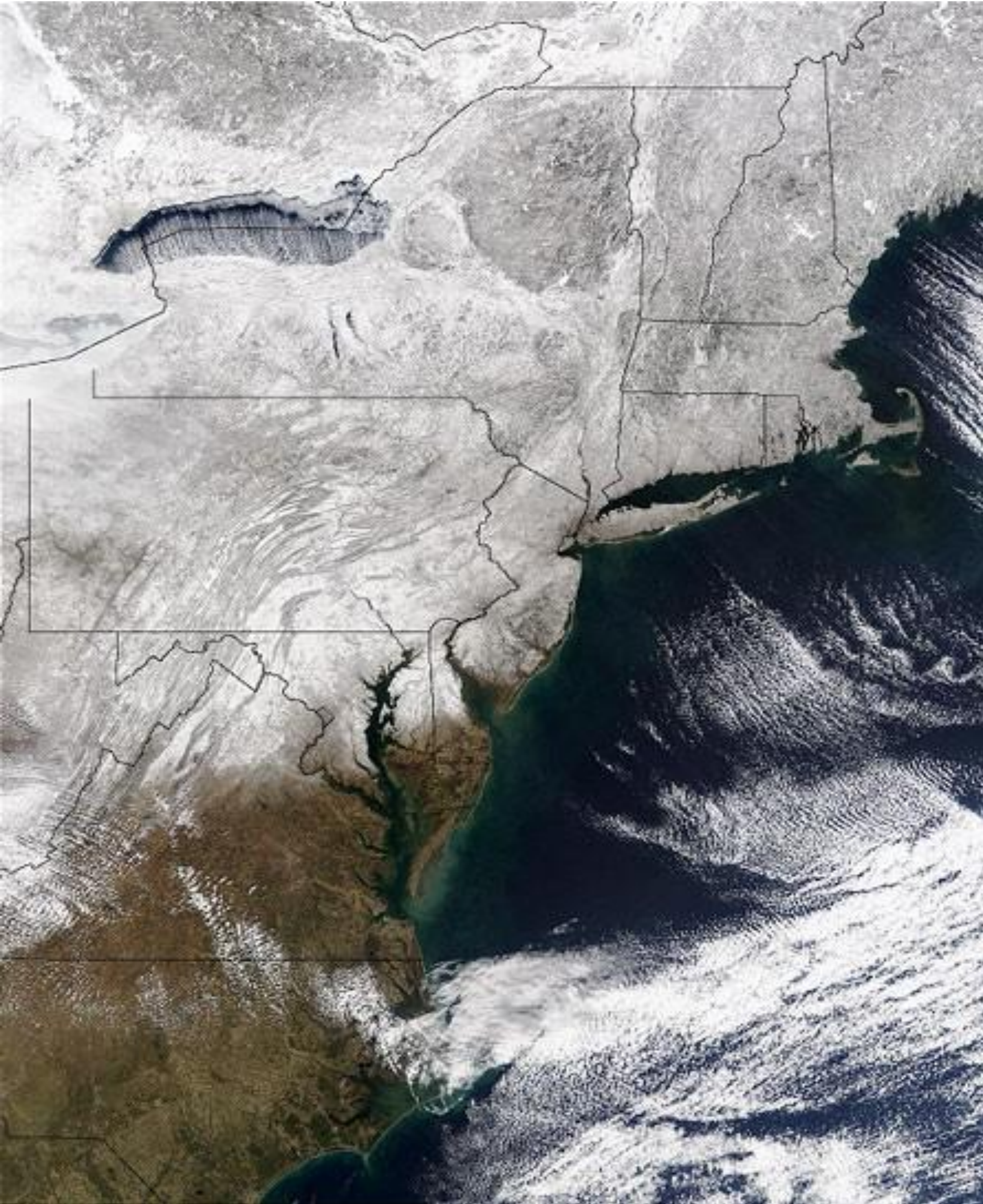

GEOCHEMISTRY AND SULFIDE MINERAL PARAGENESIS IN MARCELLUS SUBGROUP AND UTICA FORMATION GAS SHALE INTERVALS

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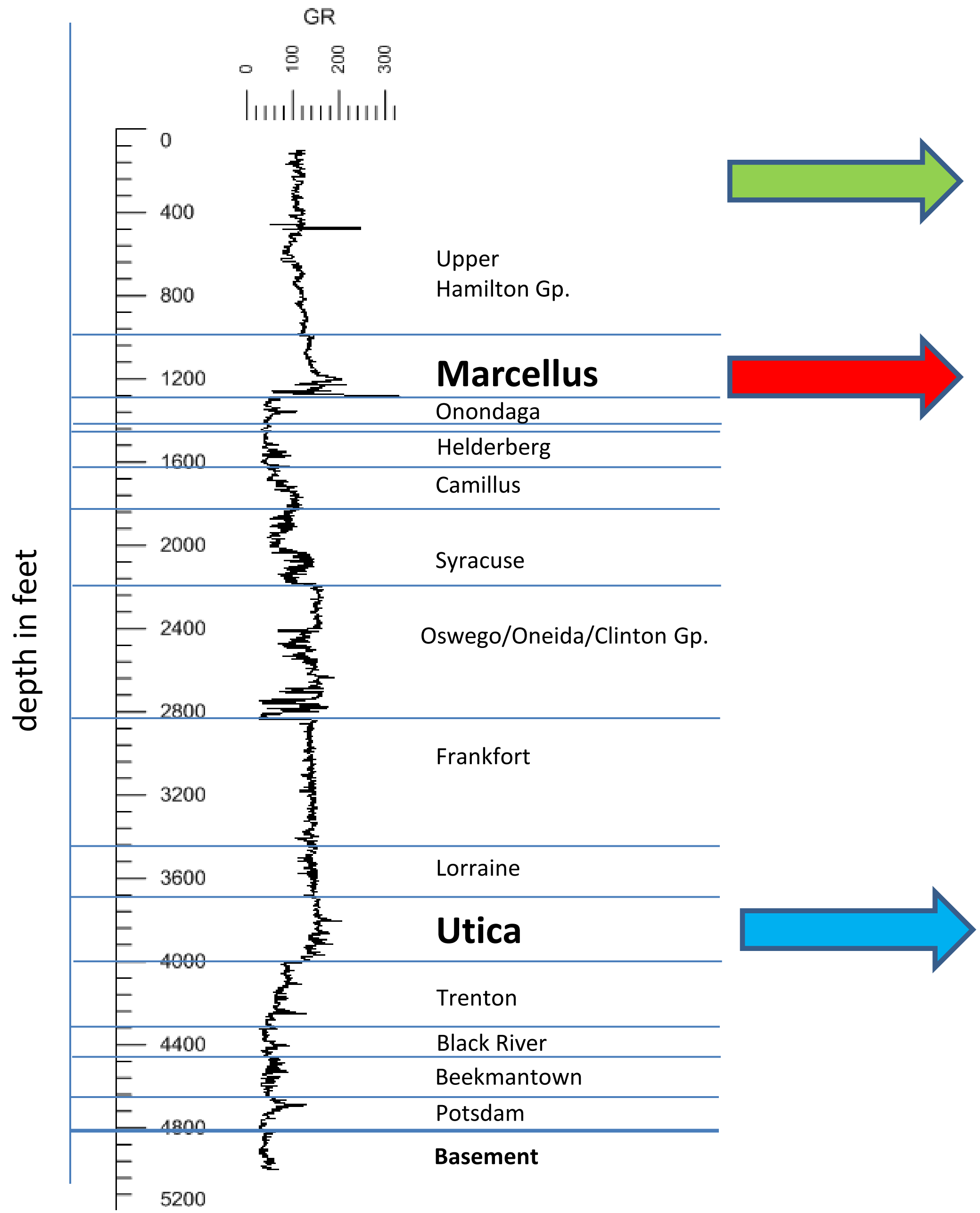
Jacky Baughman, Ali MacNamee,
Dave Linsely, Diane Keller, Brian Slater

Colgate UNIVERSITY

Marcellus Subgroup and Utica Formation

- Well cuttings - handling and disposal
- Potential sulfide/metal leachate
- Bulk mineralogy - XRD
- Major and trace element geochemistry - XRF
- Leachate studies – solute chemistry
- Sulfide mineral paragenesis – SEM/EDS

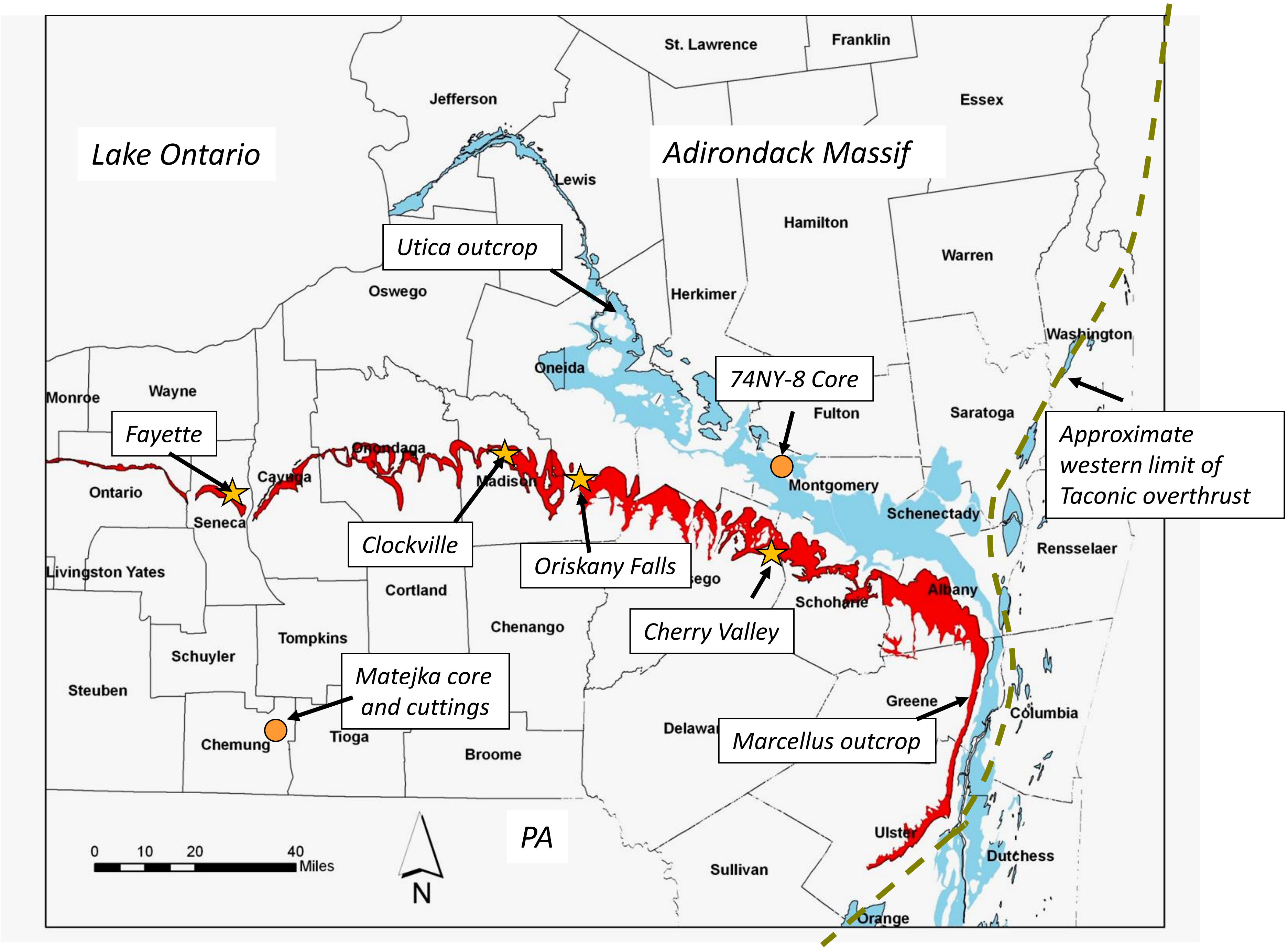
Larkin #1 Well – Madison County, NY



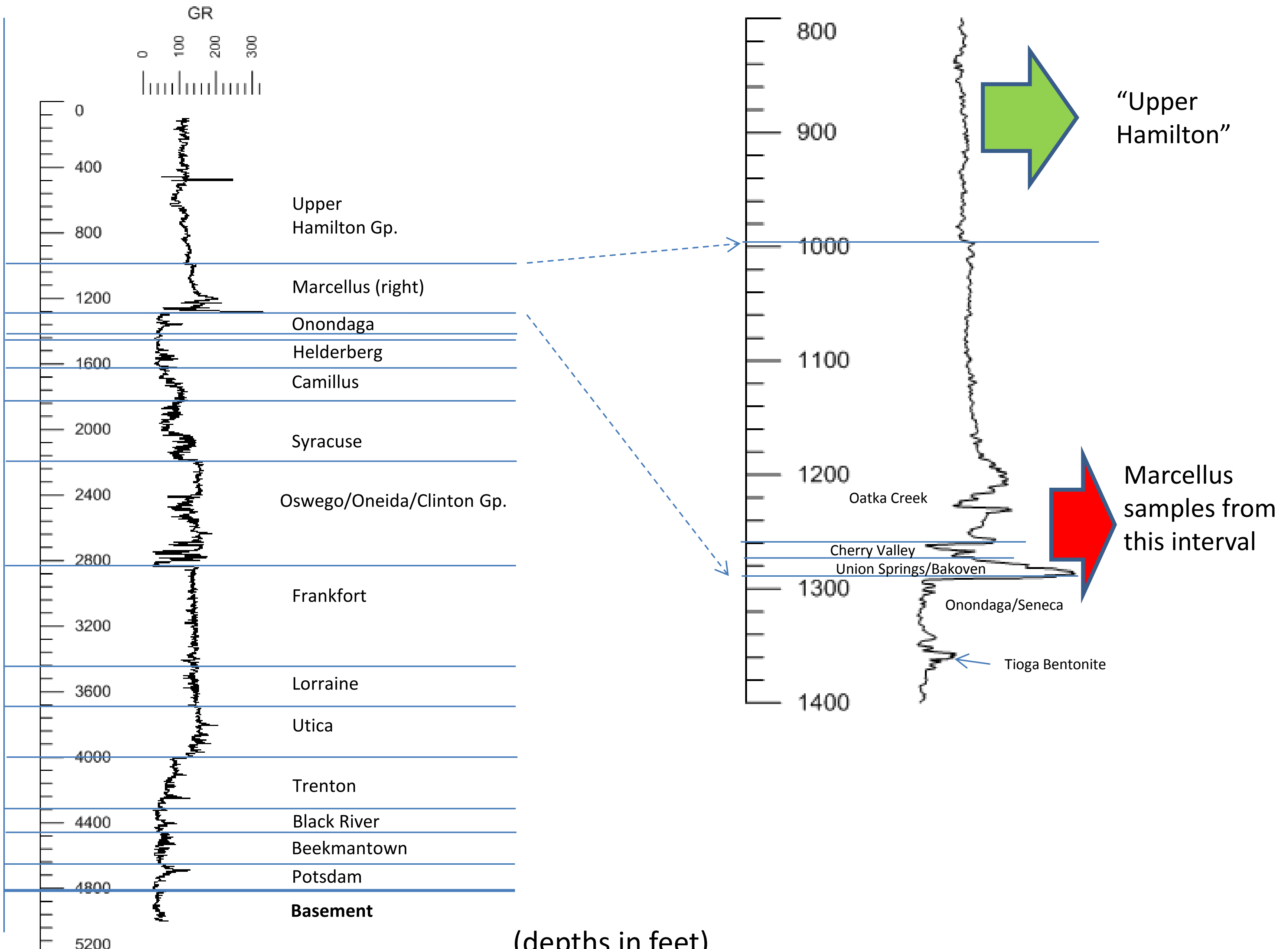
Upper Hamilton Group and overlying units – well cuttings and outcrop

