

Biogenic Silica in the Devonian Shale Succession of the Appalachian Basin, USA*

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Abstract

Opaline quartz tests of planktonic organisms such as radiolarians are unstable and commonly dissolve in bottom water undersaturated with respect to silicon. Upon dissolution, and under conditions of enhanced productivity export, silica precipitates in a more stable form often intimately associated with organic matter that, upon burial, ultimately becomes the reservoir for gas in many of these organic-rich deposits. Further, the newly precipitated silica permeates the clay fabric of mudstones providing a continuous high-modulus medium that is conducive to the initiation of, and maintenance of, high conductivity hydraulic fractures. Petrographic analysis, including thin section and SEM, and chemostratigraphic analysis of the Middle Devonian Marcellus Shale through Upper Devonian Dunkirk Shale (Lower Huron Shale equivalent) provide evidence of recurrent patterns of biogenic silica enrichment in these organic-rich deposits. Thin section analysis shows radiolarians in various states of dissolution, some being completely replaced by pyrite. Elevated molybdenum to total organic carbon ratios (Mo/TOC) coincide with excursions in silica to aluminum (Si/Al) ratios. We suggest that during times of transgression the Mo reservoir is resupplied via connection with the global ocean, resulting in elevated Mo/TOC. In addition to Mo, transgression provides silica and nutrients needed to stimulate primary productivity in the photic zone. As a result, late transgressive to early regressive systems tract deposits of the Middle and Upper Devonian shale succession become enriched in biogenic silica. These zones or condensed sections provide high gas-in-place and deliverability and should be considered for horizontal wellbore placement.

References Cited

Algeo, T.J., and N. Tribovillard, 2009, Environmental analysis of paleoceanographic systems based on molybdenum-uranium covariation: *Chemical Geology*, v. 268/3-4, p. 211-225.

Smith, C.N., and A. Malicse, 2010, Rapid Handheld X-Ray Fluorescence (HHXRF) Analysis of Gas Shales: AAPG Search and Discovery Abstract #90108. Web accessed 20 August 2013.

http://www.searchanddiscovery.com/abstracts/pdf/2010/intl/abstracts/ndx_smith.pdf



BIOGENIC SILICA IN THE DEVONIAN SHALE SUCCESSION OF THE APPALACHIAN BASIN, USA

RANDY BLOOD*, GARY LASH and LINDELL BRIDGES***

***PURE EARTH RESOURCES**

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May 21, 2013

» Every aspect of a hydrocarbon well can be related to the geology

- > Leasing: Lease position is put together where the geology suggests the reservoir/trap, etc is best developed
- > Drilling: ease of drilling, ROP, lost circulation zones, all a function of rock types, mineralogy, presence of permeable features such as faults/fractures
- > Completions: breakdown pressures, treating pressures, ability to put the job away, fluids used, are a function of reservoir pressure, lithology, structure, stress and stress orientations
- > Production: largely influenced by the reservoir pressure and mineralogy

» Understanding the geology is integral to optimizing production of a well.



- » **Introduction to chemostratigraphy**
- » **Examine data and signature for biogenic shale using the Marcellus as an example**
- » **Discuss evidence for biogenic silica in the Dunkirk Shale**
- » **Comment on biogenic silica and its influence on rock mechanics**



- » **Chemostratigraphy** – especially suited to the study of fine-grained, seemingly homogenous (often biostratigraphically barren) deposits
- » variations in elemental concentrations, elemental ratios, and elemental enrichments relative to typical shale values reflect changes in such parameters as paleoclimate, hydrographic aspects of the paleocean, paleoredox conditions (including oceanic anoxic events), and mineralogy
- » Allows for high resolution correlation of cm-scale units



» Handheld XRF (HHXRF) analyzer

- > Thermo Scientific Niton XL3t 950 GOLDD+
- > Equipped with a silicon drift detector
- > Hand (outcrop) samples, core, cuttings



» Smith and Malicse (2010)

- > Comparison of HHXRF technology with results of independent laboratory ICP-MS methodology
- > 160 sedimentary rock samples of mixed lithology

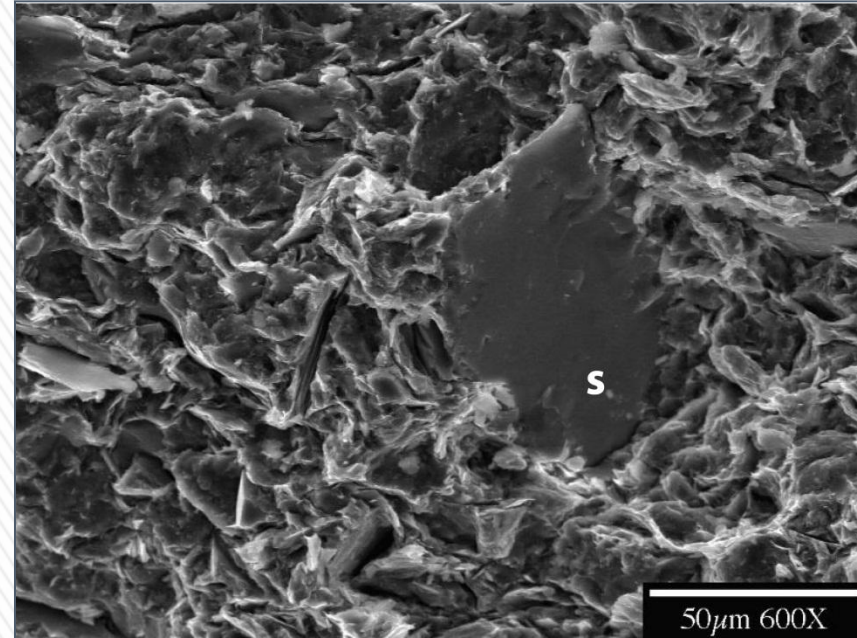


- » very strong correlations ($r^2 > 0.90$) with laboratory ICP-MS data for most major, minor and trace elements from Mg to U
- » Differences in data sets can arise from the sample preparation procedure employed by labs versus the direct measurement *in situ* by HHXRF
- » HHXRF analysis is non-destructive and enables one to readily analyze on a cm-scale
 - > Analysis of Marcellus cores at ~2.5-3 cm intervals



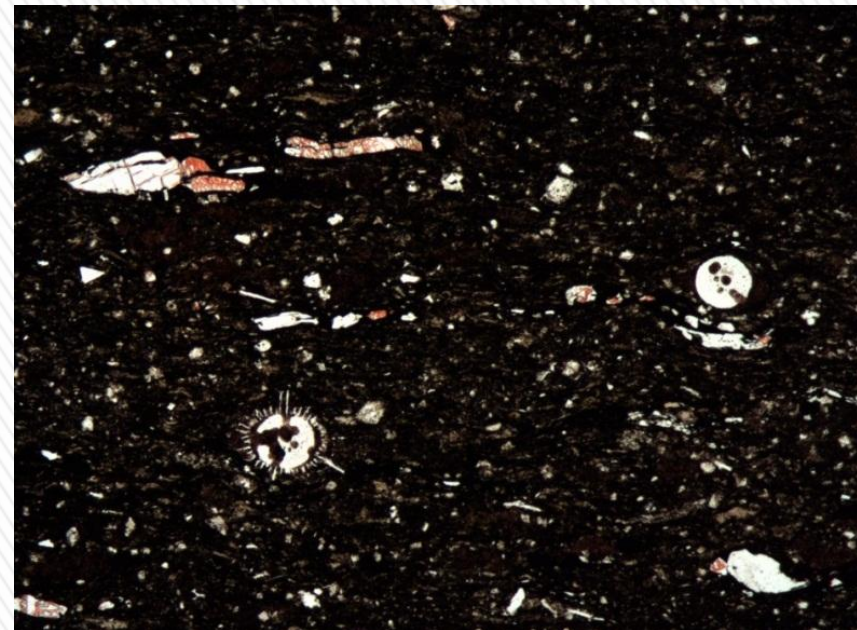
» Extrabasinal:

