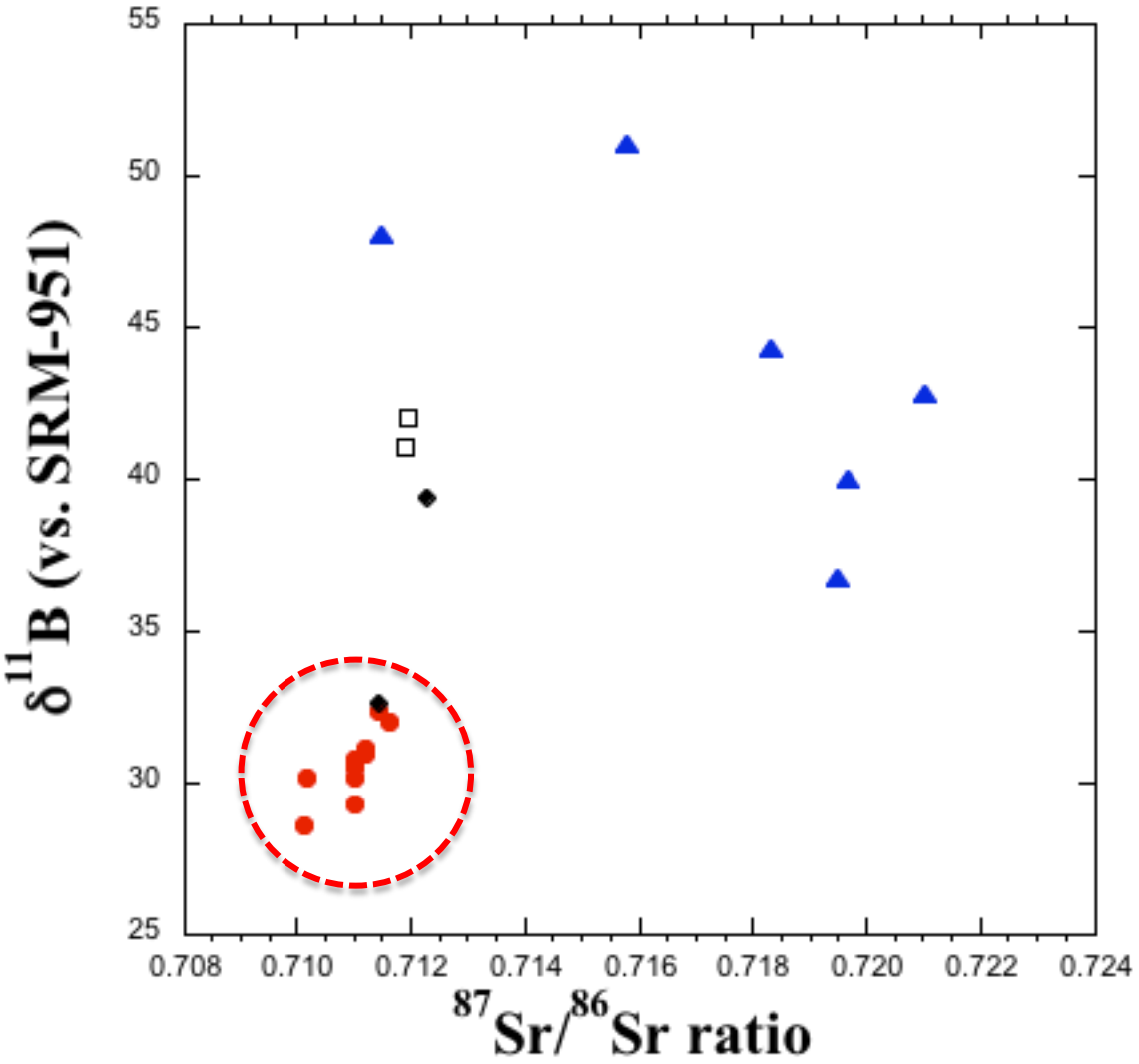
Progressively increase of $\delta^{18}O$ (and $\delta^{2}H$) in flowback water → larger proportion of the high $\delta^{18}O$ (and $d^{2}H$) formation water → **Identification of the relative mixing proportion between injected water and the original formation water.**

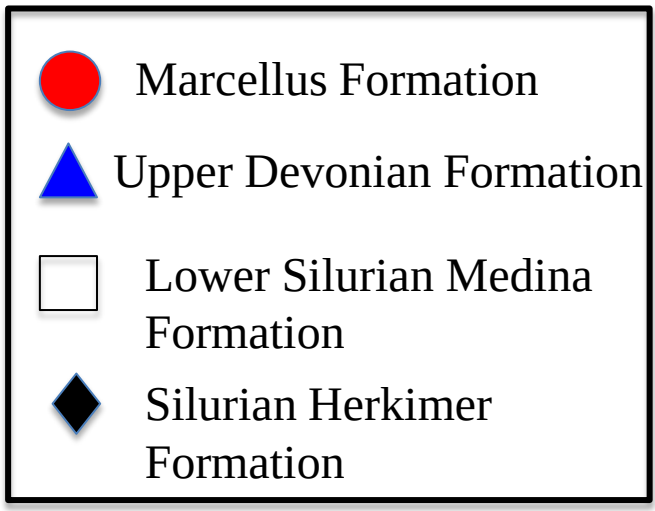
Strontium isotopes of Appalachian produced water (from Warner et al., PNAS)



