Geochemistry and Environmental Problems of Flowback Water from Marcellus Wells in Pennsylvania

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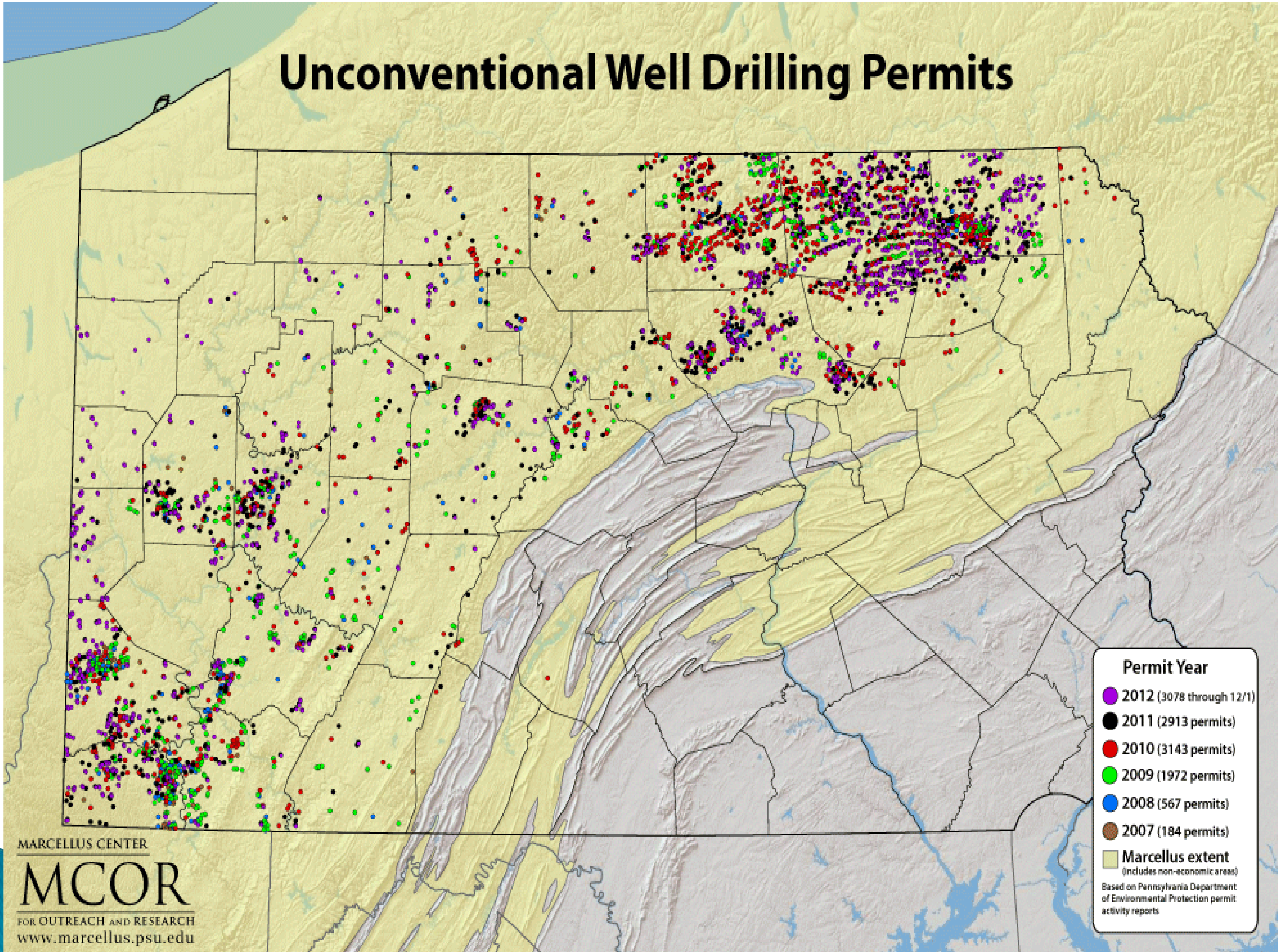
Topics

- Flowback
- Chemistry of flowback
- Source of flowback brine
- Environmental Problems

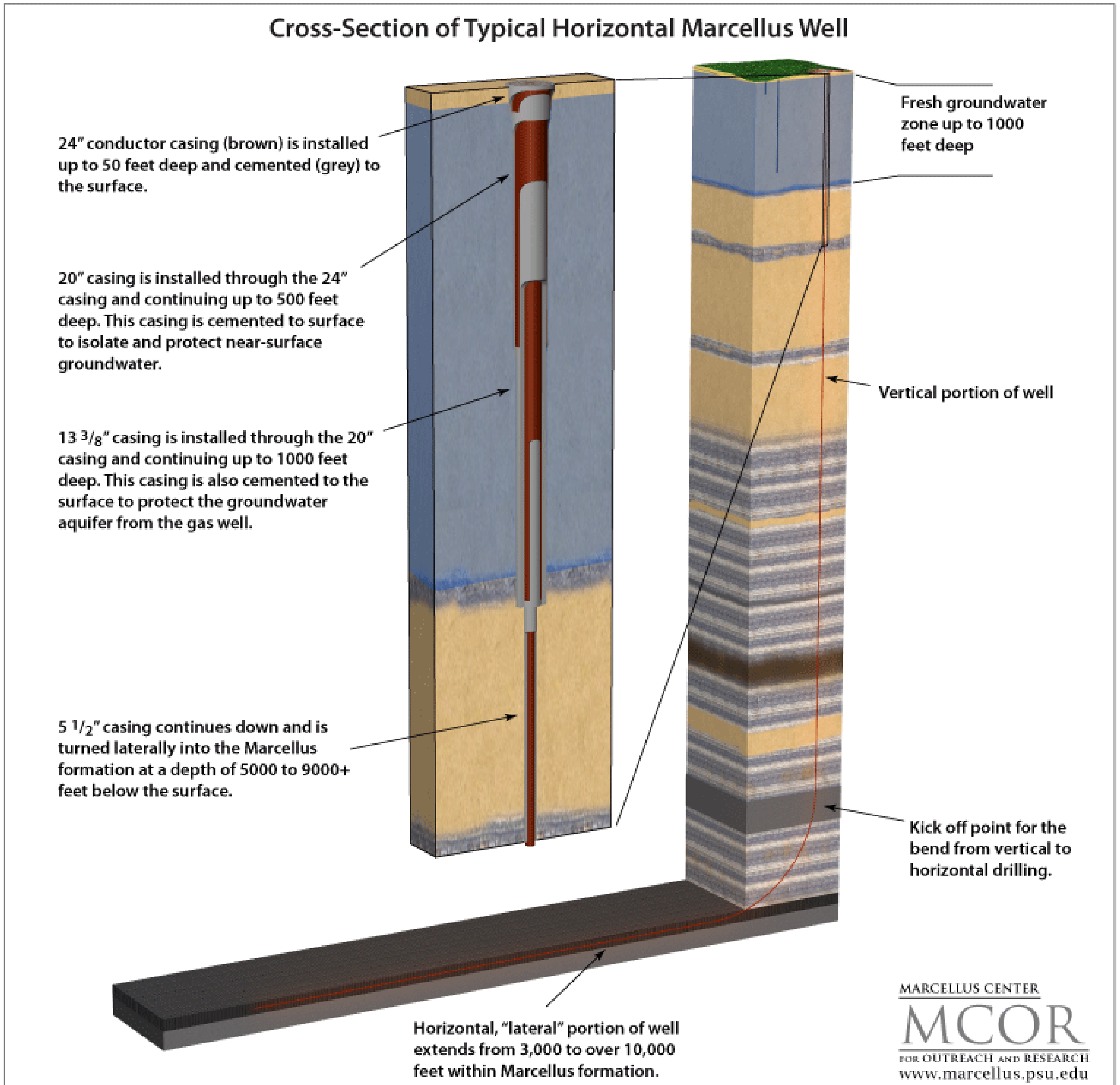
ACKNOWLEDGEMENTS

- Evan Dresel MS 1985 Conventional brines, recognition of evaporated seawater origin
- Lara Haluszczak BS 2011 Marcellus data
- PA DEP Marcellus data



Unconventional Well Drilling Permits
Permit Year
2012 (3078 through 12/1)
2011 (2913 permits)
2010 (3143 permits)
2009 (1972 permits)
2008 (567 permits)
2007 (184 permits)
Marcellus extent
(includes non-economic areas)
Based on Pennsylvania Department of Environmental Protection permit activity reports
MARCELLUS CENTER
MCOR
FOR OUTREACH AND RESEARCH
www.marcellus.psu.edu

Typical Marcellus Well



Flowback Water

- 3 to 5 million gallons of water with additives are injected into an unconventional horizontal well during fracking.
- 10 to 20% of this water commonly flows back on release of pressure, by day 14.
- This water contains the additives, and in PA much of it has extremely high salinity and high contents of many elements.
- Water after day 14 is called "production water" but typically has similar chemistry.

