

# **New Isotopic Tracers for Shale Gas and Hydraulic Fracturing Fluids**

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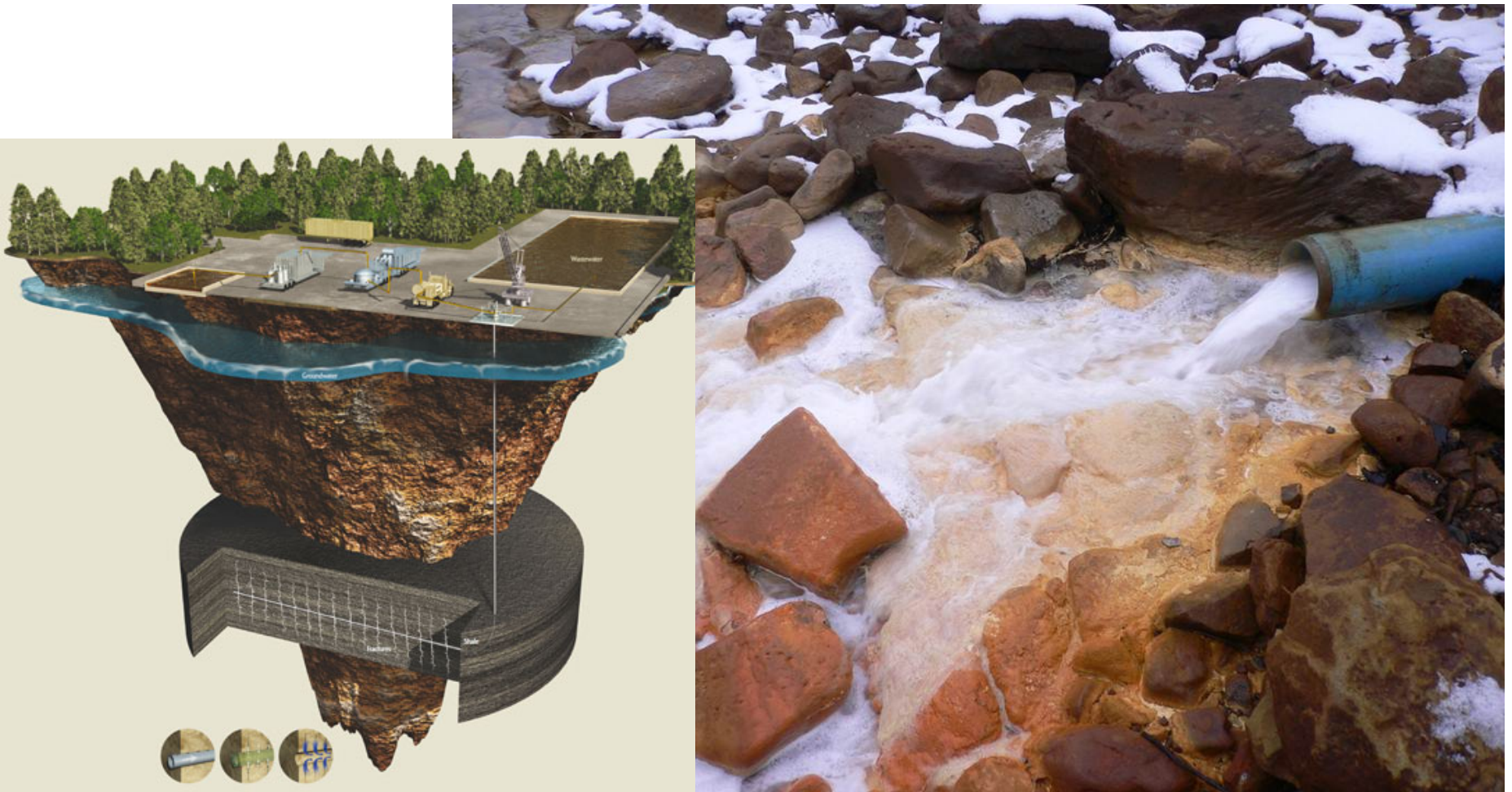


