NATIONAL ENERGY TECHNOLOGY LABORATORY

PRELIMINARY ANALYSIS OF THE WEATHERING POTENTIAL OF MARCELLUS SHALE DRILL CUTTINGS

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Geology and Environmental Science

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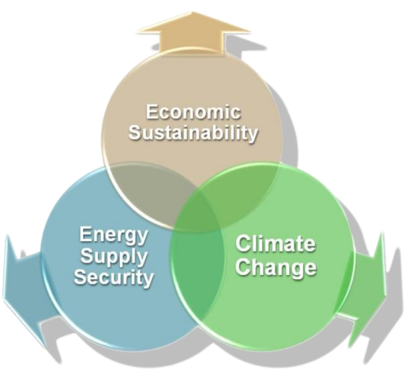
GSA Section Meeting, Pittsburgh, PA

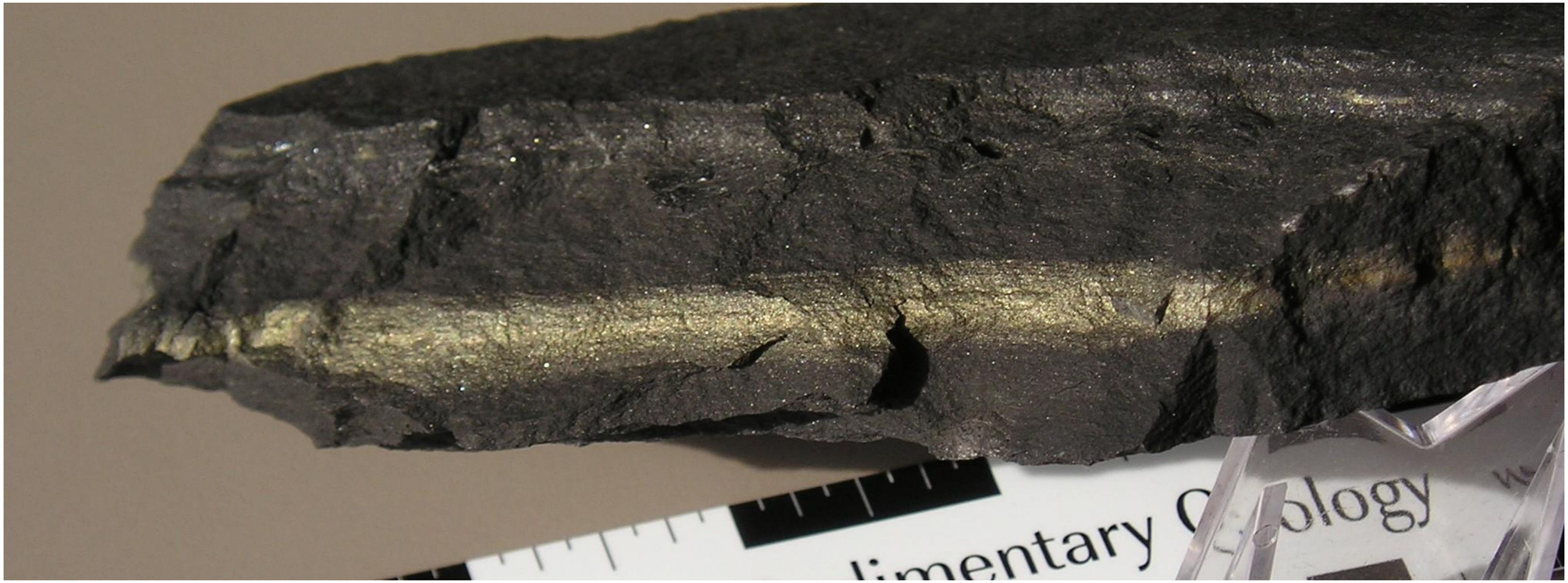


U.S. DEPARTMENT OF ENERGY

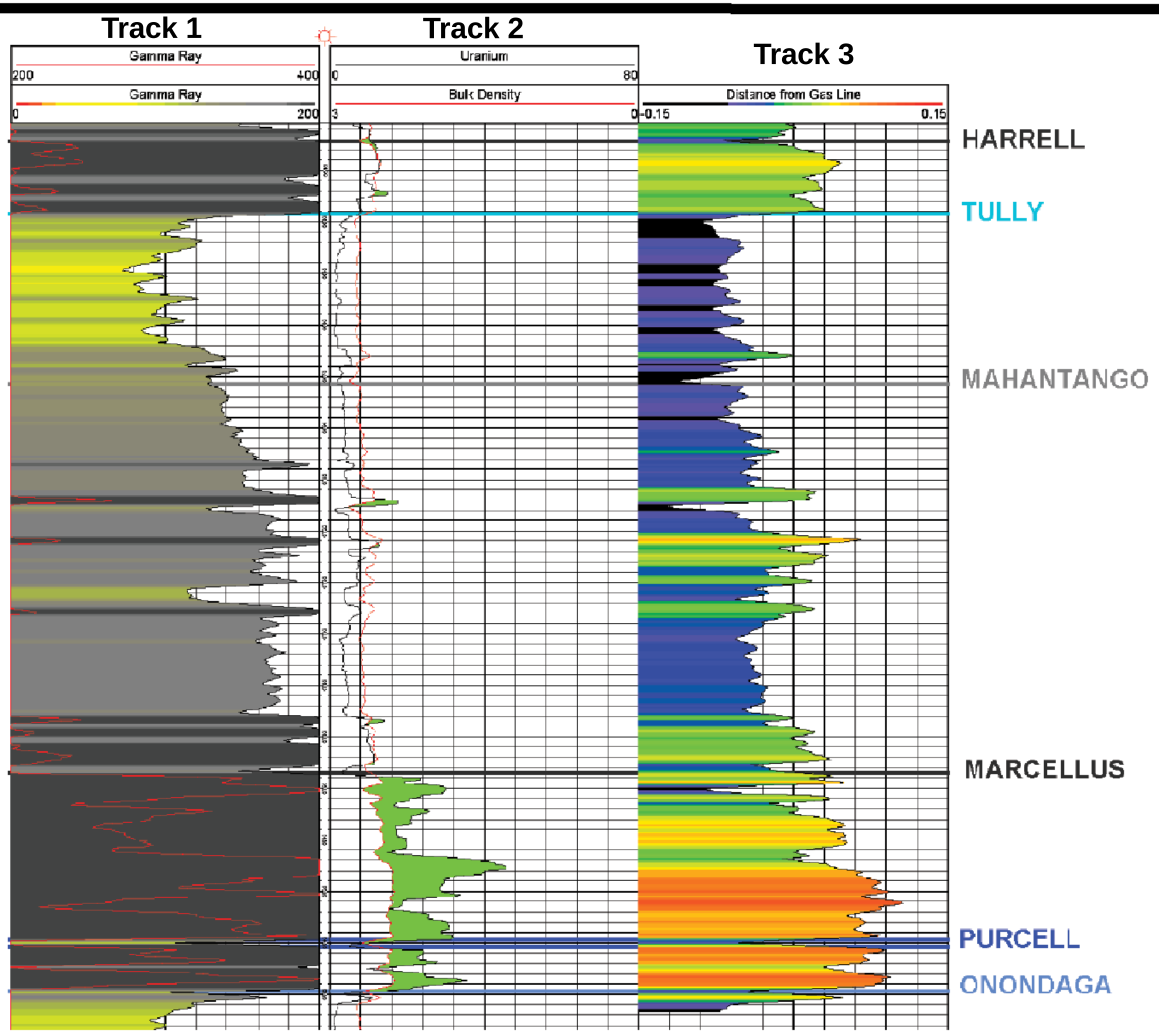

Marcellus Shale in Hanson Quarry, NY
Quaternary Till
Oatka Creek Member
Cherry Valley LS
Union Springs Member
Onondaga Limestone