- > Fluvial derived detrital quartz grains
- > Eolian derived quartz grains

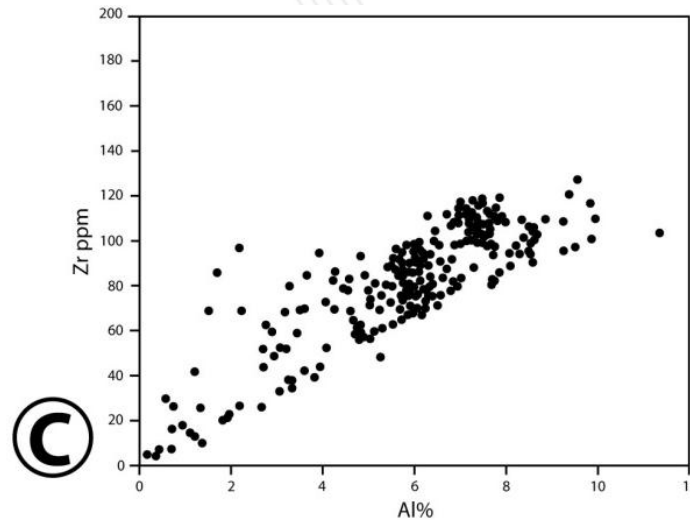
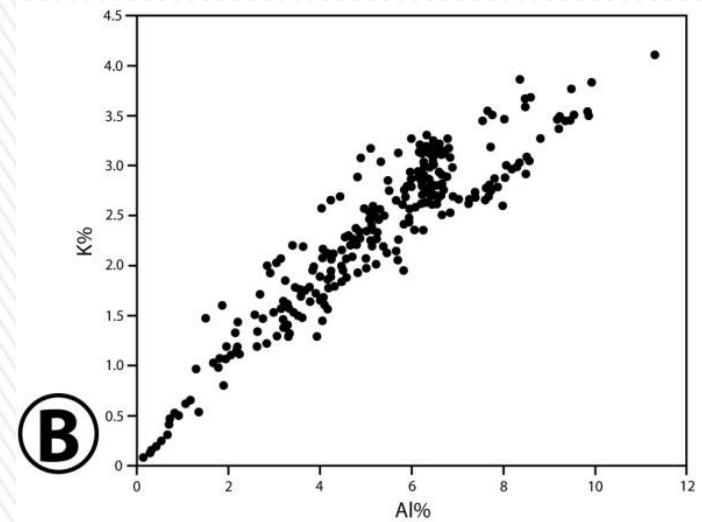
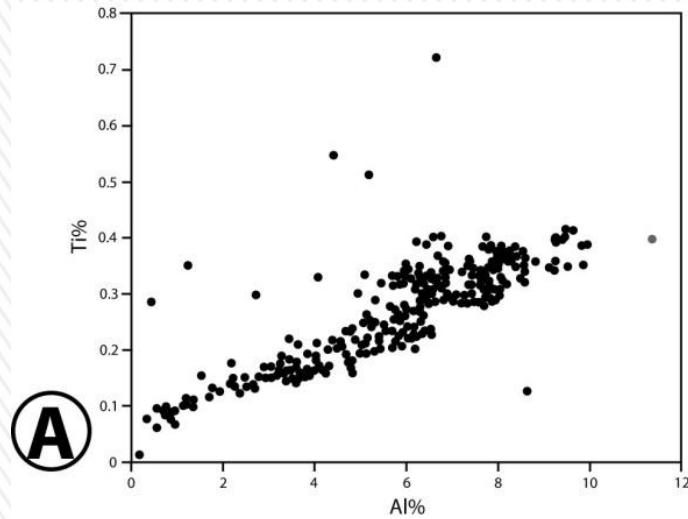


» Interbasinal:

- > Biogenic opaline quartz

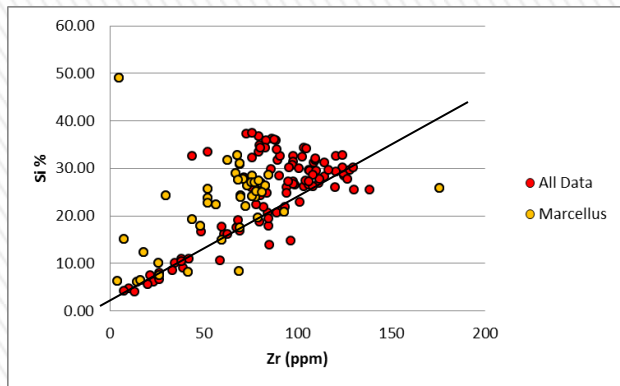
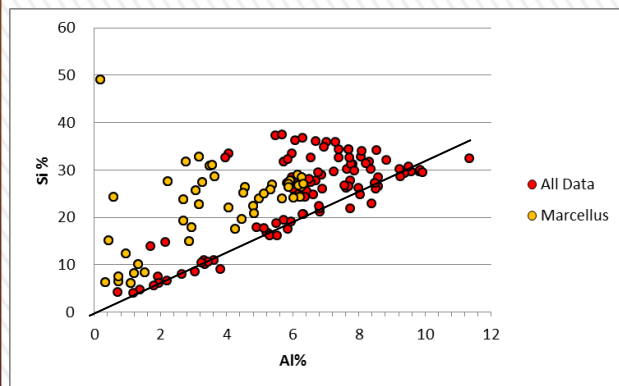
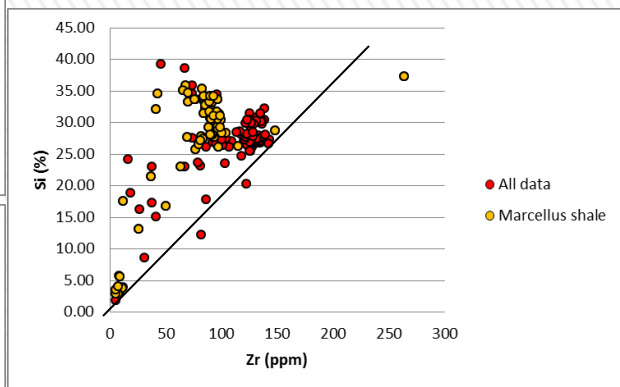
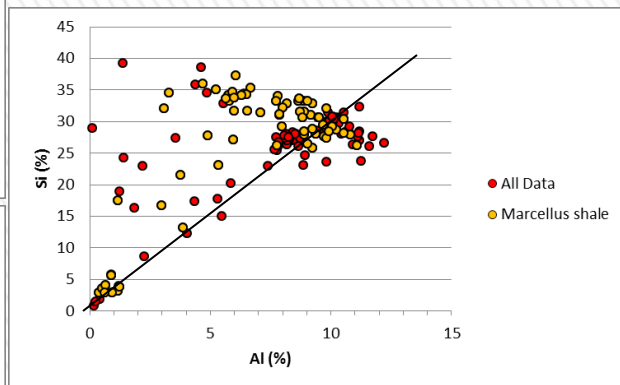
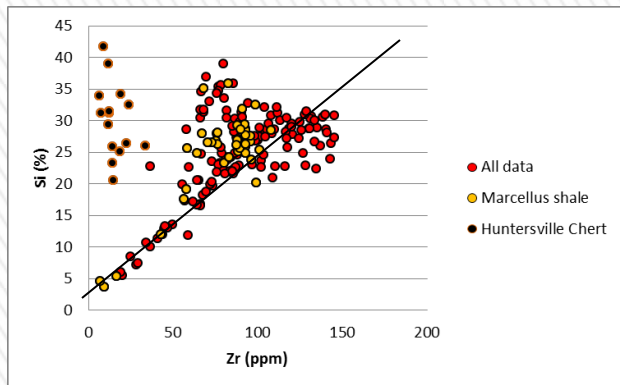
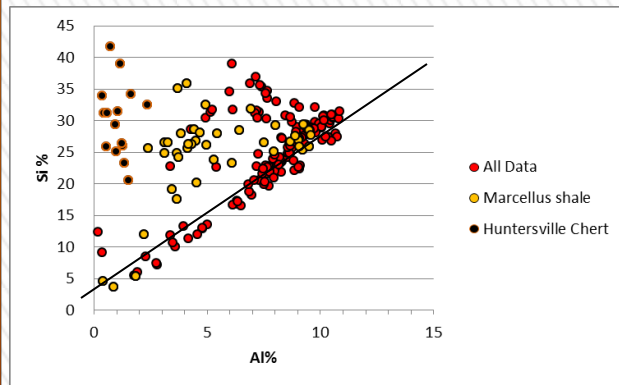
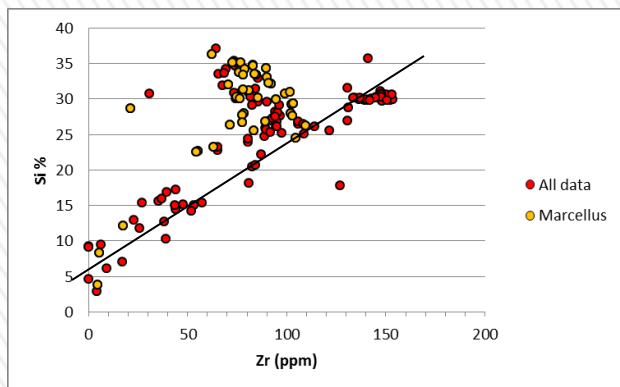
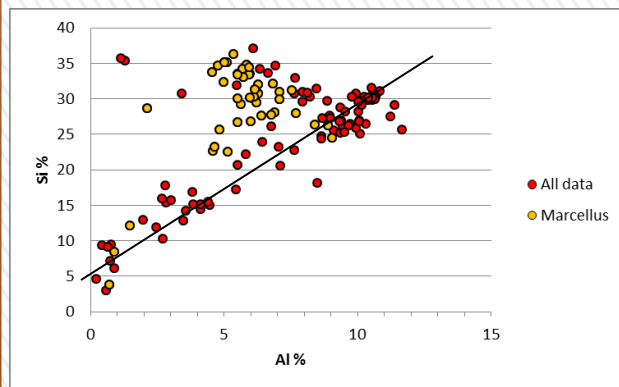


DETRITAL PROXIES



A strong correlation exists between well known detrital proxies Ti, K, Zr and Al ➤