Marcellus Subgroup – outcrop, quarry, well cuttings

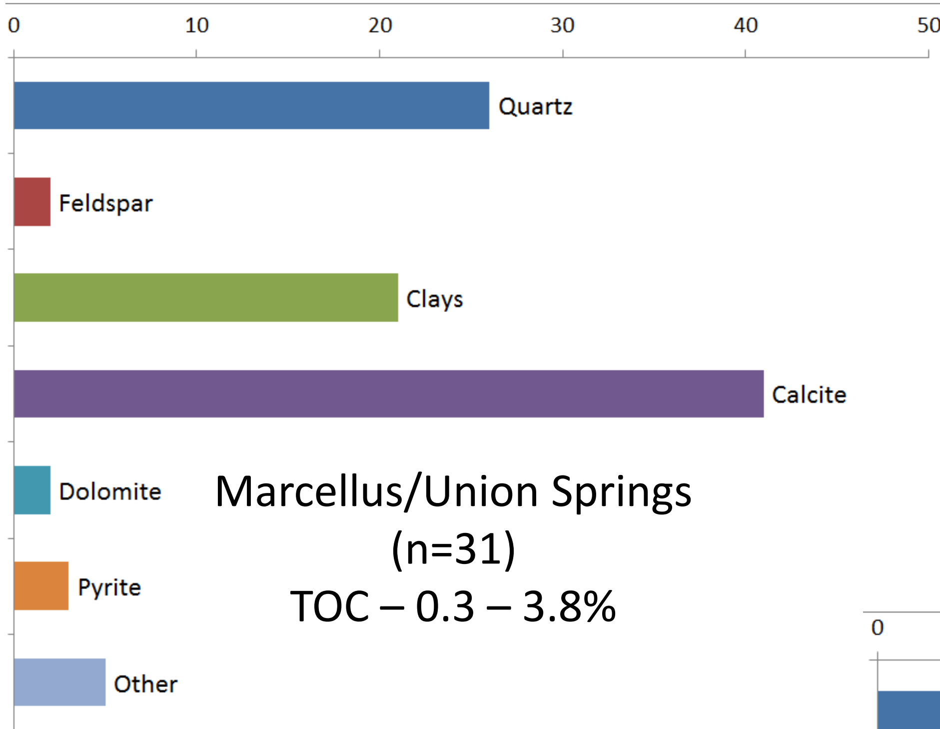
Utica Formation – outcrop, Mohawk Valley core (NYS Museum)


Lake Ontario
Adirondack Massif
St. Lawrence
Franklin
Jefferson
Essex
Lewis
Hamilton
Warren
Utica outcrop
Oswego
Herkimer
Washington
Oneida
74NY-8 Core
Fulton
Saratoga
Monroe
Wayne
Fayette
Onondaga
Cayuga
Madison
Montgomery
Approximate western limit of Taconic overthrust
Ontario
Seneca
Schenectady
Clockville
Oriskany Falls
Rensselaer
Livingston Yates
Cortland
Schoharie
Albany
Cherry Valley
Chenango
Tompkins
Schuyler
Steuben
Matejka core and cuttings
Greene
Columbia
Chemung
Tioga
Broome
Marcellus outcrop
Ulster
PA
Dutchess
Sullivan
Orange
0 10 20 40 Miles
N

Larkin #1 Well – Madison County, NY



(depths in feet)

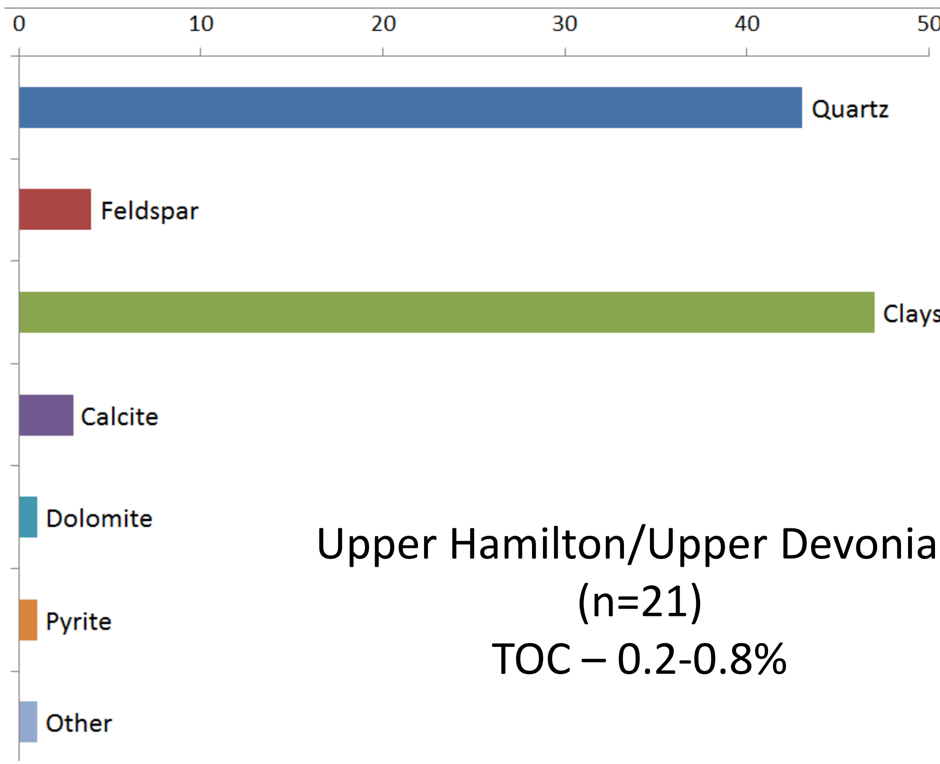


Marcellus/Union Springs
(n=31)
TOC – 0.3 – 3.8%

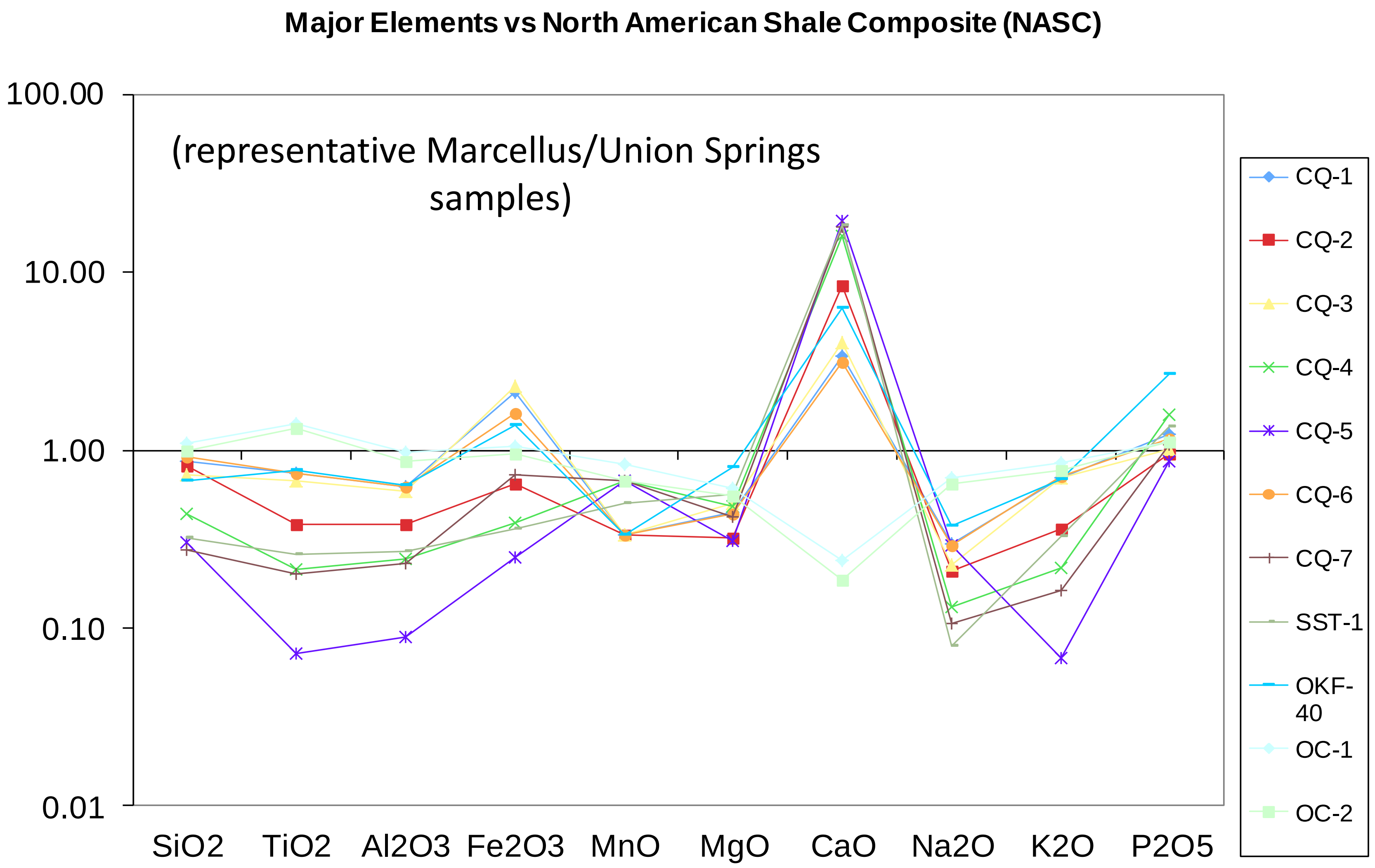
	Marcellus/ Union Springs	Upper Hamilton/ Upper Devonian
Quartz	26	43
Feldspar	2	4
Clays	21	47
Calcite	41	3
Dolomite	2	1
Pyrite	3	1
Other	5	1

Quantitative XRD - modal mineralogy (%)

- RockJock (USGS) data reduction
- Lower Marcellus – calcite-rich
- Lower Marcellus – pyrite-rich

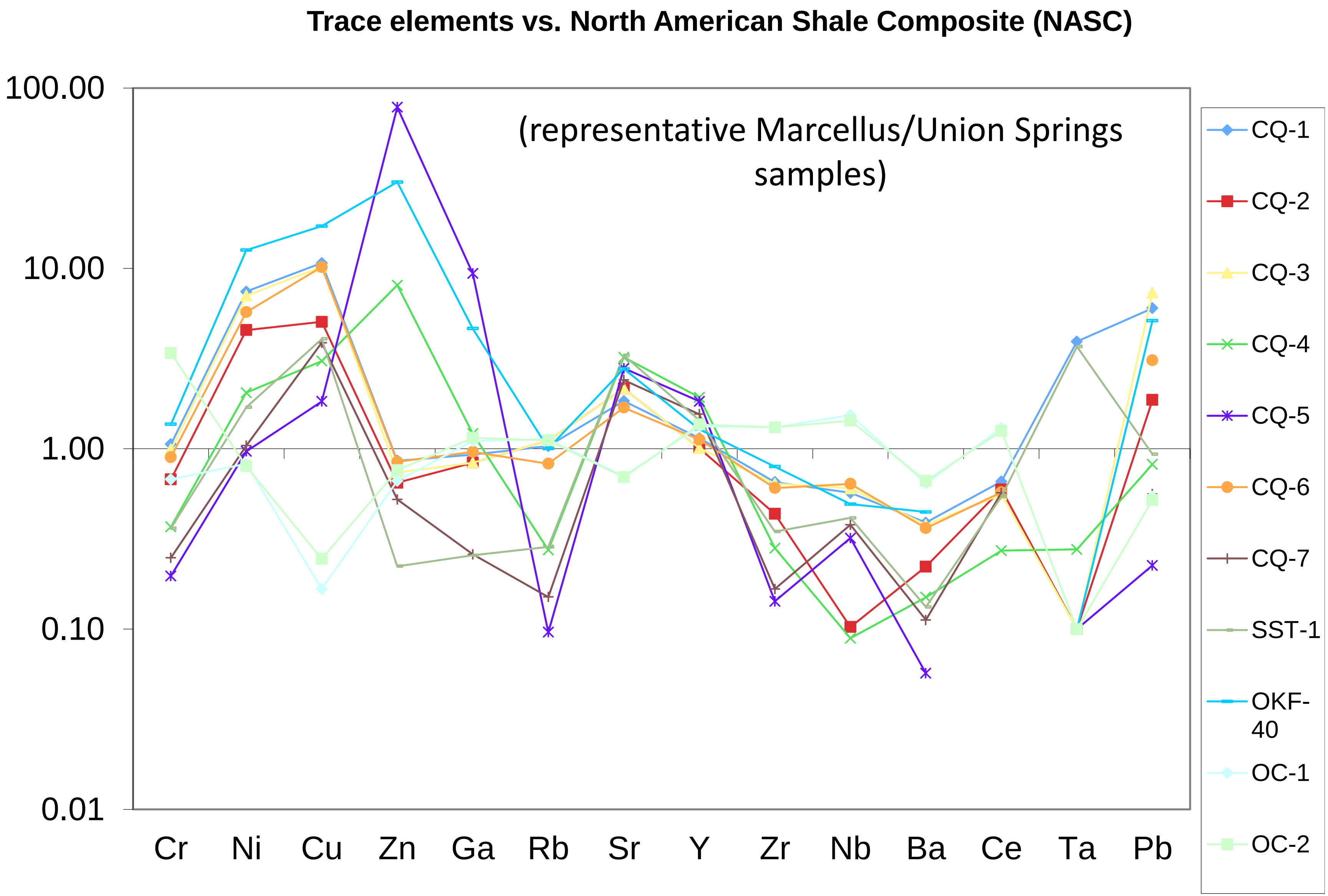


Upper Hamilton/Upper Devonian
(n=21)
TOC – 0.2-0.8%



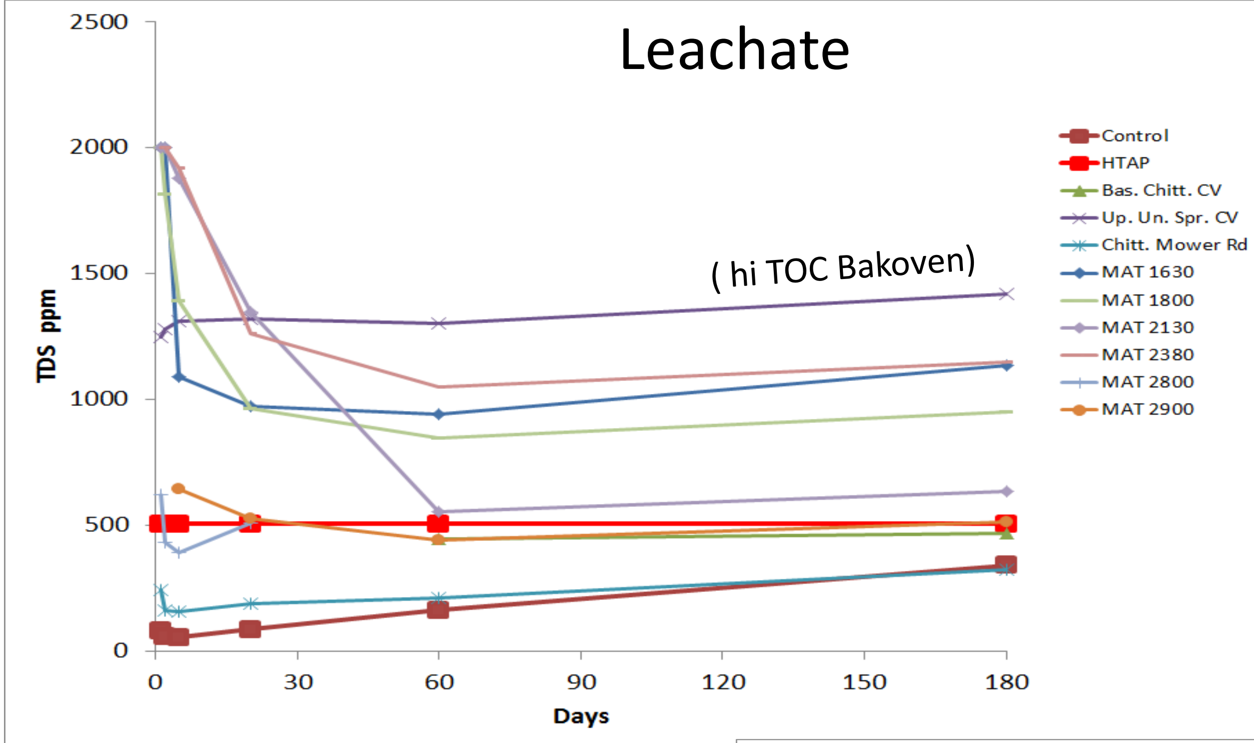
Relative to NASC

- Marcellus/Union Springs is Ca – rich (calcite)
- Slightly enriched in Fe, P



Relative to NASC

- Marcellus/Union Springs is enriched in Ni, Cu, Zn, Sr (calcite)
- Slightly enriched in Pb