Black Shale

- Black color comes from high organic content
- Organics are plant material deposited with sediment
- Organic material was preserved by anoxic bottom water
- Organic material has an affinity for radionuclides and metals
- Black shales often contain reduced minerals such as sulfides

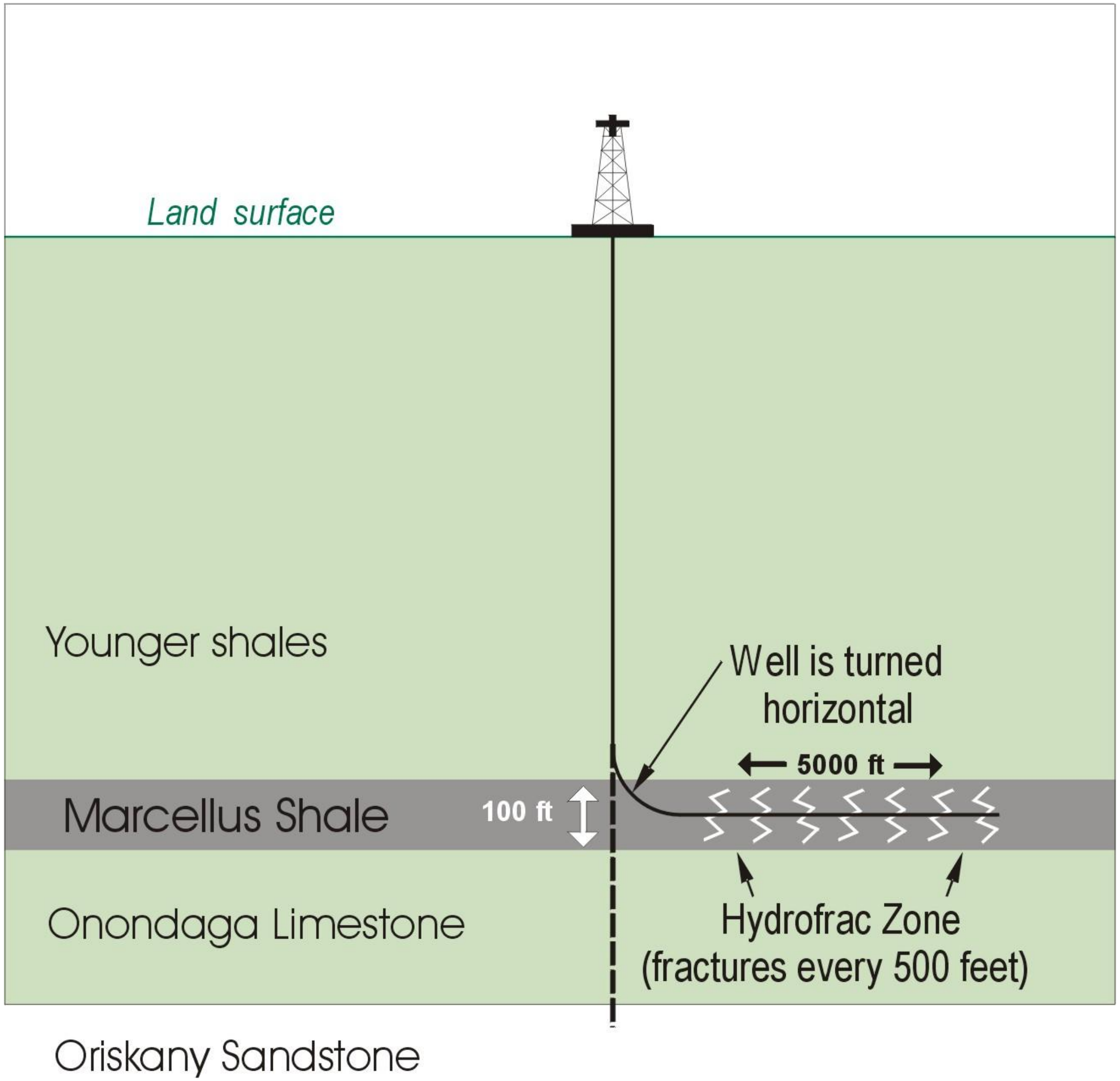


Hamilton Group Radioactivity



From Boyce, 2010

Cuttings from Horizontal Wells



Volume of Drill Cuttings

- **12 inch diameter vertical borehole through 100 feet of black shale:**
  - V= $\pi(r^2h) = \pi(0.5)^2(100ft)$= 78.54 cubic feet cuttings
  - V= $\pi(r^2h) = \pi(0.1525)^2(30.48m)$= 2.22 cubic meters cuttings

- **12 inch diameter horizontal borehole through 5,000 feet of black shale:**
  - V= $\pi(r^2h) = \pi(0.5)^2(5000ft)$= 3927 cubic feet cuttings
  - V= $\pi(r^2h) = \pi(0.1525)^2(1534m)$= 111.35 cubic meters cuttings

- **Assume shale bulk density of 2.4 g/cm^3 =**
  - 2.22 m^3 = 5,345 kg = 5.3 metric tons
  - 111.35 m^3 = 267,230 kg = 267 metric tons

A Lesson in Metal Mobility

Oxidized lead shot

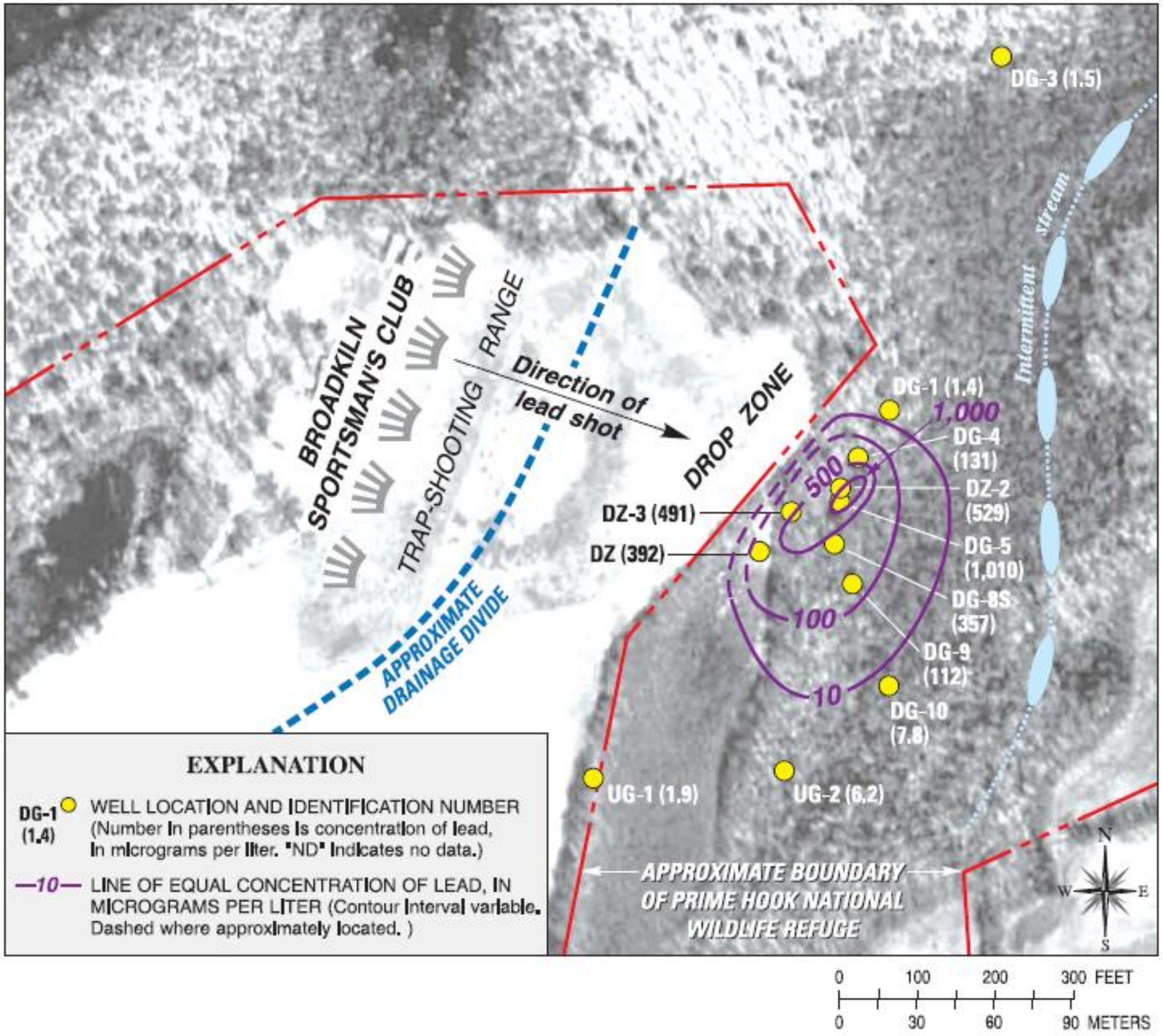
A 1999 USGS study on a wildlife refuge found lead from shotgun pellets being oxidized and transported through shallow ground water to a nearby stream.