DETRITAL SILICA IN MARCELLUS DEPOSITS



 **Clastic trend**

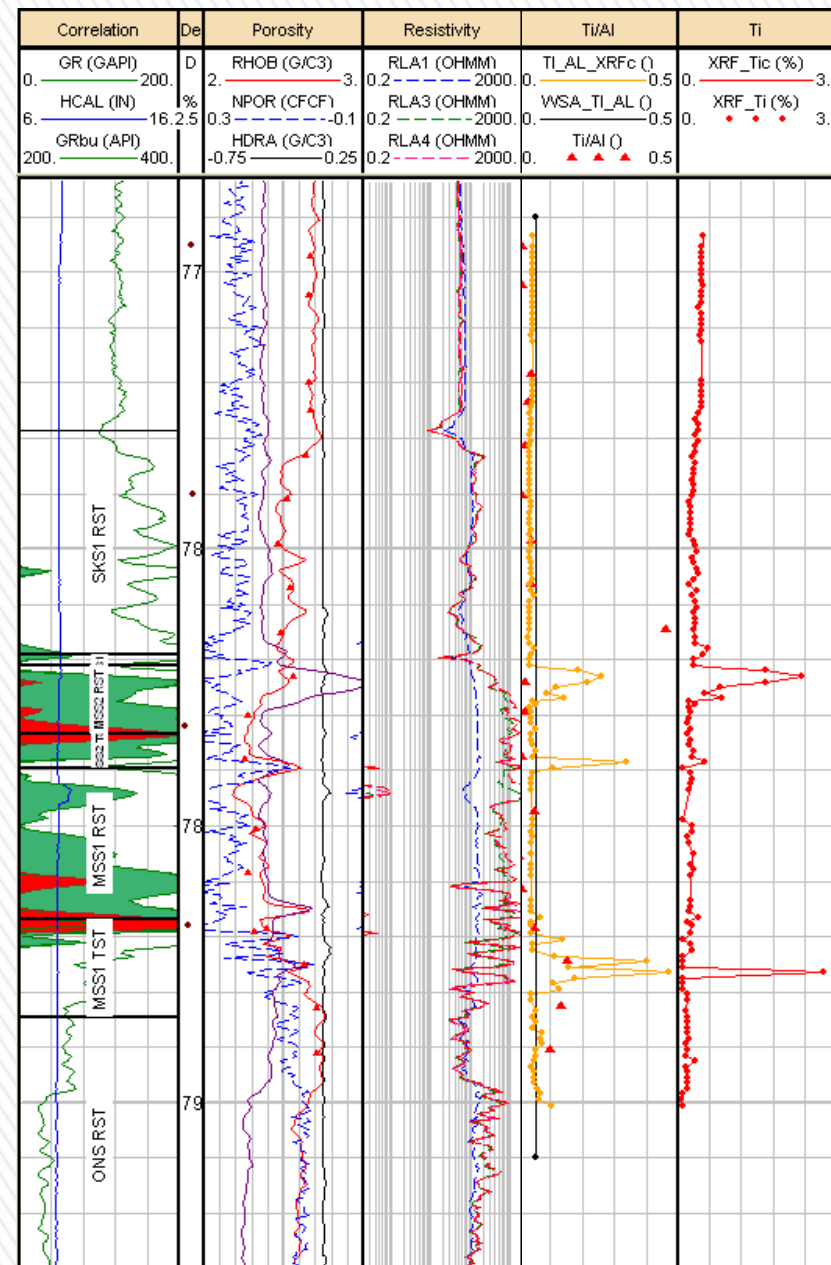
EOLIAN SILICA IN MARCELLUS DEPOSITS

The Ti/Al ratio can be used as a proxy for eolian deposition where strong winds strip away lighter material, leaving behind a sediment more enriched in heavy Ti-bearing minerals. Ti/Al values > 0.05 are indicative of eolian transport.

Ti/Al can also be used as a proxy for energy in the system and thus can be used to interpret bottom water energy, and relative changes in proximity to the paleoshoreline.

Ti/Al values of less than 0.05 suggest minimal eolian input.

The few zones of elevated Ti/Al while possibly the result of eolian transport more likely represent the winnowing of clays and/or concentration of heavier Ti-bearing minerals (these values are an order of magnitude higher than typical eolian Ti/Al values) by bottom currents

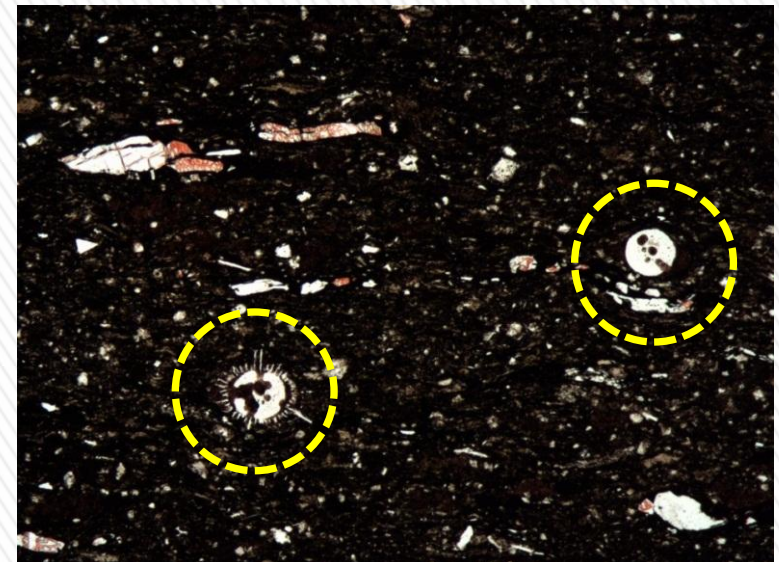
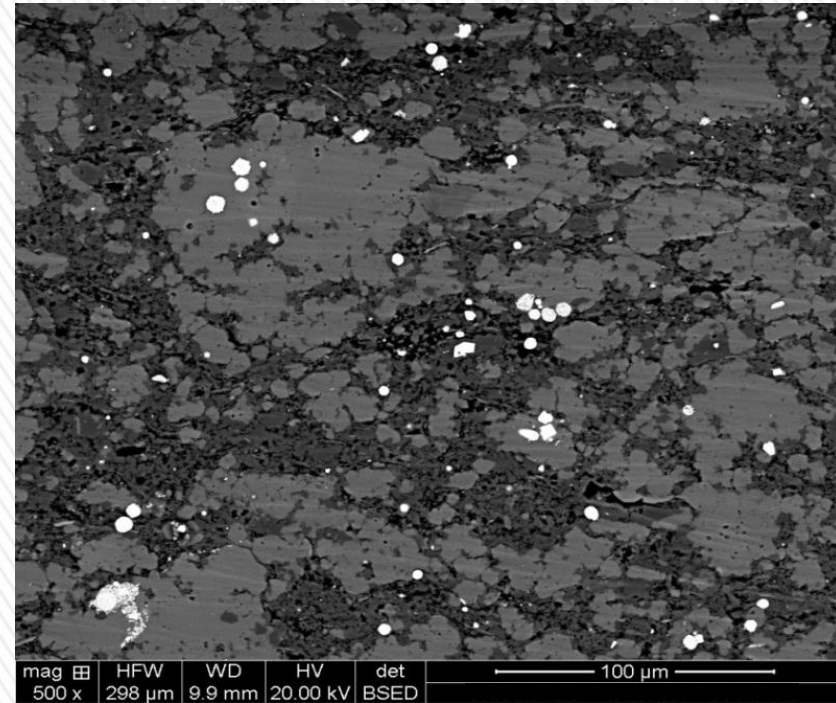