Leachate from artificial soil systems:

Rainwater added to grass-soil-crushed rock system

Leachate sampled as shown

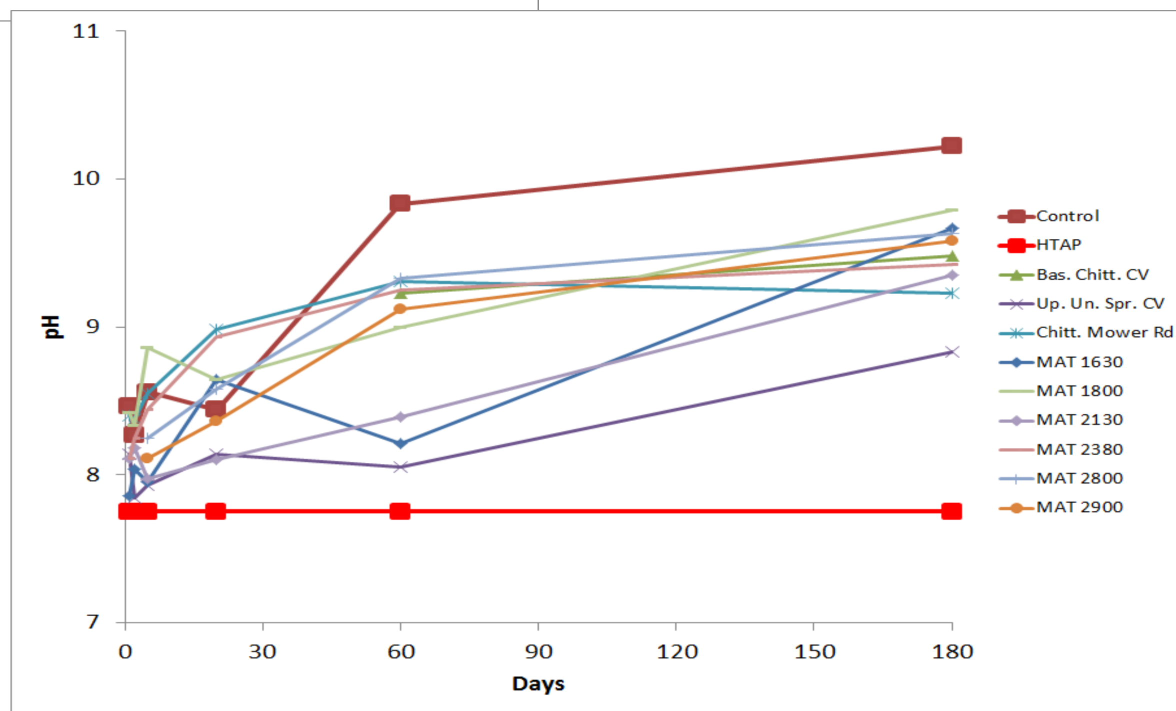
Control = granitic aquarium gravel + fiberglass mesh

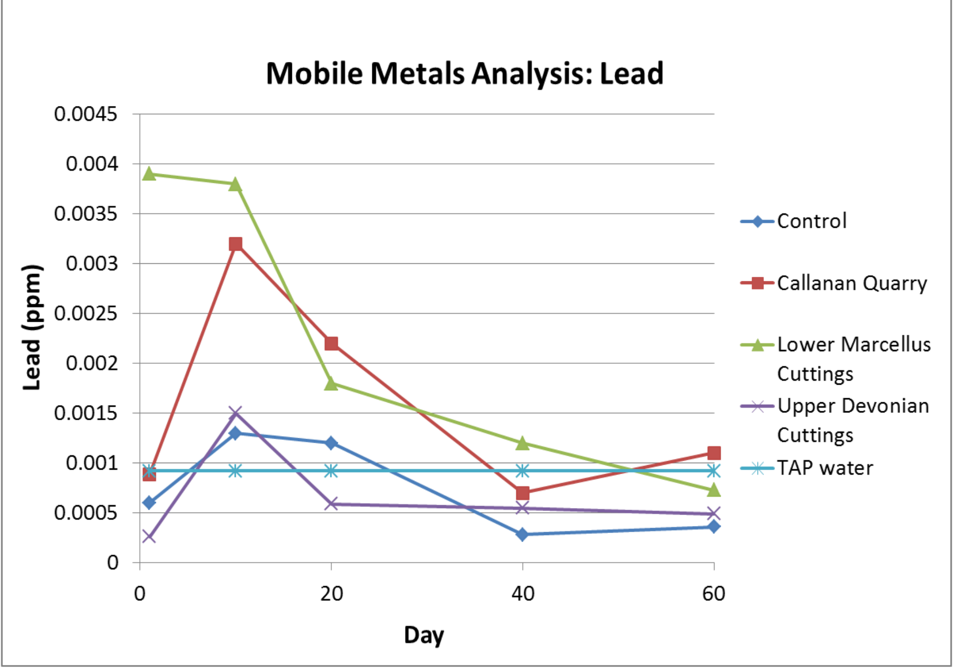
HTAP = Hamilton, NY municipal tapwater

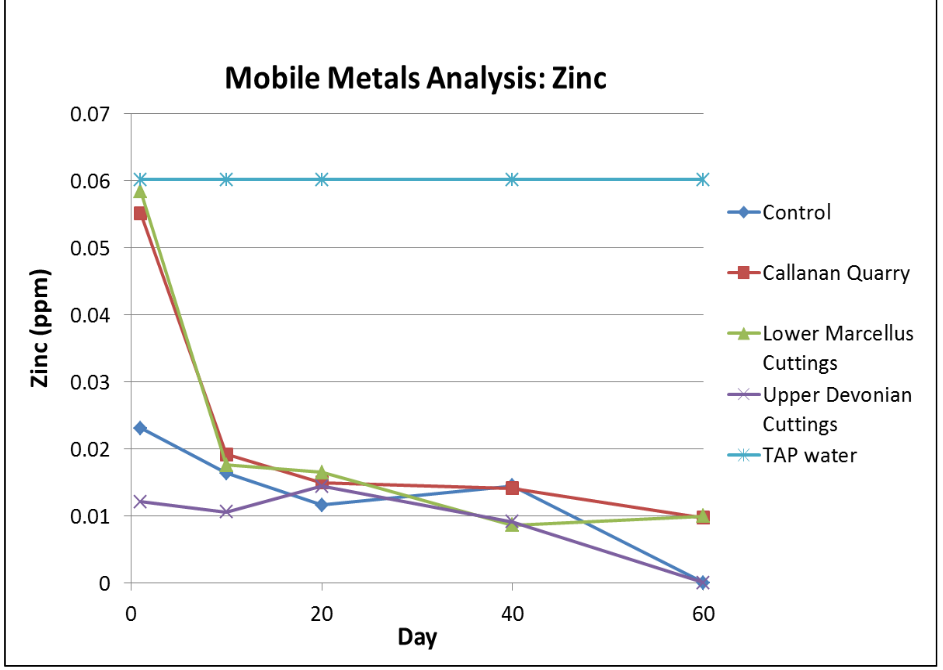
Marcellus/Union Springs, Upper Hamilton Group well cuttings leachate

- TDS ~1000 ppm after 180 days
- pH ~ 9 after 180 days
- carbonate mineral-buffered

(from Bickhart, et al 2012)

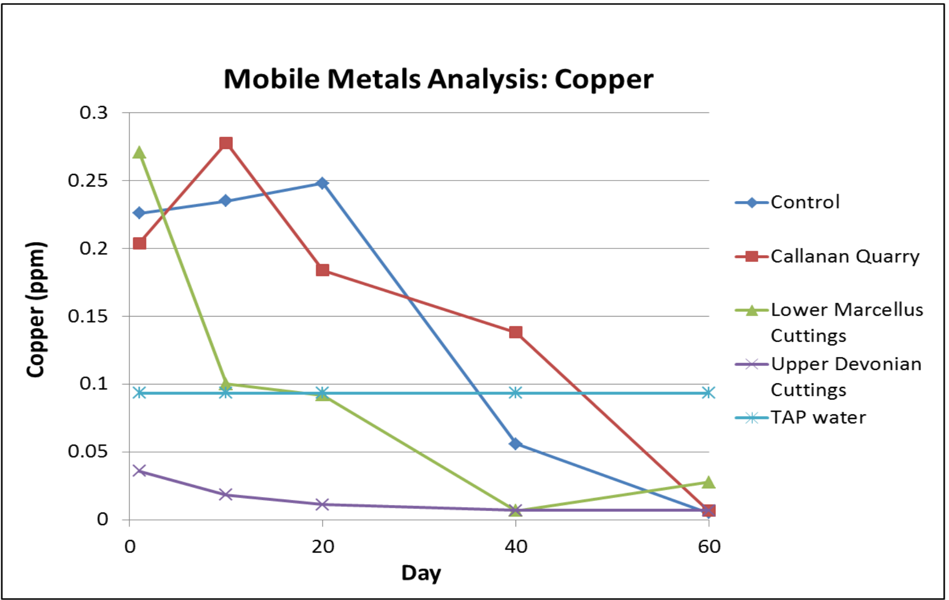


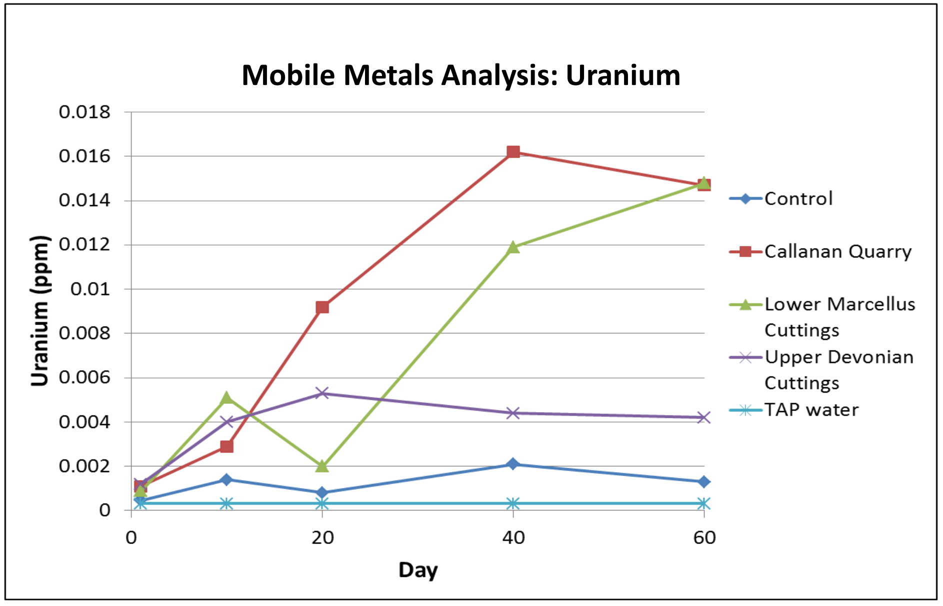




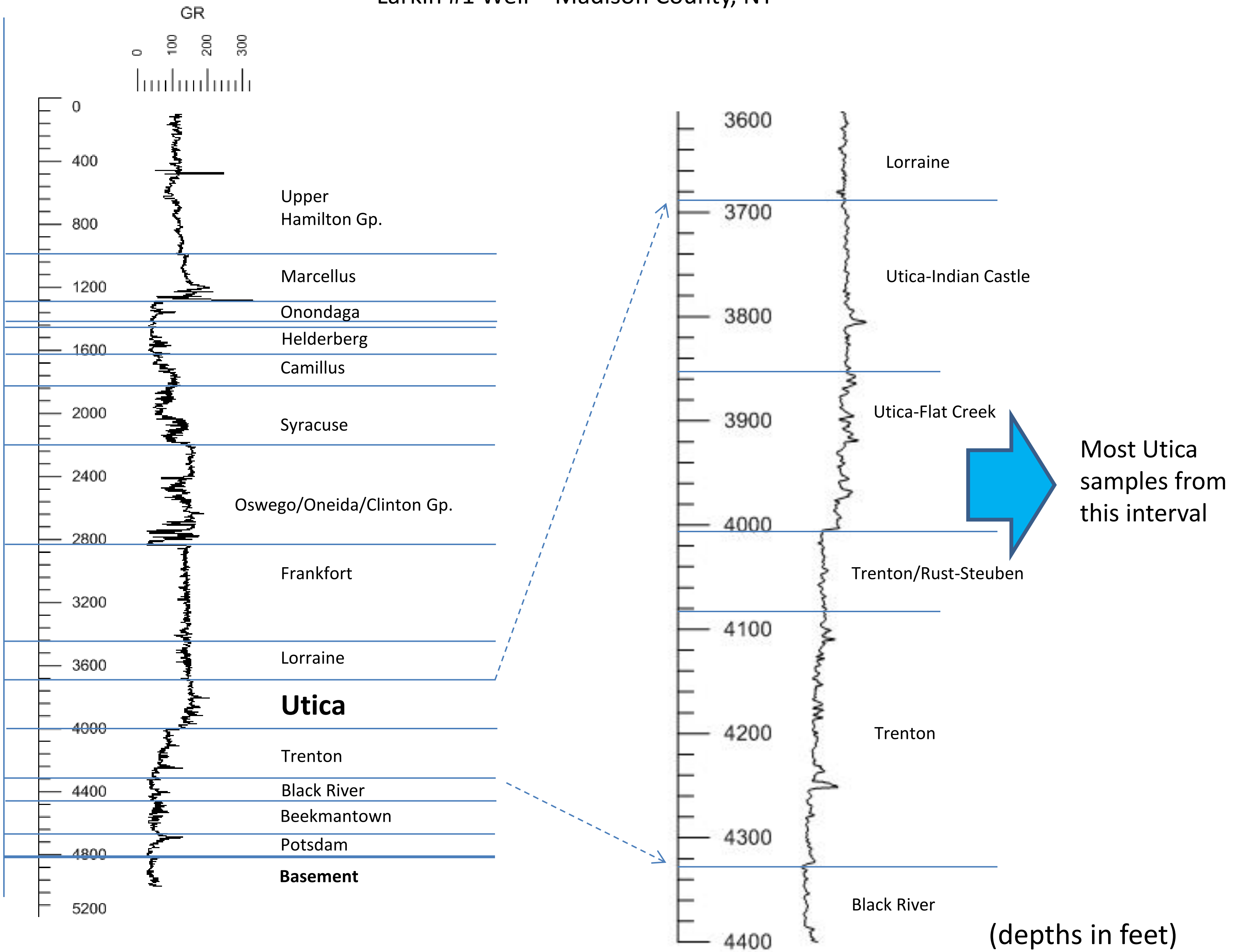
- Pb, Zn and Cu in leachate decrease (buffering of pH?) with time
- U in leachate increases (solubility of U minerals in + Eh setting?)
- (Metals analysis by Test America)