Lead in Groundwater at Prime Hook NWR

All the literature said lead was immobile.

Lead carbonate, cerussite, was forming on the pellets, and dissolving in low pH rain.

Shallow groundwater transport through a clean sand carried it to the stream.



Minerals and Metals

- Target horizons in the shales have high gamma log counts – typically above 290 API units.
- Black shale may also contain other metals, including some that are considered toxic.
- Metals in the shale have been in a reduced state for hundreds of millions of years.
- Horizontal drilling produces much greater amounts of black shale drill cuttings than vertical penetrations
- Hundreds of tons of reduced drill cuttings are exposed to oxygen and rain water on the surface.
- Oxidized forms of metals are typically more soluble in water.
- What is there, how much, and where does it go?
- Good questions.

Scope and Collaborators on Study

- USDOE-NETL: Dan Soeder and Tom Mroz
- URS Corporation (SSC): Bill Schuller
- Separation Design Group (Waynesburg): Doug Galbraith, David Walker, and Douglas Kern
- Waynesburg University: Bob LaCount and Evonne Baldauff, plus assorted students
- Project ran from April 2010 to October 2010; follow-on work is intended, as soon as budget allows.

Scope of study: Compare metals content of fresh cuttings, oxidized core and weathered outcrop samples to determine if there is a leaching process that takes place over time when black shale is exposed to air and rainfall.

Assumption: Geochemical character of the Marcellus is laterally uniform, and comparable from place to place. "Same shale; different exposures."

Research Plan - Marcellus Shale

Sample Selection:

Fresh drill cuttings "fully loaded"

- Lab had access to a Lamar Drilling rig in Greene County, PA
- Cutting samples from upper, middle and lower parts of Marcellus Shale

Old drill core "oxidized"

- DOE Eastern Gas Shales Project WV-6 core cut in 1976.
- Core has been kept dry, but minerals oxidized over time
- Samples extracted from upper, middle and lower parts of Marcellus Shale.

Outcrop samples "fully leached"

- Road cut in U.S. Silica Quarry, near Berkeley Springs, West Virginia (1905)
- Samples collected from upper, middle and lower parts of Marcellus Shale.

Analysis of Samples:

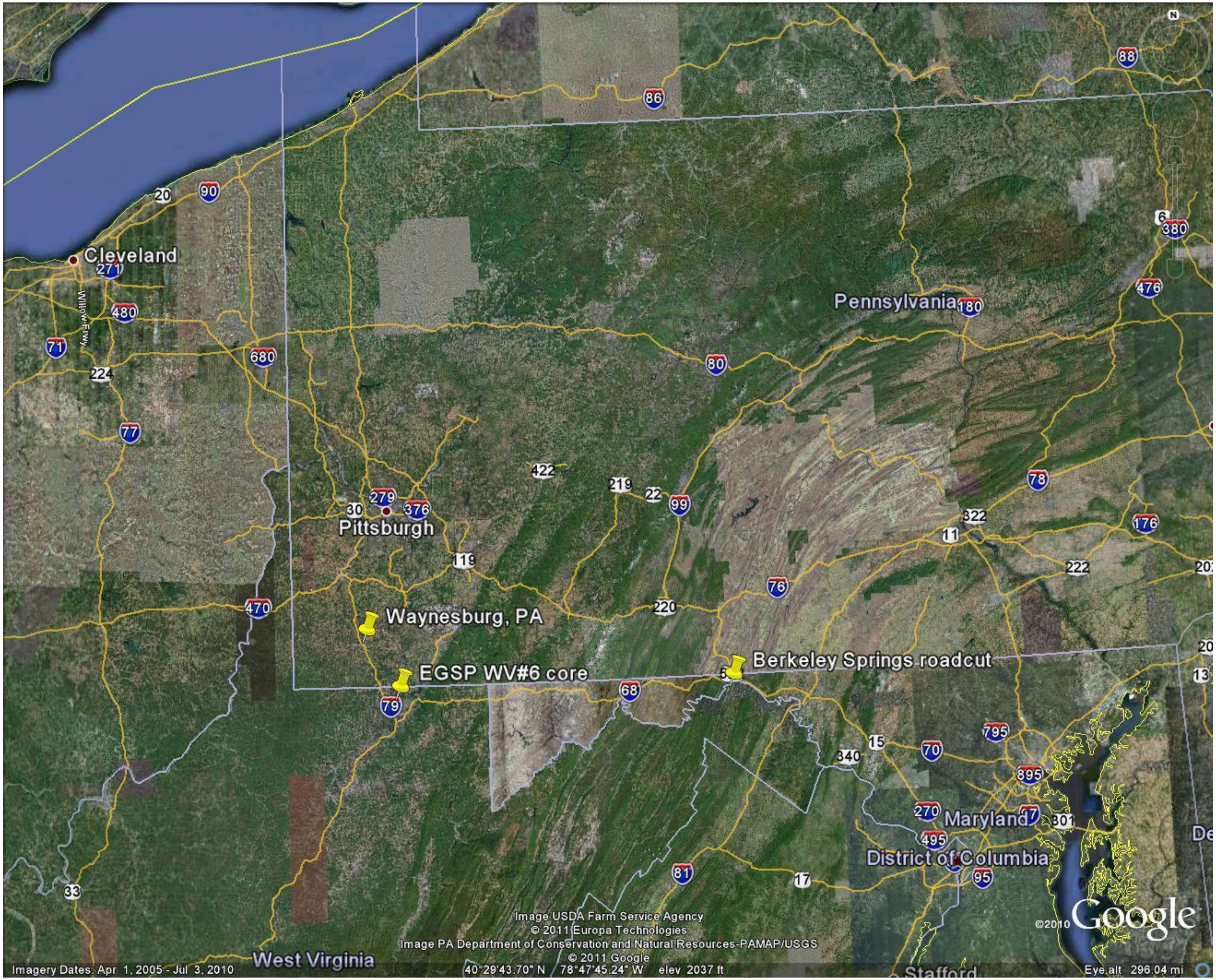
Elemental analysis and NORM

- Controlled Atmosphere Programmed Temperature Oxidation (CAPTO) analysis
- Scanning electron microscope with EDS
- Low background Alpha/Beta counter

