New Isotopic Tracers for Shale Gas and Hydraulic Fracturing Fluids

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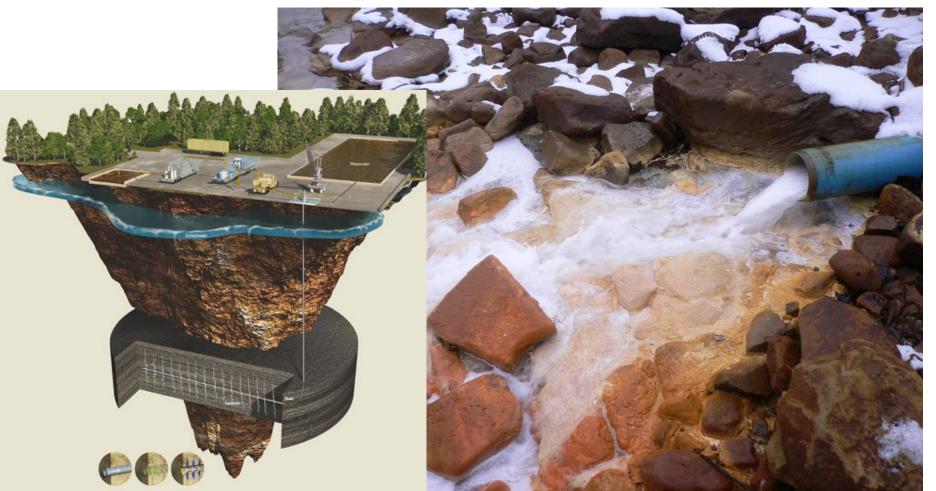


Duke study:

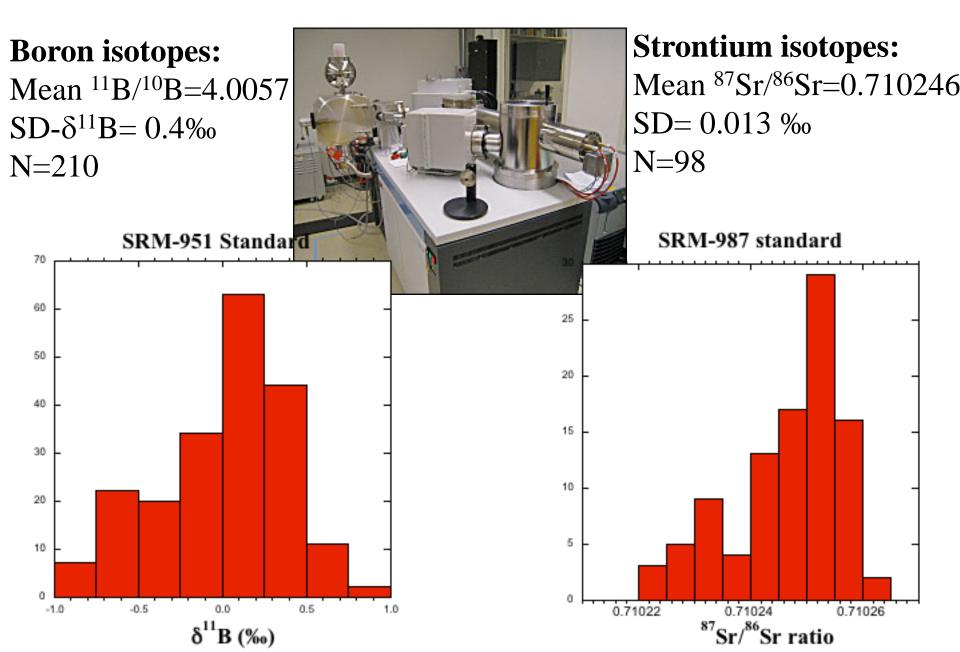
- 1. Since 2010 sampling over 600 shallow private wells in PA, NY, WV, AK, NC, TX;
- 2. Sampling produced/flowback waters from the Marcellus Shale and other formations in PA and NY;
- 3. Sampling over 100 surface waters in PA and river sediments downstream from waste waters disposal sites;
- 3. Analysis 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:

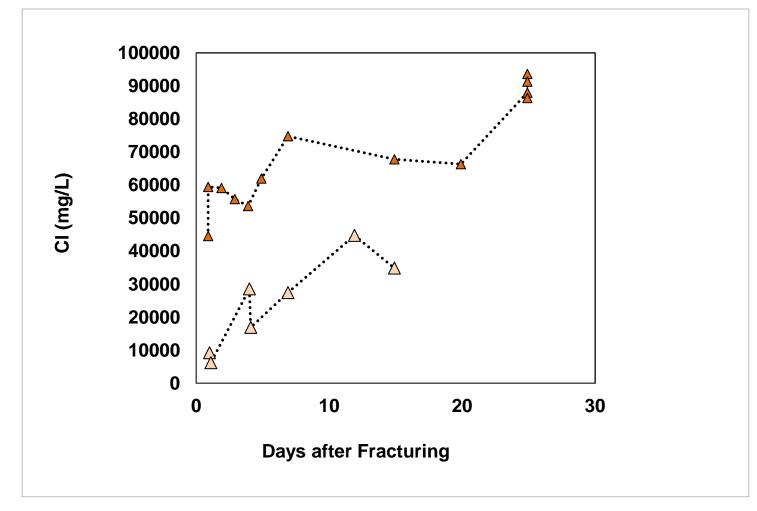
Naturally occurring tracers: 87 Sr/ 86 Sr, δ^{11} B, δ^{18} O, δ^{2} H, 228 Ra/ 226 Ra



Thermal ionization mass spectrometry



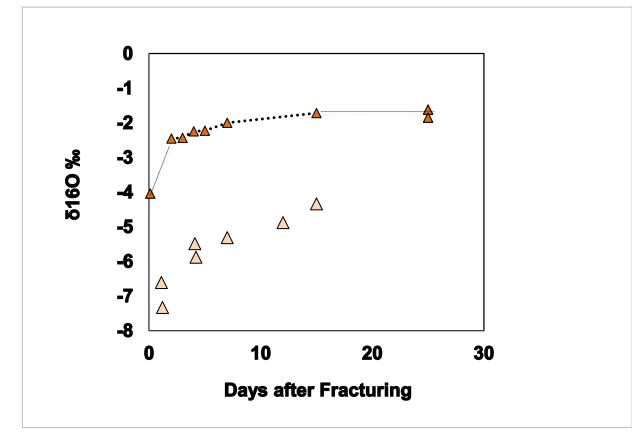
Flowback from the Marcellus gas wells



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



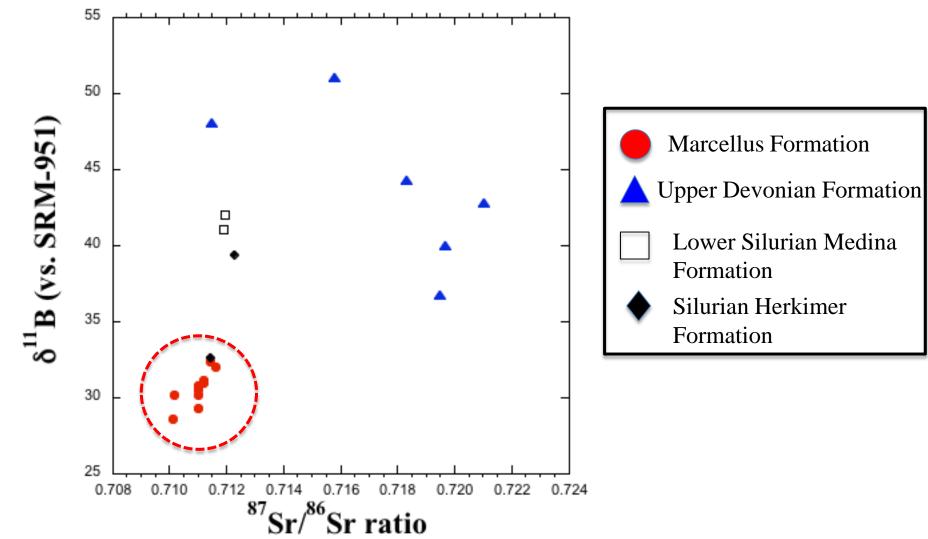
Progressively increase of δ^{18} O (and δ^{2} H) in flowback water \rightarrow larger proportion of the high δ^{18} O (and d²H) formation water \rightarrow **Identification of the relative mixing proportion between injected water and the original formation water.**

