Geochemistry of Shale Gas Basins including NORMs and Trace Elements

Jean-Philippe ‘JP’ Nicot

Bureau of Economic Geology
Jackson School of Geosciences
The University of Texas at Austin

Ground Water Protection Council UIC Conference
Houston, TX – January 23, 2012
Outline

• Basin hydrodynamics: water does flow
• Chemical composition, trace elements, NORMs
• How much is too much?
• No (easy to find) data
Hydrogeology of Sedimentary Basins

• Variable!
From Kreitler (1989)
>30,000 wells fraced in the past 5 years

- **Barnett Shale**
- **Haynesville Shale**
- **Eagle Ford Shale**
- **Pearsall Shale**
- **Bossier Shale**
- **Woodford Shale**
- **Canyon Sands**
- **Olmos**
- **Cotton Valley, Travis Peak**
- **Granite wash, Cleveland, Marmaton**

**Tight Gas**

**Shales**
Hydrogeology of Sedimentary Basins

- Variable!
- Water/Brine are highly mobile (geologic scale)
- Driving forces: compaction, gravity (uplift), convection (density-driven by salinity or temperature contrasts), diffusion of chemical species
- Flow is not restricted along layers; regional leakage across aquitards ("shales" / mudrocks)
Cross-section of Gulf Coast Basin

From Galloway (1982)
Hydrogeology of Sedimentary Basins

• Variable!
• Water/Brine are highly mobile (geologic scale)
• Driving forces: compaction, gravity (uplift), convection (density-driven by salinity or temperature contrasts), diffusion of chemical species
• Flow is not restricted along layers; regional leakage across aquitards (“shales” /mudrocks)
• Source of water: connate (“born with”), meteoric, deeper brines, or mixed
Chemical Composition

• Salinity in general increases with depth to a maximum value variable for each basin; however salinity reversal are not uncommon and salinity may stay <seawater

• Na-Cl or Na-Ca-Cl w/ or w/o SO4

• Controlled by presence of evaporites in the basin, reflux of bitterns, water-rock interactions (Ba from degraded feldspar could precipitate if SO4), diffusion, organic carbon and microbial activity, mixing

• NATCARB database; USGS database: http://energy.cr.usgs.gov/prov/prodwat/data2.htm
Mineral Composition

- Mineral make up: quartz, clays (illite, smectite, kaolinite), carbonates (feldspar, pyrite, OM, etc) in variable quantity
- Much finer, slower flow, increased water-rock interactions, increased surface area for sorption (a few percent organic carbon, smectites)
- Local conditions (minerals present, P, T, pH, Eh) add local flavor to the formation water
- Variable across plays and within plays
- Geologic time
Total Organic Carbon – Sorbing Clays

- TOC: 0.5 to 1.5 %, common range for shales
- TOC: 2-5% common for gas shales; black shales
- Smectites: a few to >10%

Dan Jarvie (2010) website

<table>
<thead>
<tr>
<th>Formation</th>
<th>Non-Generative Organic Carbon</th>
<th>Generative Organic Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cretaceous Eagle Ford</td>
<td>2.76</td>
<td>1.48</td>
</tr>
<tr>
<td>Ordovician Utica</td>
<td>1.33</td>
<td>0.63</td>
</tr>
<tr>
<td>Triassic Montney</td>
<td>0.93</td>
<td>1.86</td>
</tr>
<tr>
<td>Devonian Muskwa</td>
<td>2.16</td>
<td>1.72</td>
</tr>
<tr>
<td>Devonian Marcellus</td>
<td>4.67</td>
<td>3.53</td>
</tr>
<tr>
<td>U. Jurassic Haynesville</td>
<td>3.01</td>
<td>4.78</td>
</tr>
<tr>
<td>U. Jurassic Bossier</td>
<td>1.64</td>
<td>0.91</td>
</tr>
<tr>
<td>Devonian Woodford</td>
<td>5.34</td>
<td>3.99</td>
</tr>
<tr>
<td>Mississippian Fayetteville</td>
<td>3.77</td>
<td>1.97</td>
</tr>
<tr>
<td>Mississippian Barnett</td>
<td>4.42</td>
<td>2.50</td>
</tr>
</tbody>
</table>

Dan Jarvie (2010) website

- TOC: 2-5% common for gas shales; black shales
- Smectites: a few to >10%
Laminated calcareous mudrock
Harbor’s MS thesis UT 2011
Eagle Ford
(>50% carbonates)
Harbor’s MS thesis UT 2011

Barnett
(~quartz + clays)
Chelini et al. SPE134292
Produced Water

• Not a new problem, produced water was 21 billion bbls in 2007 (Veil and all) >80% injected for disposal or waterflood/EOR

• Elements of concern: TDS; As, Ba, Fe, Mn, Se, B, SiO$_2$, Sr; organics (natural and introduced – additives); NORMs

• Flowback water: highly variable TDS increasing from that of frac water to resident water TDS

• Barnett average of 80,000 ppm (max >150,000) Marcellus aver. of 120,000 ppm (max >250,000)
Comparison to MCLs – How high are trace elements concentrations?