Toxicity analysis

- Toxicity Characteristic Leaching Procedure (USEPA 1311 - extraction in dilute acid)
- Inductively Coupled Plasma elemental analysis

Sample Locations



68
40
Hancock
144
E Main St
Western Pike
National Fwy
Redrock Crossing
Co Route 1
Berkeley Springs roadcut
Co Route 4
Co Route 2
9
522
Ridersville
Berkeley Springs
Cacapon Rd
Image U.S. Geological Survey
© 2011 Google
Image USDA Farm Service Agency
©2010 Google
Imagery Dates: Jun 8, 2005 - Jun 8, 2009
39°39'52.83" N 78°12'21.10" W elev 657 ft
Eye alt 38439 ft

U.S. Silica Quarry Roadcut

Outcrop Sample - Lower Marcellus

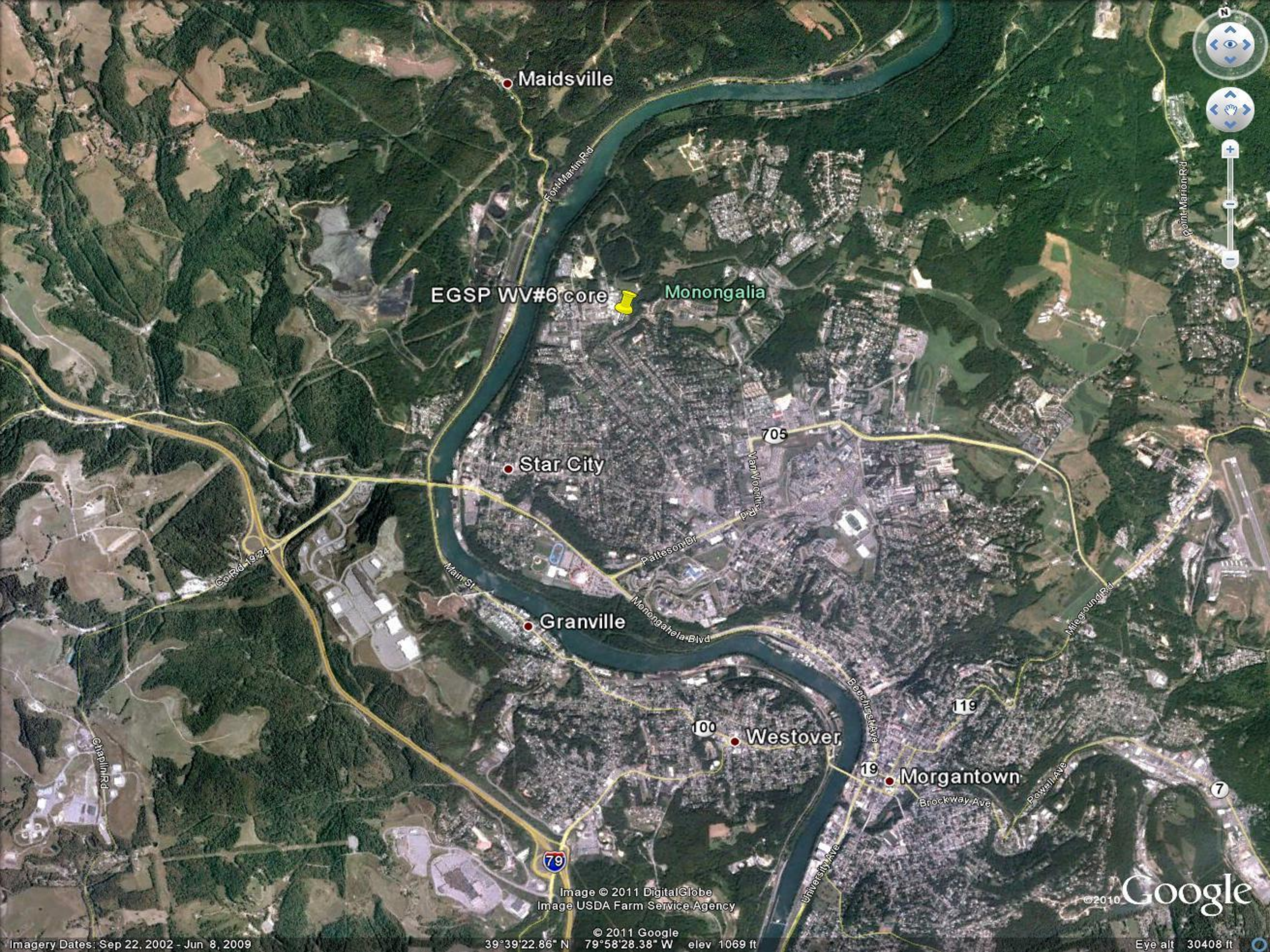
Sample collected from lower Marcellus Shale about 1 foot above contact with Needmore Shale.

Outcrop Sample – Middle Marcellus

Sample collected at the top of a foot-thick carbonate bed in Marcellus Shale, about 30 feet above contact with Needmore shale

