

TestAmerica

THE LEADER IN ENVIRONMENTAL TESTING

Radiochemical Analytical Challenges with Hydrofrac Fluids

Terry Romanko
Technical Director
TestAmerica St. Louis

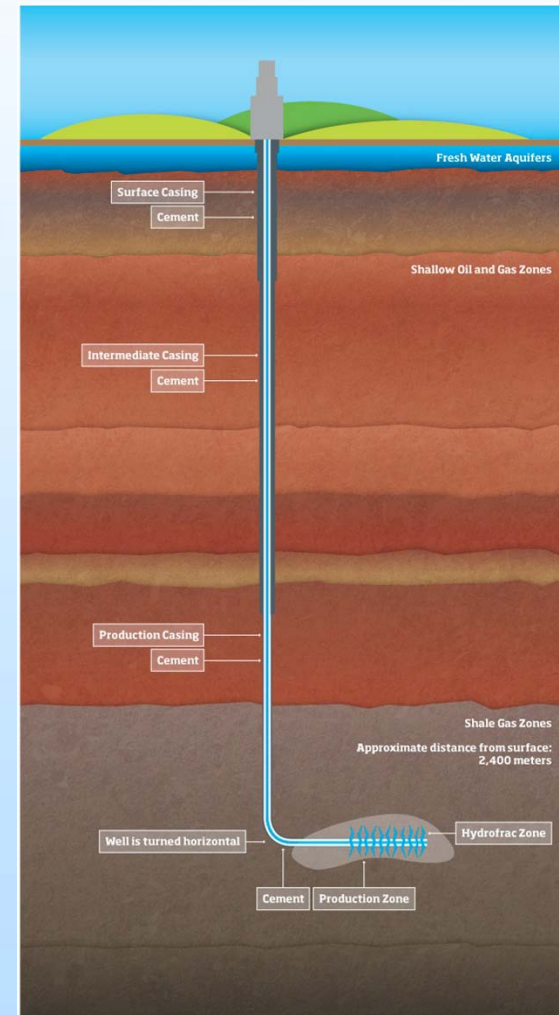
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Feb 24-25, 2011

- **Relatively High TDS**
(some >250,000 mg/L)
 - ~ Barium (>4,000 mg/L)
 - ~ Calcium (>31,000 mg/L)
 - ~ Strontium (>2,000 mg/L)
 - ~ Iron (>100 mg/L)



- **Gross Alpha/Beta**
(EPA 900.0/SW846 9310)
 - ~ “Rough” screening
 - ~ Mass on planchet limited to 100 mg for alpha
 - ~ High solids leads to reduced aliquot and counting efficiency
 - ~ EPA 900.1/SM 7110C can help, but ...



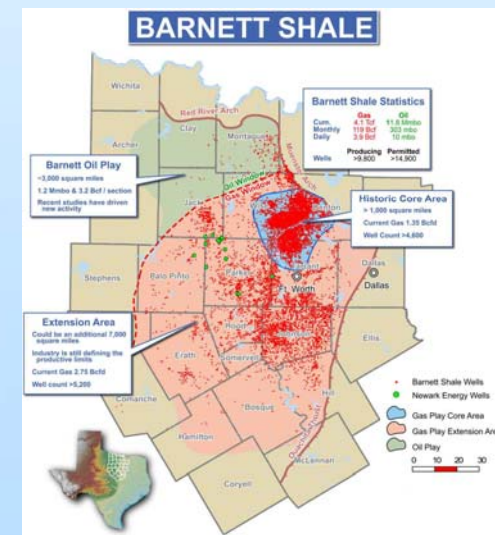
Periodic Chart of the Elements

File Help

IA		88		226		Physical Properties										VIII A	
H		Ra		Radium		Density 5.00 g/cc										He	
Li Be						Abundance - ppm										Ne	
Na Mg						Melting Point 700.00 C										Ar	
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr																	
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe																	
Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn																	
Fr Ra Rf Db Sg Bh Hs Mt Un Uu																	
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu																	
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr																	