# Duke study:

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 ( $\delta^{13}C_{CH_4}$ ,  $\delta^2H_{CH_4}$ )
4. Analysis of the chemistry (major and trace elements) and isotopes ( $^{87}Sr/^{86}Sr$ ,  $\delta^{11}B$ ,  $\delta^{18}O$ ,  $\delta^2H$ ,  $\delta^{13}C$ -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:  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{11}\text{B}$ ,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ,  $^{228}\text{Ra}/^{226}\text{Ra}$**



# Thermal ionization mass spectrometry

## Boron isotopes:

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

SD- $\delta^{11}\text{B}= 0.4\text{‰}$

N=210



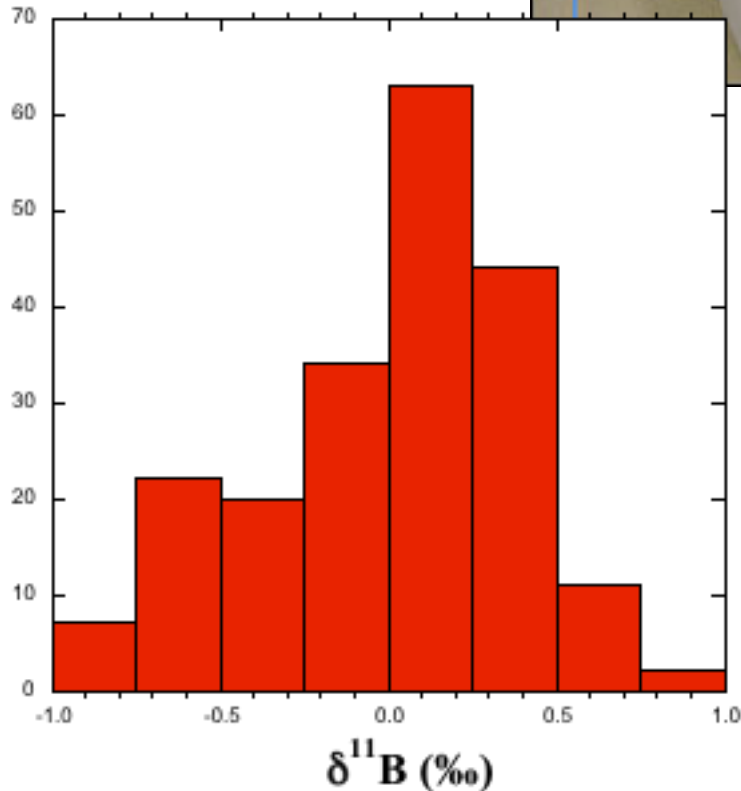
## Strontium isotopes:

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

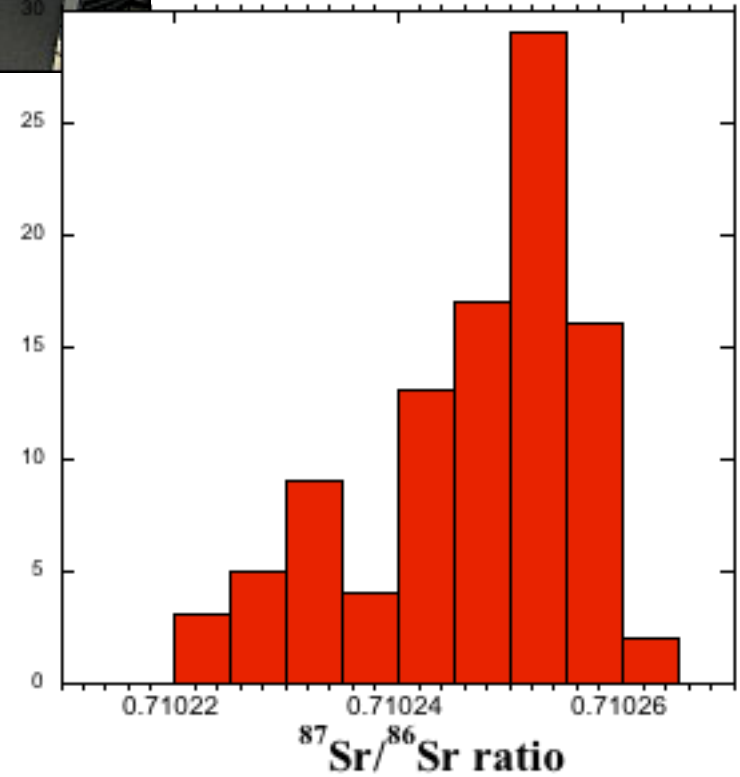
SD= 0.013 ‰

N=98

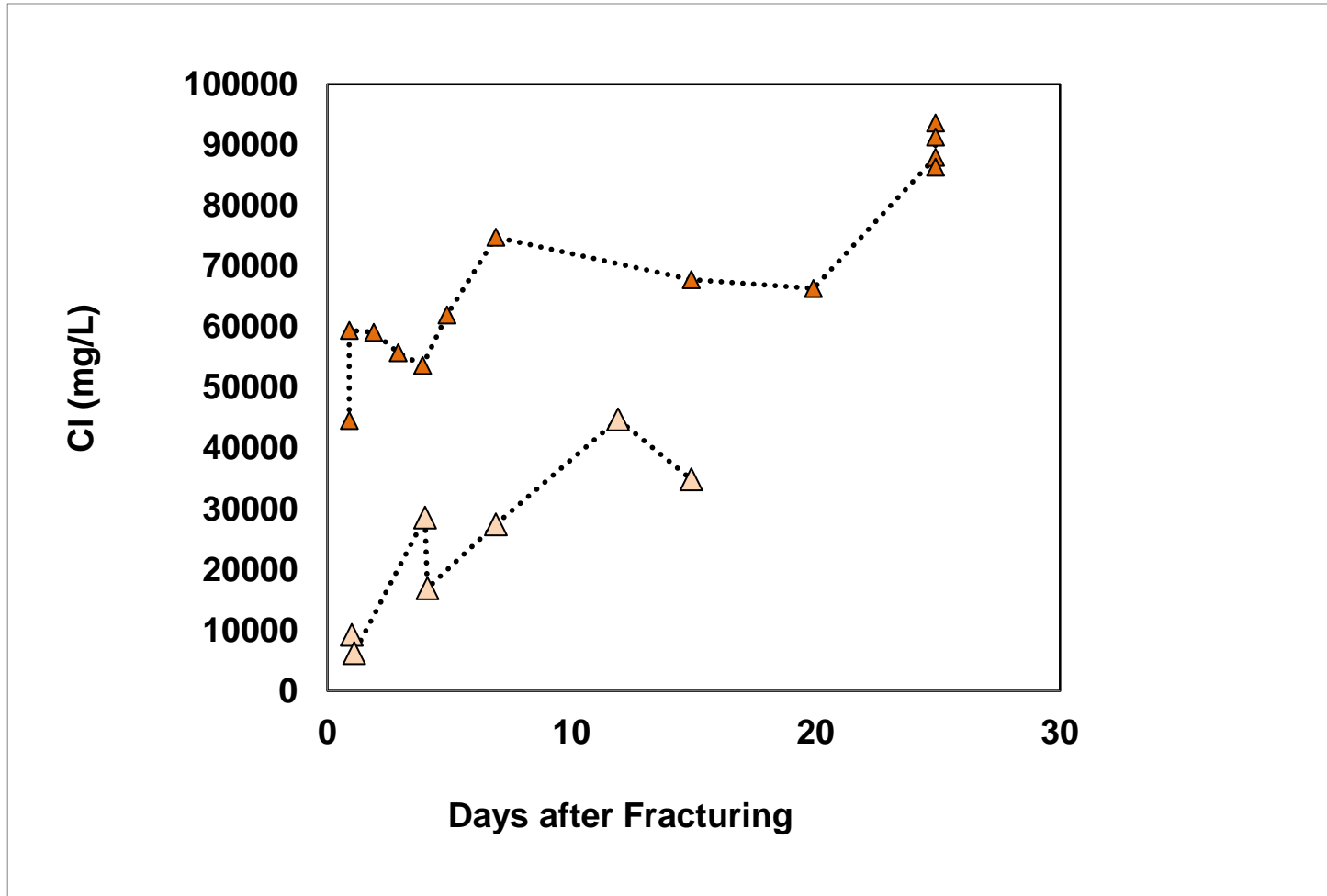