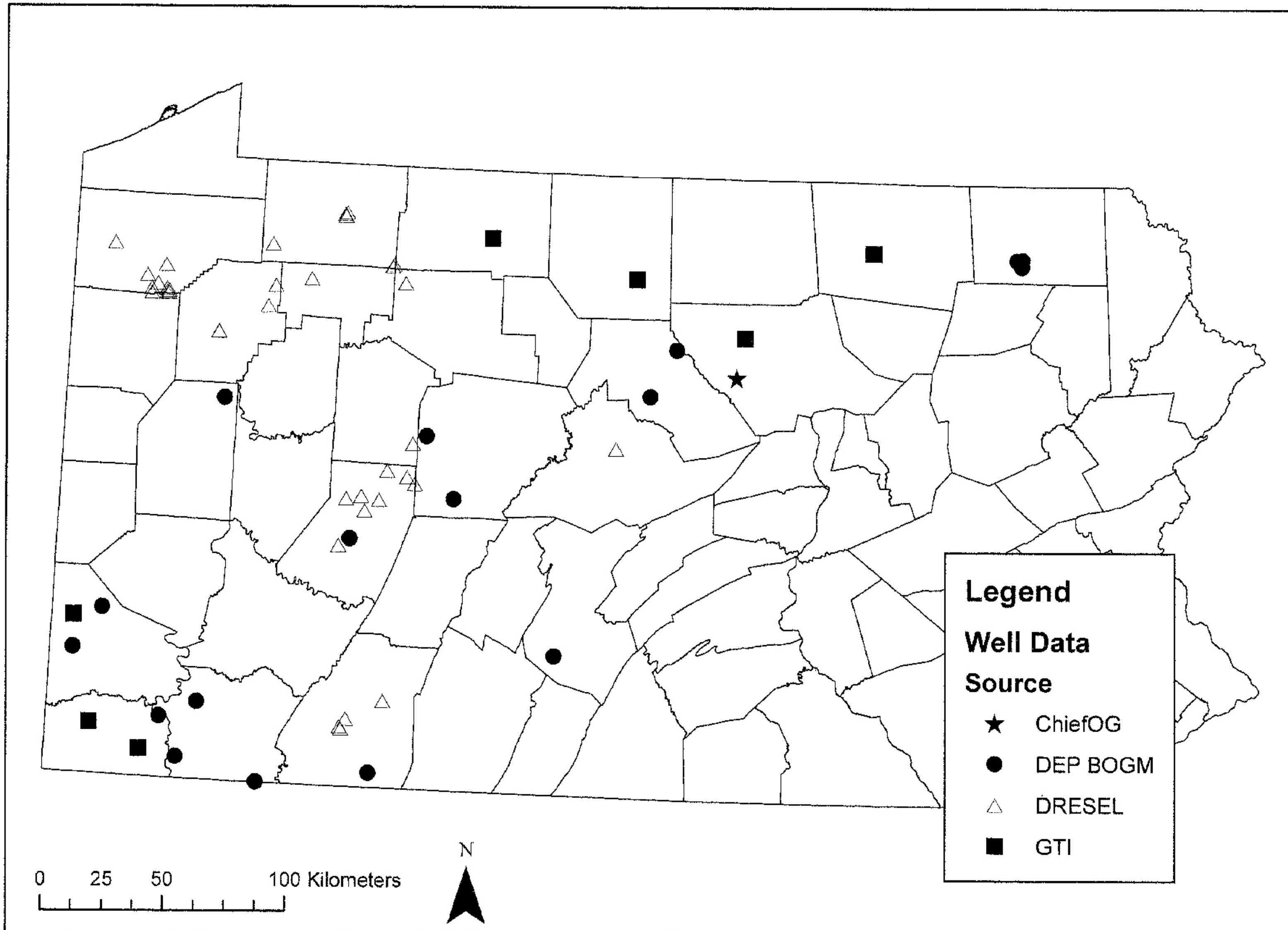
Questions on Flowback Water

- What constituents are present in hazardous amounts?
- What to do with this water?
- What is the origin of the high salinity and related constituents?
- Is the brine actually coming from the Marcellus?

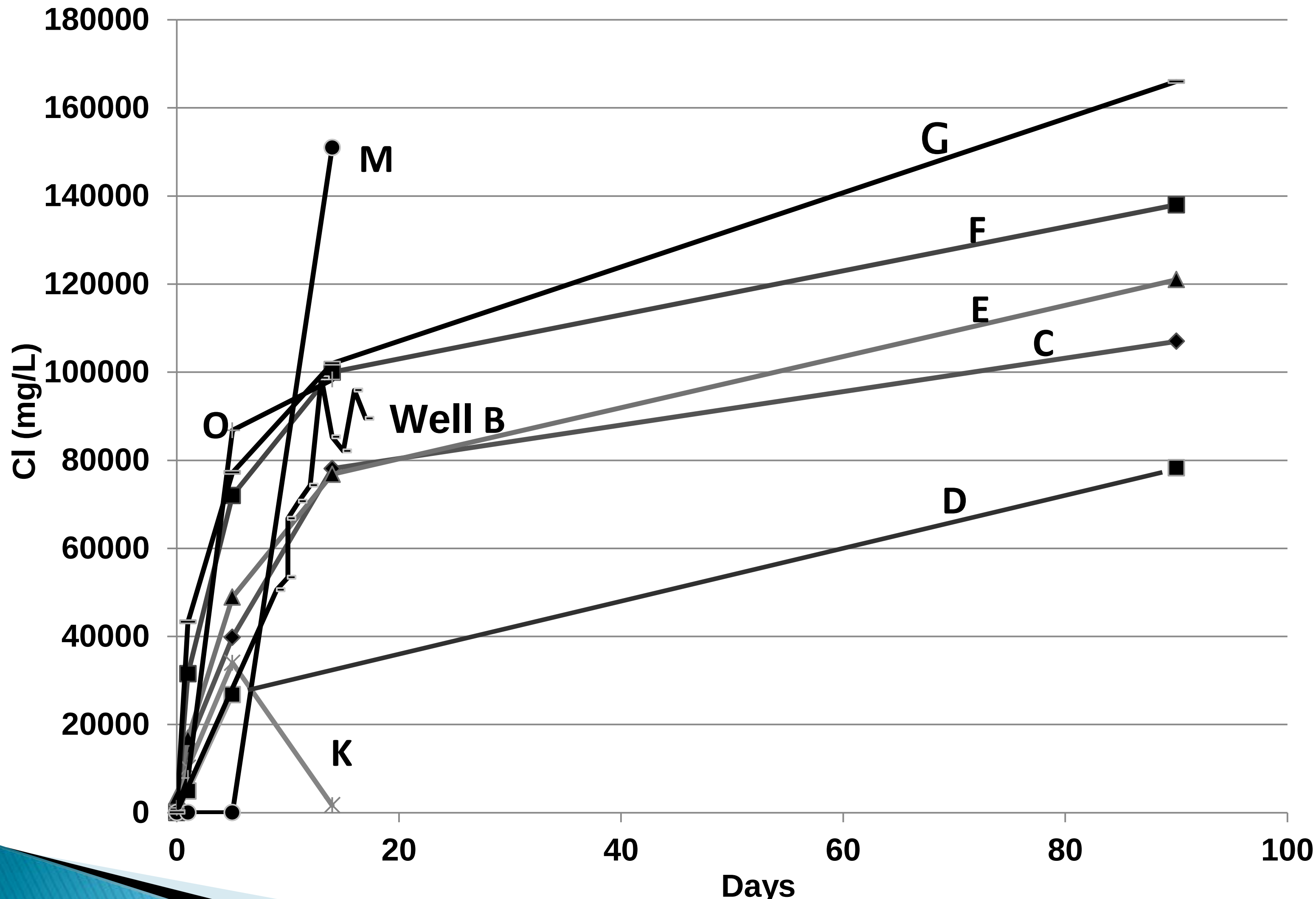
Sources of Data

- Dresel, E. and Rose, A.W., 2010, PA Geol. Survey, OFOG 10-01.0, 40 conventional oil and gas wells.
- Hayes, T., 2009, Gas Techn. Inst., 7 horizontal Marcellus wells, time sequence, additives.
- PA DEP, 2011, data for 22 Marcellus wells, analyses in Haluszczak et al., 2013.
- Rowan, E.L. et al., 2011, US Geol. Survey Sci. Inv. Rept. 2011-5135, Ra data for many wells.

Wells Providing Chemical Data



Cl in flowback vs. days after fracking (GTI study)