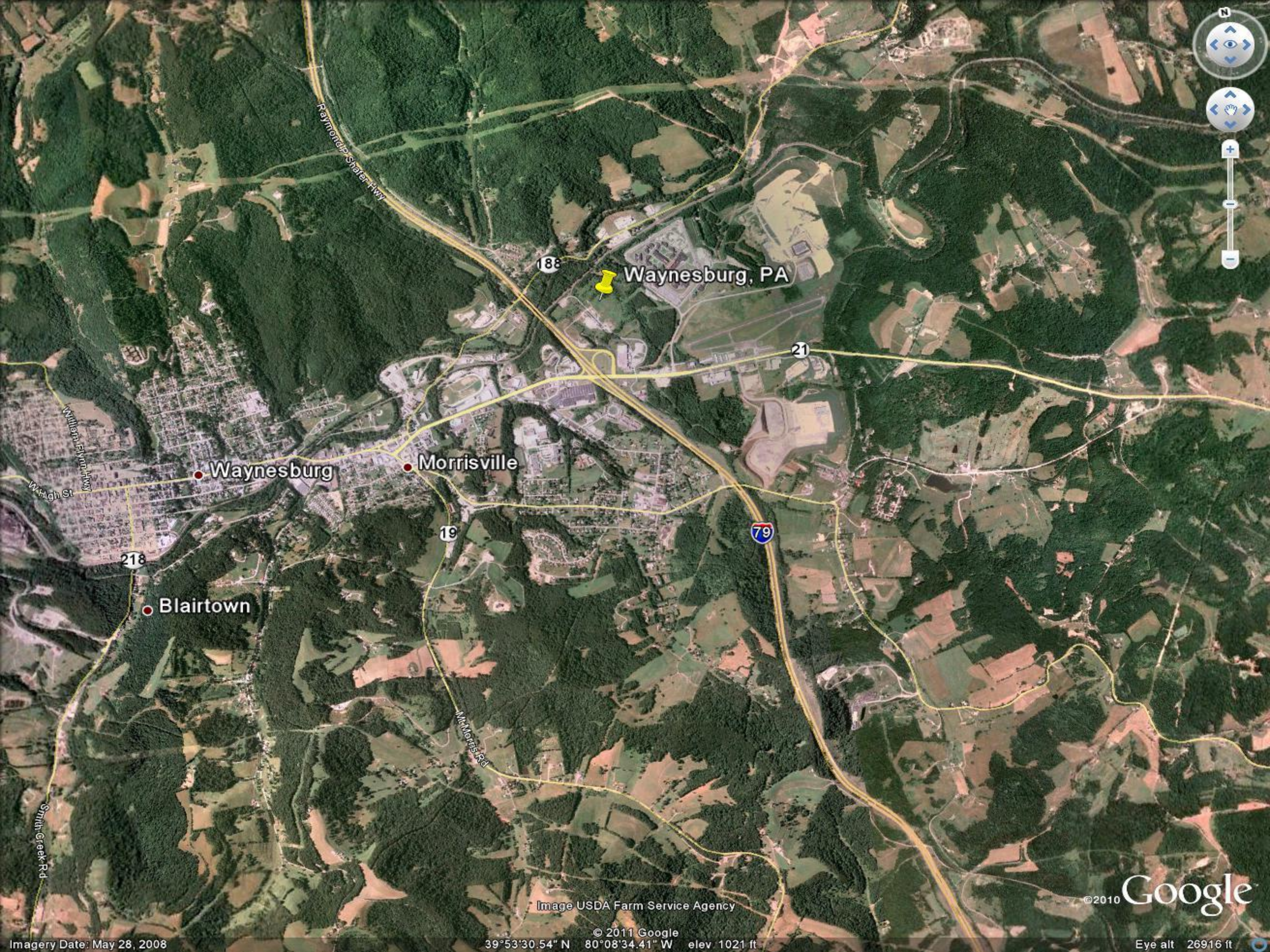
Outcrop Sample – Upper Marcellus

Sample collected in a fissile black shale resembling the Oatka Creek about 250 feet above the Marcellus Shale contact with the Needmore Shale. Faulting suggests this is Marcellus in a repeat section, but it could possibly be Mahantango Shale



Maidsville
Fort Martin Rd
EGSP WV#6 core
Monongalia
Star City
705
Van Voorhis Rd
Patteson Dr
Co Rd 19/24
Main St
Granville
Monongahela Blvd
Mileground Rd
Point Marion Rd
Beechurst Ave
119
100
Westover
19
Morgantown
Brockway Ave
Powell Ave
7
Chaplin Rd
79
University Ave
Image © 2011 DigitalGlobe
Image USDA Farm Service Agency
© 2011 Google
©2010 Google
Imagery Dates: Sep 22, 2002 - Jun 8, 2009
39°39'22.86" N 79°58'28.38" W elev 1069 ft
Eye alt 30408 ft

EGSP WV-6 Well and Core (MERC#1)



Raymond P Shafer Hwy
188
Waynesburg, PA
21
Waynesburg
Morrisville
William Flynn Hwy
W High St
19
79
218
Blairtown
Mt Morris Rd
Smith Creek Rd
Image USDA Farm Service Agency
©2010 Google
© 2011 Google
Imagery Date: May 28, 2008
39°53'30.54" N 80°08'34.41" W elev 1021 ft
Eye alt 26916 ft

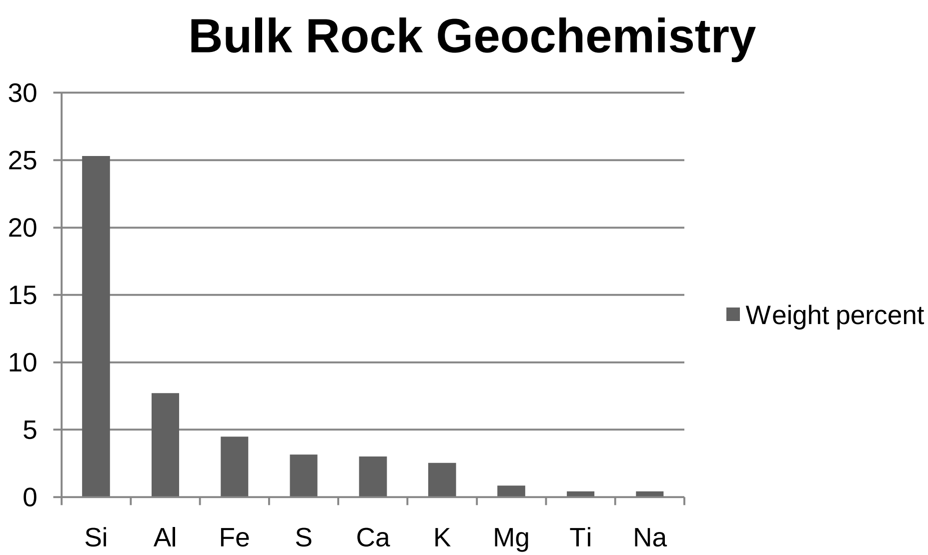
Drill Cuttings

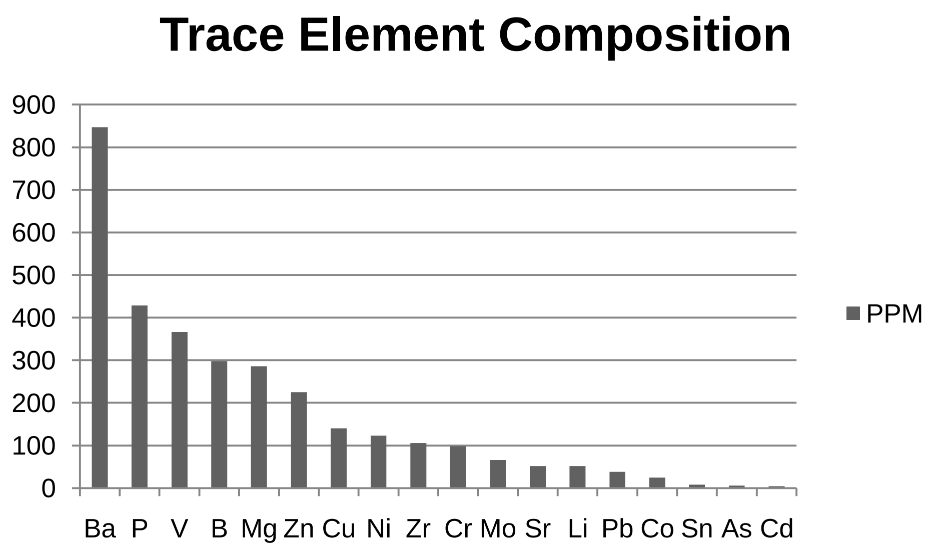
Limited usefulness
Small size chips
Somewhat co-mingled stratigraphy
Difficulties with depth control

However,
Considered a waste product and usually free
A good mud logger is reasonably certain of stratigraphy
Useful in applications requiring small sample size (SEM, XRD, Hgφ, Pet)

Results - Composite Sample

- Bulk rock geochemistry consists of Si, Al, Fe, S, Ca, K, Mg
- About what is expected for quartz/clay shale.
- Trace metals measured in Marcellus above MRL include the following: As, Ba, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, P, Pb, Sn, Sr, V, Zn, and Zr