SRM-951 Standard



SRM-987 standard



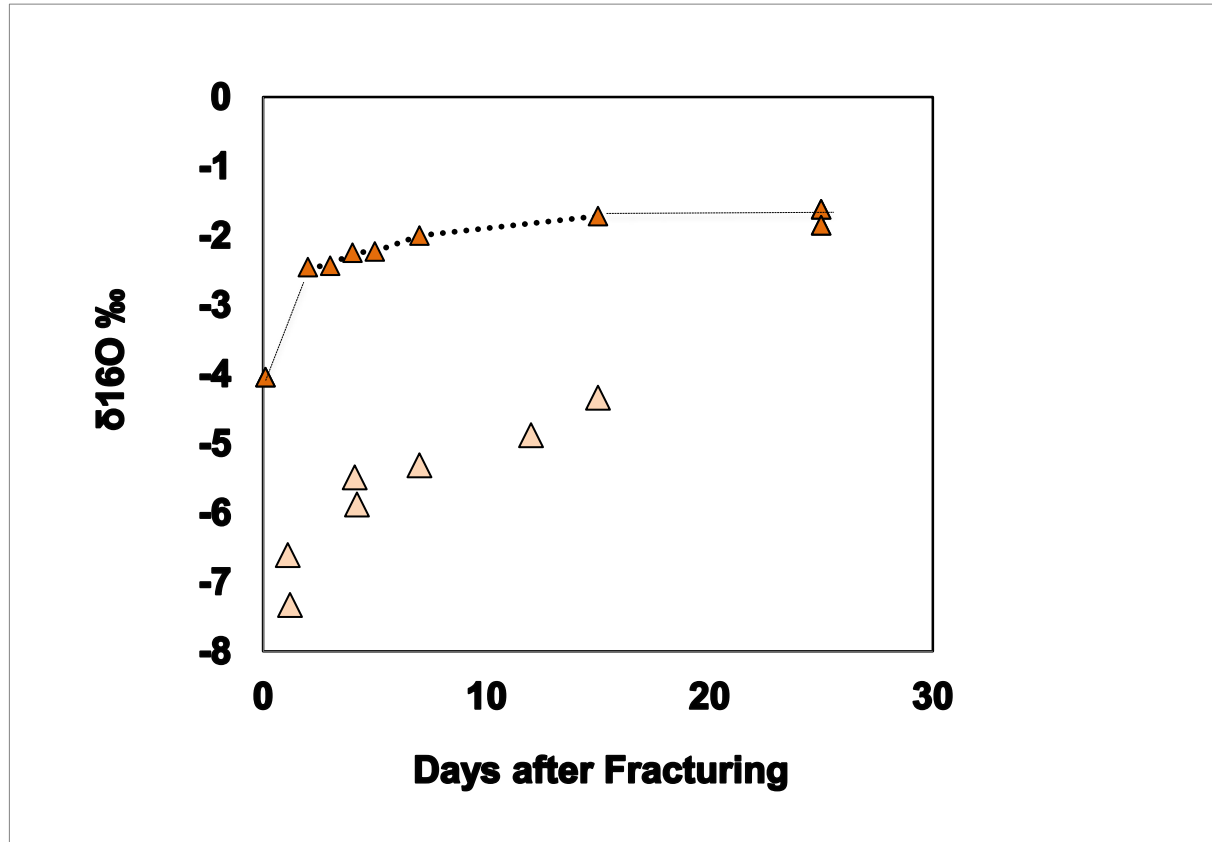
# Flowback from the Marcellus gas wells



Two types of flowback waters:

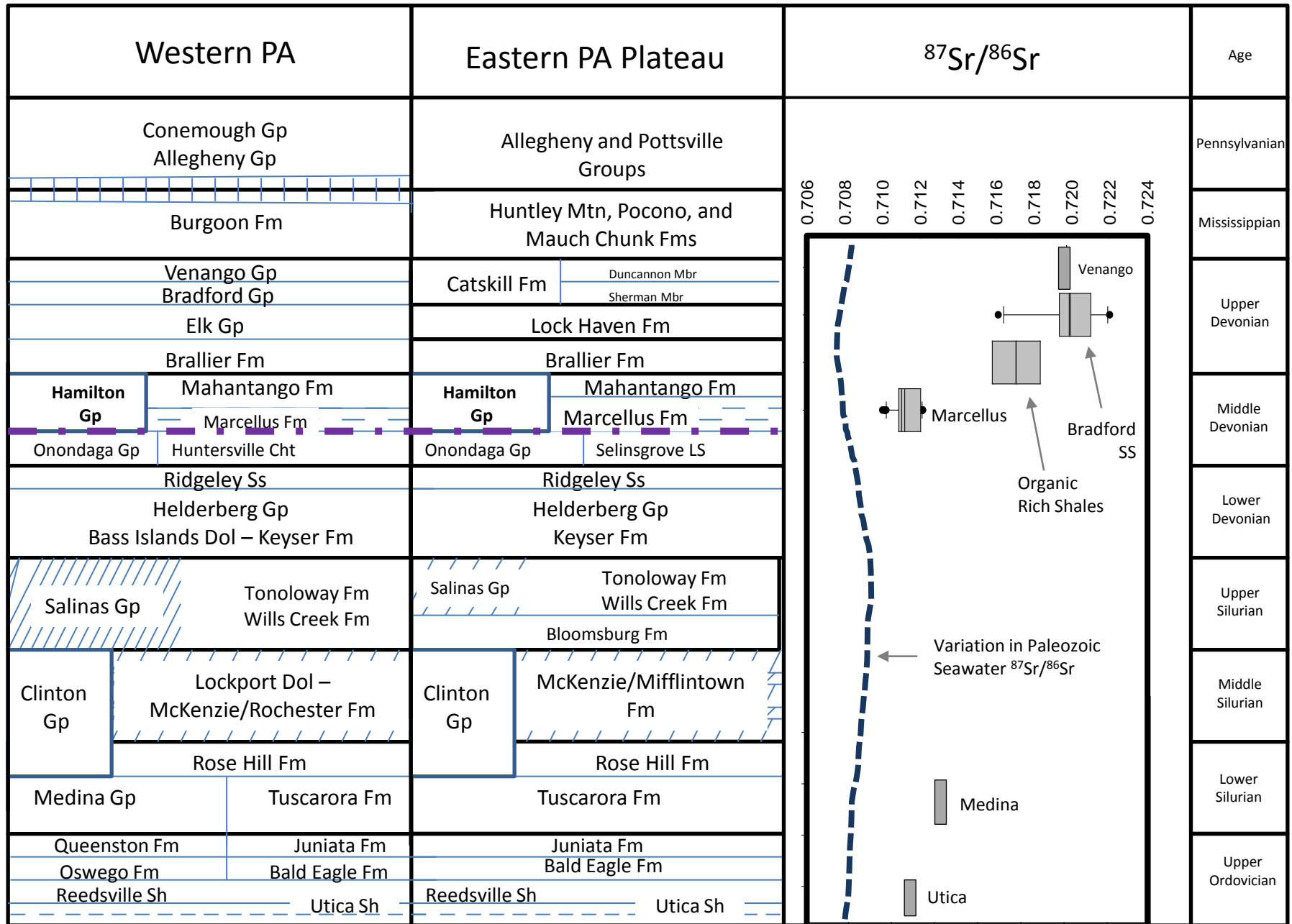
- 1) Injection water for fracturing was fresh water;
- 2) Injection water for fracturing was recycled (saline) frack water