Cl vs. Flow

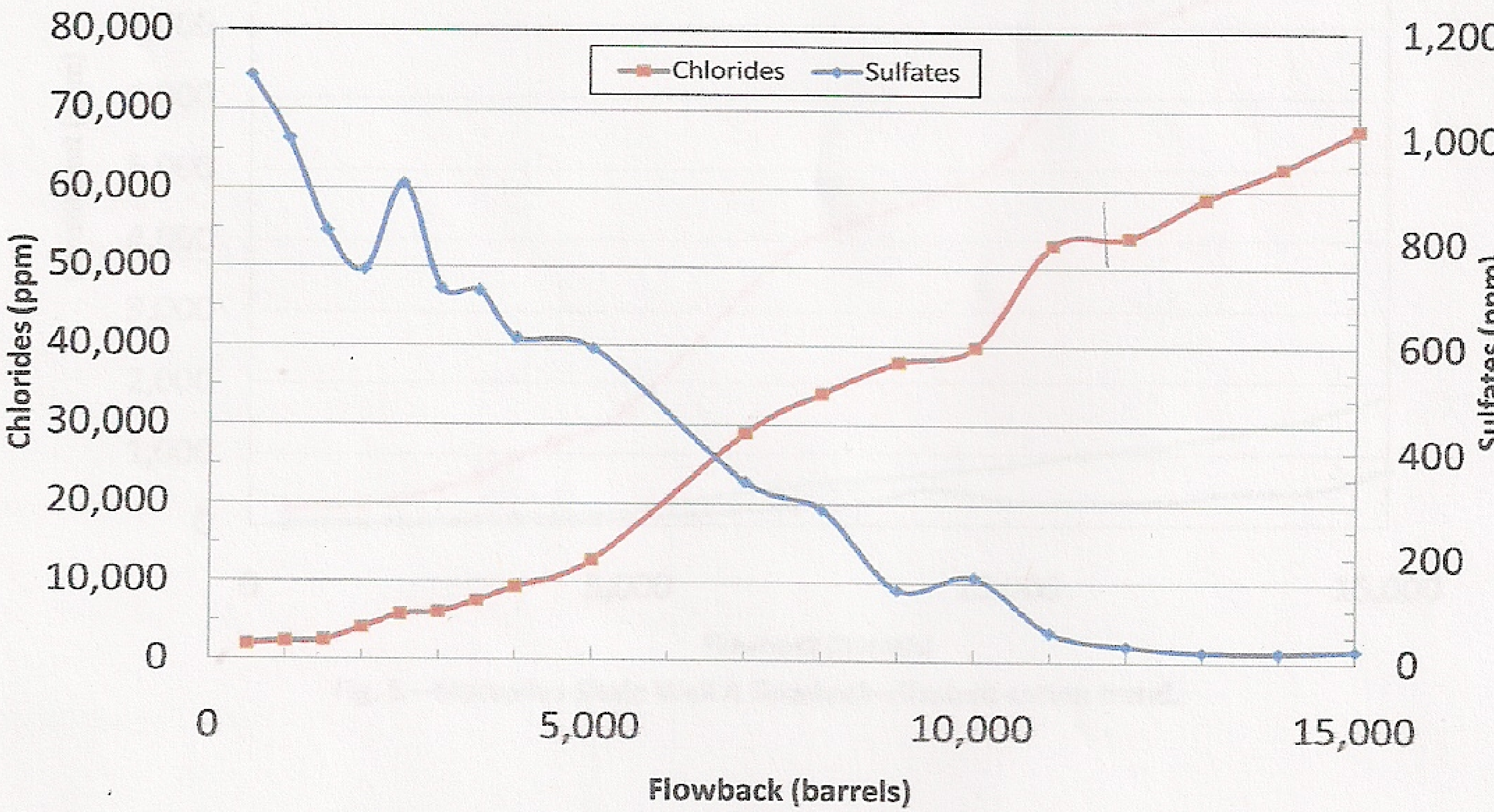
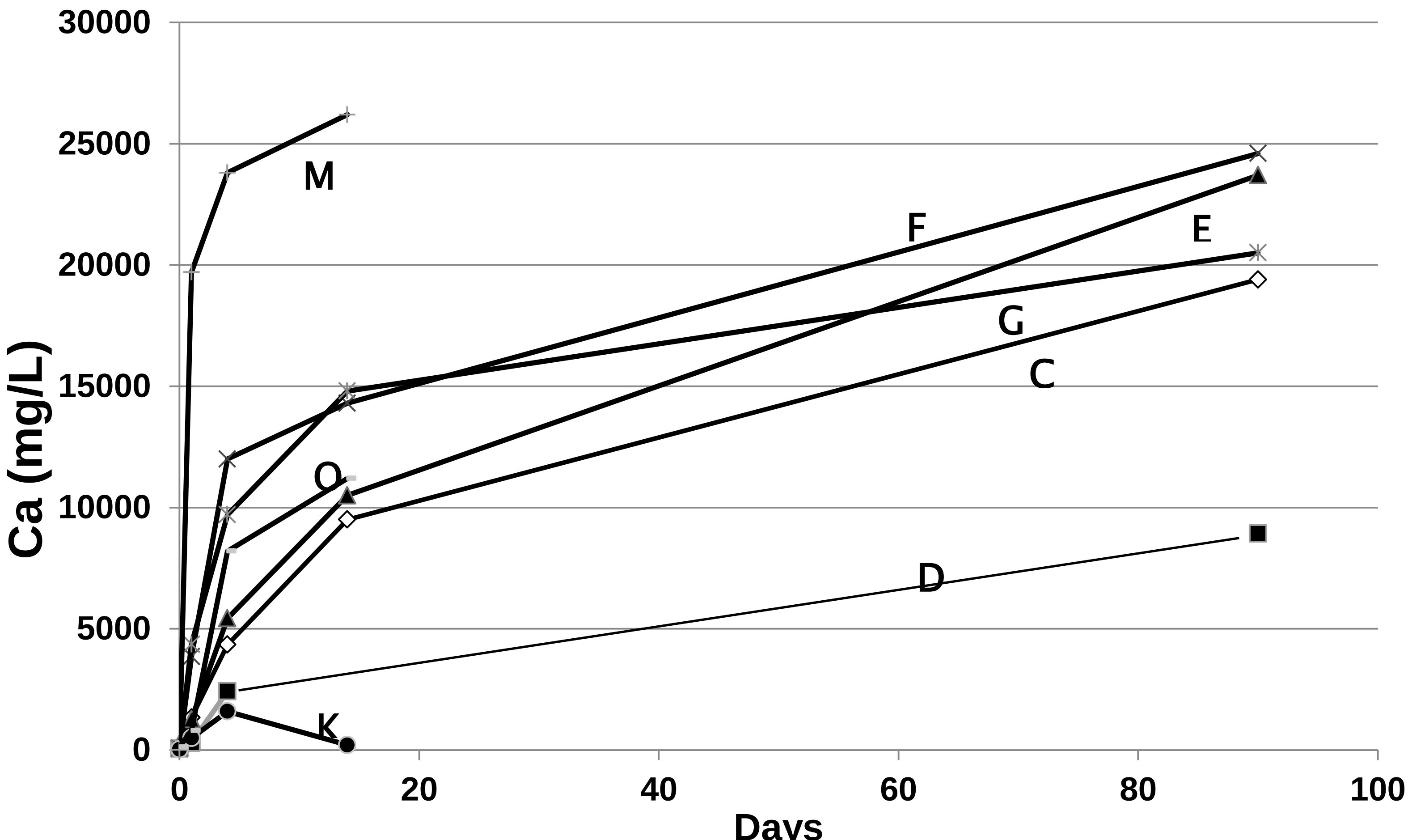


Fig. 3—Marcellus Shale Well A flowback analysis–anion trend.

Ca vs. days after Fracking



Chemistry–Injected Water and Day 14 Flowback

Medians, GTI study, 7 wells, mg/L

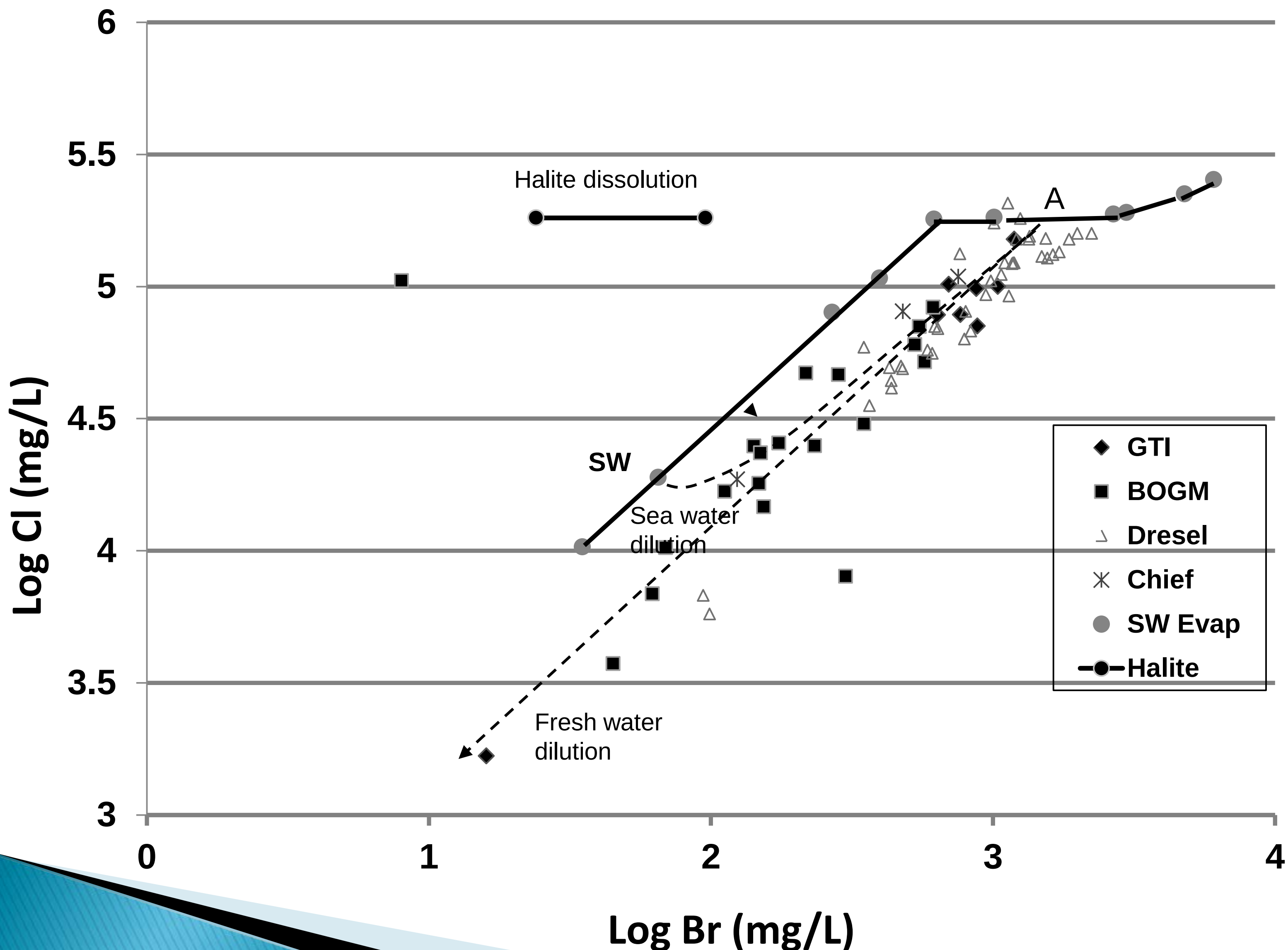
Constituent	Injected Fluid	Flowback Day 14	Seawater
pH	7.0	6.2	~8
Cl	82	98,300	19,400
Br	<10	872	67
SO4	59	<50	2700
Ca	32	11,200	410
Mg	3.7	875	1290
Na	80	36,400	10,800
K	0.7	281	390
Fe	<50	47	0.0034

Chemistry – Minor Elements

Medians, mg/L, GTI Study, 7 samples

Element	Injected fluid	Flowback, Day 14	Seawater
N	14	140	15
P	0.36	0.55	0.09
Al	0.3	0.5	0.001
B	0.5	20	4.4
Li	0.04	95	0.17
Sr	0.82	2330	8.1
Ba	0.6	1990	0.021
Mn	0.07	5.6	0.0004
Zn	0.08	0.09	0.005
Ra		2640 pCi/L*	