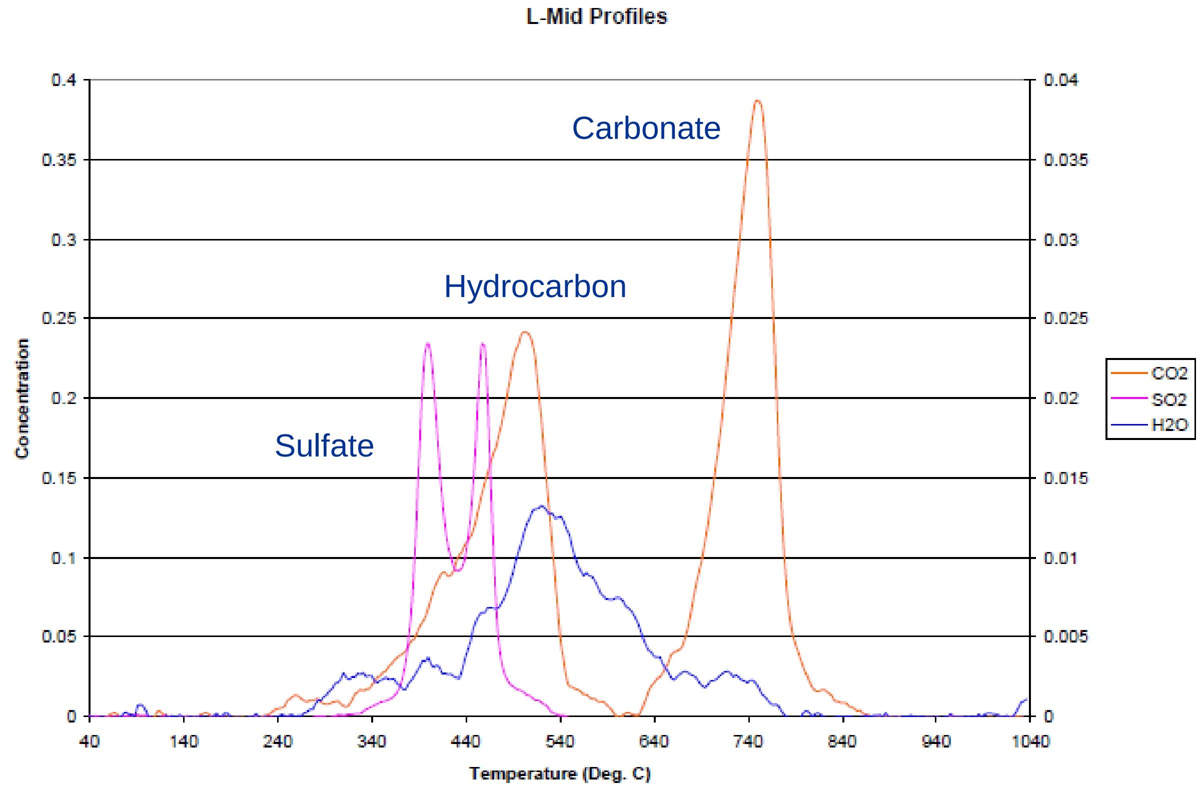


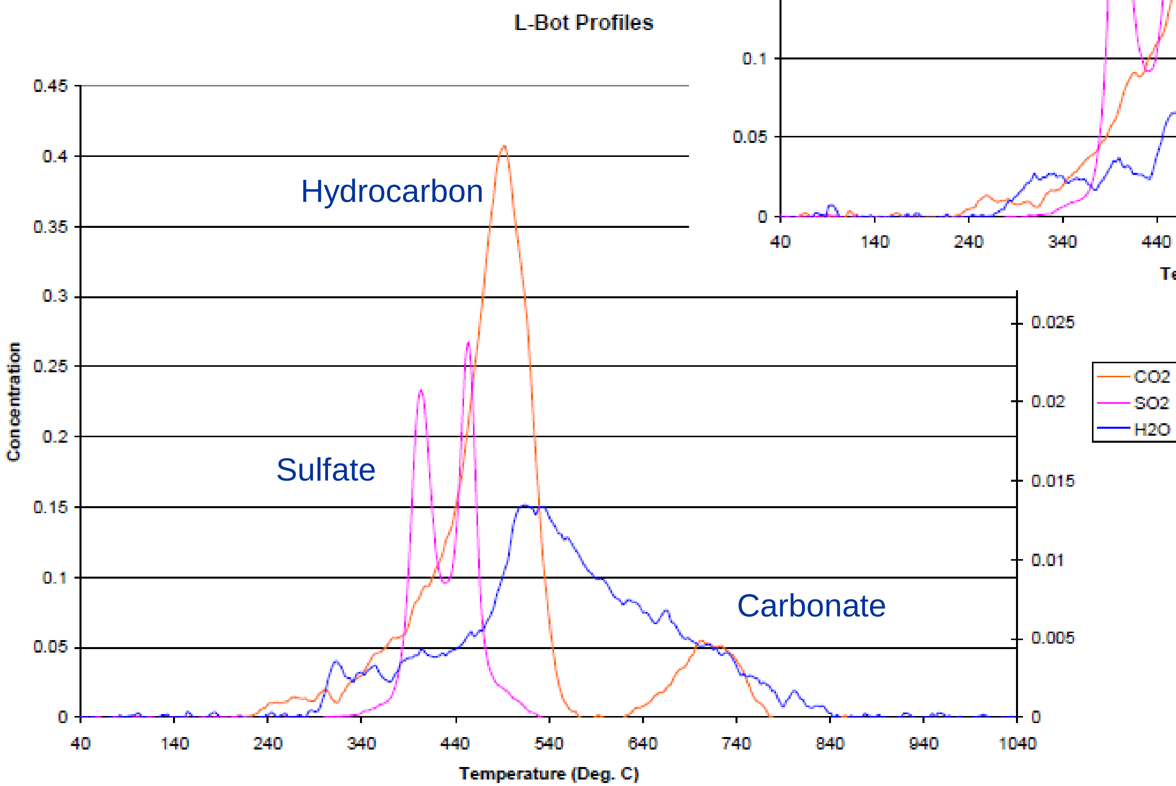
NORM Analyses

- The outcrop samples had the lowest α count and lowest β count.
- Cuttings were more radioactive than the outcrop, but less than parts of the core
- Upper part of core was the most radioactive sample

SDGroup Sample ID	RJLee Sample ID	Sampling Date	Alpha rate (raw cpm)	Beta rate (raw cpm)	Sample mass (g)	Alpha rate (μCi/kg)	Beta rate (μCi/kg)
C-Top	xxx-001	10/13/2010	4.80	6.73	0.02470	0.478	0.165
C-Mid	xxx-002	10/13/2010	1.07	4.10	0.04088	0.034	0.052
C-Bot	xxx-003	10/13/2010	1.47	5.73	0.03686	0.068	0.091
O-Top	xxx-004	10/14/2010	0.67	1.87	0.03162	0.008	0.016
O-Mid	xxx-005	10/14/2010	0.53	1.85	0.02900	at bkg	0.017
O-Bot	xxx-006	10/14/2010	0.57	2.67	0.03728	at bkg	0.029
L-Top	xxx-007	10/14/2010	1.40	5.37	0.03763	0.061	0.082
L-Mid	xxx-008	10/14/2010	1.30	5.23	0.03574	0.056	0.083
L-Bot	xxx-009	10/14/2010	1.57	3.23	0.01594	0.174	0.094
	average background		0.58 +/- 0.08	1.19 +/- 0.18			
	alpha efficiency		16.26% +/- 3.25				
	beta efficiency		61.65% +/- 12.33				