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

Western PA			Eastern PA Plateau				⁸⁷ Sr/ ⁸⁶ Sr								Age	
Conemough Gp Allegheny Gp			Allegheny and Pottsville Groups			ű	٥	x	0	2	4	6	ø	0004		Pennsylvanian
Burgoon Fm			Huntley Mtn, Pocono, and Mauch Chunk Fms				0.700	0.708	0.71	0.71	0.71	0.71	0.718	0.720		Mississippian
Venango Gp Bradford Gp Elk Gp			Catskill Fm Duncannon Mbr Sherman Mbr Lock Haven Fm									●⊢		Venango		Upper Devonian
Brallier Fm			Brallier Fm				ļ									Devoluti
Hamilto Gp	Ma	antango Fm arcellus Fm	Hamilton Gp	Ν	Mahantango Fm Marcellus Fm			Marcellus Bradford							Middle Devonian	
Onondaga Gp Huntersville Cht			Onondaga Gp Selinsgrove LS					1					1	SS		
<u>Ridgeley Ss</u> Helderberg Gp Bass Islands Dol – Keyser Fm			<u>Ridgeley Ss</u> Helderberg Gp Keyser Fm				Organic Rich Sha							-		Lower Devonian
Salinas Gp Wills Creek Fm		, Salinas Gp Tonoloway Fm Wills Creek Fm Bloomsburg Fm							,	Varia	ation i	in P:	aleozoic		Upper Silurian	
Clinton Gp	McKenzi	Lockport Dol – McKenzie/Rochester Fm		Clinton Gp					•	_		iation in Paleozoic water ⁸⁷ Sr/ ⁸⁶ Sr				Middle Silurian
Rose Hill FmMedina GpTuscarora Fm		Rose Hill Fm Tuscarora Fm			-	Medina								Lower Silurian		
Queenston Fm Juniata Fm Oswego Fm Bald Eagle Fm Reedsville Sh		Juniata Fm Bald Eagle Fm <u>Reedsville Sh</u> Utica Sh							l	Jtica					Upper Ordovician	

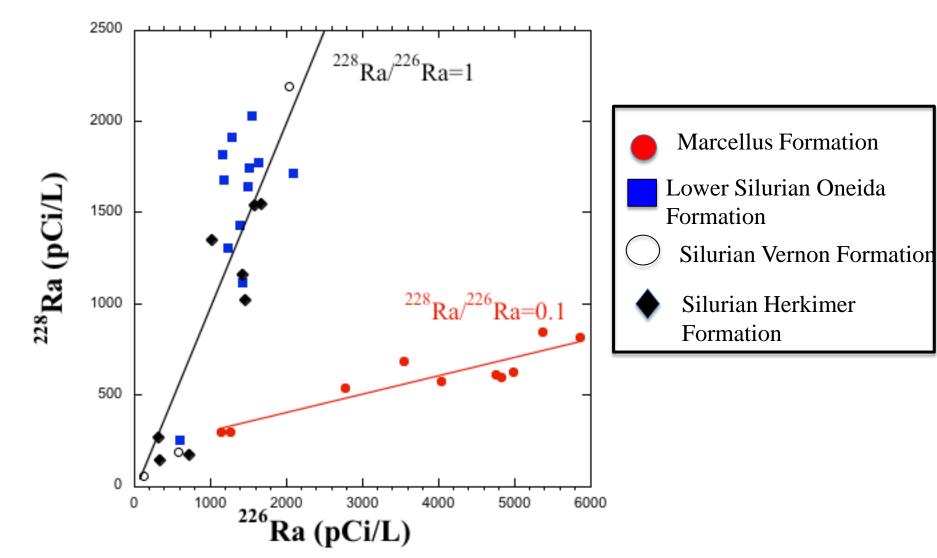
The combined used of boron and strontium isotopes

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 ($\delta^{18}O, \delta^{2}H$), 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.