BIOGENIC SILICA IN MARCELLUS DEPOSITS

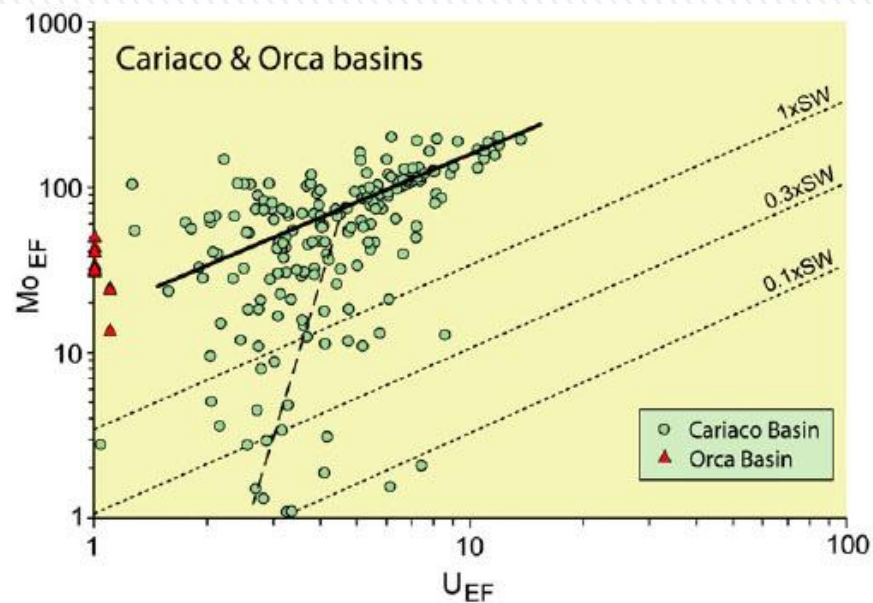
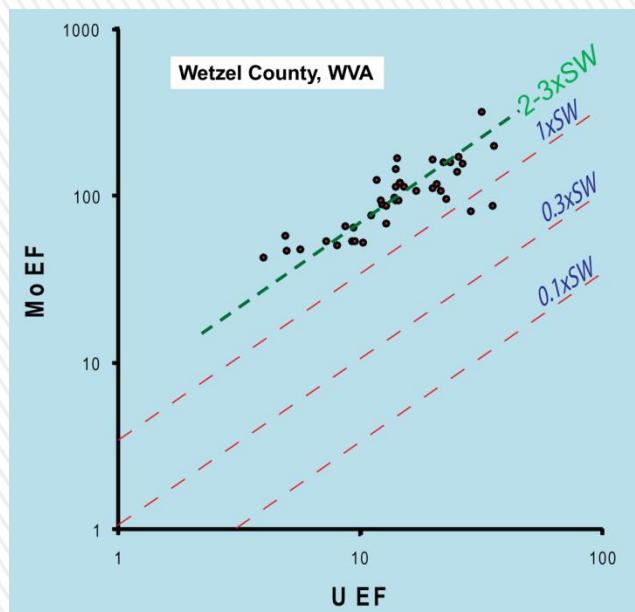
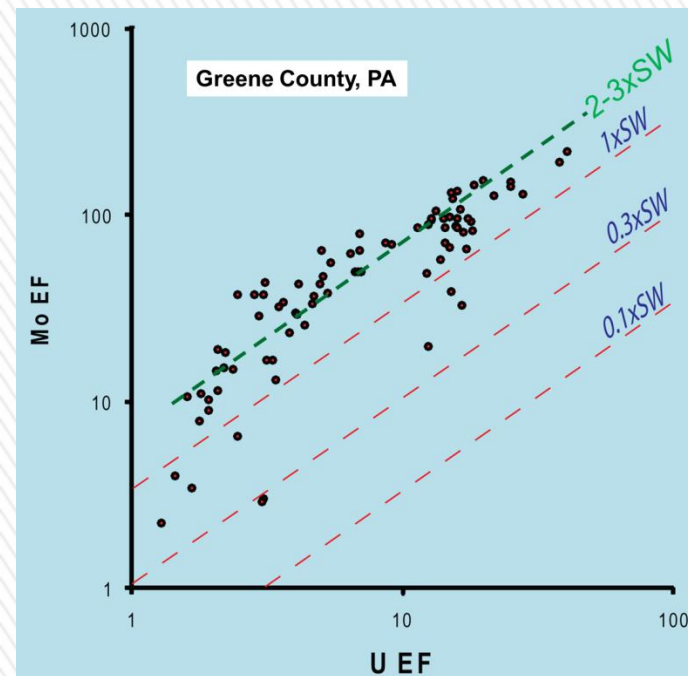
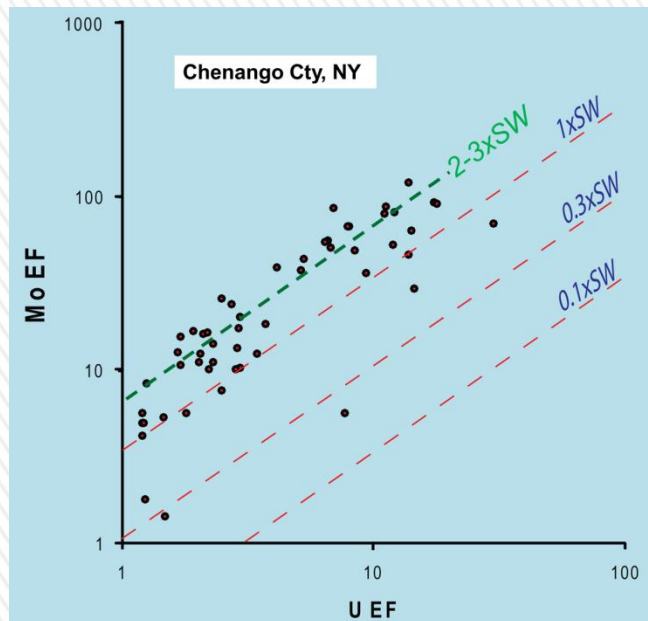
Opaline quartz produced by radiolarians is unstable under the temperature and redox conditions of the bottom water.

As a result the opaline quartz dissolves and re-precipitates in a more stable form.

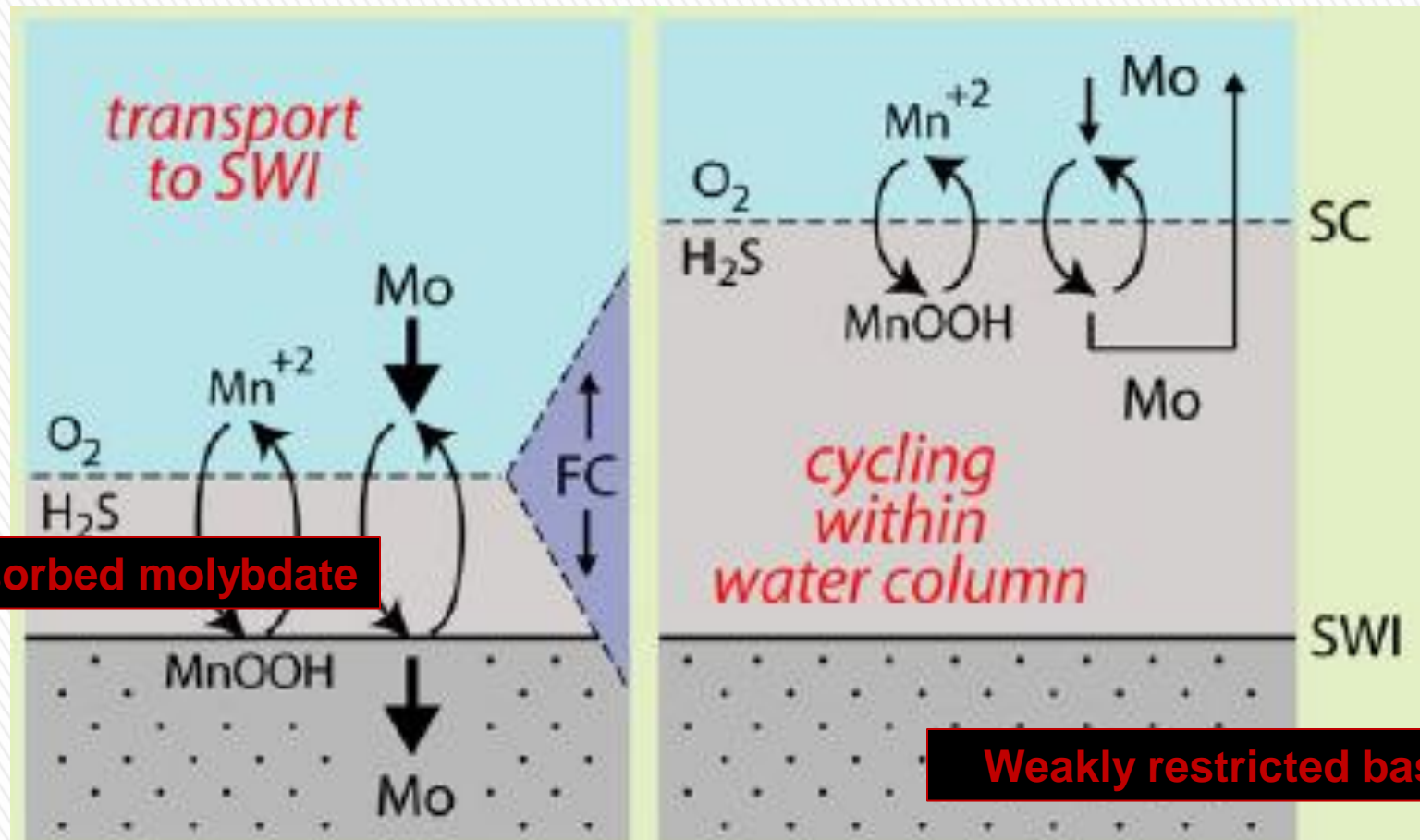
This biogenic quartz permeates the fabric creating a strong interlocking matrix of high modulus, brittle rock.