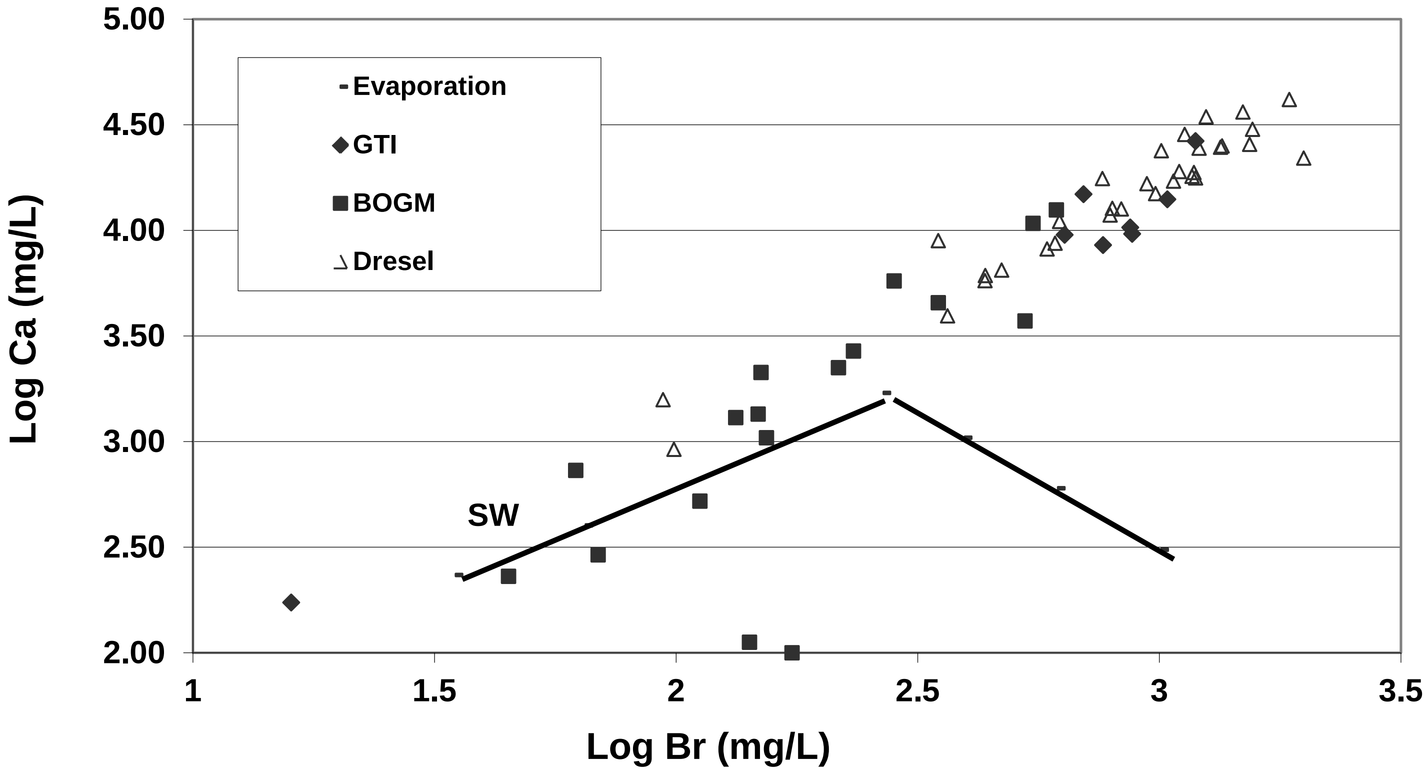
Br/Cl indicates ancient brine



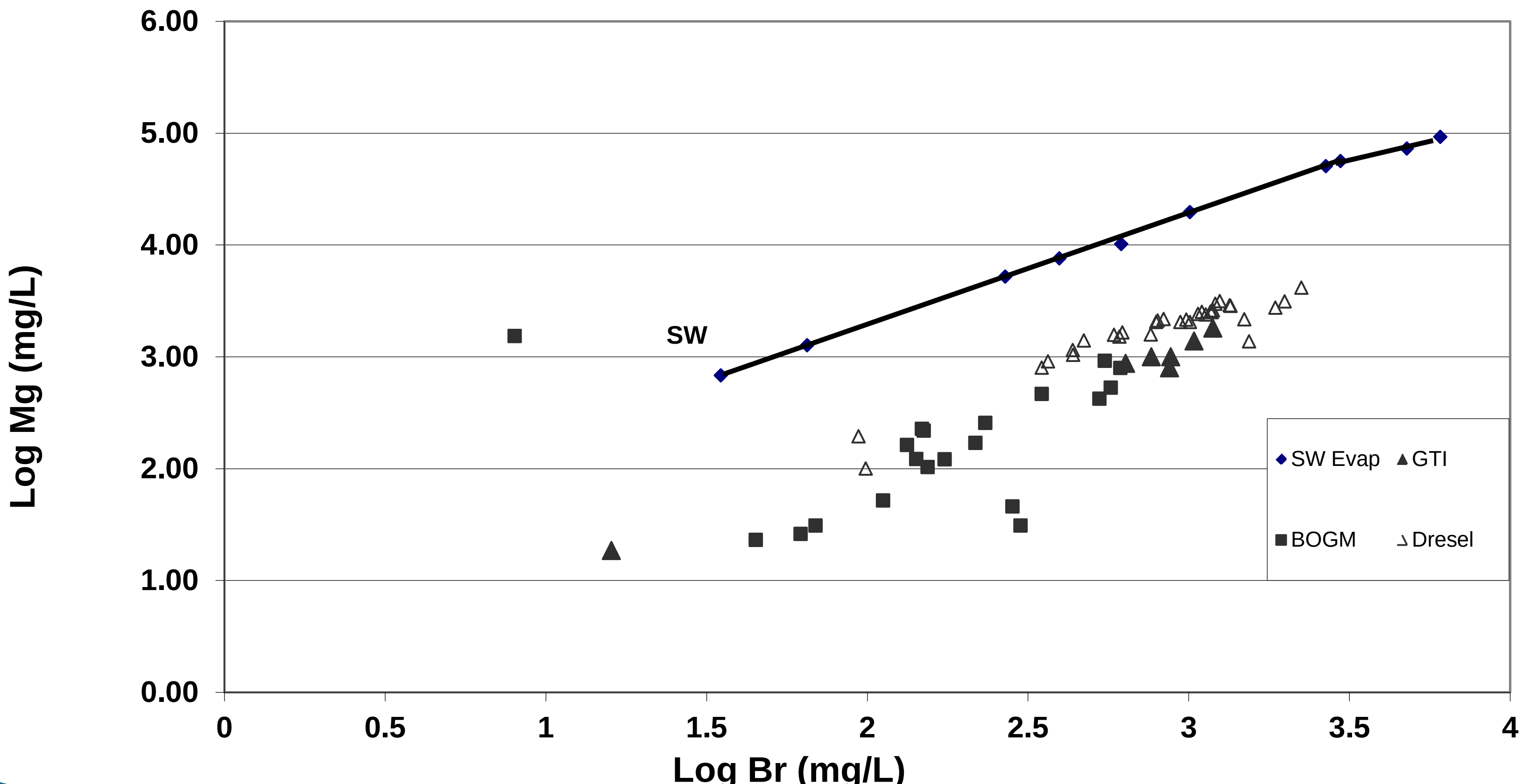
Alternatives – Dissolution of halite or acid attack?

- Blauch et al. (2010) suggest that the high NaCl comes from dissolution of halite (NaCl)
- But Br/Cl would be much lower.
- GTI data does not show acid in the injected water – pH is near-neutral in both input and flowback.

Ca is enriched over evaporated seawater



Mg is depleted from evaporated seawater – dolomitization



Origin – Step 1

- Evaporation of seawater through gypsum precipitation into halite precipitation
- Probable timing and locale – Silurian Salina formation

- Step 2 – dolomitization ($CaMg(CO_3)_2$

- Other Steps
- – Mobilization out of Salina Fm. into overlying and underlying sediments (Ord. to Miss.)
- – Dilution with connate seawater in other formations, fresh water, injected water
- – Sulfate reduction and pyrite oxidation