- **Radium Co-precipitation**

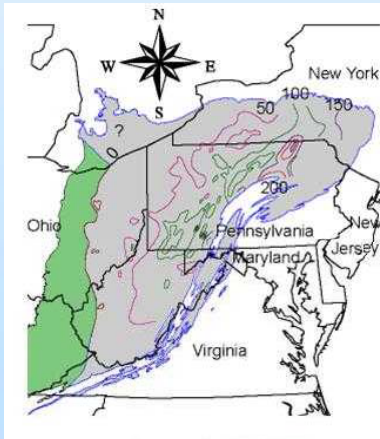
- ~ Most “traditional” precipitation chemistry methods employ sulfate co-precipitation
- ~ Various Pb/Sr/Ba concentrations added
- ~ EDTA cleanup
- ~ Eventually barium sulfate
 - carrier for chemical recovery calculation
 - ~30 mg barium



- **Interferences**

- ~ TDS and Ba/Ca/Sr all cause problems

- General competition in chemistry
- Large qty of barium sulfate precipitate



- Spoils gravimetric chemical recovery
- For GFPC creates flaking issue
- For GFPC increases self-absorption

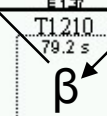
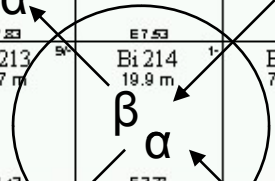
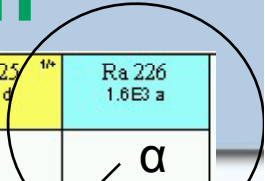
- **Possible Solutions**
 - ~ Reduce aliquot (increases MDC)
 - ~ Ba-133 as tracer for chemical yield
 - Still have large qty of precipitate
 - ~ Use “non-traditional” method
 - Gamma Spectroscopy (direct count)
 - Gamma Spectroscopy (Ga. Tech method)

- Ra-226 has one weak gamma emission
 - ~ 3% abundance at 186 keV
- U-235 has several gamma emissions
 - ~ 11% at 144 keV
 - ~ 54% at 186 keV

U-235 is large interference for Ra-226!!

Ra-226 Decay Chain

Ra 215 ⁽⁵⁺⁾ 1.60 ms	Ra 216 1.8E-7 s	Ra 217 ⁽⁵⁺⁾ 1.6E-6 s	Ra 218 1.4E-5 s	Ra 219 ⁽⁷⁺⁾ 10.0 ms	Ra 220 23.0 ms	Ra 221 ⁵⁺ 28.0 s	Ra 222 38.0 s	Ra 223 ³⁺ 11.4 d	Ra 224 87.8 h	Ra 225 ¹⁺ 14.8 d	Ra 226 1.6E3 a
E826	E953	E916	E855	E813	E780	E629	E668	E556	E579	E357	E427
⁽²⁻⁾ Fr 214 ⁽¹⁻⁾ 3.40 ms 5.00 ms	Fr 215 ⁵⁺ 9.0E-8 s	Fr 216 ⁽¹⁻⁾ 7.0E-7 s	Fr 217 ⁵⁺ 2.2E-6 s	Fr 218 ⁽¹⁻⁾ 7.0E-4 s	Fr 219 ⁵⁺ 20.0 ms	Fr 220 ¹⁺ 27.5 s	Fr 221 ⁵⁺ 4.80 m	Fr 222 ²⁻ 14.8 m	Fr 223 ⁽³⁻⁾ 21.8 m	Fr 224 ⁽¹⁻⁾ 160 s	Fr 225 ⁽³⁻⁾ 3.00 m
E859	E954	E918	E847	E801	E745	E620	E646	E203	E115	E282	E187
Rn 213 ⁽⁵⁺⁾ 25.0 ms	Rn 214 2.7E-7 s	Rn 215 ⁵⁺ 2.3E-6 s	Rn 216 45.0 s	Rn 217 ⁵⁺ 5.4E-4 s	Rn 218 35.0 ms	Rn 219 ⁵⁺ 3.96 s	Rn 220 55.6 s	Rn 221 ⁽⁷⁺⁾ 25.0 m	Rn 222 91.8 h	Rn 223 ⁽⁷⁻⁾ 43.0 m	Rn 224 107 m
E824	E921	E884	E820	E789	E726	E695	E641	E122	E559		
⁽²⁻⁾ At 212 ⁽¹⁻⁾ 122 ms 315 ms	At 213 ⁵⁺ 1.1E-7 s	At 214 ¹⁻ 2.0E-6 s	At 215 ⁵⁺ 1.0E-4 s	At 216 ⁽¹⁻⁾ 3.0E-4 s	At 217 ⁵⁺ 32.0 ms	At 218 ⁽²⁻⁾ 2.00 s	At 219 54.0 s				
E783	E925	E859	E818	E795	E720	E627	E639				
⁽²⁵⁺⁾ Po 211 ⁵⁺ 25.5 s 520 ms	⁽¹⁸⁺⁾ Po 212 45.0 s 3.0E-7 s	Po 213 ⁵⁺ 4.2E-6 s	Po 214 1.0E-4 s	Po 215 ⁵⁺ 2.00 ms	Po 216 150 ms	Po 217 10.0 s	Po 218 183 s				
E780	E856	E854	E783	E753	E691	E695	E612				
⁵⁻ Bi 210 ¹⁻ 3.5E5 a 5.01 d	Bi 211 ⁵⁺ 130 s	Bi 212 ⁽¹⁻⁾ 60.6 m	Bi 213 ⁵⁺ 45.7 m	Bi 214 ⁽¹⁻⁾ 19.9 m	Bi 215 7.40 m						
E116	E675	E225	E143	E327	E225						
Pb 209 ⁵⁺ 3.25 h	Pb 210 20.4 a	Pb 211 ⁵⁺ 36.1 m	Pb 212 10.6 h	Pb 213 ⁽⁵⁺⁾ 10.2 m	Pb 214 26.8 m						
E644	E054	E137	E574	E207	E107						
Tl 208 ⁵⁺ 186 s	Tl 209 ⁽¹⁺⁾ 132 s	Tl 210 ⁽⁵⁺⁾ 79.2 s									
E500	E396	E548									



