New Isotopic Tracers for Shale Gas and Hydraulic Fracturing Fluids

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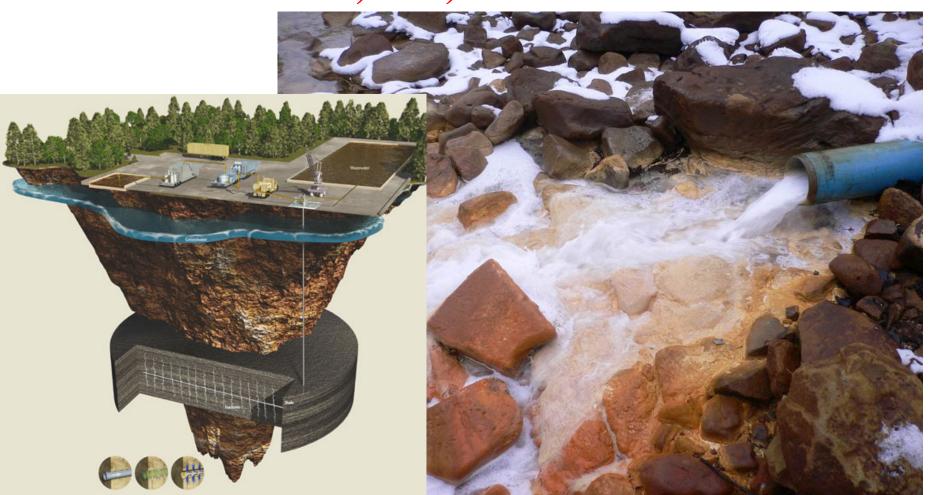


Duke study:

- 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 ($\delta^{13}C_{CH4}$, δ^2H_{CH4})
- 4. Analysis of the chemistry (major and trace elements) and isotopes (87 Sr/ 86 Sr, δ^{11} B, δ^{18} O, δ^{2} H, δ^{13} C-DIC)
- 5. Measurements of naturally occurring radium (²²⁶Ra, ²²⁸Ra) 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, δ^{11} B, δ^{18} O, δ^{2} H, 228 Ra/ 226 Ra



Thermal ionization mass spectrometry

Boron isotopes:

Mean ¹¹B/¹⁰B=4.0057

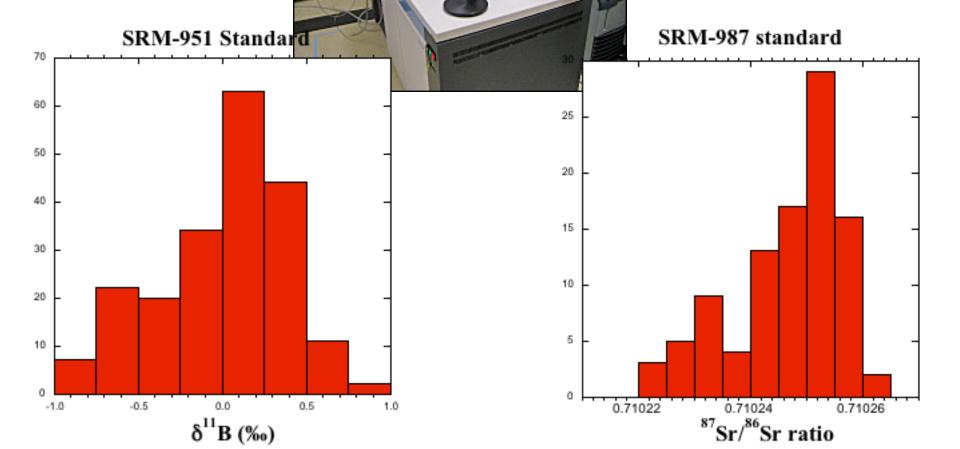
 $SD-\delta^{11}B = 0.4\%$

N=210

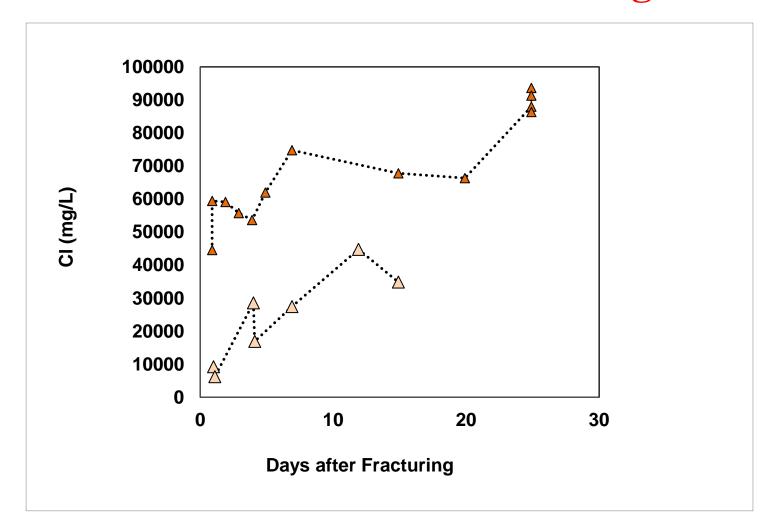
Strontium isotopes:

Mean ⁸⁷Sr/⁸⁶Sr=0.710246 SD= 0.013 %

N=98



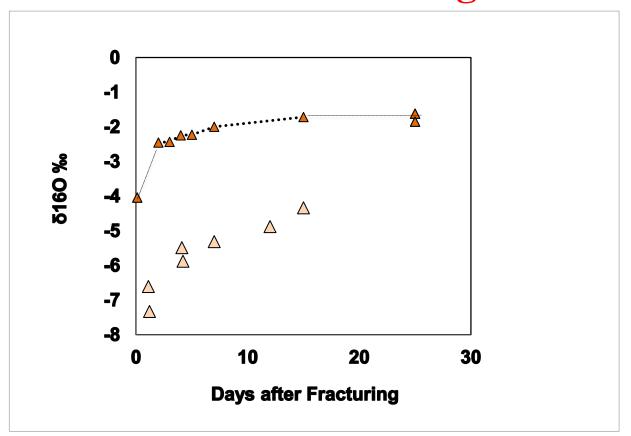
Flowback from the Marcellus gas wells



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



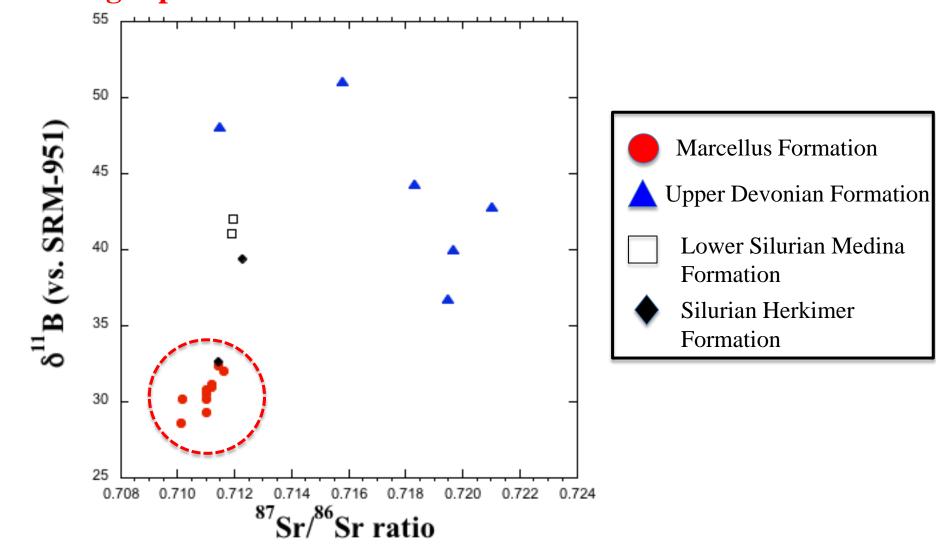
Progressively increase of $\delta^{18}O$ (and $\delta^{2}H$) in flowback water \rightarrow larger proportion of the high $\delta^{18}O$ (and $d^{2}H$) formation water \rightarrow **Identification of the relative mixing proportion between injected** water and the original formation water.