Stratigraphy in SW PA

16,000 ft of sed. rock

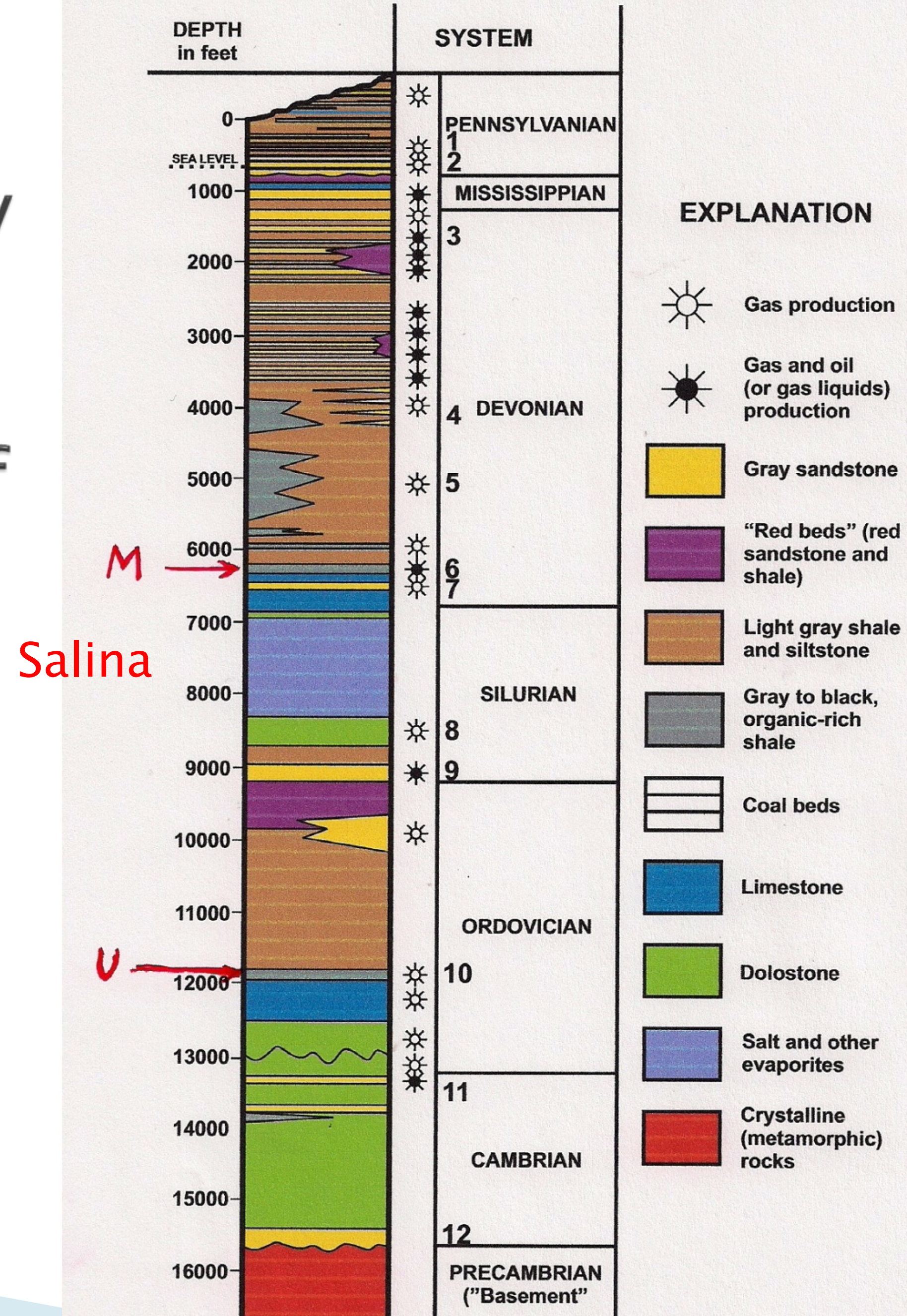
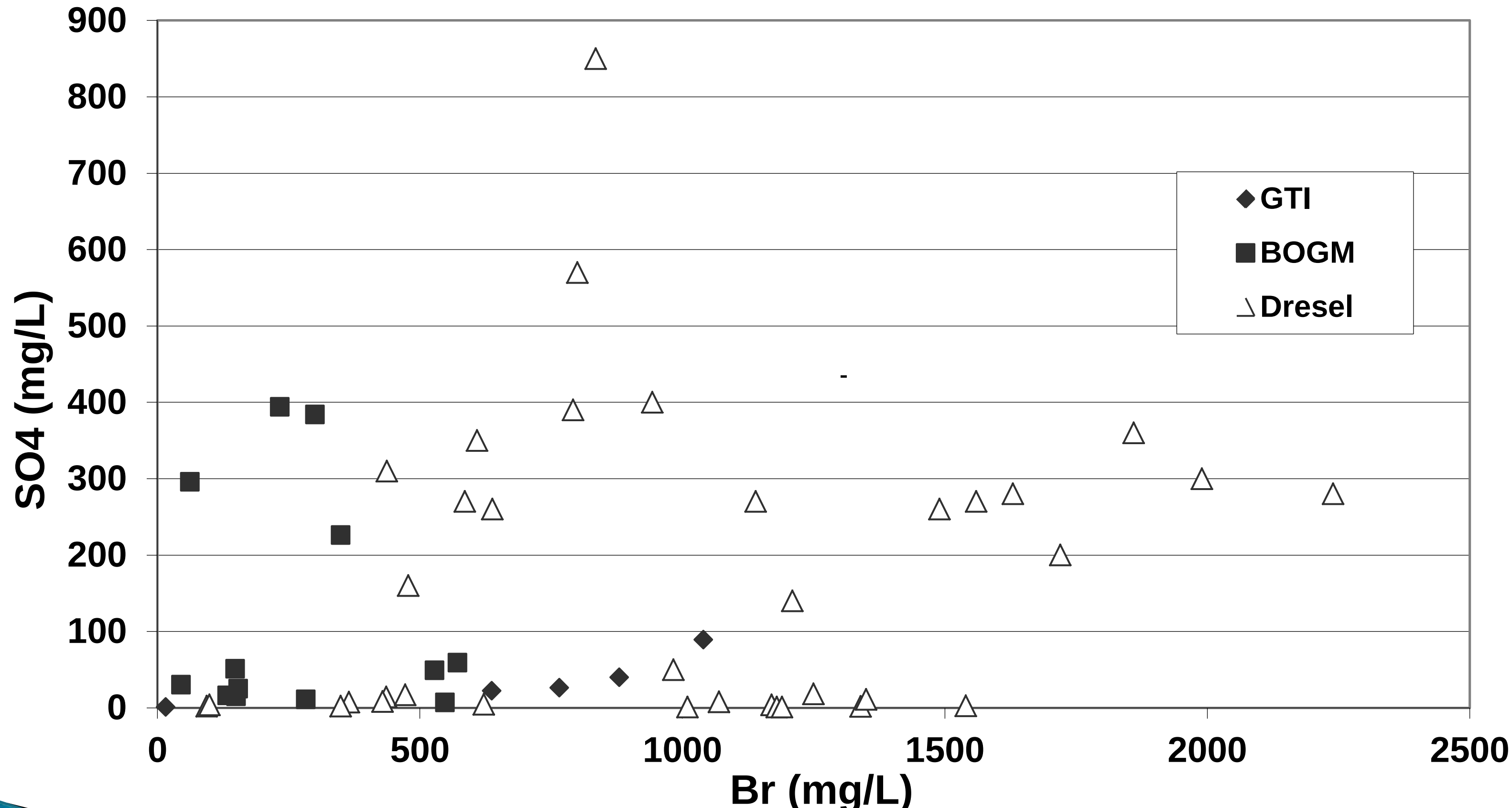
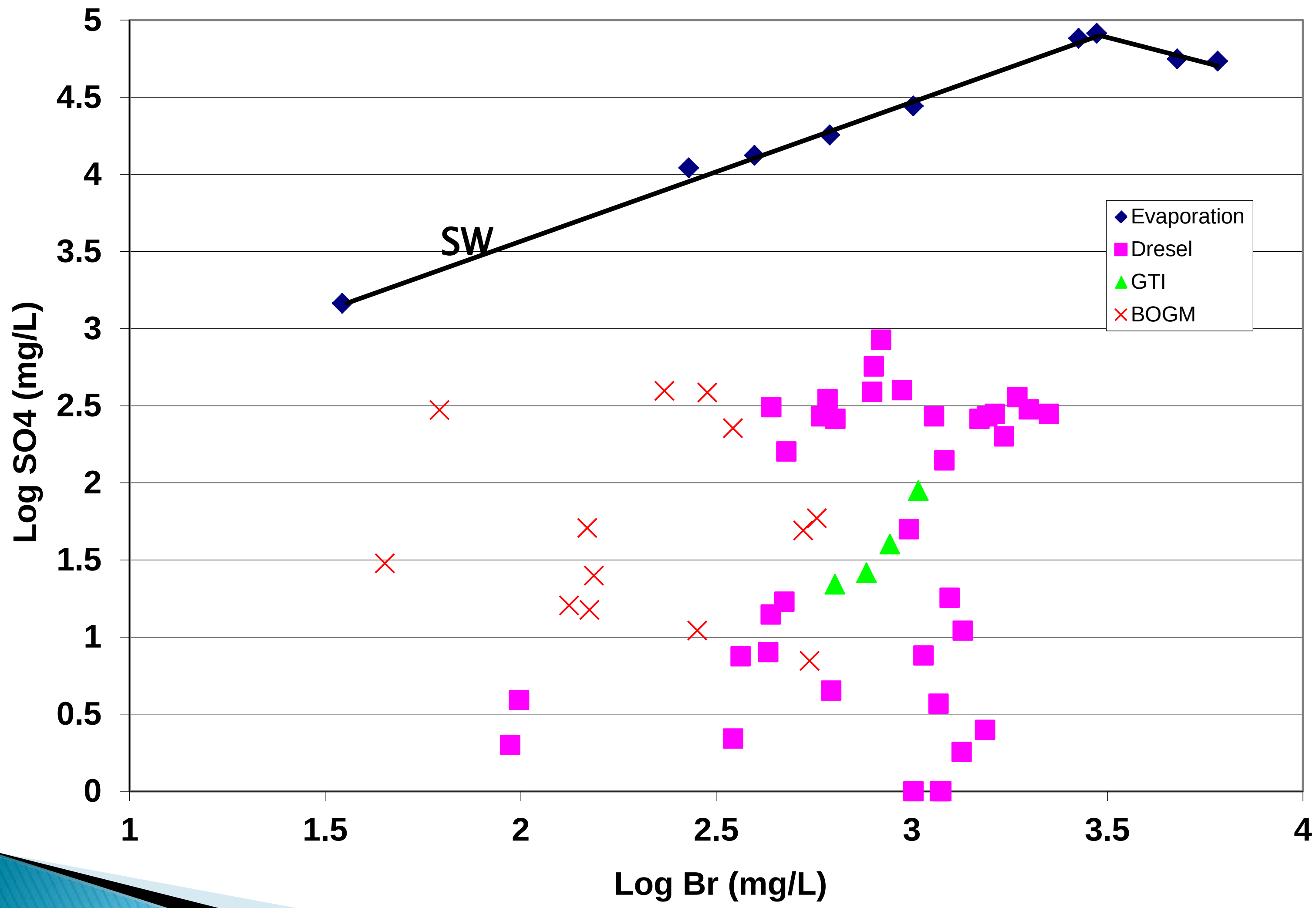


Figure 2. Generalized stratigraphic column of rocks in southwestern Pennsylvania. Numbers indicate geologic units referred to in this article: 1, Pennsylvanian and Permian coal beds; 2, Pottsville Formation Salt sands; 3, Venango Group oil sands; 4, Huron Shale; 5, Rhinestreet Shale; 6, Marcellus Formation; 7, Oriskany Sandstone; 8, Lockport Dolomite; 9, Medina Group and equivalent Tuscarora Formation; 10, Utica Shale; 11, Gatesburg Formation sandstones; and 12, Potsdam Sandstone.