The combined used of boron and strontium isotopes

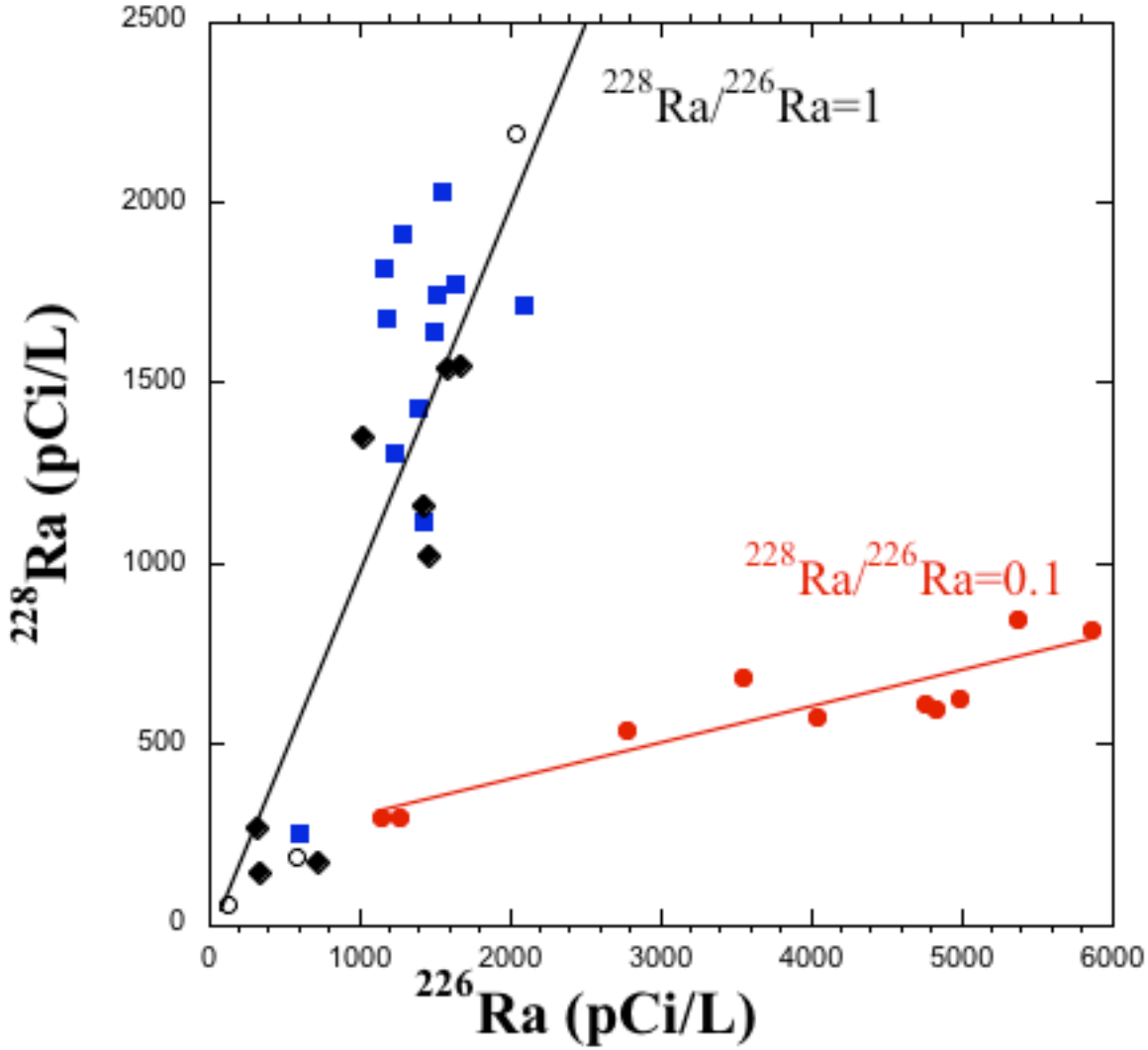
Distinction between the Marcellus brines and other (conventional) oil and gas produced waters

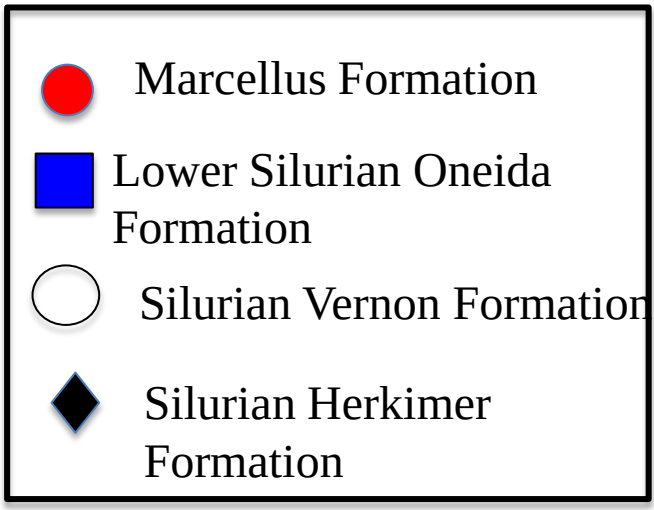




The used of radium isotopes

Distinction between the Marcellus brines and other (conventional) oil and gas produced waters





Conclusions

The combined application of geochemistry, stable isotopes ($\delta^{18}O$, $\delta^{2}H$), strontium isotopes ($^{87}Sr/^{86}Sr$), boron isotopes ($\delta^{11}B$), and radium isotopes ($^{228}Ra/^{226}Ra$) provides a unique methodology for tracing and monitoring shale gas and fracking fluids in the environment.