MARCELLUS MO EF VS U EF SIGNATURES

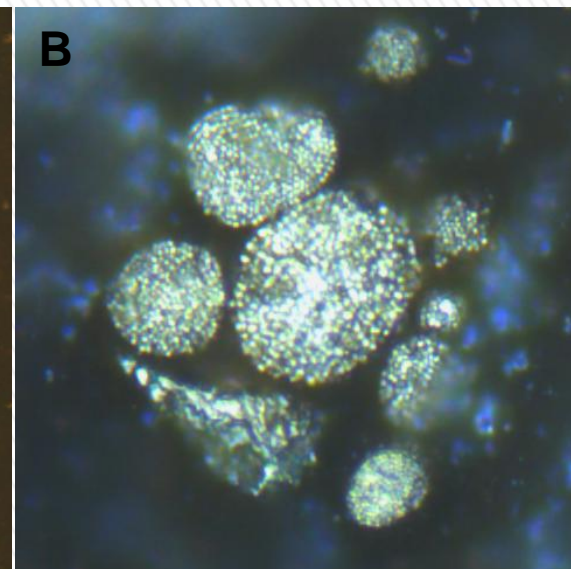
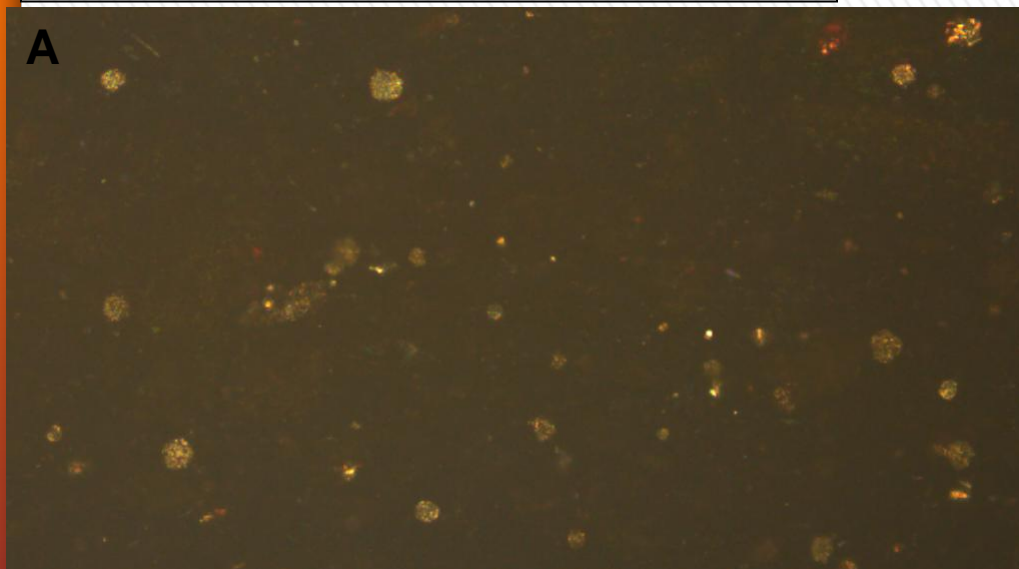
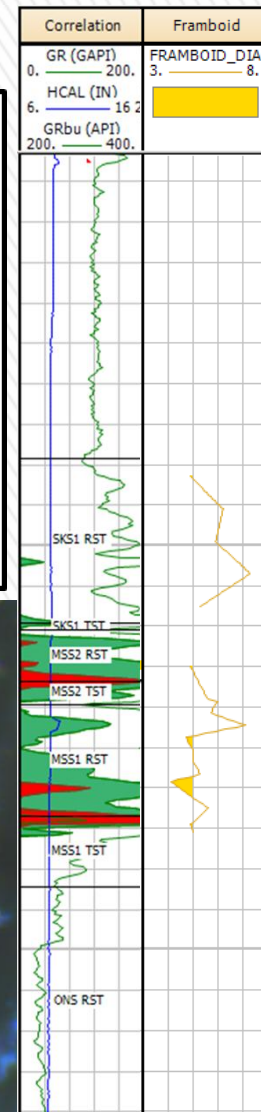
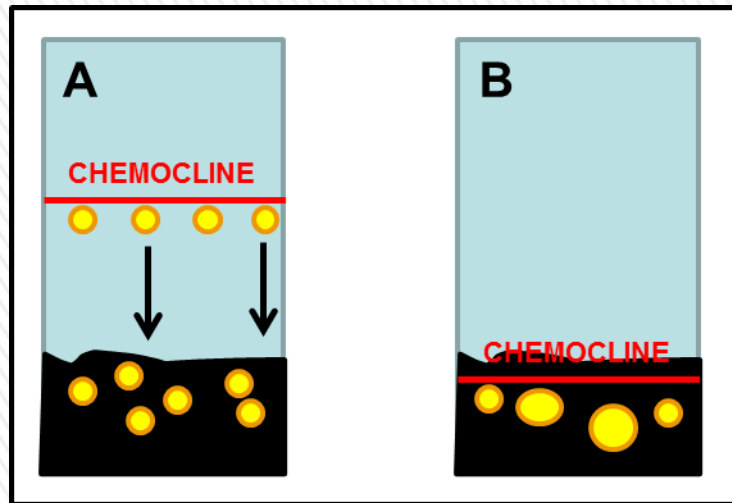


Mn (Fe)-OXYHYDROXIDE PARTICULATE SHUTTLE



PYRITE FRAMBOID FORMATION

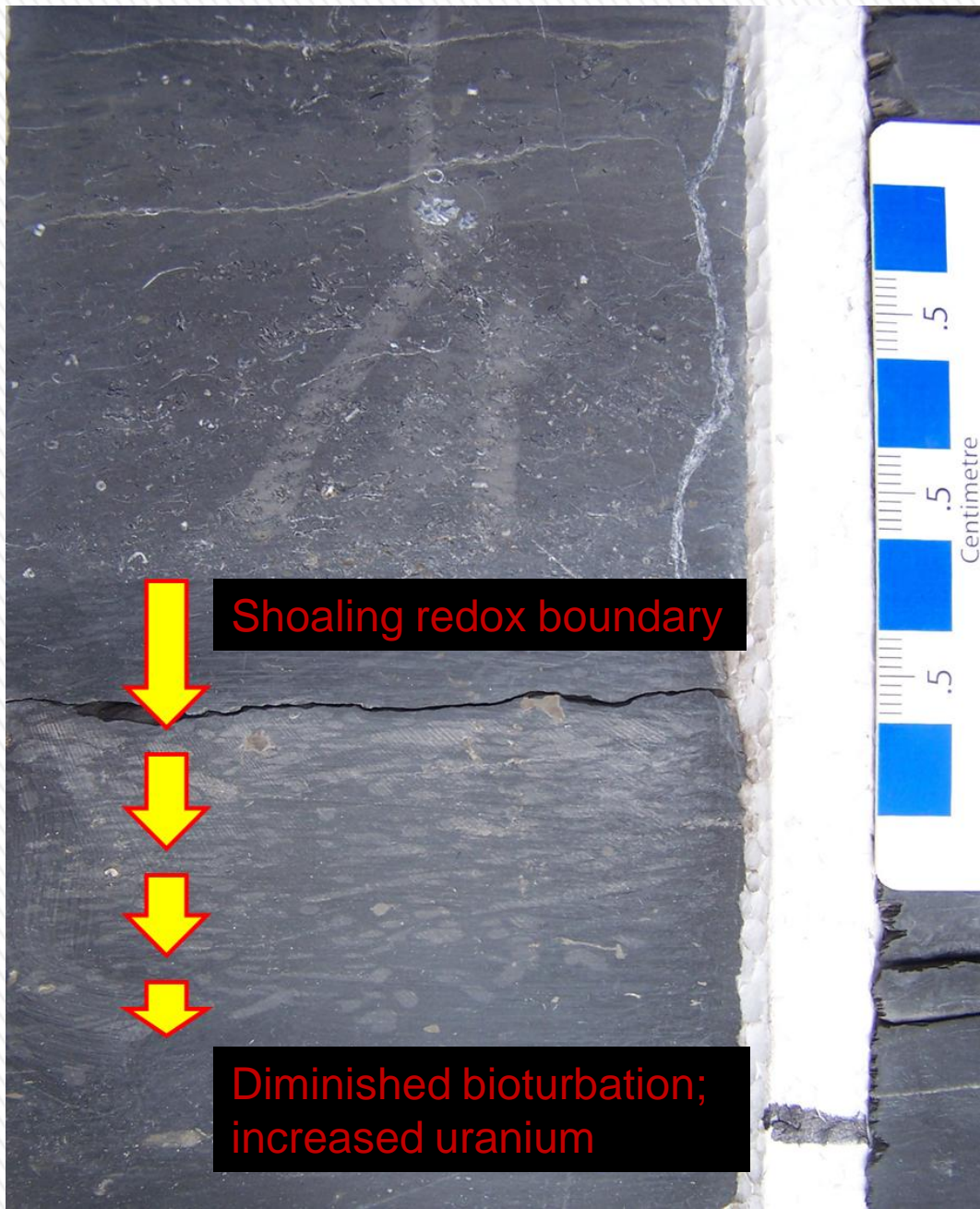
- Pyrite framboids form at the chemocline
- Framboids that form in the water column can grow to ~5µm before the water cannot support their weight and they sink
 - Statistical analysis of the framboid diameters show that under these conditions mean diameter is ~5µm, with a narrow range
- Framboids forming in euxinic sediment are limited by availability of reactants and can grow to much larger and diverse sizes.