# Stable isotopes in Flowback waters from the Marcellus gas wells



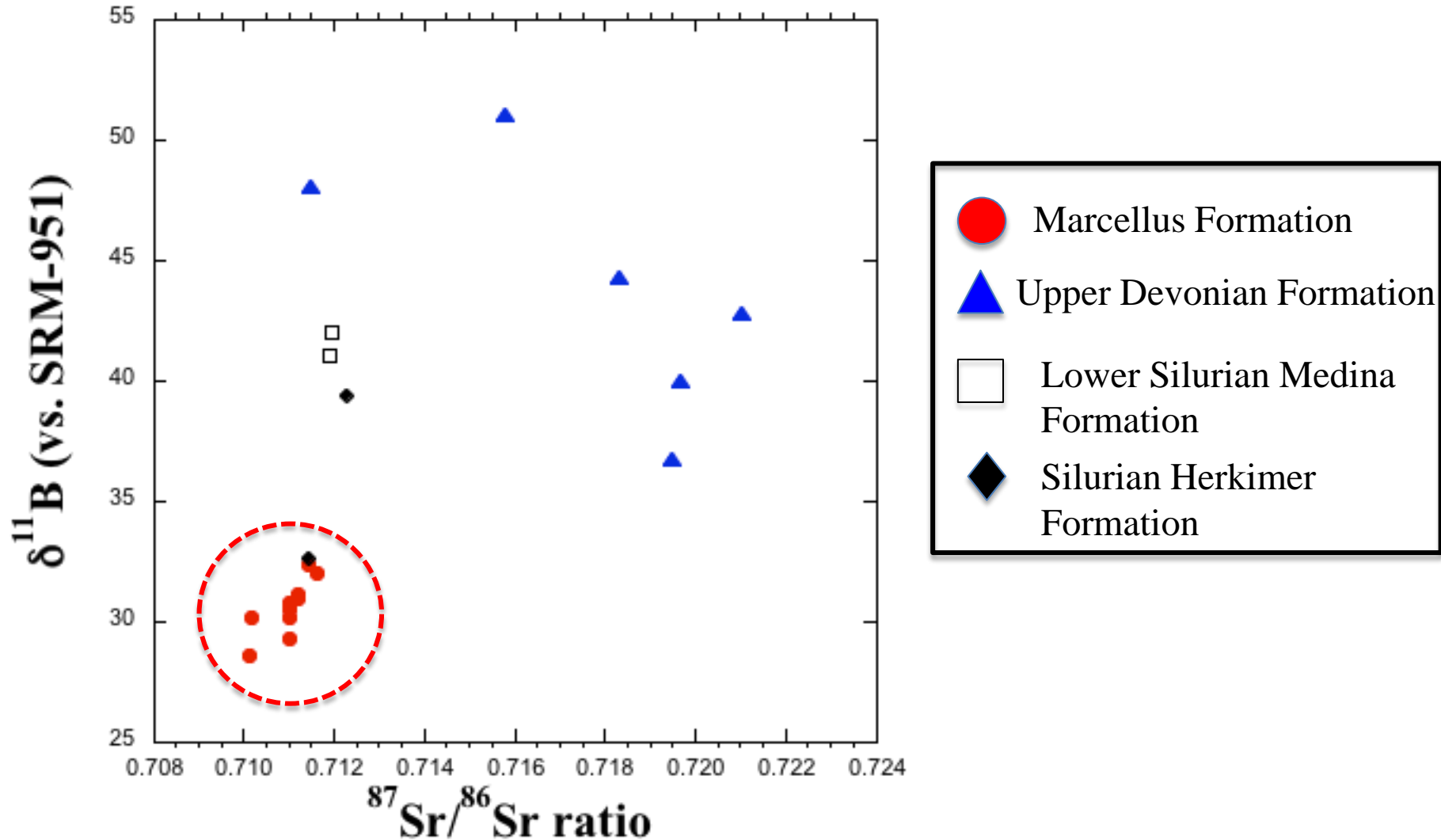
Progressively increase of  $\delta^{18}\text{O}$  (and  $\delta^2\text{H}$ ) in flowback water →  
larger proportion of the high  $\delta^{18}\text{O}$  (and  $\delta^2\text{H}$ ) formation water →  
**Identification of the relative mixing proportion between injected  
water and the original formation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