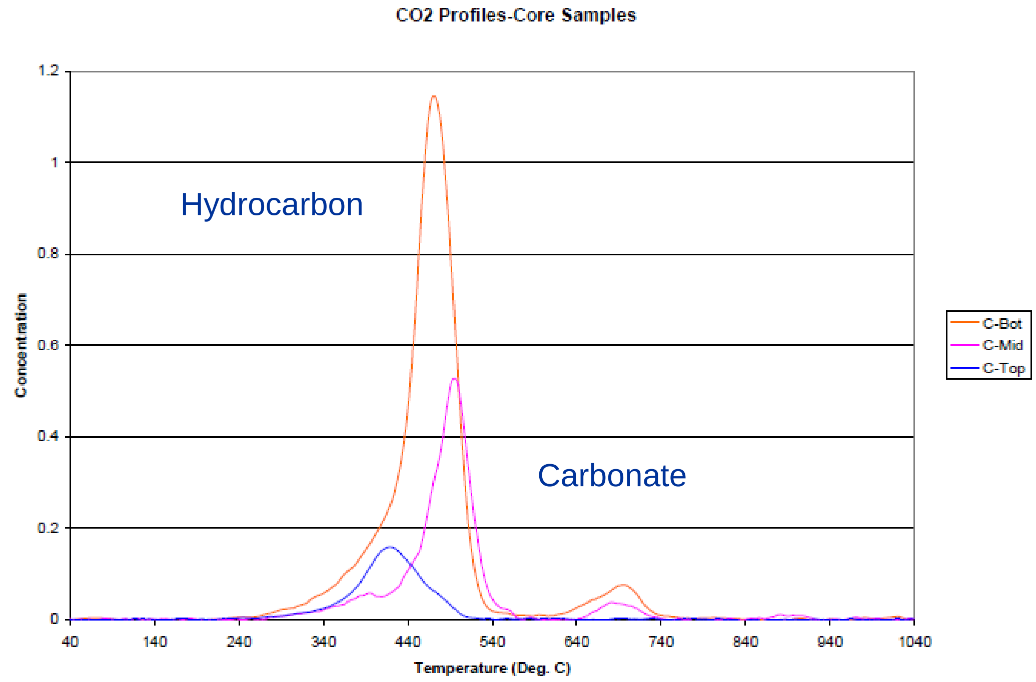
CAPTO oxidation and evolution results:

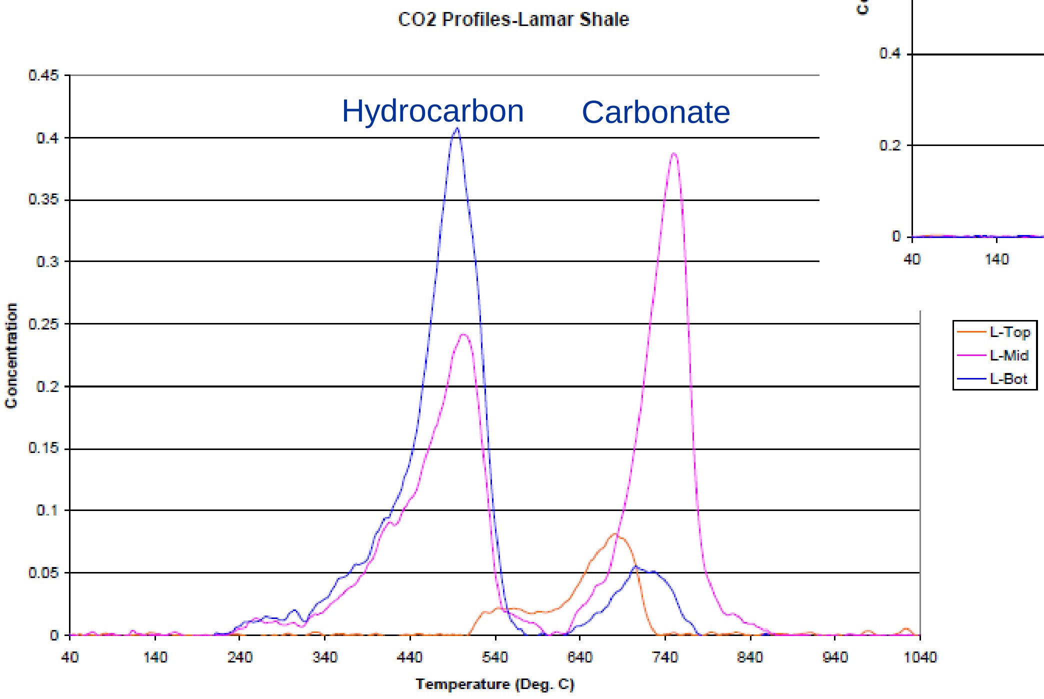




Cuttings from lower Marcellus (left); Cuttings from middle Marcellus (above)

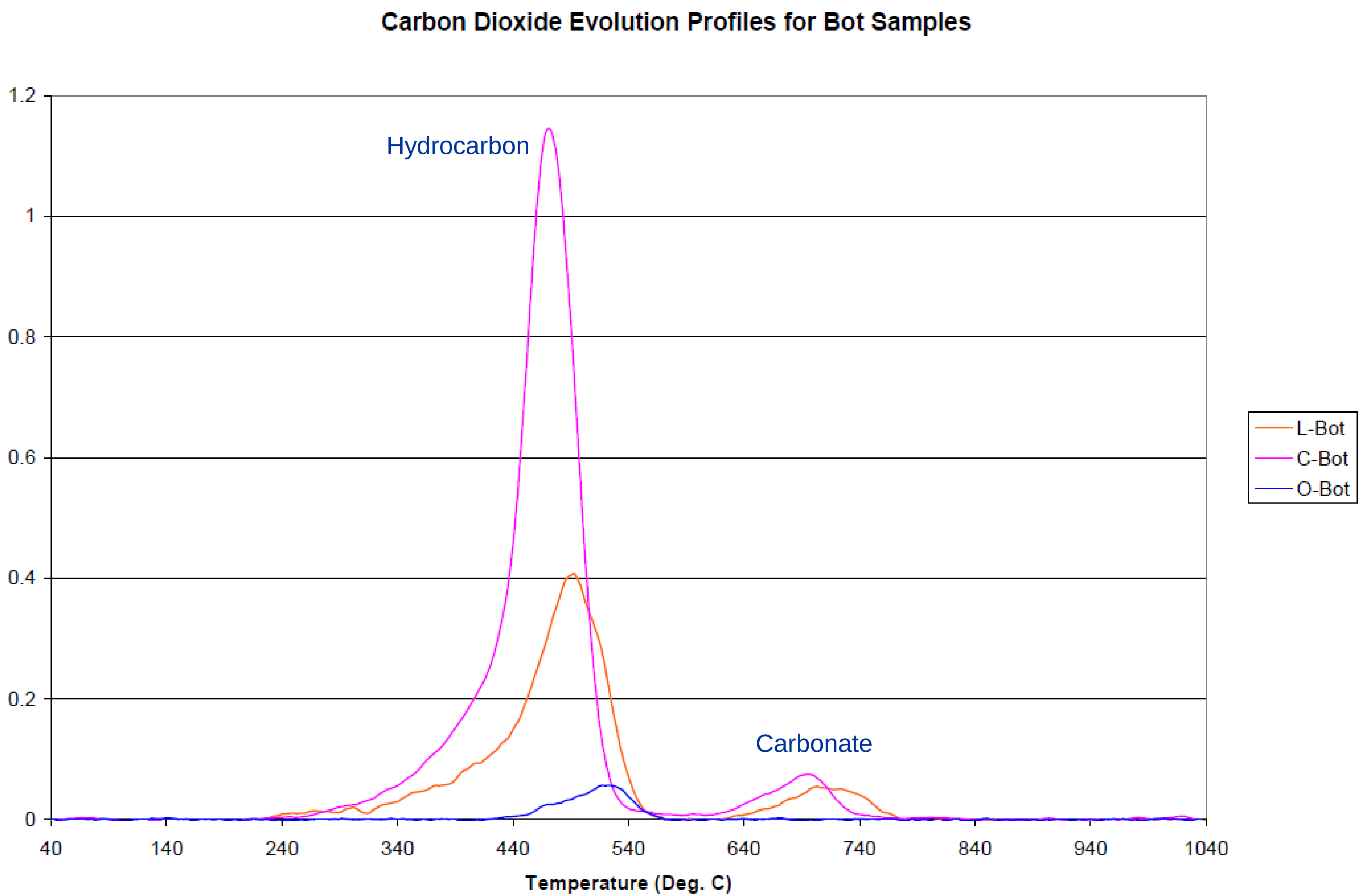
CO2 Evolution – Cuttings/Core





Cuttings from Lamar drilling rig (left);
Core from EGSP WV-6 (above)