SO4 vs. Br – No pattern



SO_4 vs Br – Major S loss

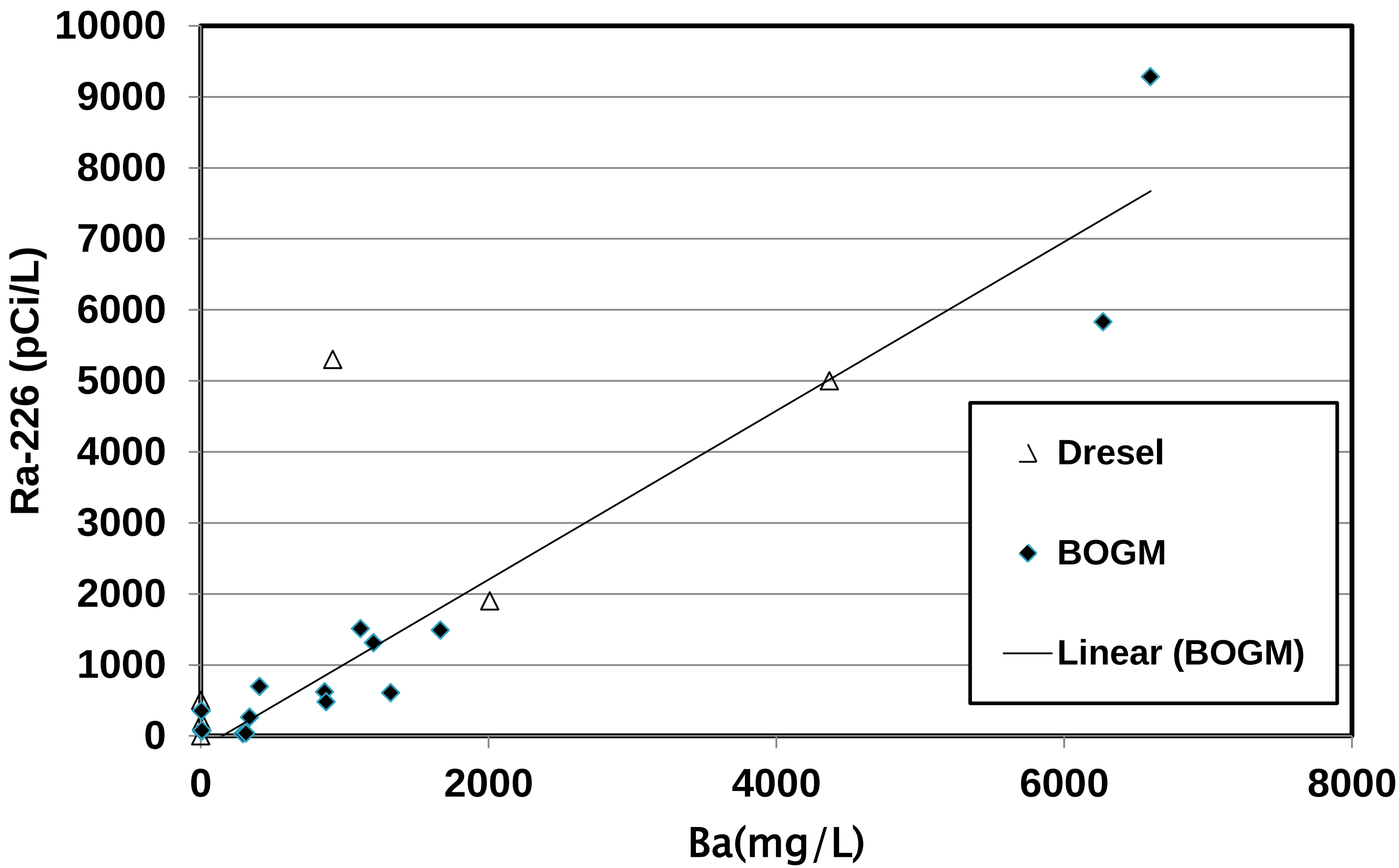


Ra and Ba Problems

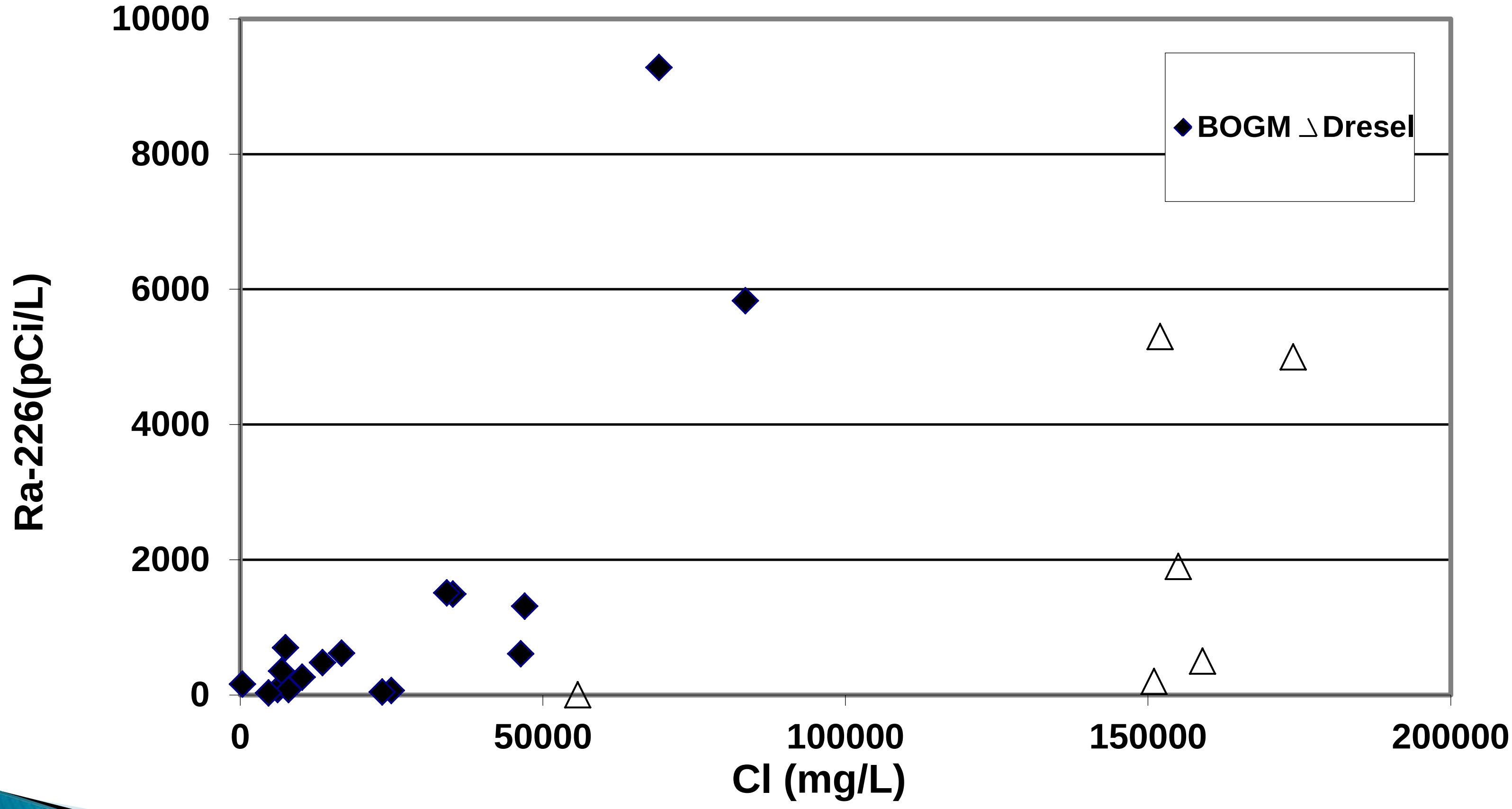
Element	Flowback	Drinking water Limit
Ba (mg/L)	1990* (Day 14)	2
Ra (pCi/L)#	2460*	5