(from Bickhart, et al 2012)

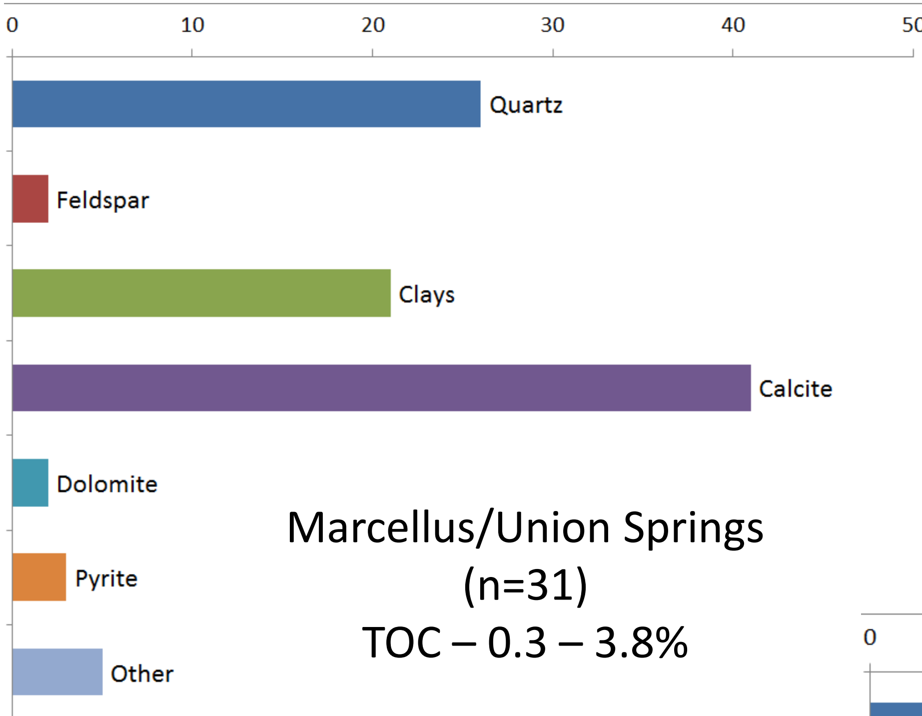




Larkin #1 Well – Madison County, NY



Selleck/Colgate – 8/2012

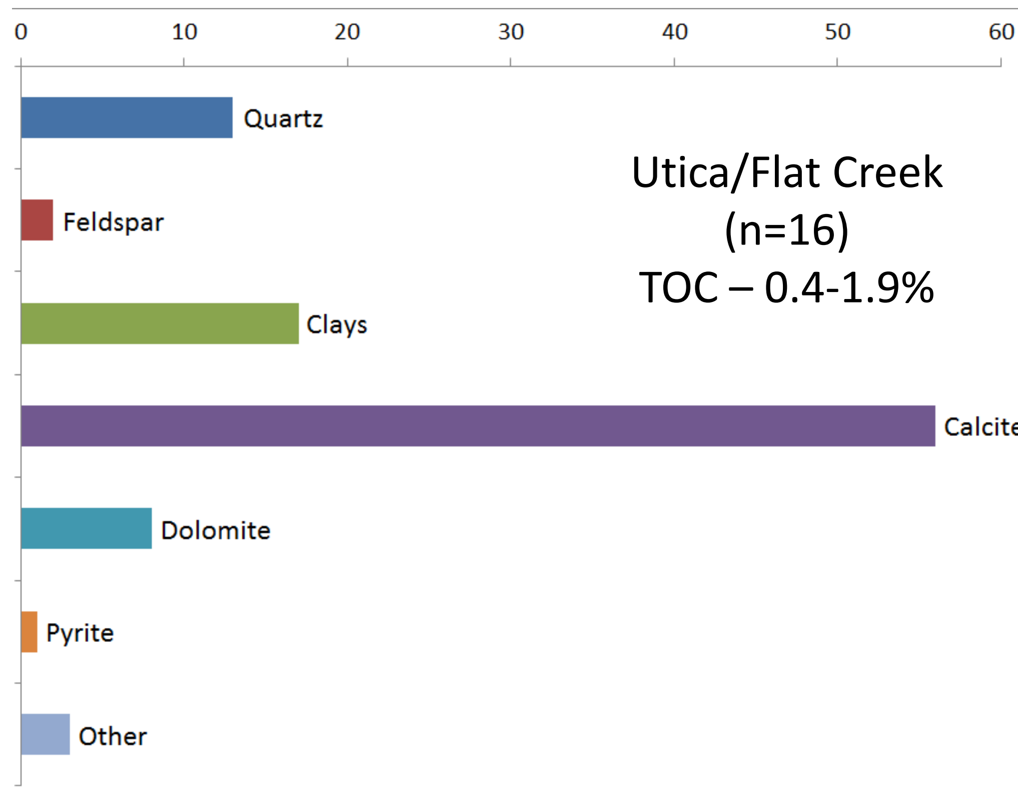


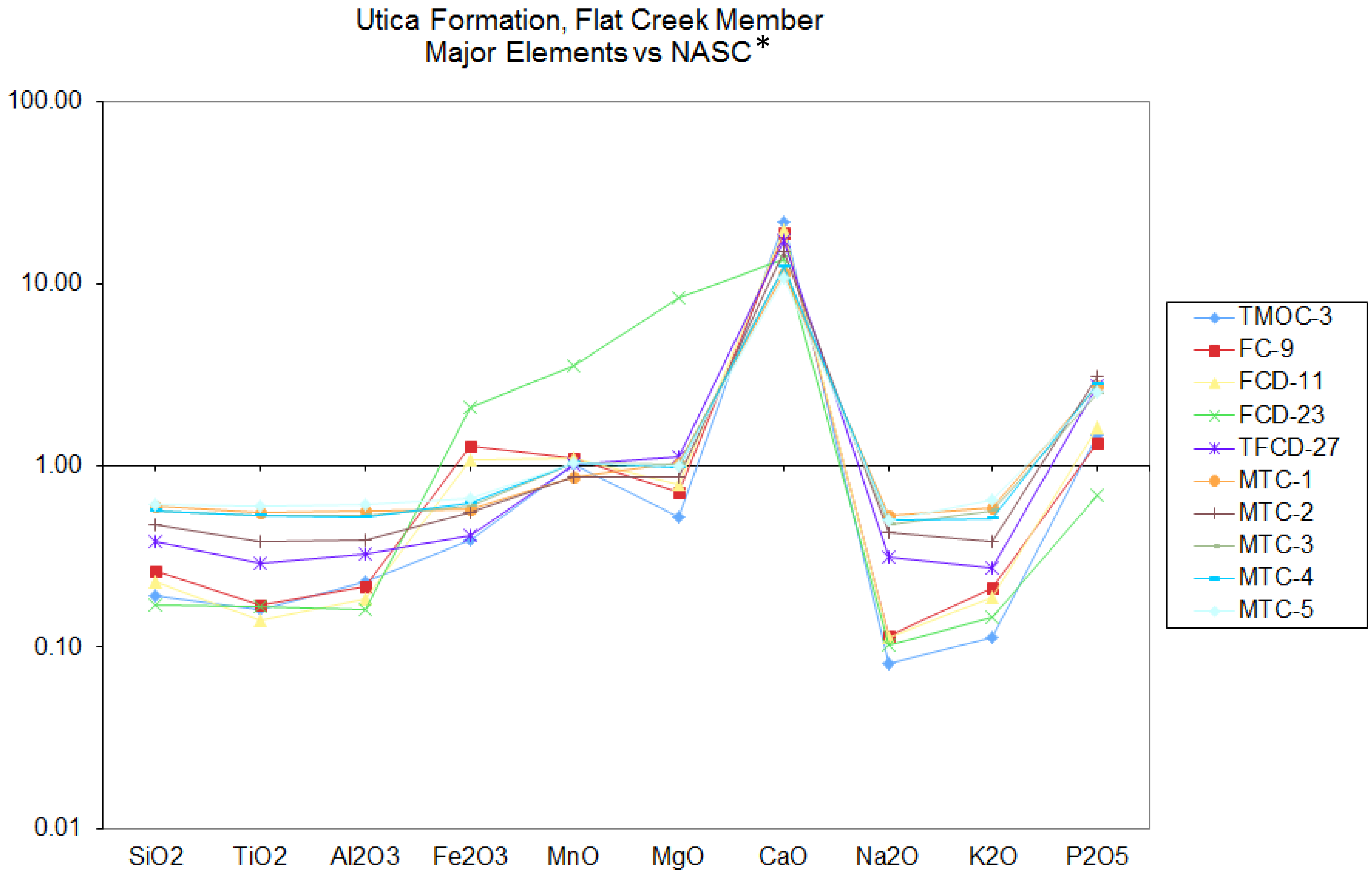
	Marcellus/ Union Springs	Utica/Flat Creek
Quartz	26	13
Feldspar	2	2
Clays	21	17
Calcite	41	56
Dolomite	2	8
Pyrite	3	1
Other	5	3

Quantitative XRD - modal mineralogy (%)

Utica/Flat Creek

- calcite-rich
- relatively lower % pyrite

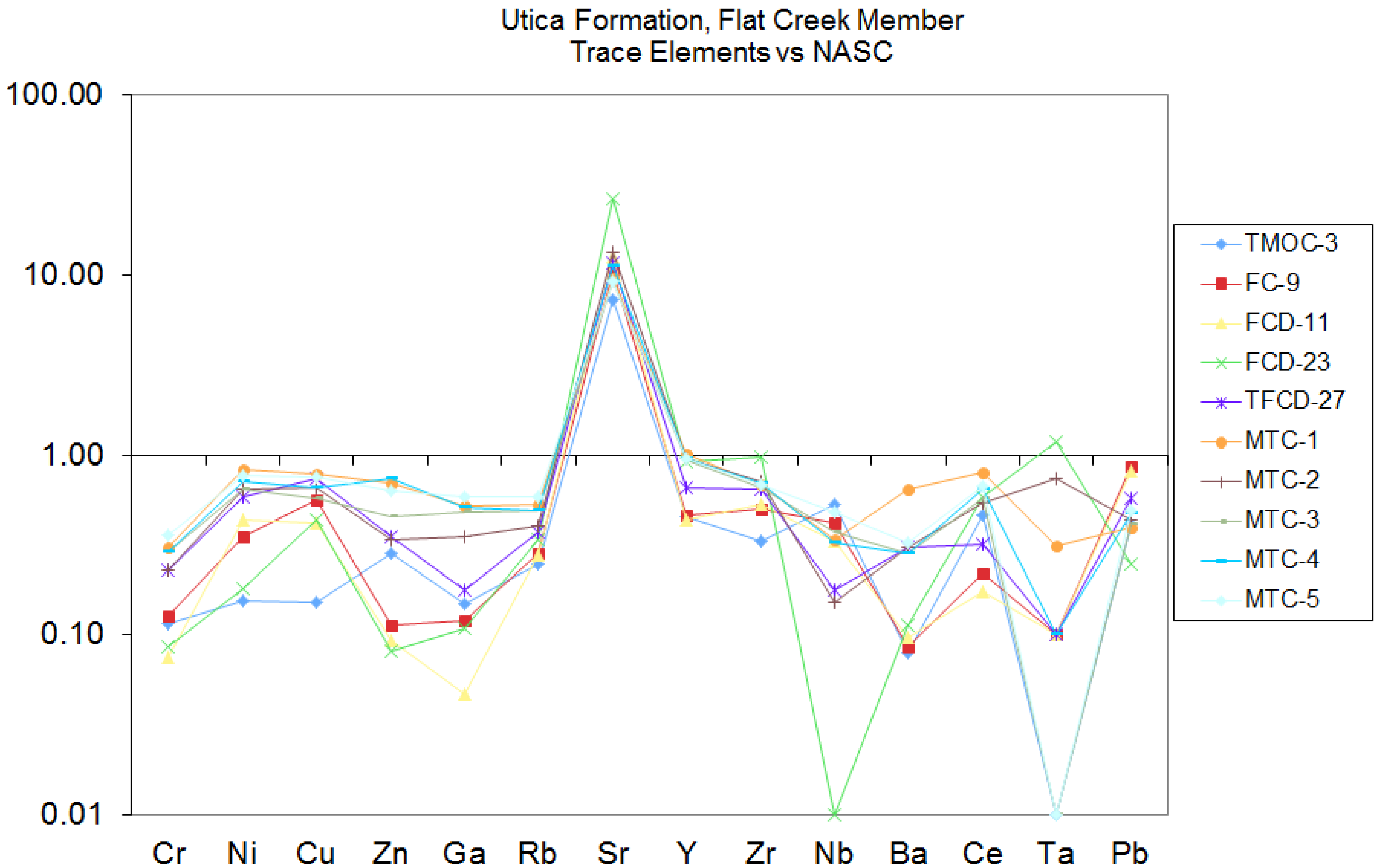




Relative to NASC* Utica/Flat Creek :

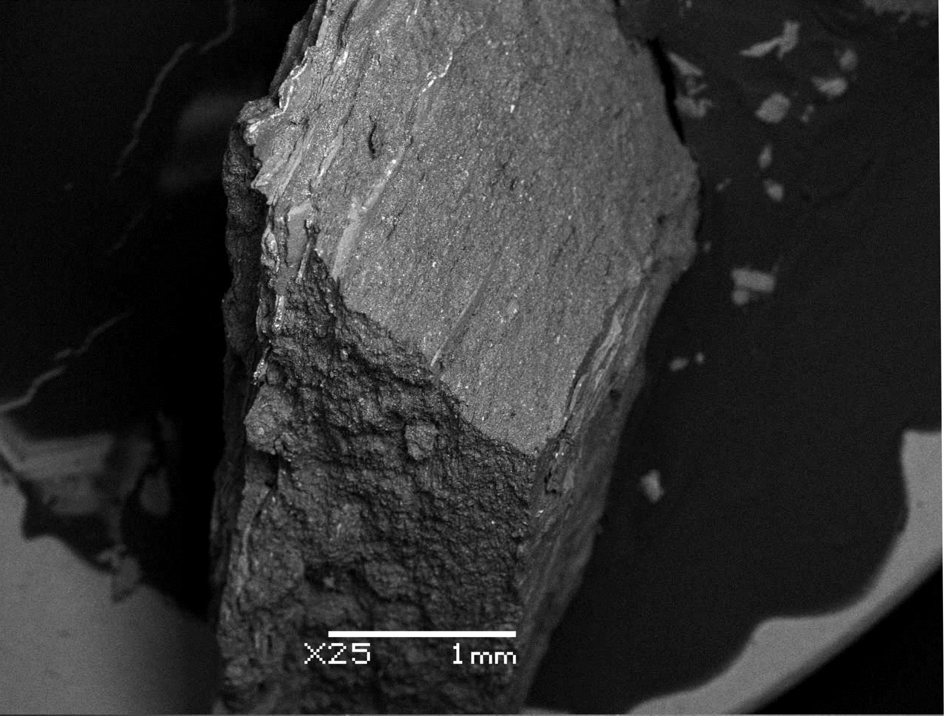
- is Ca-enriched (carbonates)
- slightly Fe, P –enriched (like Marcellus/Union Springs)