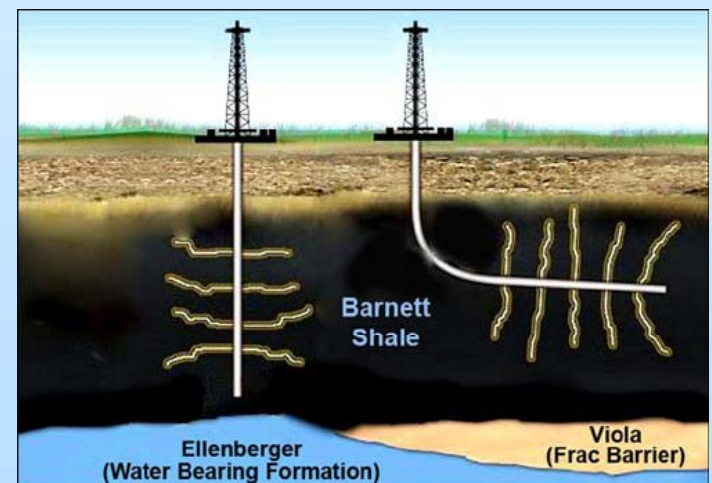
- First progeny of Ra-226, Rn-222 (gas), can escape matrix.
- Seal in a geometry, then allow for decay chain to ingrow
- Measure Bi-214 (46% gamma at 609 keV)



Secular equilibrium

- ~ Half-life of Ra-226 (1600 years) is much greater than of Rn-222 (91.8 hrs)
- ~ Rest of decay chain down to Pb-210 has short half-life (<30 min.)
 - 7 days = 72% ingrowth
 - 14 days = 92% ingrowth
 - 21 days = 98% ingrowth

- **Direct Count (No Preparation)**
 - ~ Place sample (e.g. 1L) in geometry
 - ~ Count after ingrowth
 - ~ MDC of 30-50 pCi/L
 - ~ Ra-226/228 concentration:
 - Flowback duration
 - Ba content



- Georgia Tech Research Institute (Bernd Kahn, Robert Rosson)
 - ~ Coprecipitate Radium with barium sulfate
 - ~ Modify by adding Ba-133 as tracer
 - ~ Allow ingrowth (can use any time)
 - ~ Ra-226, Ra-228, and Ba-133 recovery from single analysis
 - ~ Should allow for lower MDC (<5 pCi)

Other Considerations

- **What is actual sample matrix?**
- **What is ultimate goal of analysis?**
- **What are regulatory requirements?**
- **?????**



Questions?

- Terry Romanko – Radiochemistry Technical Director
 - St. Louis Laboratory
 - terry.romanko@testamericainc.com
 - 314-298-8566