- *Median
- #Rowan et al., 2011

Ra vs Ba – Correlation



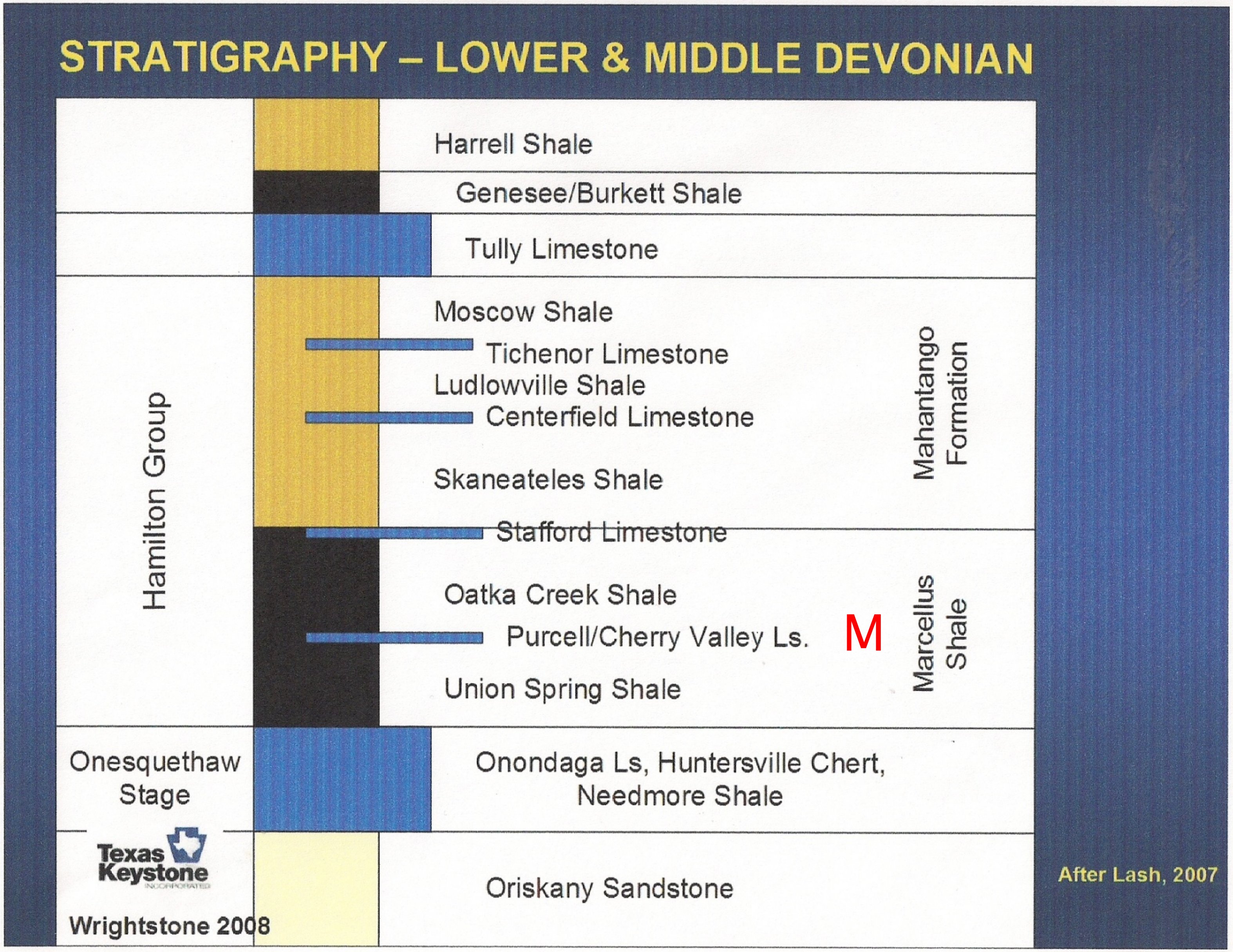
Ra vs. Cl



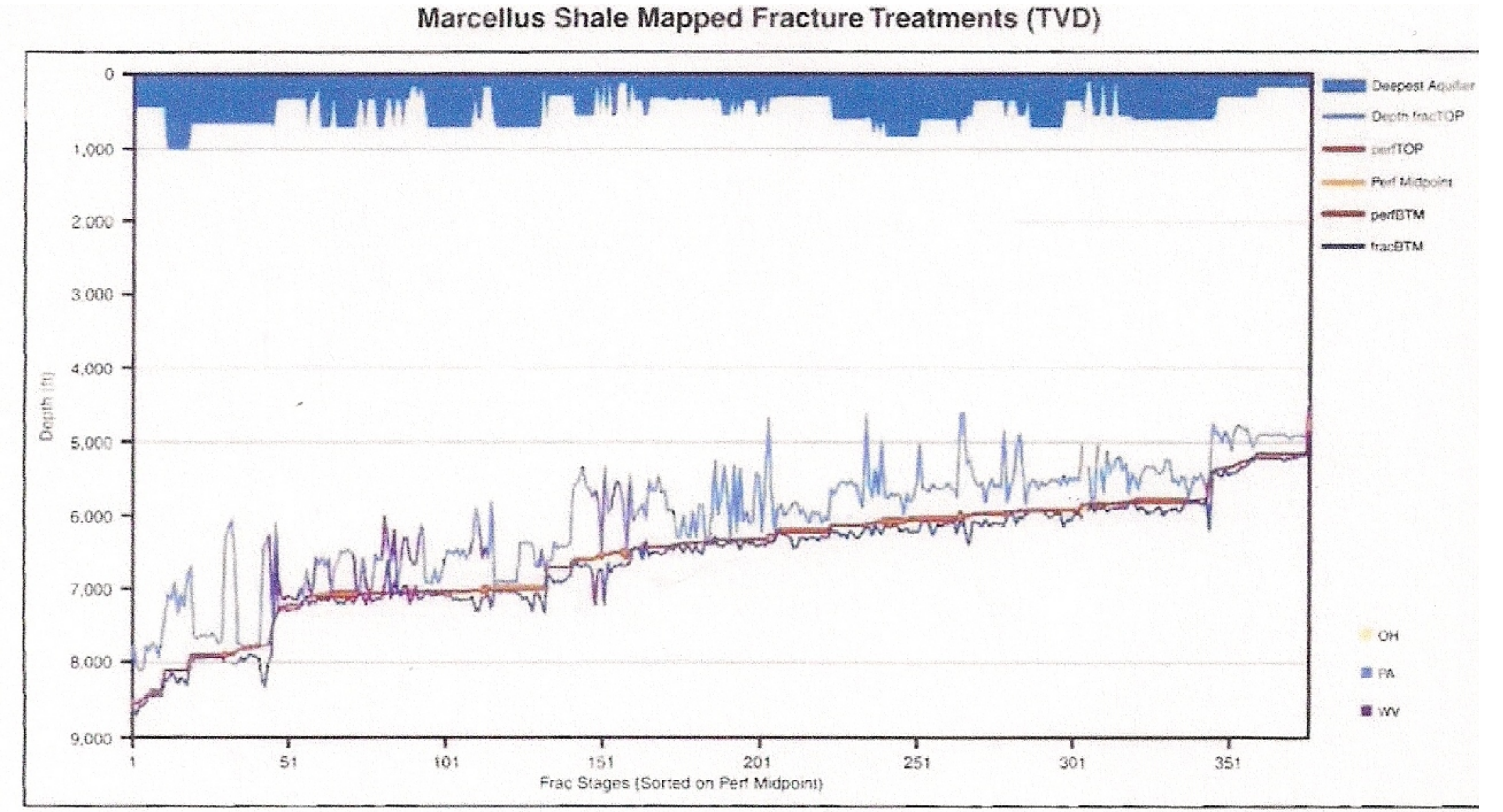
10000
8000
6000
4000
2000
0
BOGM
Dresel
Ra-226(pCi/L)
0
50000
100000
150000
200000
Cl (mg/L)

Host for concentrated brine entering Marcellus wells?

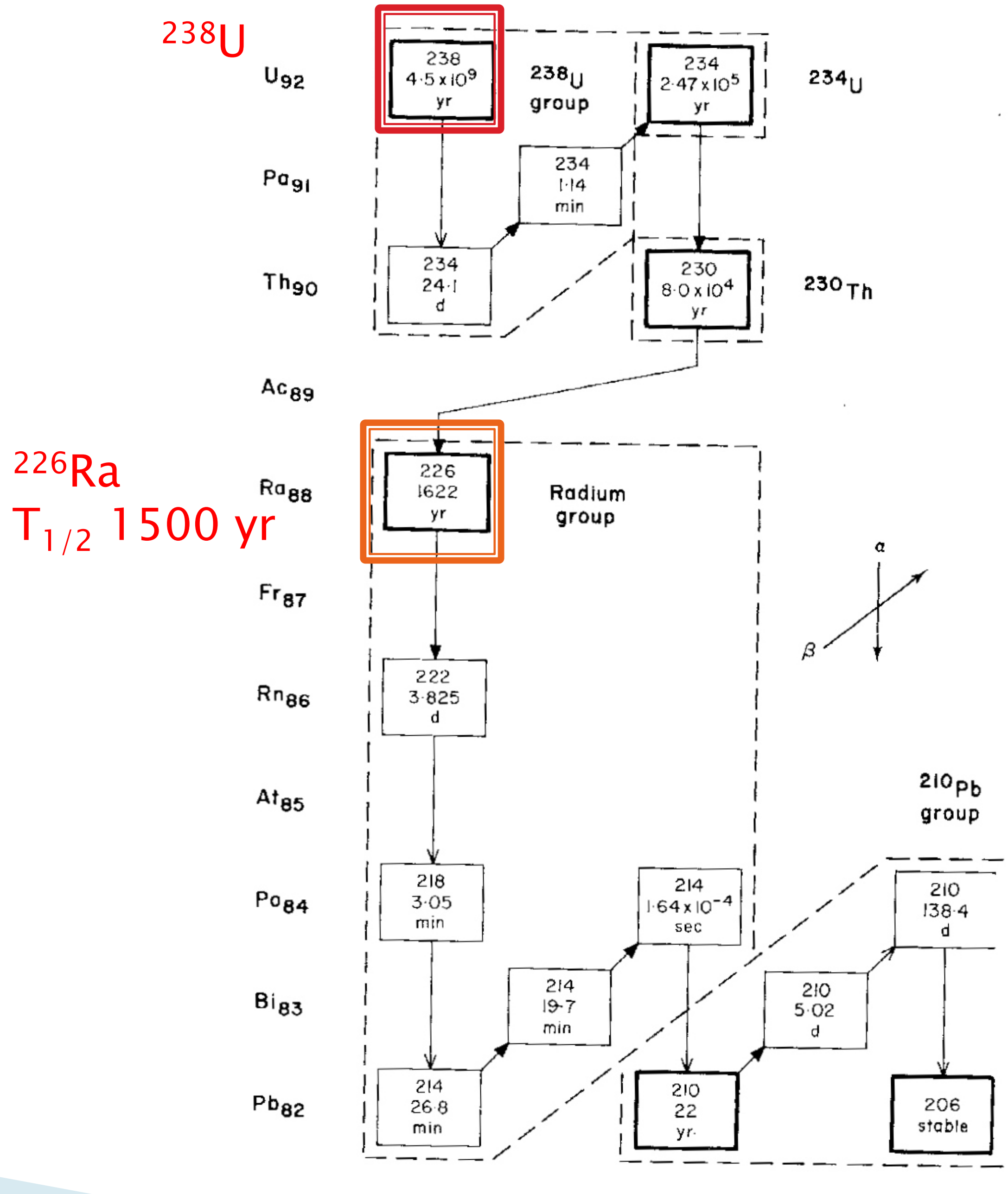
- Marcellus Formation? But this is a relatively impermeable tight shale. Little pore space. Electric logs suggest essentially no saline pore fluid. Fractures?
- Adjacent formations? But radium isotopes suggest Marcellus as host. Porosity/fractures in limestones and calcareous zones?


STRATIGRAPHY – LOWER & MIDDLE DEVONIAN
Harrell Shale
Genesee/Burkett Shale
Tully Limestone
Hamilton Group
Moscow Shale
Tichenor Limestone
Ludlowville Shale
Centerfield Limestone
Skaneateles Shale
Mahantango Formation
Stafford Limestone
Oatka Creek Shale
Purcell/Cherry Valley Ls.
M
Union Spring Shale
Marcellus Shale
Onesquethaw Stage
Onondaga Ls, Huntersville Chert, Needmore Shale
Texas Keystone
Oriskany Sandstone
Wrightstone 2008
After Lash, 2007