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

			T		1	•	1	
Western PA			Eastern PA Plateau			⁸⁷ Sr/ ⁸⁶ Sr	Age	
Conemough Gp Allegheny Gp			Allegheny and Pottsville Groups			0.706 0.708 0.710 0.714 0.716 0.720 0.722		
Burgoon Fm			Huntley Mtn, Pocono, and Mauch Chunk Fms					
Venango Gp Bradford Gp			Catskill Fm Duncannon Mbr Sherman Mbr		Venango	Upper Devonian		
Elk Gp Brallier Fm			Lock Haven Fm Brallier Fm				Devoman	
Hamilto Gp			Hamilton Gp	Mahantango Fm Marcellus Fm		Marcellus		
Onondaga Gp Huntersville Cht		Onondaga (Gp Selinsgrove LS	SS		Devonian		
Ridgeley Ss			Ridgeley Ss		11	Organic		
Helderberg Gp			Helderberg Gp		Н	Rich Shales	Lower Devonian	
Bass Islands Dol – Keyser Fm			Keyser Fm		Ш	i		
Salinas Gp / Wills Creek Fm		, Salinas Gp Tonoloway Fm , Vills Creek Fm Bloomsburg Fm			Upper Silurian			
Clinton Gp	McKenzi	Lockport Dol – McKenzie/Rochester Fm		McKenzie/Mifflintown 7		Variation in Paleozoic Seawater ⁸⁷ Sr/ ⁸⁶ Sr		
	Rose Hill Fm			Rose Hill Fm		!		
Medina Gp Tuscarora Fm		Tuscarora Fm			Medina	Lower Silurian		
Queenston Fm Juniata Fm Oswego Fm Bald Eagle Fm Reedsville Sh Utica Sh		Juniata Fm Bald Eagle Fm Reedsville Sh Utica Sh			Utica	Upper Ordovician		

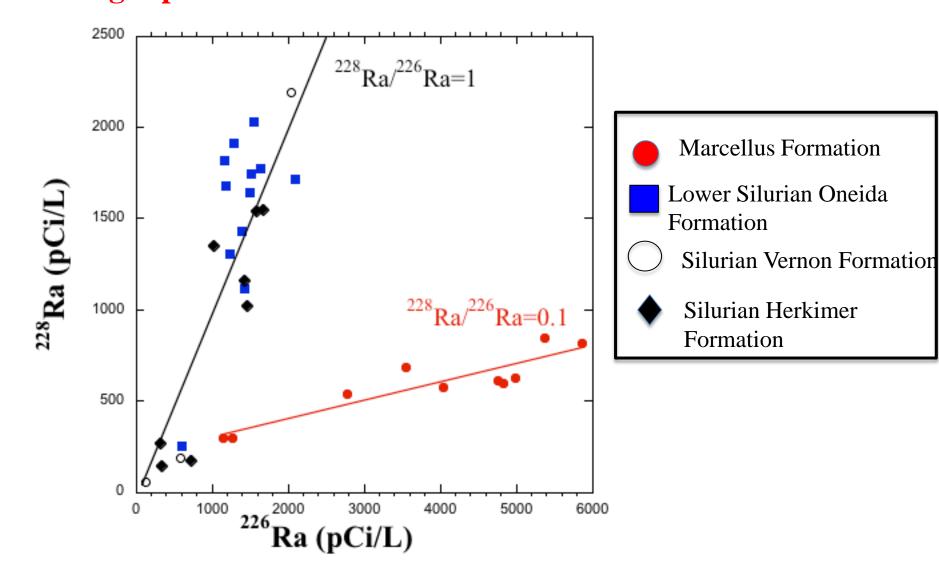
The combined used of boron and strontium isotopes

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 (δ^{18} O, δ^{2} H), strontium isotopes (87 Sr/ 86 Sr), boron isotopes (δ^{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.