FREQUENT REDOX FLUCTUATIONS

fossil debris

Bioturbated dark-grey shale

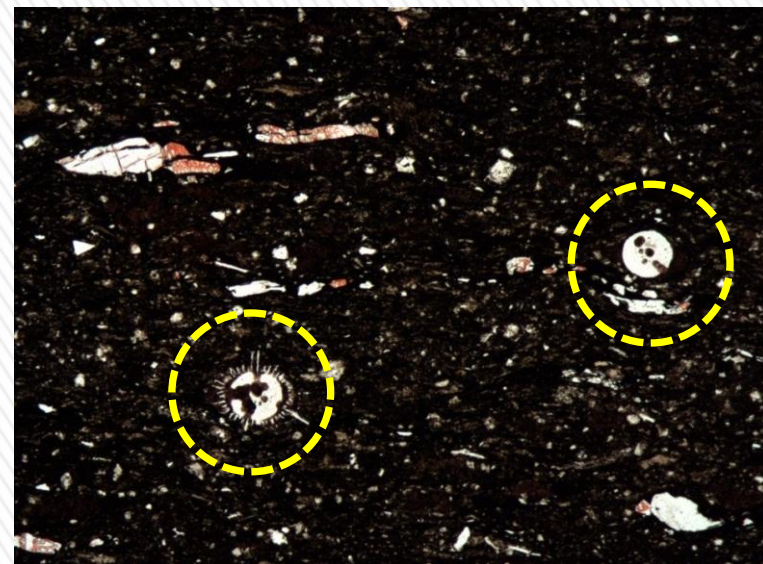
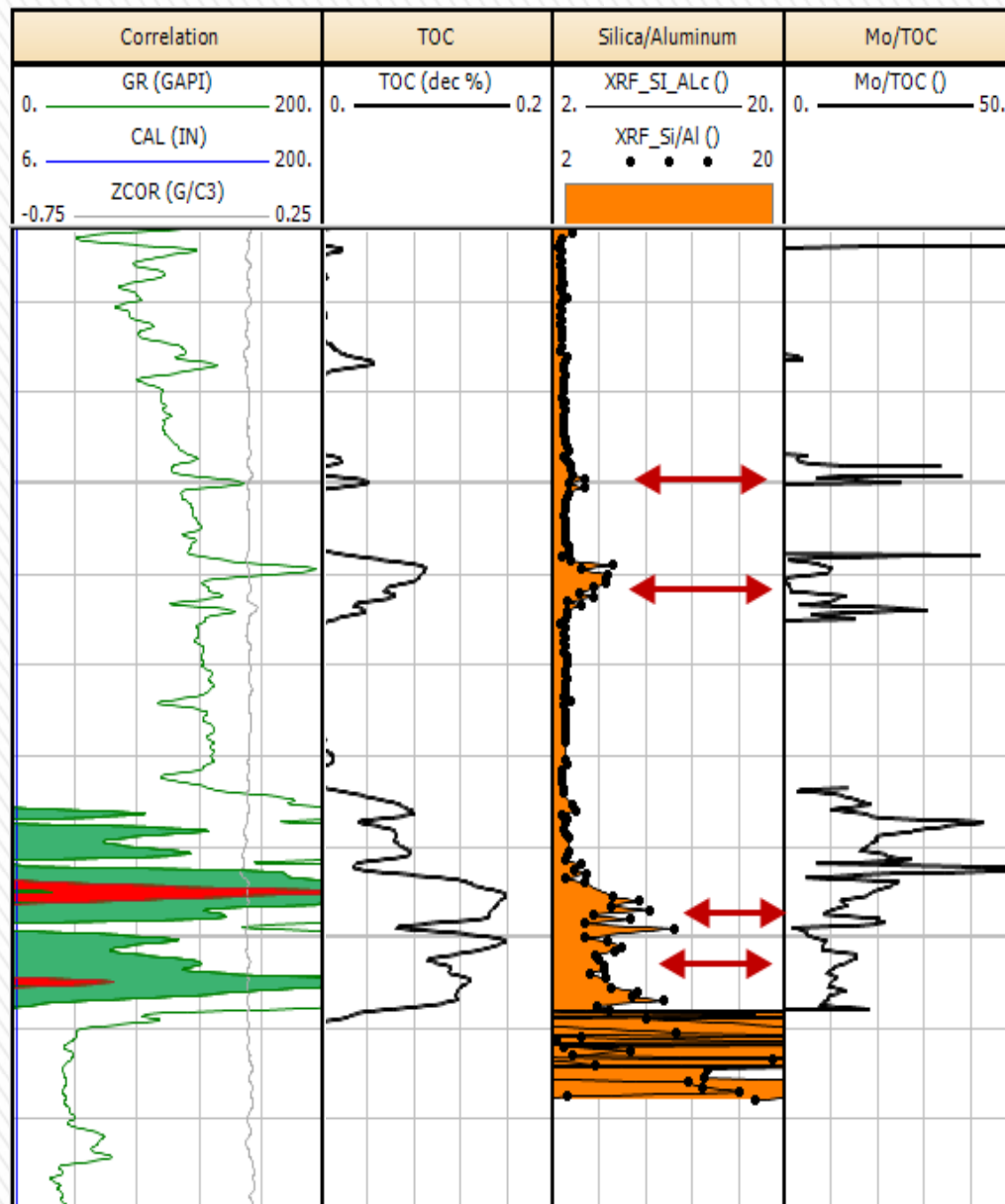


Shoaling redox boundary

Diminished bioturbation;
increased uranium



QUARTZ, TOC, AND Mo IN THE MARCELLUS



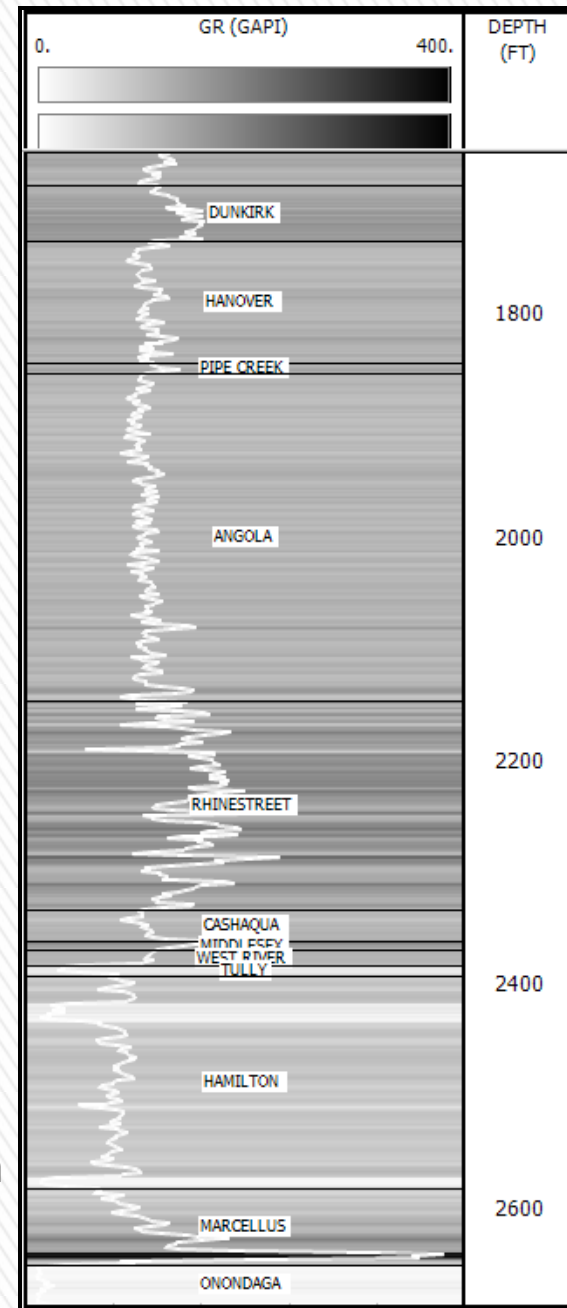
- Prominent occurrence of biogenic quartz coinciding with elevated TOC and Mo/TOC values.