Vertical extent of fractures



Radium isotopes



^{232}Th–^{228}Ra Decay Series

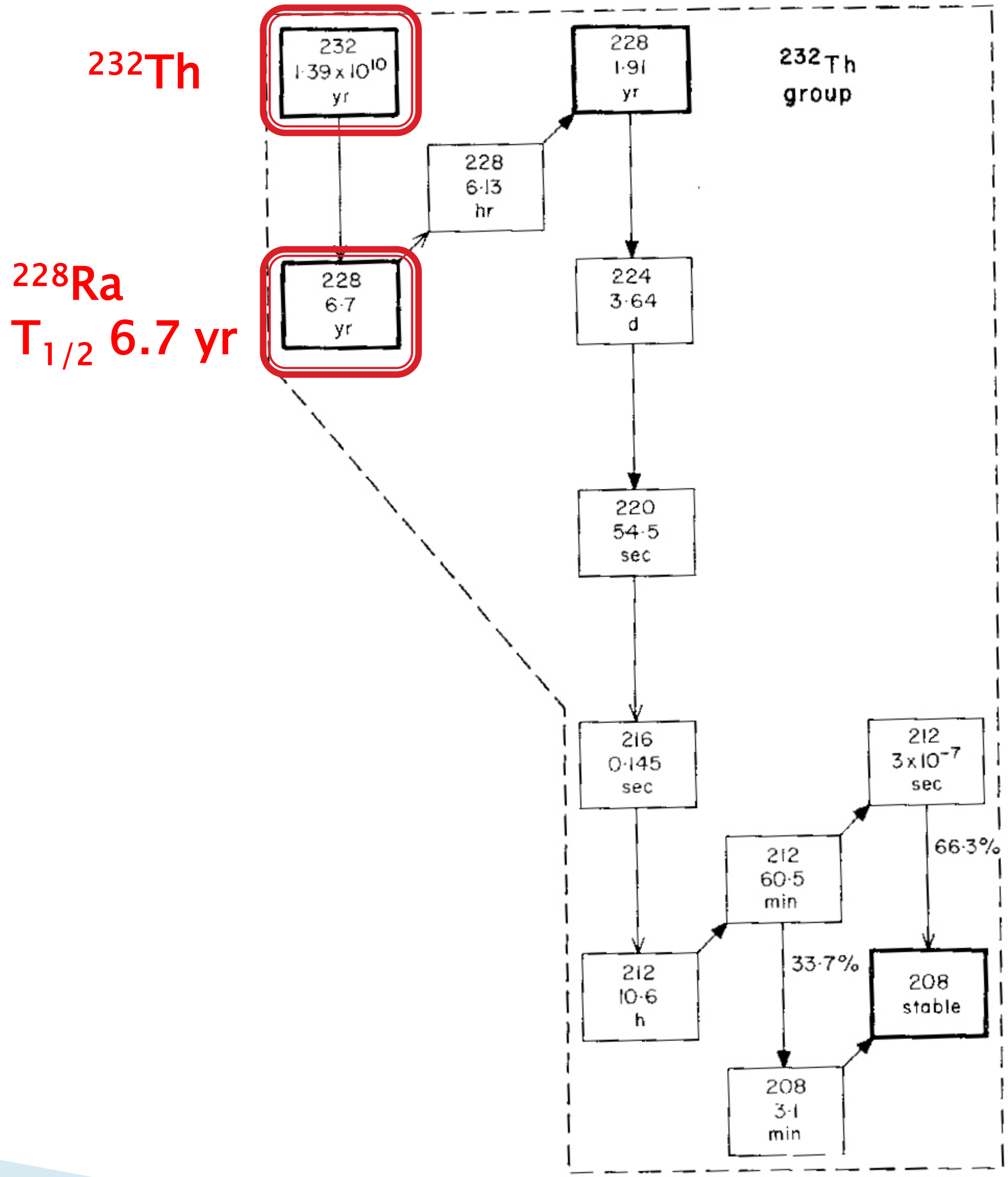
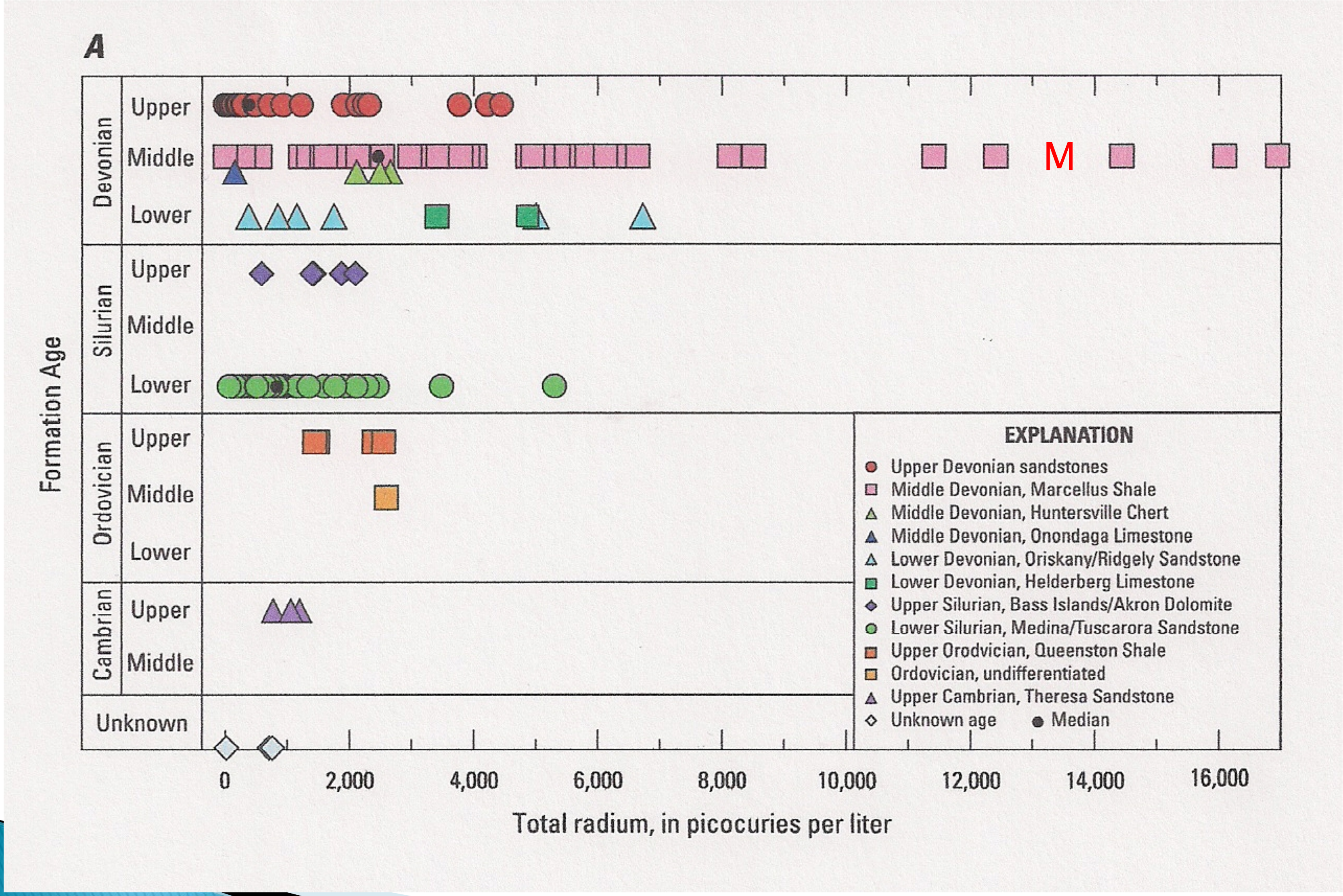
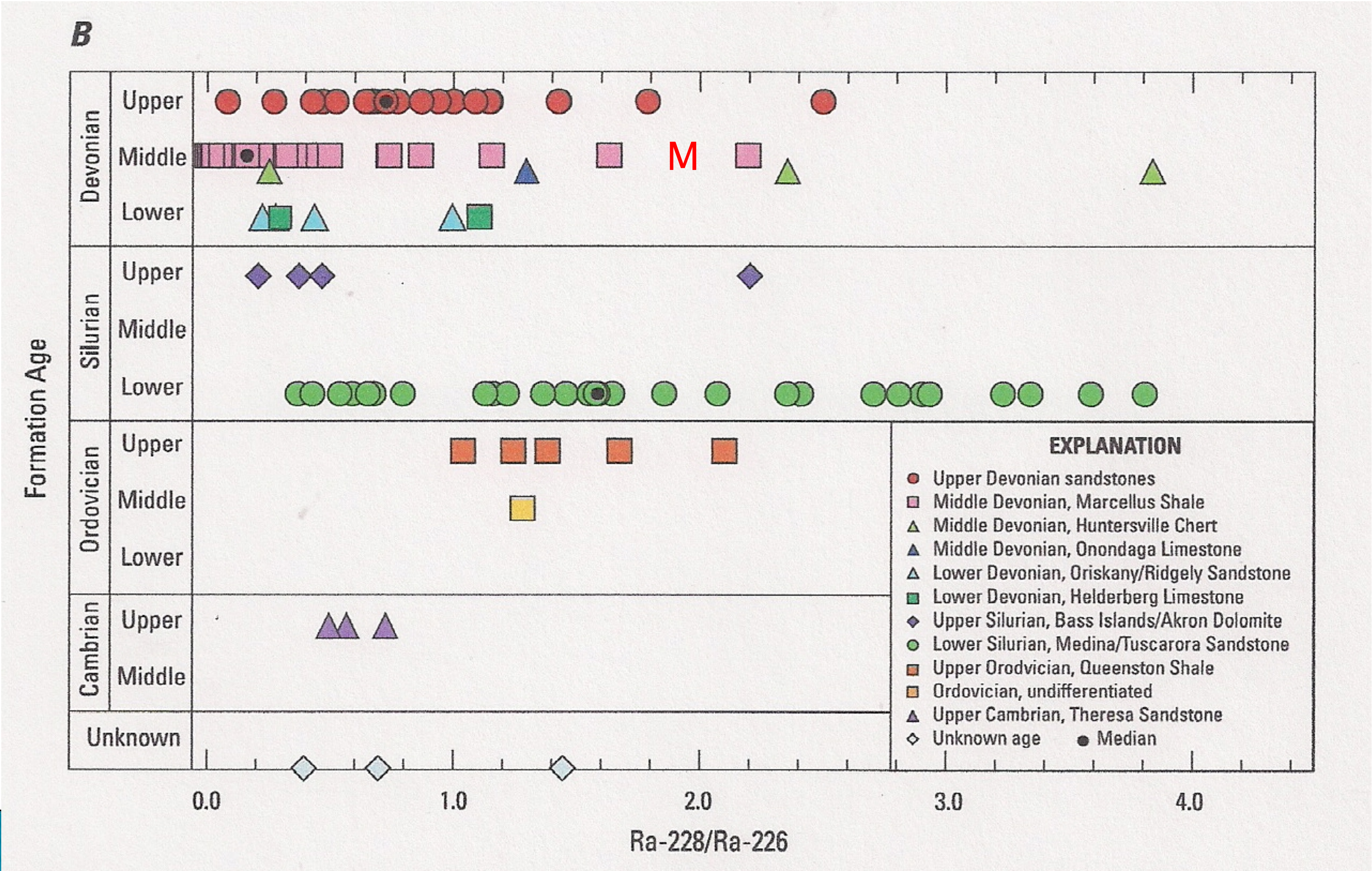


Fig. A 1c Thorium-232 disintegration

Radium in brine vs. host (Rowan, 2010)



$^{228}Ra/^{226}Ra$ in brine vs. host



Abundance of ^{226}Ra vs ^{228}Ra

- A typical shale has 10 ppm Th and 3.7 ppm U
- In radioactivity units, this translates to about 1.3 pCi/g of each parent.
- At radioactive equilibrium, amounts of ^{226}Ra and ^{228} Ra would be equal.
- Equal leaching of Ra isotopes would result in equal concentrations or ^{226}Ra and ^{228}Ra in solution.
- But ^{226}Ra is far higher than ^{228}Ra in brines.
- Implies U host is more abundant or more easily leached than Th host.
- ^{226}Ra is from Marcellus with high U?

Removal/Disposal of Ra and Ba

- Sulfate precipitation – but 3 truckloads of sludge is lifetime Ra limit for a normal landfill.
- Release to streams- Probable adsorption on Fe oxides and uptake by biota.
- Ra and Rn hazards for workers.
- Coat wellbore and proppants w/ Ra-exchange resin (Ra in brine is a widespread problem).
- Re-use of flowback.

Water Supply and Disposal Solutions

- Re-use of prior flowback
- Use abandoned mine drainage (Effect of high sulfate?)
- Ship to deep injection wells (very few in PA, possible EQ triggering)

Leakage of brine

- Natural salt springs in deep valleys.
- Minor groundwater component in many valleys (Warner et al., 2012).
- Control by lineaments – deep fault zones.
- Possible contamination from depth by fracking??

Summary

- Extremely saline brine flows back from Marcellus wells, will be Production Water.
- Origin as evaporated seawater from Salina Salt Formation.
- Migration from Salina, extensive interaction with other rocks (dolomitization, S reduction)
- High levels of Ra, Ba greatly exceed drinking water standards.
- Lack of good disposal methods.
- Flowback may be derived largely from overlying and underlying formations rather than Marcellus.