*North American Shale Composite



Relative to NASC, Utica/Flat Creek:

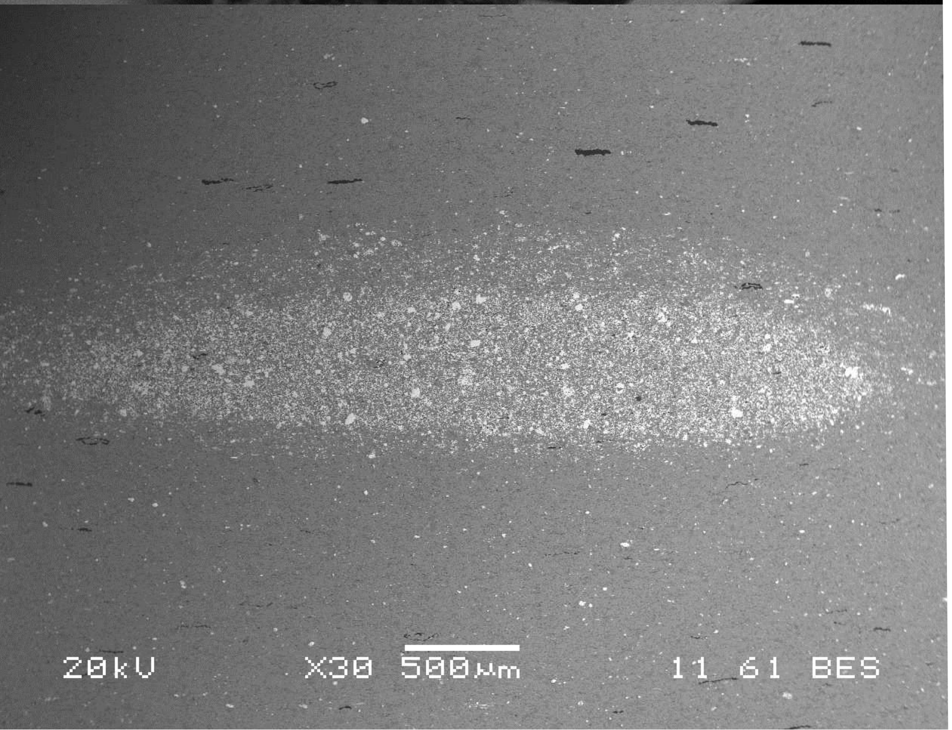
- Sr-enriched (calcite)
- not enriched in Ni, Cu, Zn, Pb (unlike the Marcellus/Union Springs)

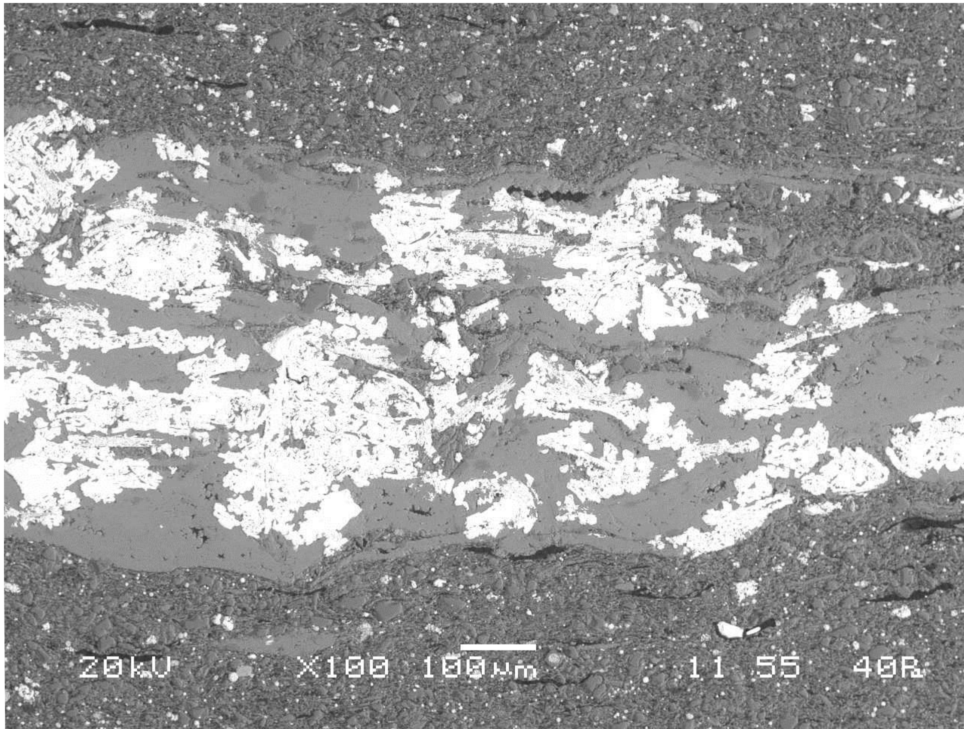


Sulfide mineral paragenesis
Marcellus/Union Springs

Early framboidal pyrite
Coarsely crystalline 'later' pyrite
Both reworked as clastic particles
Coarse pyrite replacement of carbonate bioclasts; concretionary segregations

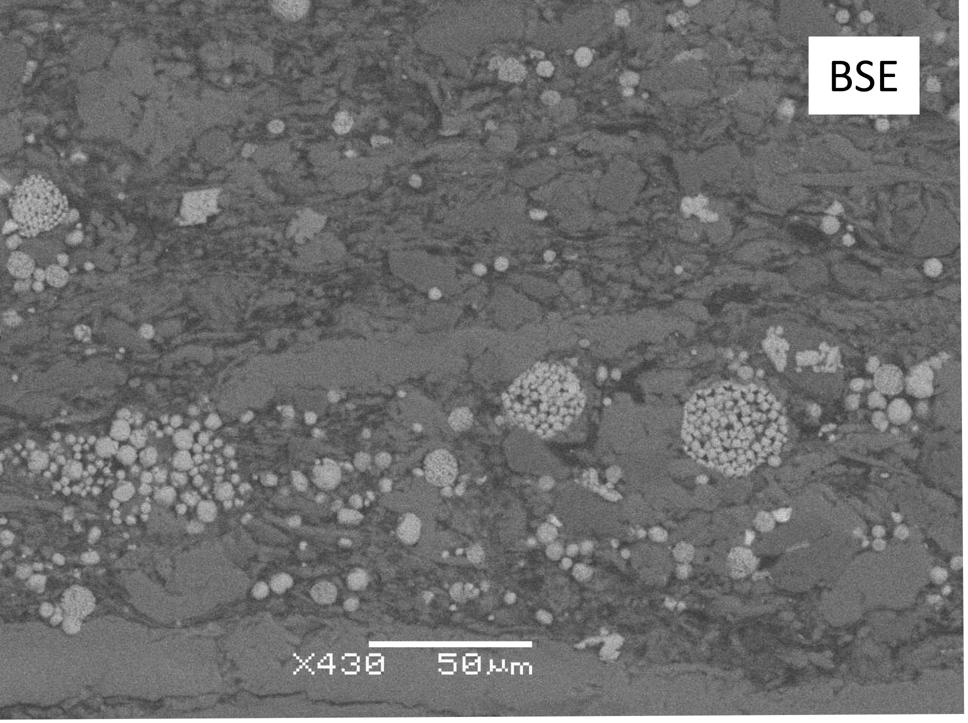
Other sulfides – sphalerite (common); chalcopyrite (present), galena (rare)