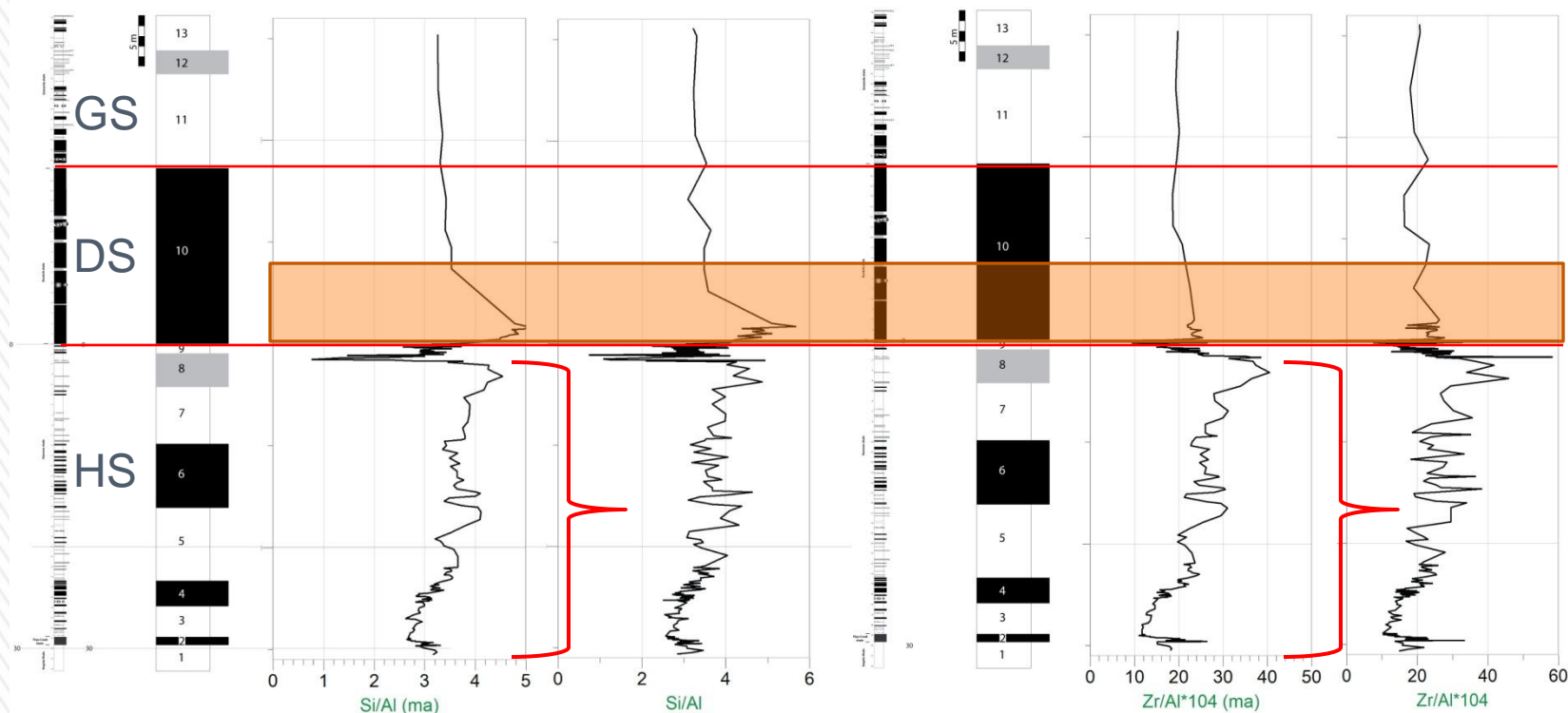
DUNKIRK SHALE OUTCROPS AND TYPE LOG



- Extensive chemostratigraphic data set collected through the Hanover – Dunkirk shale sequence along two outcrop sections in western New York
- Well log from western New York showing the Middle and Upper Devonian shale succession (Dunkirk shale is the equivalent of the basal Lower Huron shale)



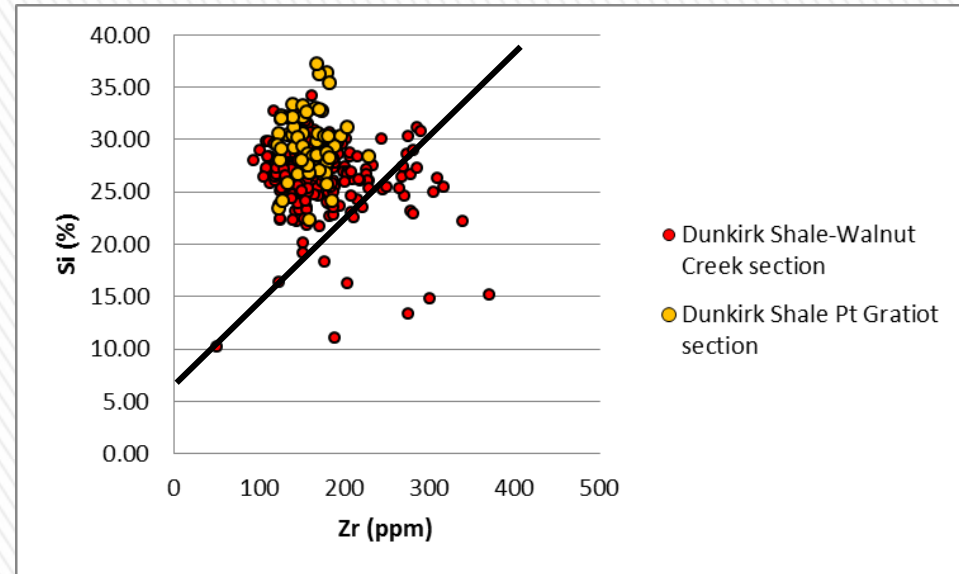
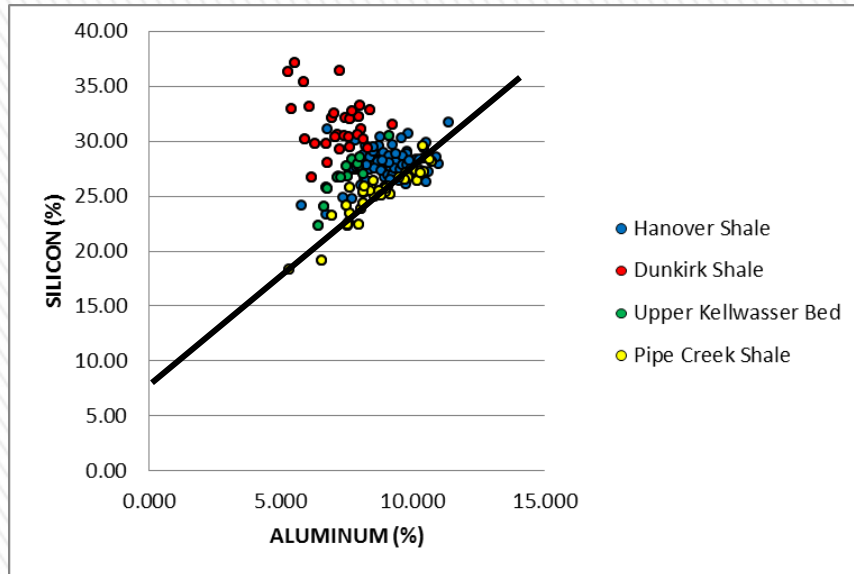
Dunkirk Shale –Walnut Creek Section



- Note that Si/Al and Zr/Al co-vary through the Hanover Shale (HS) implying that the silica in the system is related to the zircon in the system and thus is of detrital origin
- At the base of the Dunkirk Shale (DS) there is a marked deviation of the trends in Si/Al from Zr/Al showing an over abundance of silica in the Dunkirk shale, suggesting it is not of detrital origin
- In the upper part of the Dunkirk shale into the Gowanda Shale (GS) Si/Al and Zr/Al co-vary again suggesting the silica in the system is of detrital origin.