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



# The combined use of boron and strontium isotopes

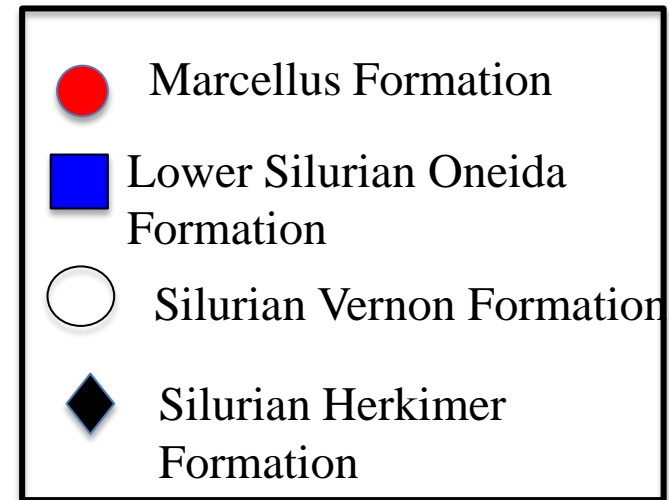
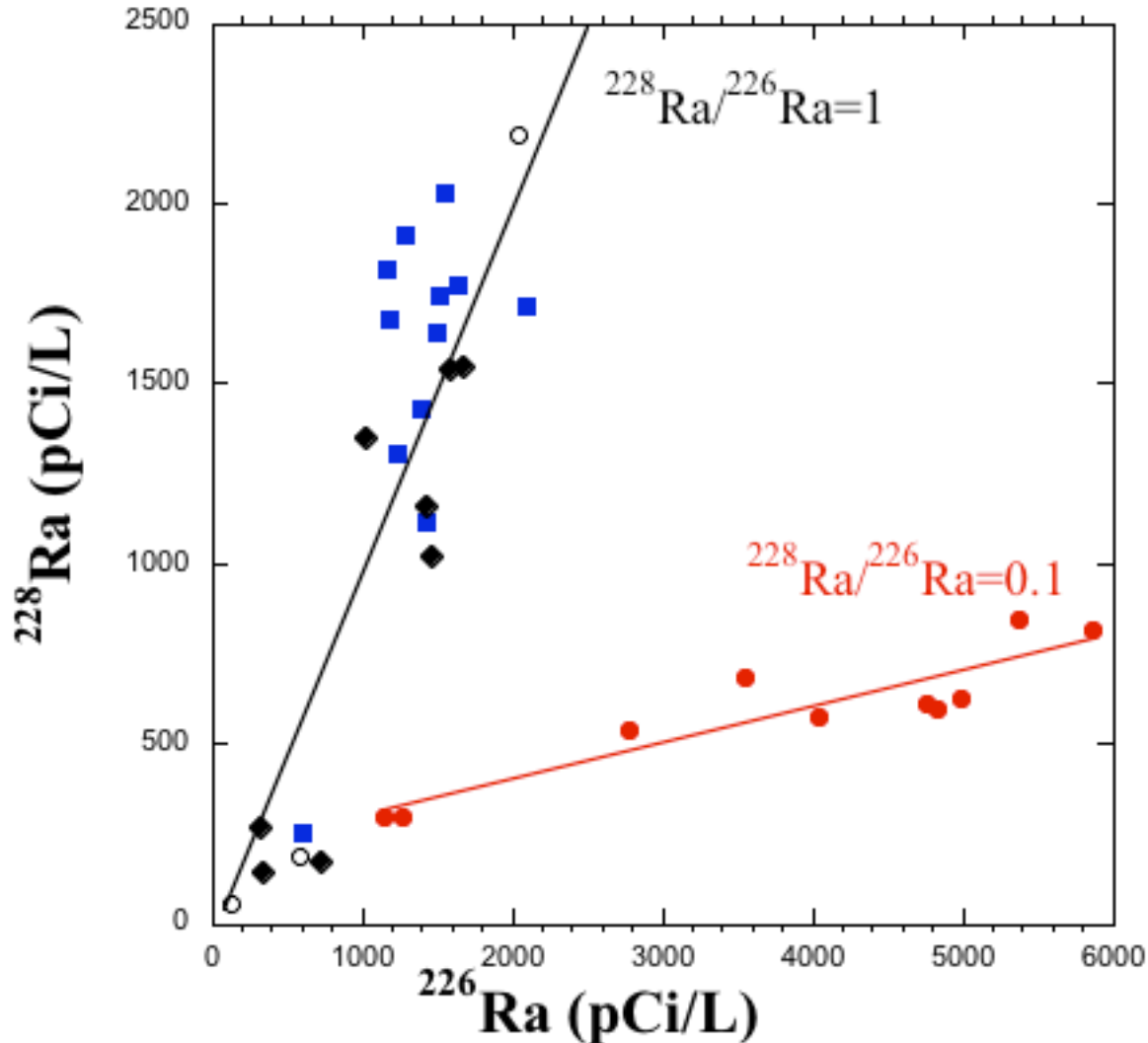
## Distinction between the Marcellus brines and other (conventional) oil and gas produced waters





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