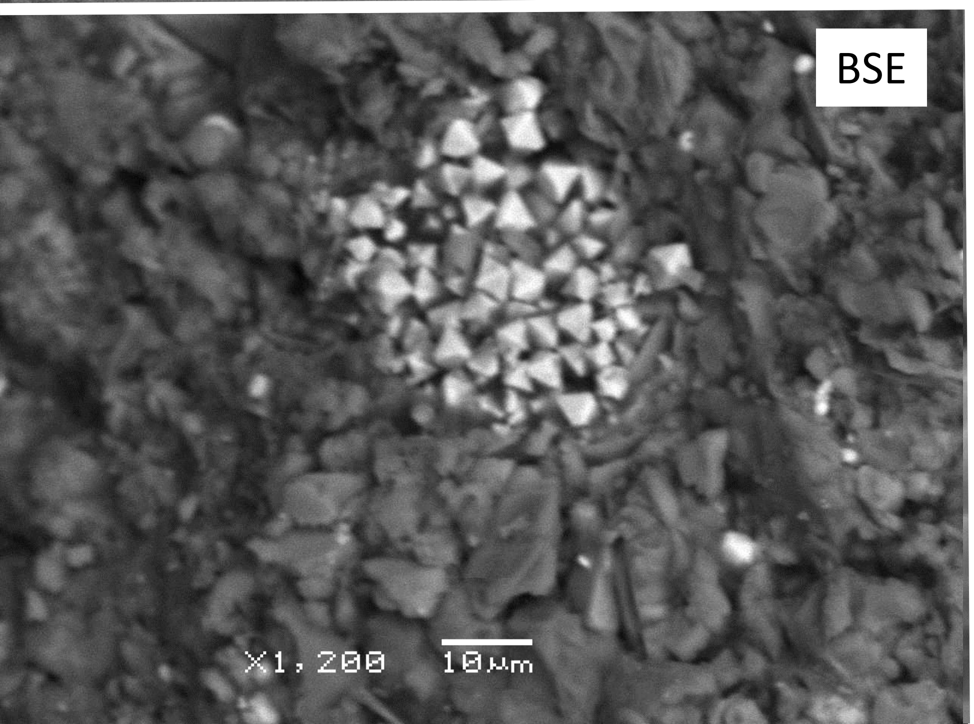


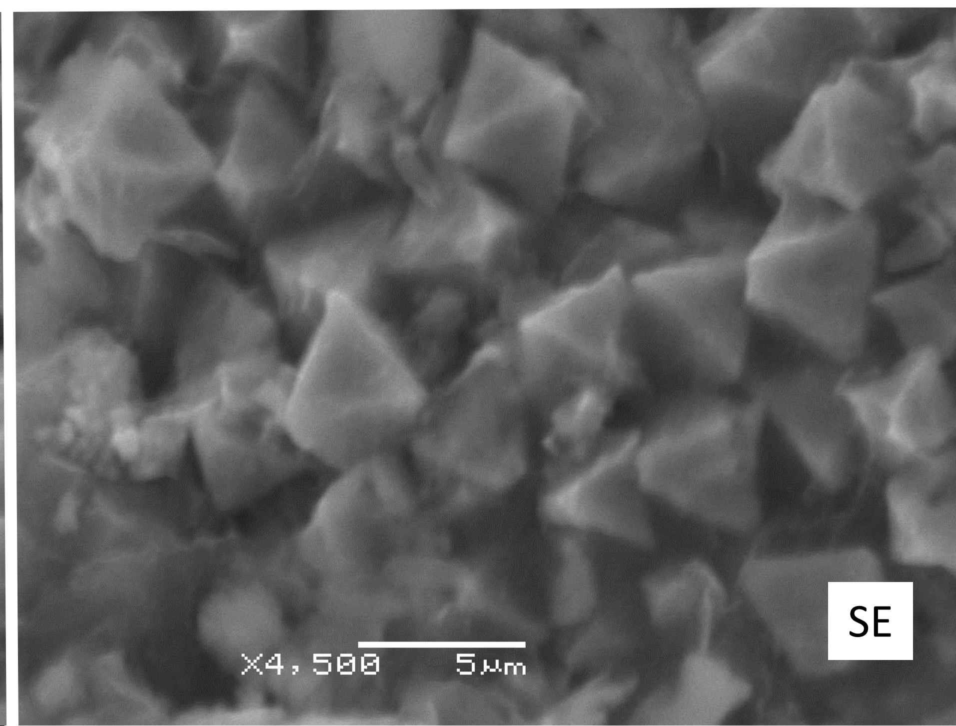


Marcellus/Union Springs

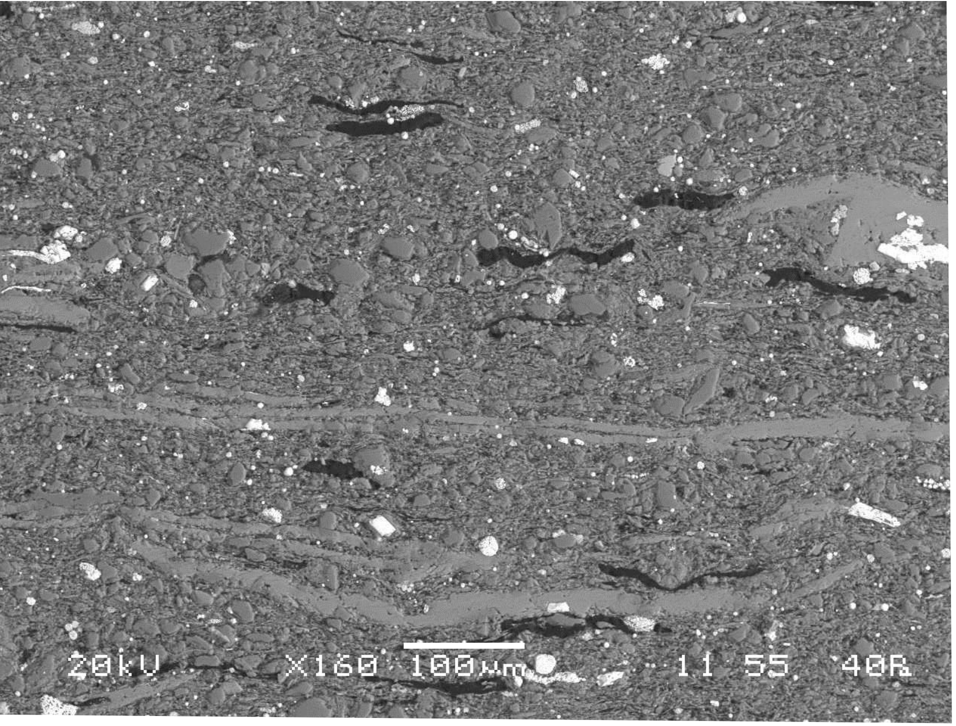
Pyrite framboids preserve porosity







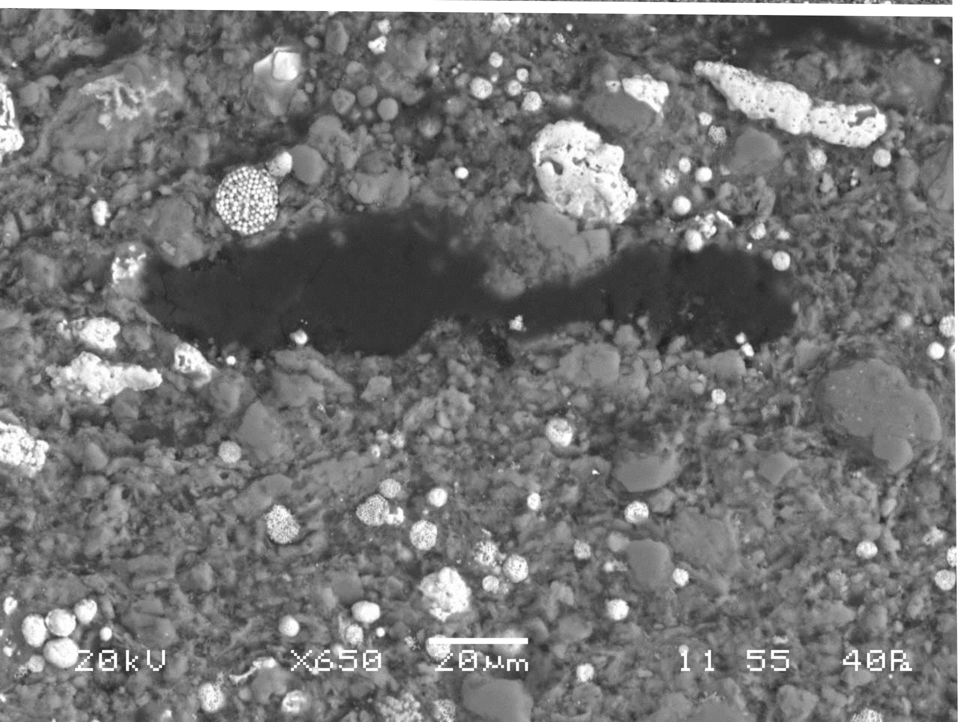
Marcellus/Union Springs

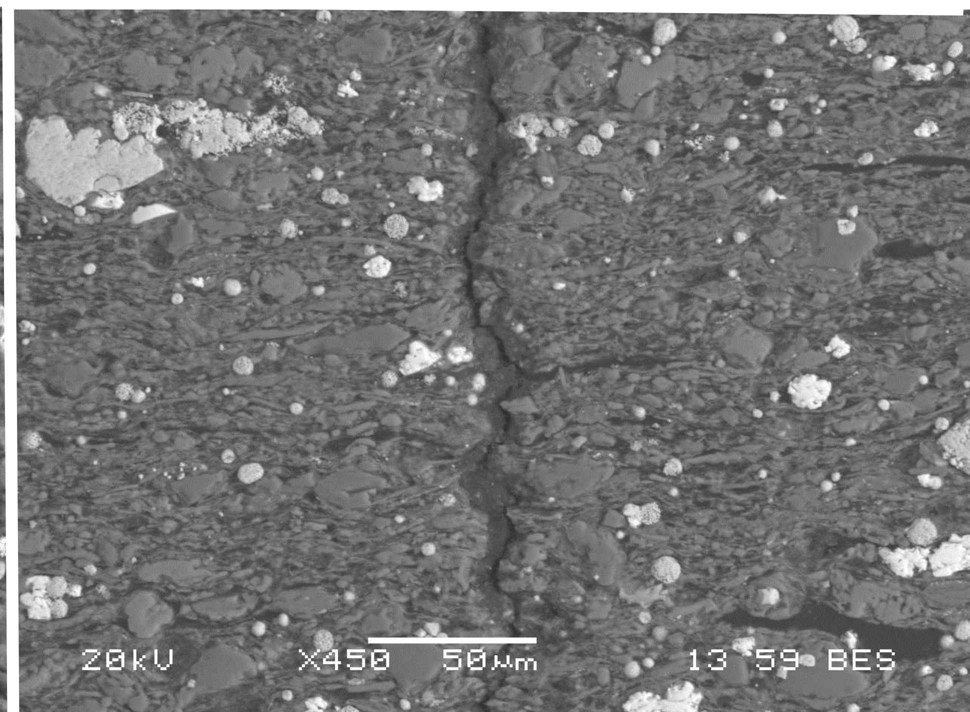


Left: flattened algal cysts and bioclasts

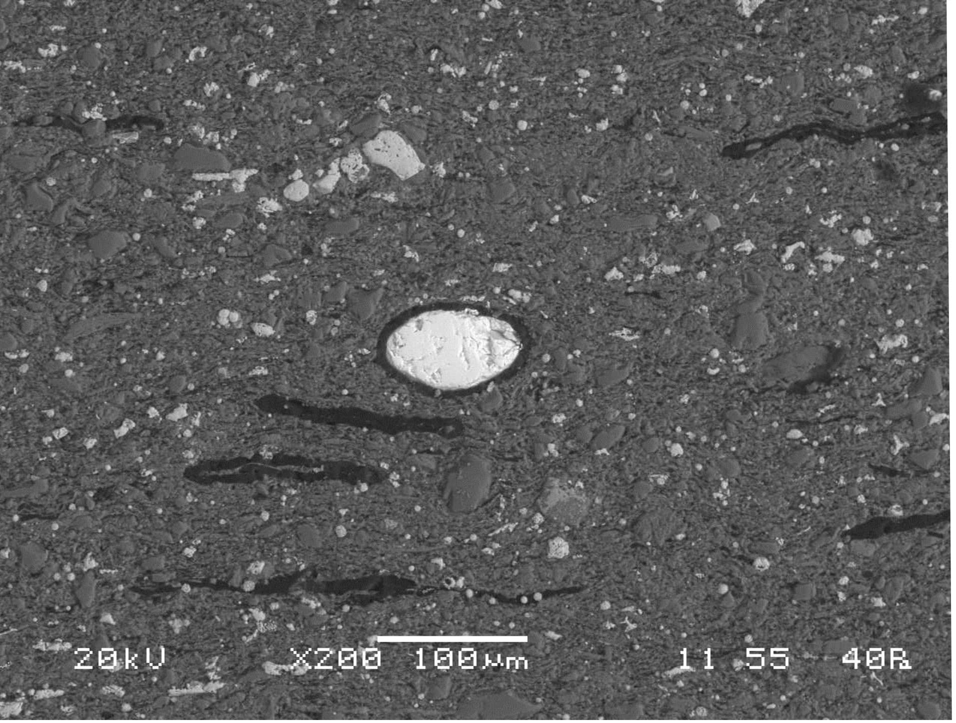
Below left: Bitumen (algal cyst?)
with reworked sulfide particles

Below: Vertical bitumen (dead oil) vein
marking petroleum pathway in pyrite- and
organic-rich carbonate mudstone.



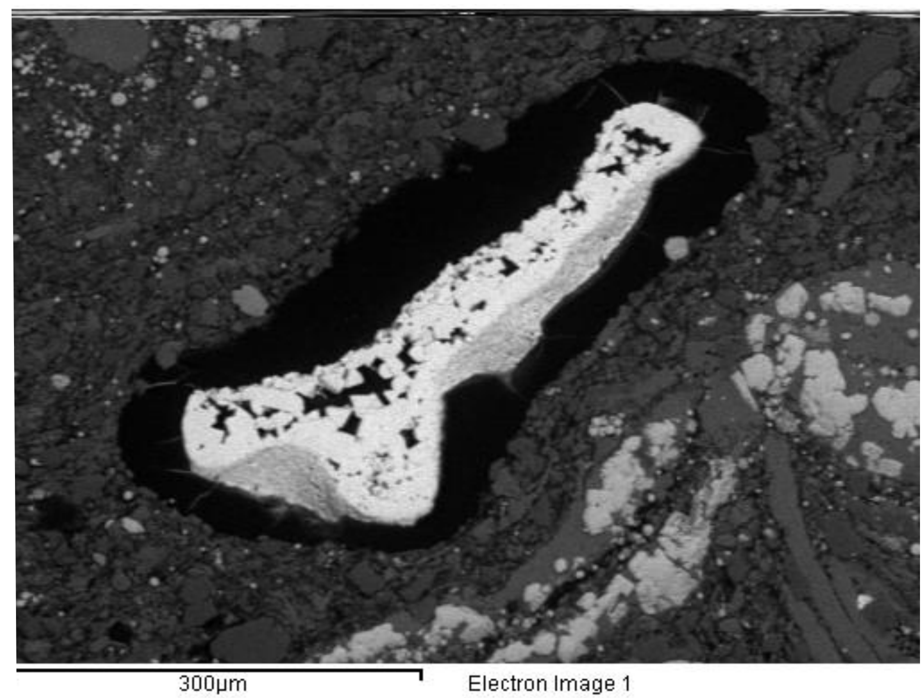


Marcellus/Union Springs



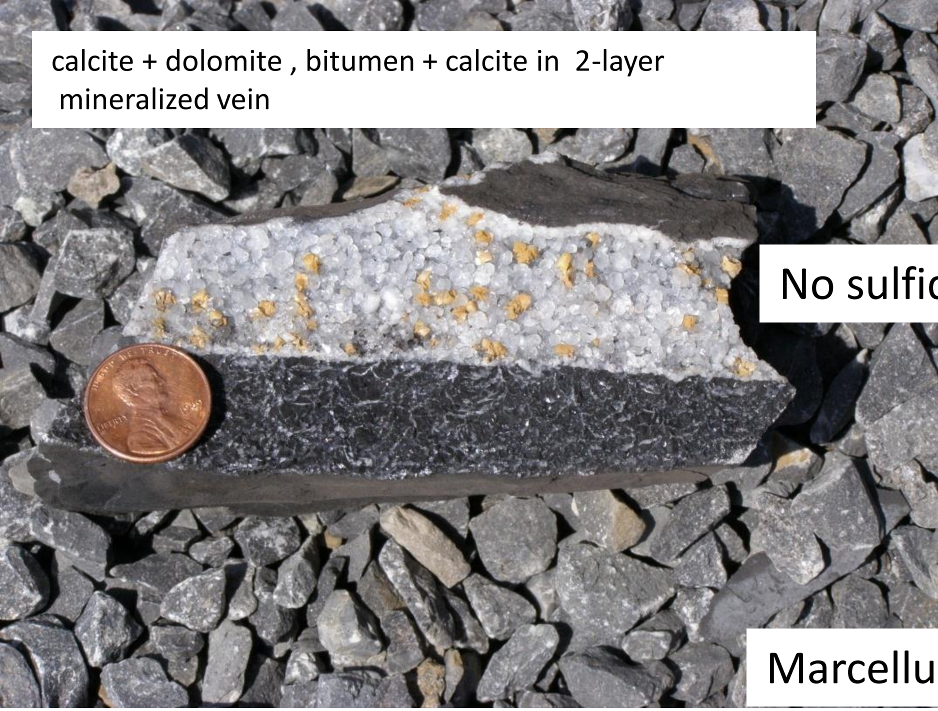
Left and below left:
sphalerite filling algal cysts

Below: Pyrite and sphalerite, plus
'anthraxolite' line bitumen (dead oil)
'tube'

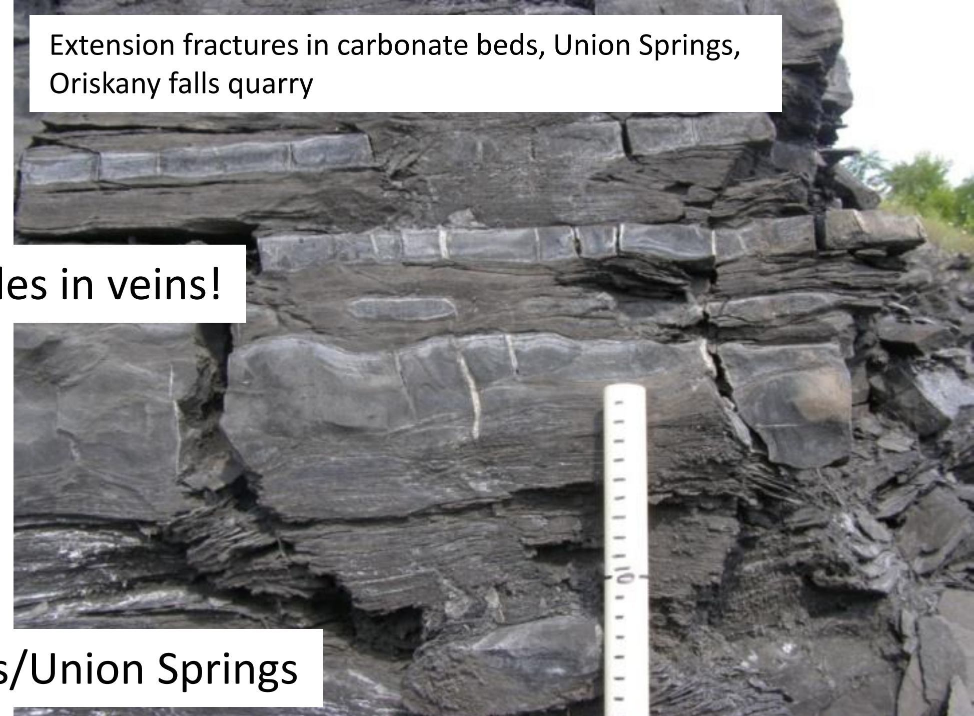


Marcellus/Union Springs

No sulfides in veins!



calcite + dolomite , bitumen + calcite in 2-layer mineralized vein



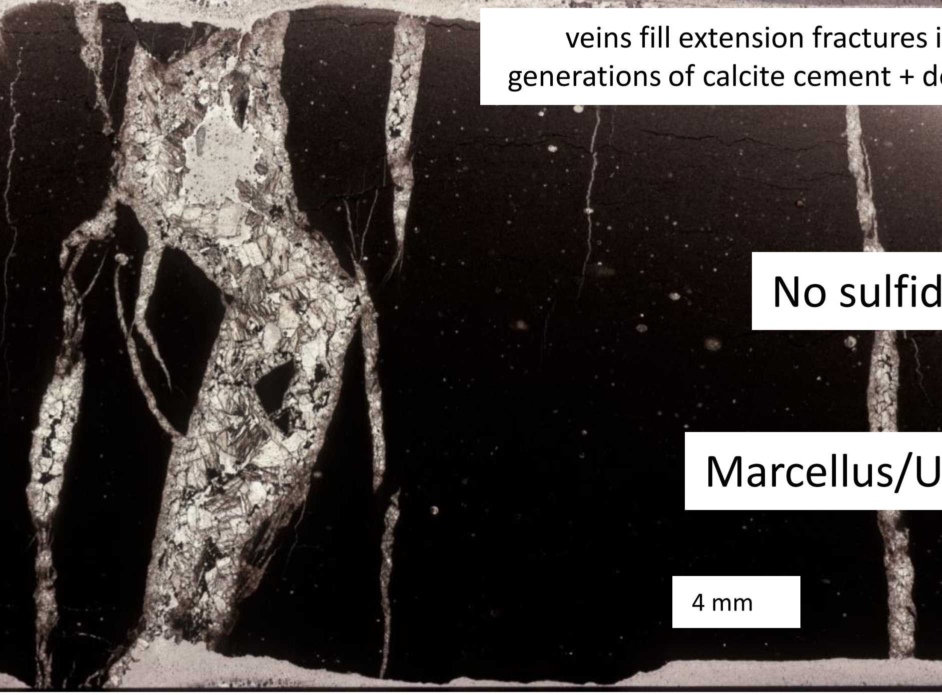
Extension fractures in carbonate beds, Union Springs, Oriskany falls quarry

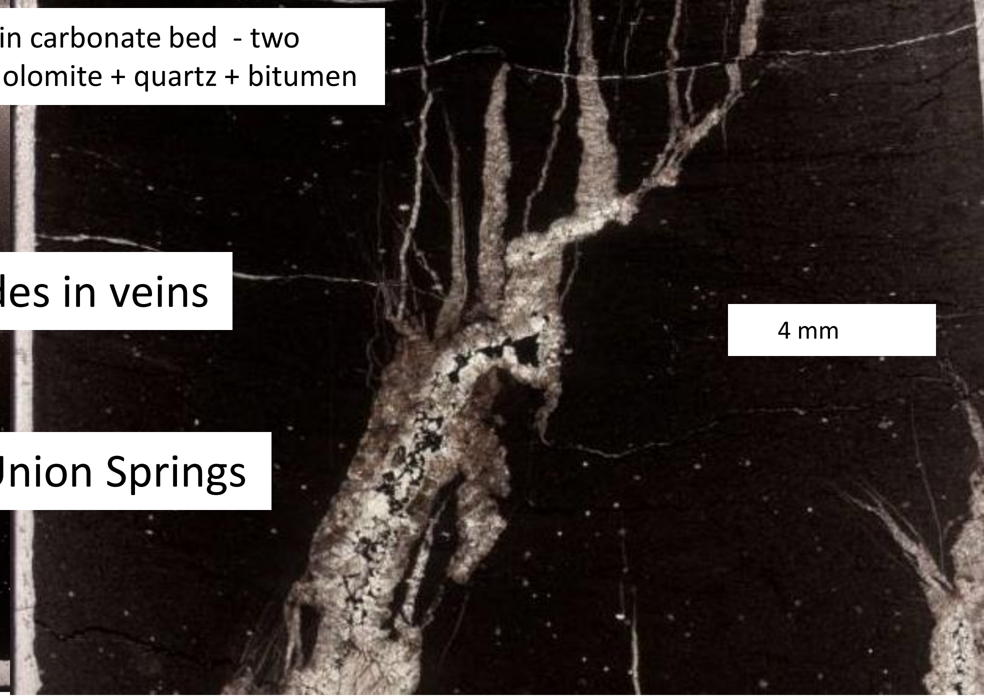
calcite + aligned saddle dolomite, bitumen + calcite in 2-layer vein with quartz at layer boundary