- MCLs – TTs
- TDS: 500-1000 ppm
- Sr: 4 ppm
- F: 4 ppm
- Ba: 2 ppm
- As: 10 ppb
- B: 1400 ppb
- Br: 100 ppb

EPA drinking water MCL
- Ra-226+Ra-228: 5 pCi/L
- Gross alpha: 15 pCi/L
- Gross beta: 5 mrem
- Uranium: 30 ppb
How much is too much?

- Marcellus samples (Vidic, U. of Pittsburgh)

<table>
<thead>
<tr>
<th></th>
<th>Ba (ppm)</th>
<th>0</th>
<th>2300</th>
<th>3310</th>
<th>4700</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sr (ppm)</td>
<td>0</td>
<td>1390</td>
<td>2100</td>
<td>6830</td>
</tr>
<tr>
<td></td>
<td>TDS (ppm)</td>
<td>500</td>
<td>69,400</td>
<td>175,600</td>
<td>248,000</td>
</tr>
</tbody>
</table>

- Are Ba and Sr concentrations high?
- Ba, Sr > MCL
- Ca, Mg, Sr increase with TDS, Ba, Ra too but are more strongly inversely correlated with sulfate.
Black Shales

• Rich in organic matter; good source rock if right conditions; good trace metal scavenger (Ag, B, Co, Cr, Cu, Mo, Ni, U, V, Zn) during deposition
• Elevated Th=30-40 ppm and U=10-25 ppm; Sr=250-500 ppm (XRF analyses, Harbor, 2011)
• Crust aver.: Th ~10 ppm; U ~3 ppm ; Sr ~400 ppm
• U, Th not soluble in water in reducing conditions but decay products (Ra-226 and Ra-228) are soluble
• Injection of fresh/brackish water: some defloculation (additives?), trace metal mobilization/leaching
• Fracking: quickly exposed a large surface area
NORM metrics

• Curie: unit of radioactivity measuring the number of disintegrations per second
• 1 Ci =~ 1g Ra-226, that is, 1 pCi/L =~ 1 ppt Ra-226
• Another concept: dose (mrem/time) = f(energy, impact on living tissue)
• Produced water: from ~0 to >10,000 pCi/L (10 ppb Ra-226)
### Radium in Marcellus

The image shows a scatter plot with two red circles highlighting data points from different formations:

- **Upper Devonian**
- **Middle Devonian**
- **Lower Devonian**
- **Silurian**
- **Ordovician**
- **Cambrian**
- **Unknown**

The x-axis represents the total radium in picocuries per liter, ranging from 0 to 16,000. The y-axis represents the formation age.

**USGS SIR-2011-5135**
A

Total dissolved solids (TDS), in milligrams per liter

EXPLANATION
- □ Marcellus Shale Data
- □ Non-Marcellus Shale Data
- □ Marcellus ND
- □ Non-Marcellus ND

Log total Ra = 1.55 x Log TDS – 4.86

Log total Ra = 1.55 x TDS – 5.26

Log total dissolved solids (TDS), in milligrams per liter

Log total radium, in picocuries per liter

Log total radium, in picocuries per liter

USGS SIR-2011-5135
Woodford – OK:
TDS = 13,833 mg/L
TSS = 64.5 mg/L
Ra-226: 81.8 pCi/L
Ra-228: 7.34 pCi/L
U-234: 1.12 pCi/L
U-238: 0.96 pCi/L
G. alpha: 265 pCi/L
G. beta: 72 pCi/L
in SPE #121104
Horn et al. 2009
5 pCi/L with TDS = 1000 ppm
Conclusions

• Immense variability in the geochemistry
• Shale richer in trace elements (whole rock), not clear how much partitions into the water
• Better knowledge of trace elements, (organics) and NORMs is needed to better understand relationship between suite of elements detrimental to treatment
• [Scaling of pipe/tanks]