CO2 Evolution - Base of Marcellus



Leachable Toxic Elements

Toxicity geochemistry by sample and location				TCLP EPA 1311						mg/l
	outcrop			core			cuttings			
element	base	mid	top	base	mid	top	base	mid	top	MRL
arsenic	<MRL	<MRL	<MRL	<MRL	<MRL	0.073	<MRL	<MRL	<MRL	0.050
barium	0.136	0.425	0.135	0.181	0.164	0.300	1.330	1.380	1.400	0.020
cadmium	<MRL	<MRL	<MRL	0.085	0.011	0.020	<MRL	<MRL	<MRL	0.010
chromium	<MRL	<MRL	<MRL	<MRL	0.026	0.077	<MRL	<MRL	<MRL	0.020
lead	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	0.050
selenium	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	0.050
silver	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	0.020
mercury	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL	0.0002

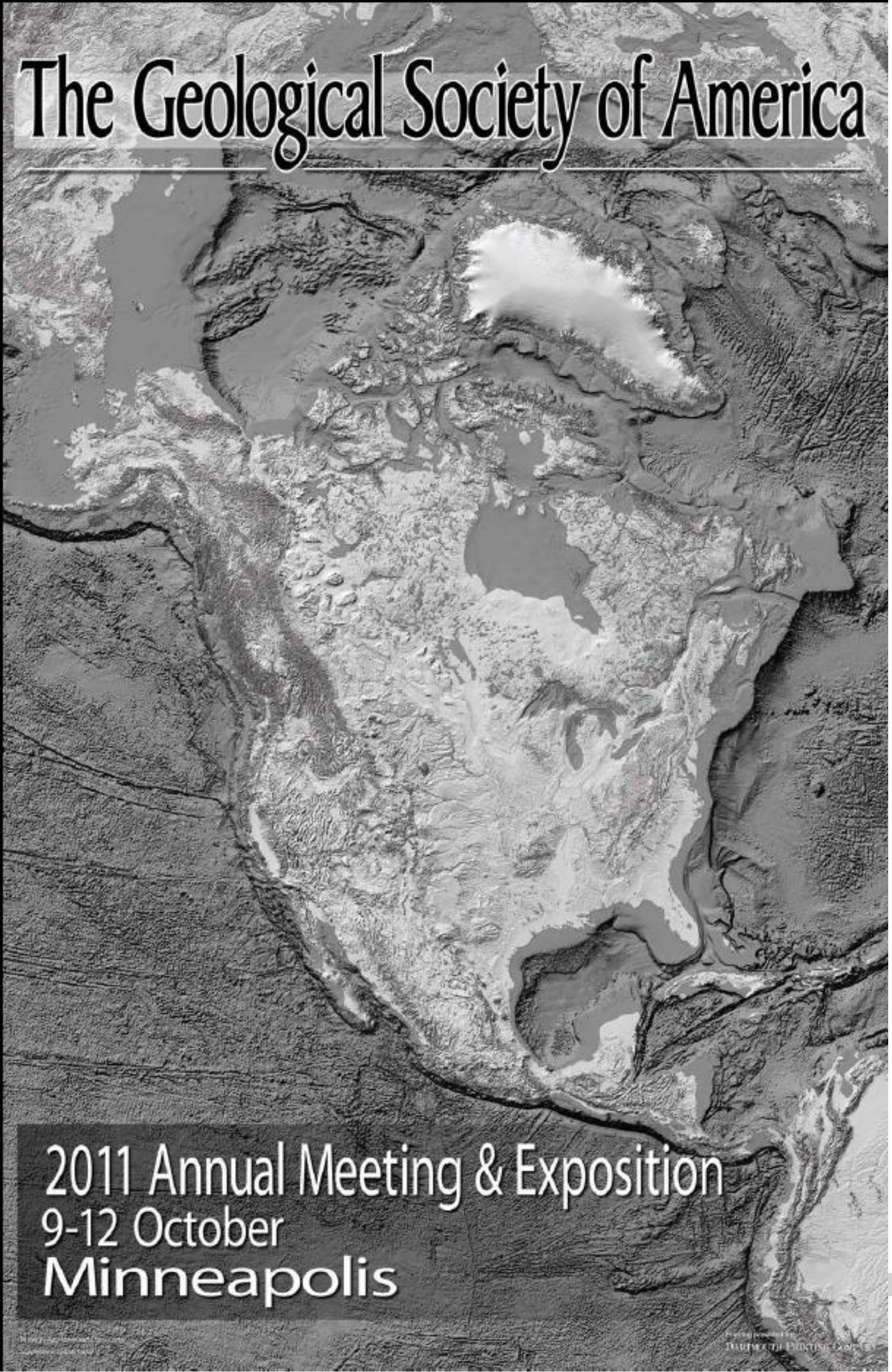
red signifies concentration in leachate below minimum reporting limit

Interim Conclusions

- Marcellus Shale samples from locations tens of miles apart are more different than similar, and samples from different sites cannot be assumed to be the "same" rock.
- The Marcellus Shale does contain a variety of trace elements, toxic metals and radionuclides associated with organic matter, some of which are leachable.
- The 30 year old core showed the greatest propensity for leachable metals – possibly because of oxidation state, or possibly just because it contained more.
- The outcrop samples contained the least leachable metals, and fresh cuttings were intermediate.
- Nine samples can't take us much farther.

Next Steps

- Run artificial weathering experiments on fresh cuttings – oxidation and leaching under controlled conditions in laboratory.
- Collect samples covering a much wider variety of geographic locations, lithotypes and formations.
- Determine if core vs. cuttings geochemistry and metals content are the same in the same rock – NETL test well.
- Need better and more detailed analysis of NORM in cuttings with potential for leaching.
- Investigate potential for acid "mine" drainage from cuttings.
- Investigate possible oxidation reactions of organics in cuttings.
- Attempt to link weathering and leachability of metals to geologic/geochemical properties in order to improve predictability.
- Additional collaborators for follow-on: Tracy Bank (Univ. Buffalo), Cathy Enomoto and Liz Rowan (USGS), Brian Stewart and Rosemary Capo (Pitt), Shikha Sharma (WVU)



Special Topical Session T111 at 2011 GSA Annual Meeting:

Geology of Unconventional Fossil Energy Resources

Sponsored by GSA Sedimentary Geology Division
Tom Mroz and Dan Soeder, co-chairs

Seeking abstracts on:

Marcellus, Barnett, Bakken, Utica, Eagle Ford, International resources, plus many others...

Depending on response, this may be both an oral and poster session.

Call for Papers will be out in April-May edition of GSA Today

Abstracts deadline 26 July 2011