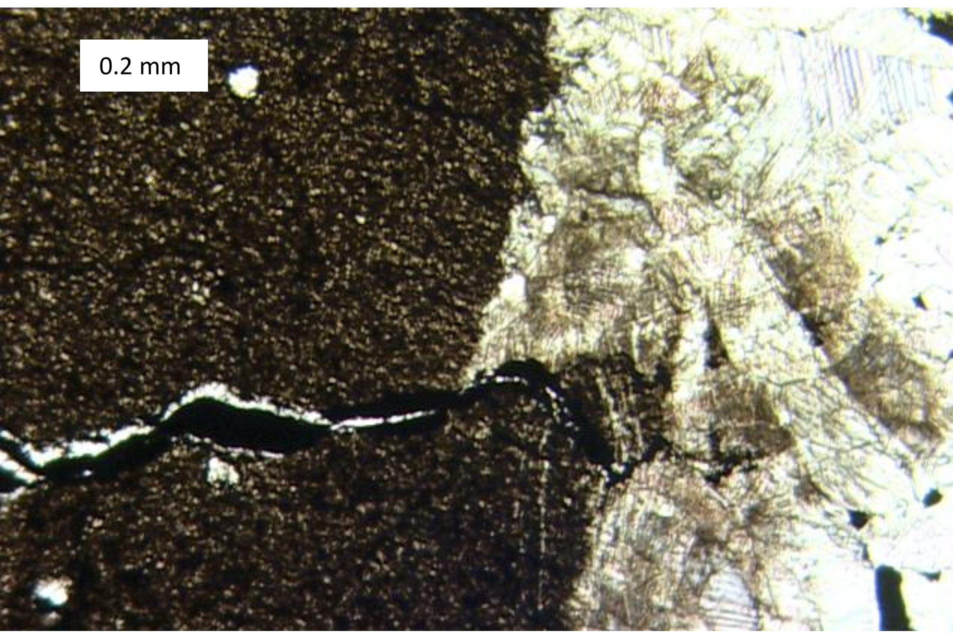
mineralized dilatent voids on bedding-plane fault surface veins fill extension fractures in carbonate bed - two generations of calcite cement + dolomite + quartz + bitumen

No sulfides in veins

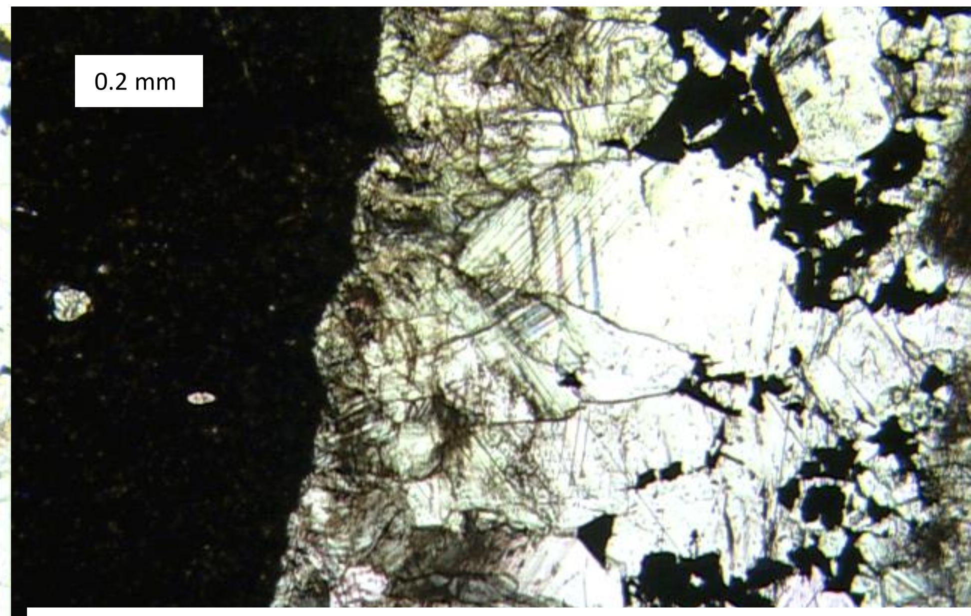
Marcellus/Union Springs







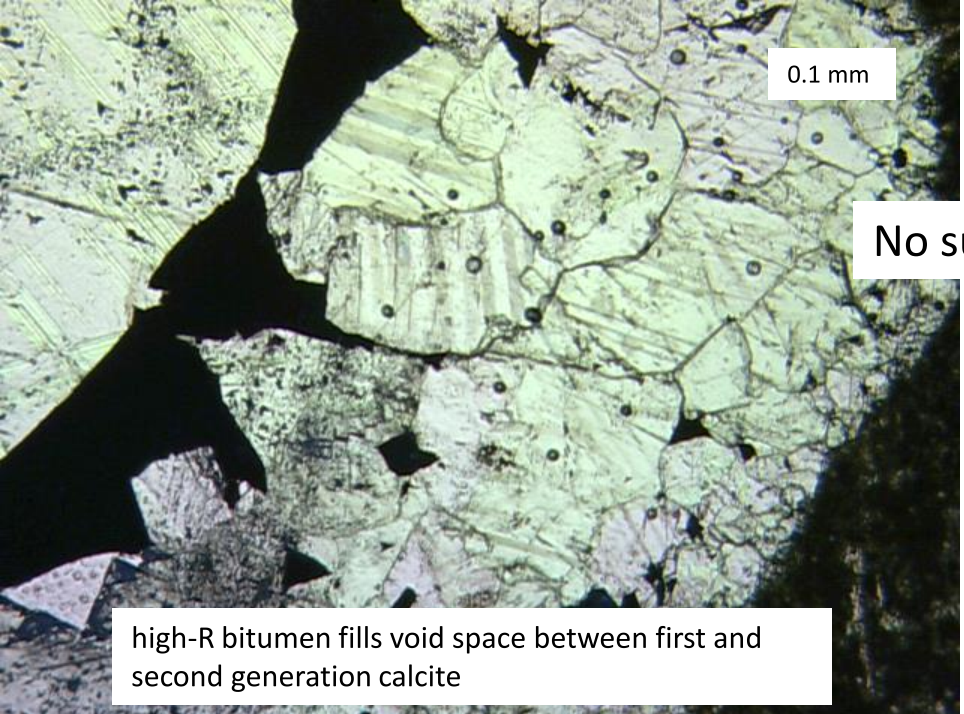
bitumen layer with calcite-filled shrinkage void intersects calcite vein; note brown staining of first-generation calcite cement



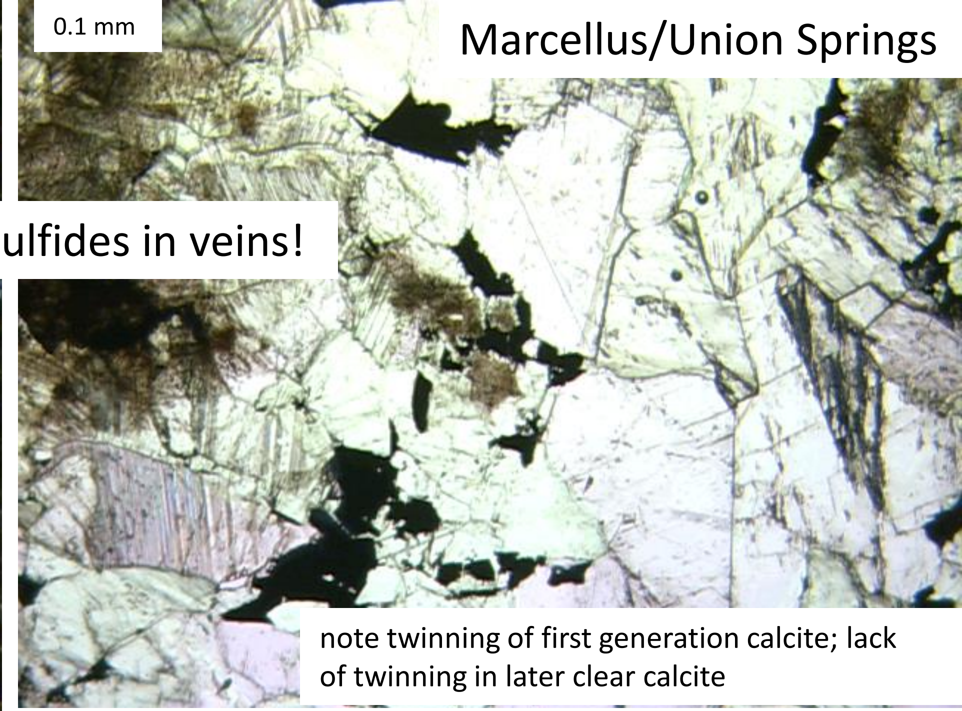
2 generations of calcite in vein; early generation stained by disseminated hydrocarbon; second generation clear and associated with high-reflectance (hi-R) bitumen (‘anthraxolite”)

Marcellus/Union Springs

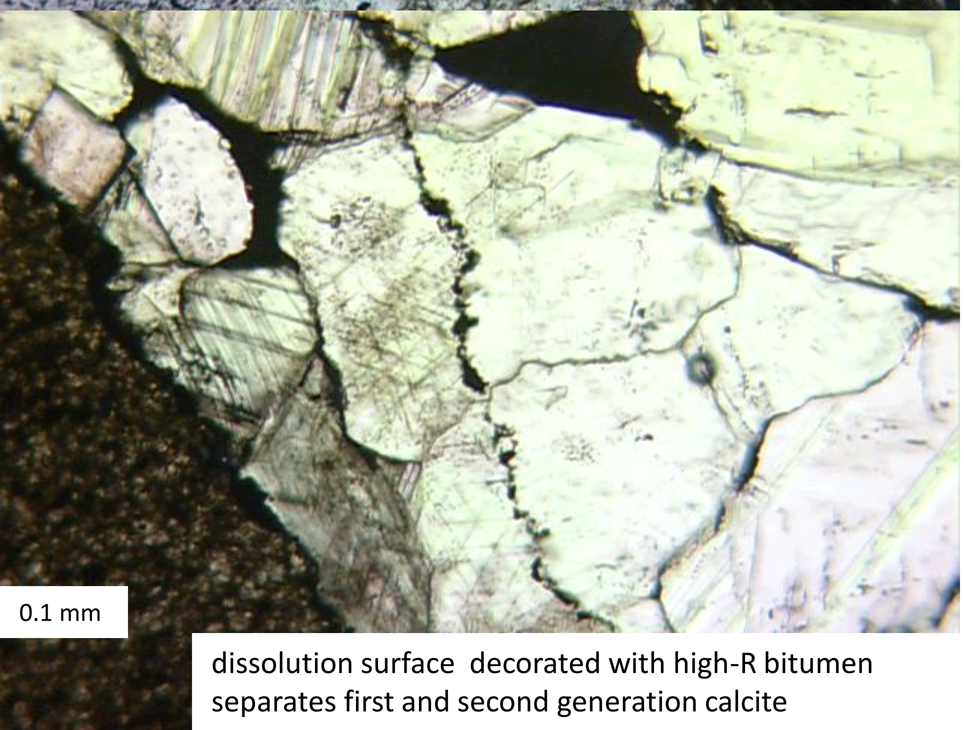
No sulfides in veins!



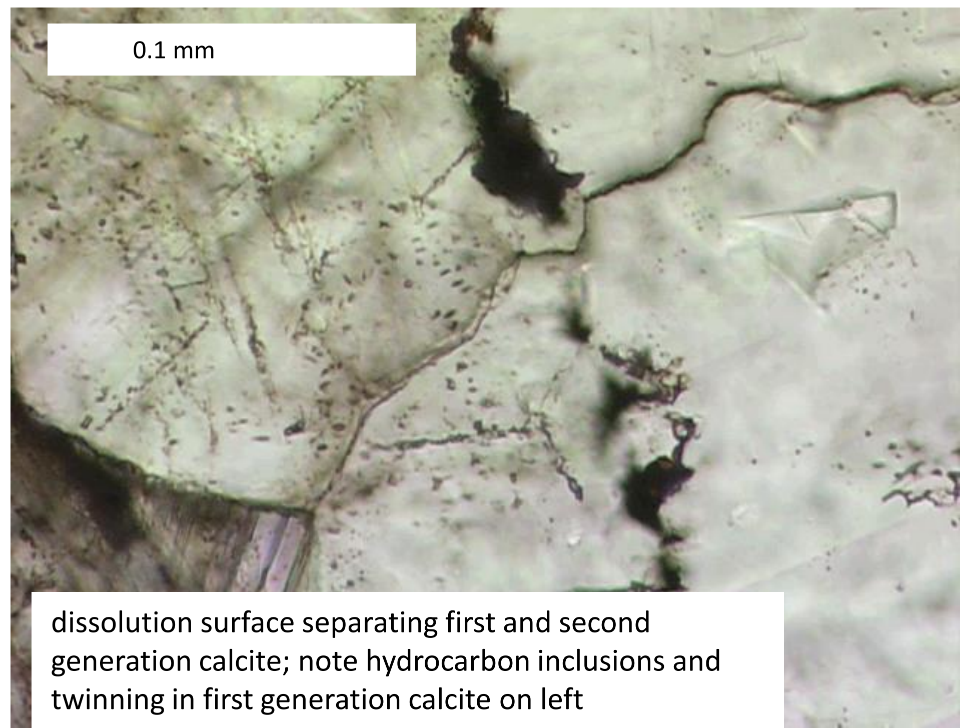
high-R bitumen fills void space between first and second generation calcite



note twinning of first generation calcite; lack of twinning in later clear calcite

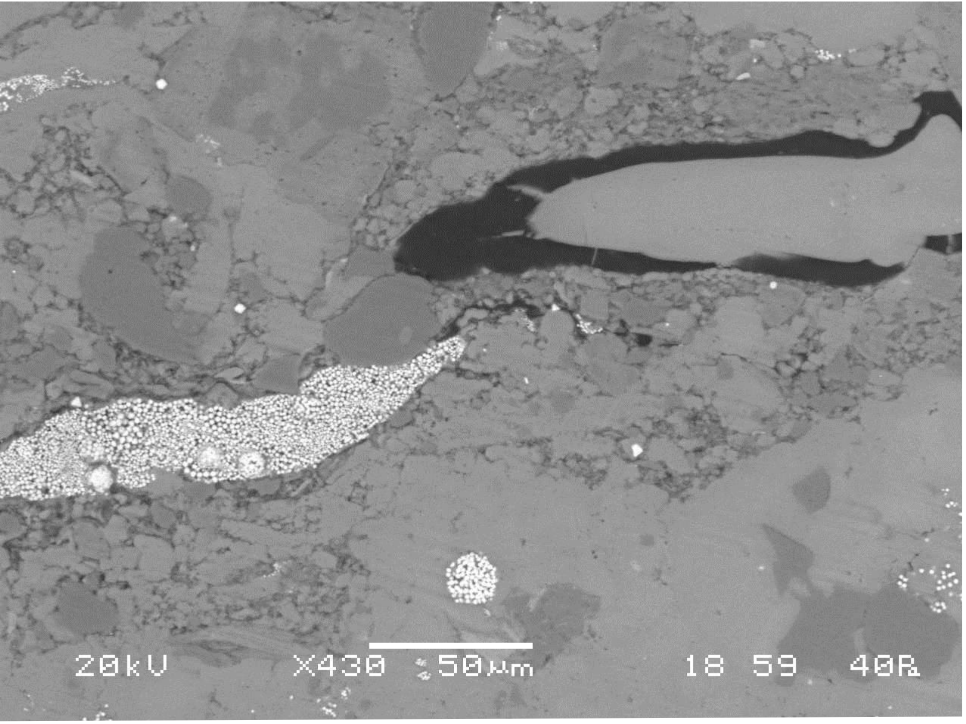


dissolution surface decorated with high-R bitumen separates first and second generation calcite



dissolution surface separating first and second generation calcite; note hydrocarbon inclusions and twinning in first generation calcite on left

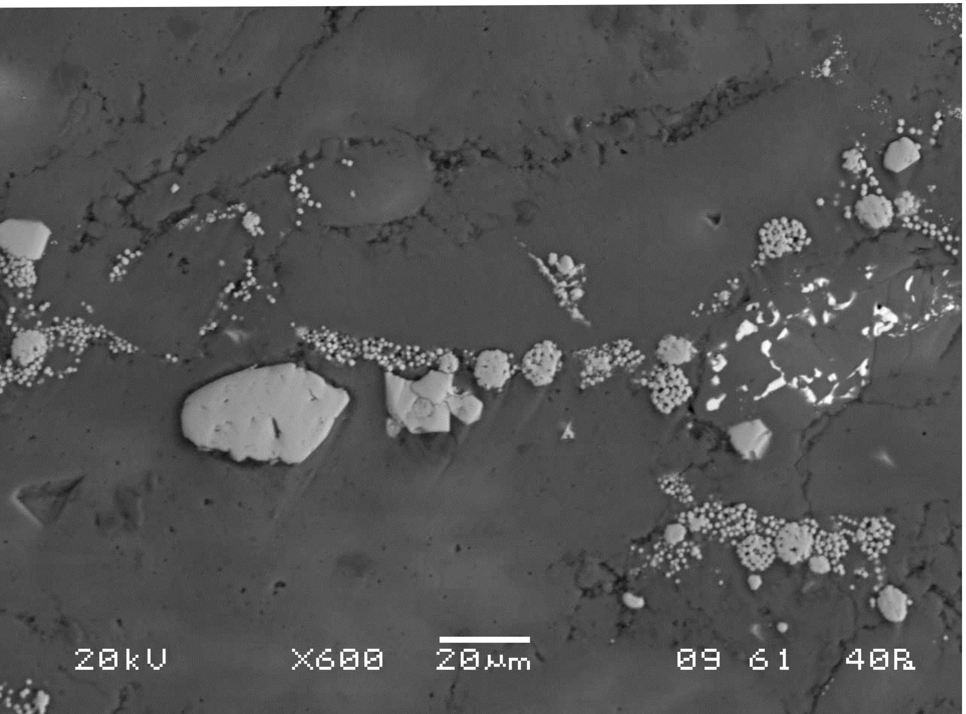
Utica/Flat Creek

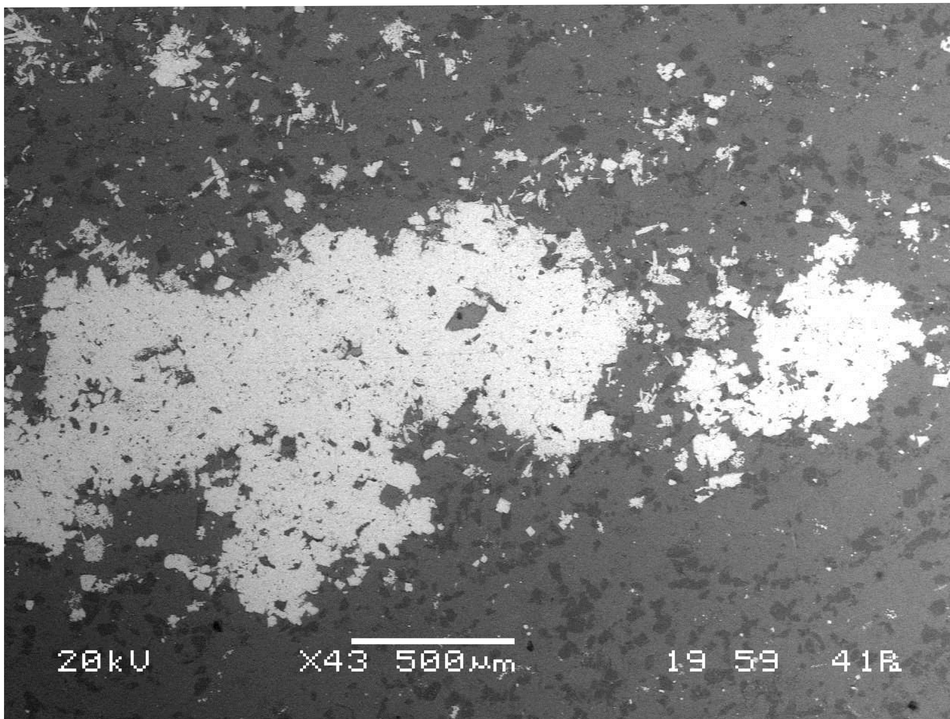


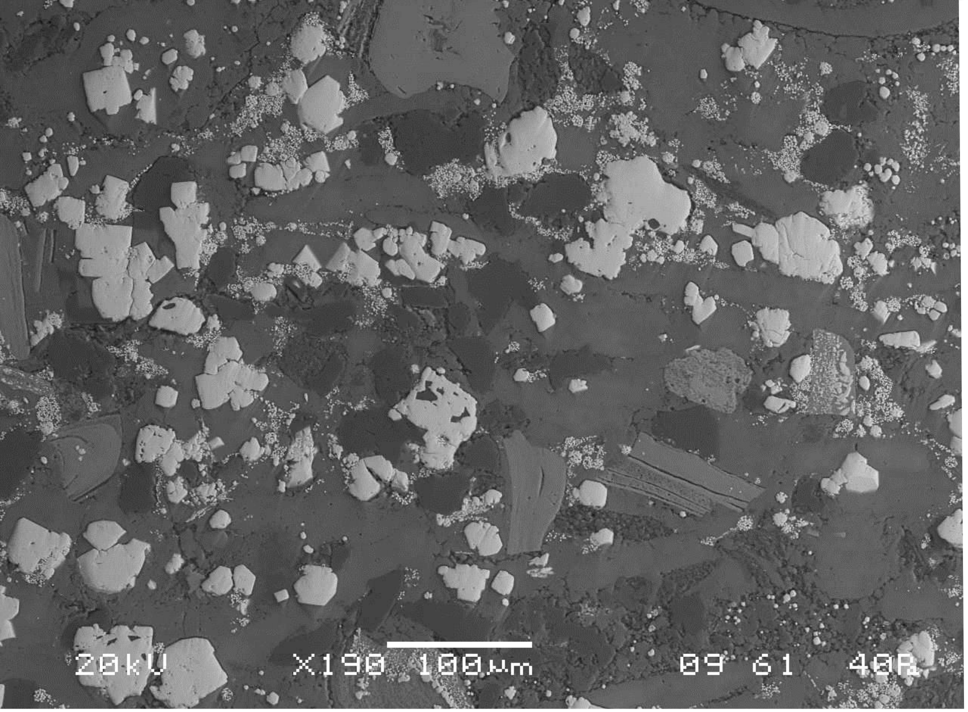
Left: pyrite framboids and microcrystalline pyrite mass, coarser pyrite crystals; calcite cement fills organic fragment (graptolite?)

Below left: pyrite framboids, microcrystals and reworked(?) pyrite clasts; barite

Below: coarsely crystalline pyrite mass





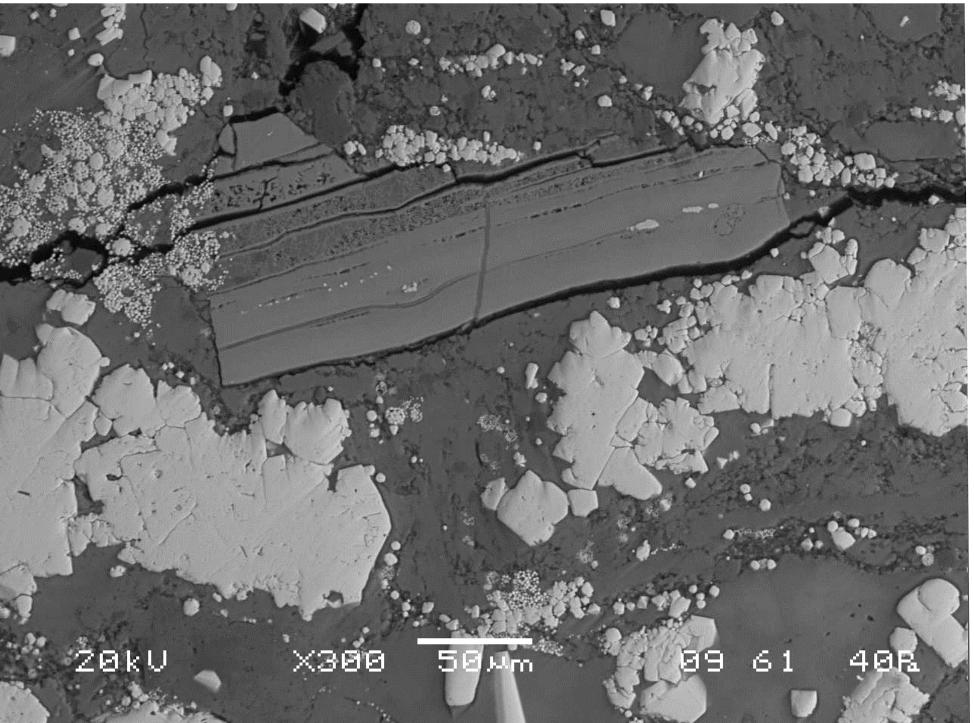


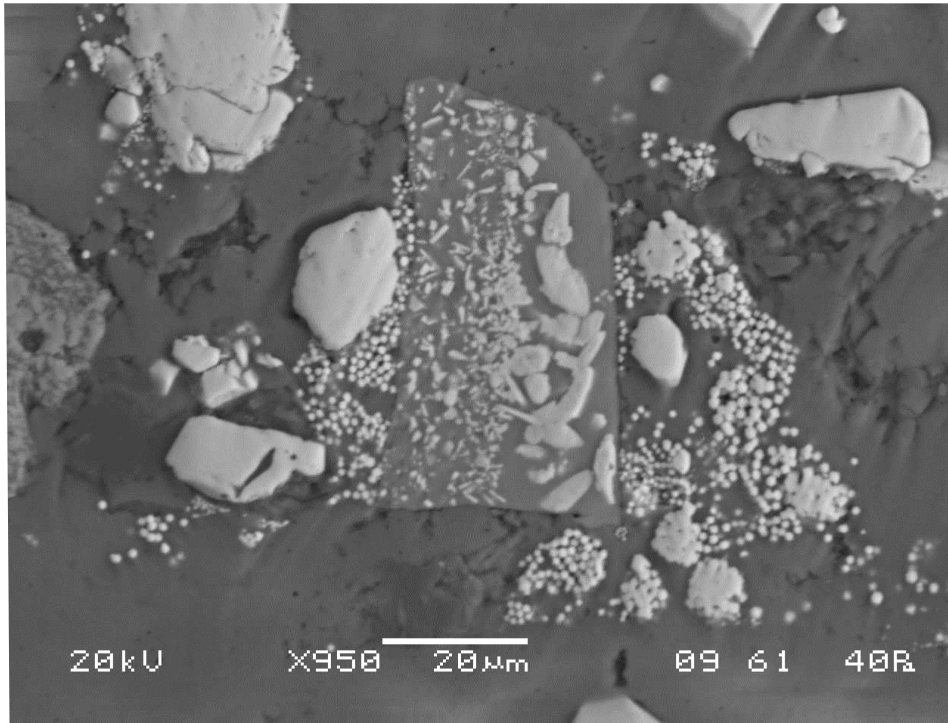
Utica/Flat Creek

Sand injectite

Left and below left: Microcrystalline pyrite, coarser pyrite, pyrite clasts(?), quartz, feldspar, carbonate and apatite grains, bioclasts.

Below: Pyrite partially replaces biogenic (?) apatite; pyrite framboids, microcrystals and grains





Summary:

Marcellus/Union Springs:

- enriched in Ca, P, Fe relative to NASC; also Sr, Ni, Cu, Pb, Zn
- carbonate-buffered
- sulfides include pyrite, sphalerite, galena, chalcopyrite
- pyrite framboids and coarser crystals reworked as clasts
- pyrite framboids preserve porosity
- sulfides rarely mobilized in vein systems related to décollement

Utica/Flat Creek:

- enriched in Ca, P, Fe, Sr, relative to NASC; not Cu, Pb, Zn
- sulfides other than pyrite rare; found in late veins
- pyrite framboids and coarser crystals reworked as clasts

Organic-rich mudrocks of the Utica Formation (Upper Ordovician) and Marcellus Subgroup (Middle Devonian) are sources of natural gas and related liquids in the Appalachian Basin. Sulfide mineralization and associated enrichment of certain trace metals in the target intervals in the Utica and Marcellus are widespread. Sulfide mineral distribution controls important rock properties including fracturing behavior, porosity and permeability, and potential metal/acid leachate from well cuttings. Whole-rock major and trace element chemistry, bulk mineralogy from X-ray diffraction, and SEM-EDS analyses of outcrop, core and cutting samples of the Flat Creek Member of the Utica Formation, and Union Springs Formation of the Marcellus Subgroup reveal a variety of sulfide mineral species, and paragenetic histories. In the Flat Creek Member (Utica), early diagenetic framboidal pyrite is widespread. Burial recrystallization produced coarser, blocky pyrite in the mudrock matrix. Other sulfide minerals, including sphalerite and minor galena, are rarely observed in mudrock, but present and associated with coarse pyrite in carbonate-sulfide veins. Flat Creek Member sulfide-carbonate veins often contain aromatic hydrocarbons, and are related in time to fluid hydrocarbon generation. Later, apparently higher-temperature carbonate veins lack sulfides, but contain methane fluid inclusions.

In the Union Springs Formation (Marcellus), early framboidal and coarser, blocky pyrite are also common, and are accompanied by abundant sphalerite in some mm-scale laminae and flattened concretionary masses. Sphalerite occurs as equant to irregular-blocky aggregates of the same size as detrital clasts. Sphalerite infills uncompacted algal cysts (‘*Tasmanites*’), suggesting a synsedimentary or early diagenetic origin. Chalcopyrite and minor galena are also relatively common, and associated with sphalerite. The common occurrence of this sulfide mineral suite suggests that Union Springs bottom waters were metal-enriched. Later carbonate veins associated with thrust fault systems in the Marcellus are generally sulfide mineral-poor, and sulfide mobility was relatively limited during fluid hydrocarbon migration and subsequent thermal over-maturation.