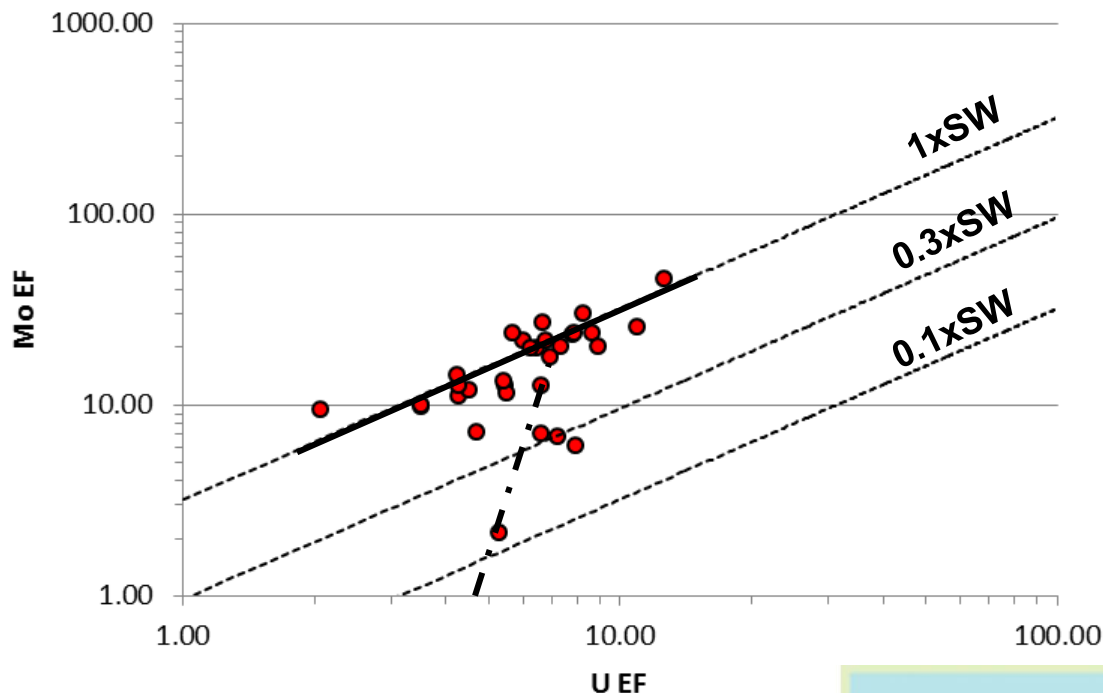
SOURCES OF SILICA-DUNKIRK SHALE



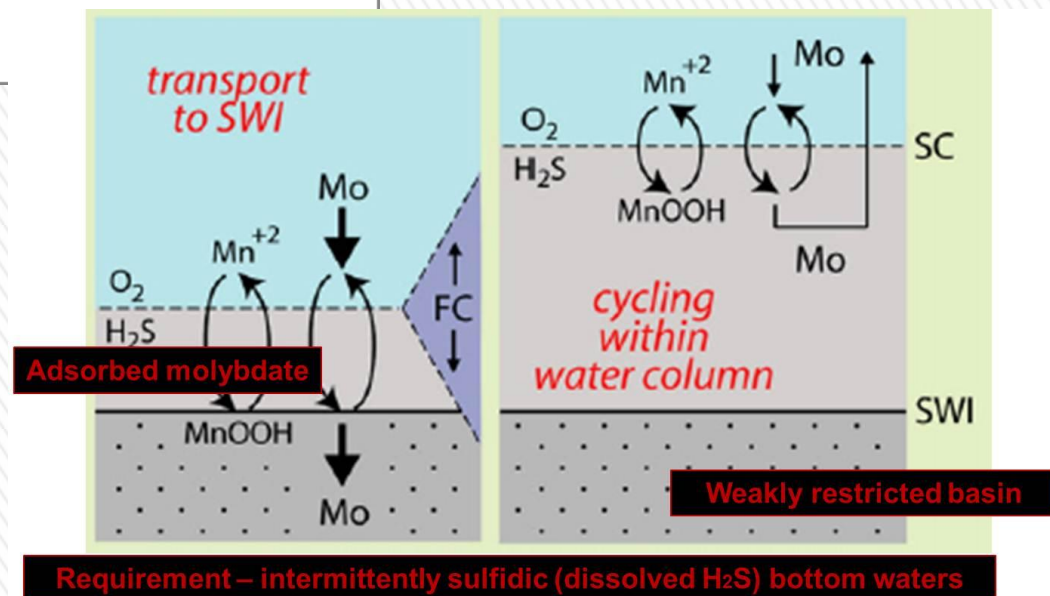
- Both scatter plots of aluminum vs. silicon and zirconium vs. silicon show excess silica



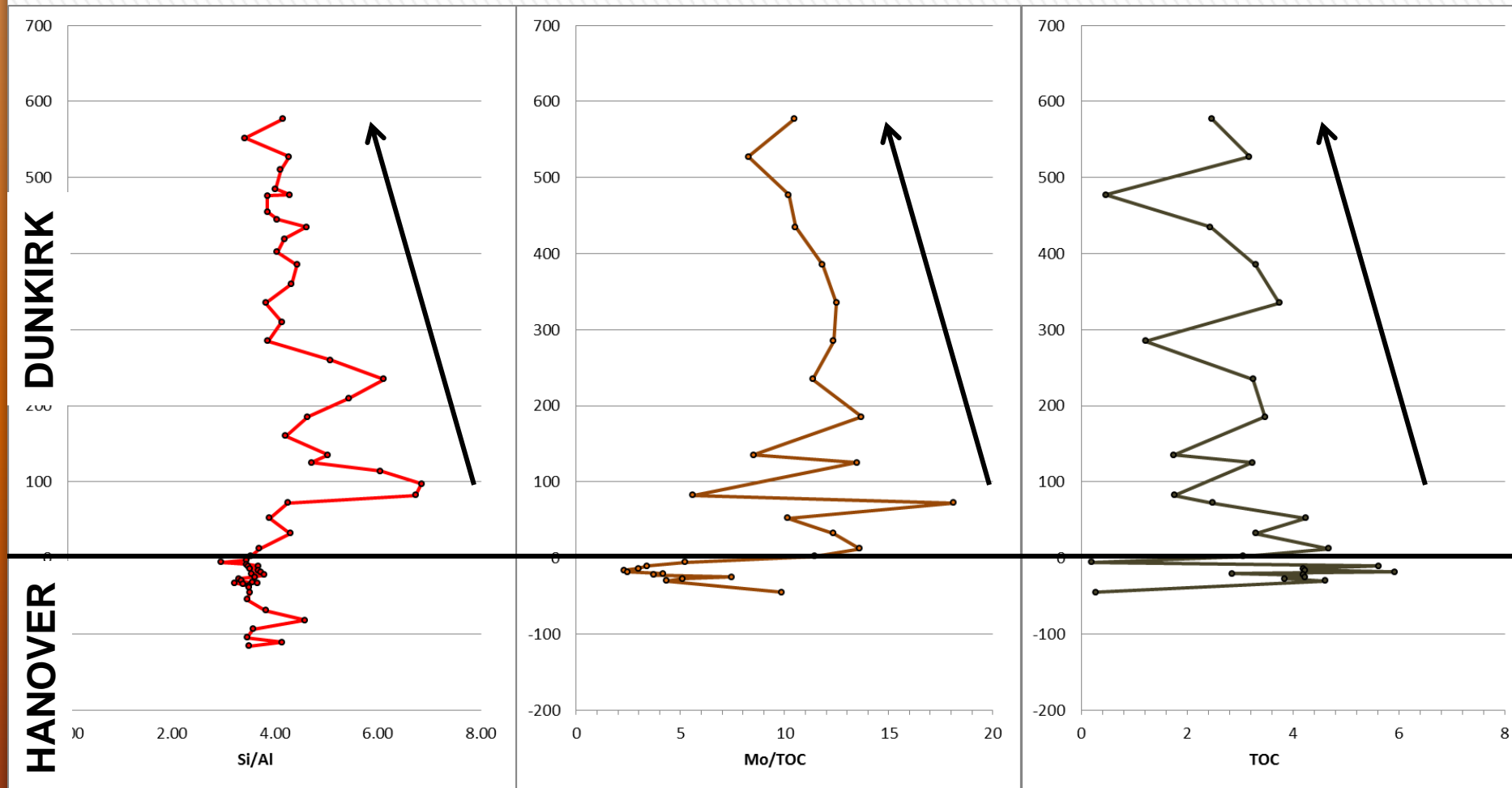
DUNKIRK SHALE MO EF VS U EF SIGNATURE



- U EF vs Mo EF of the Dunkirk shale is consistent with the particulate shuttle mechanism that operated during Marcellus deposition



DUNKIRK MO EF VS U EF SIGNATURE

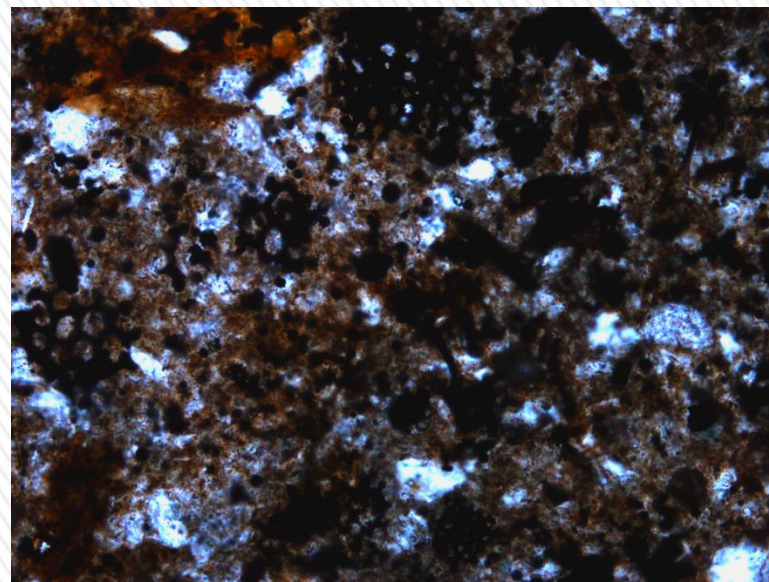
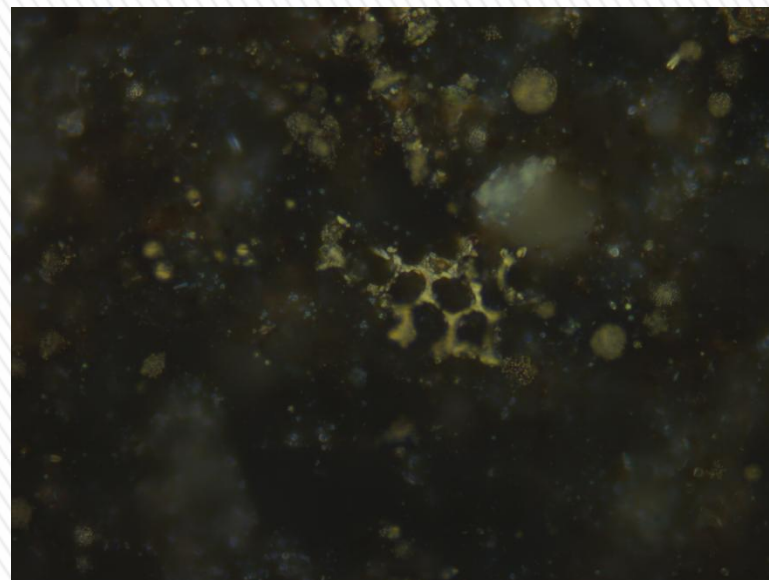
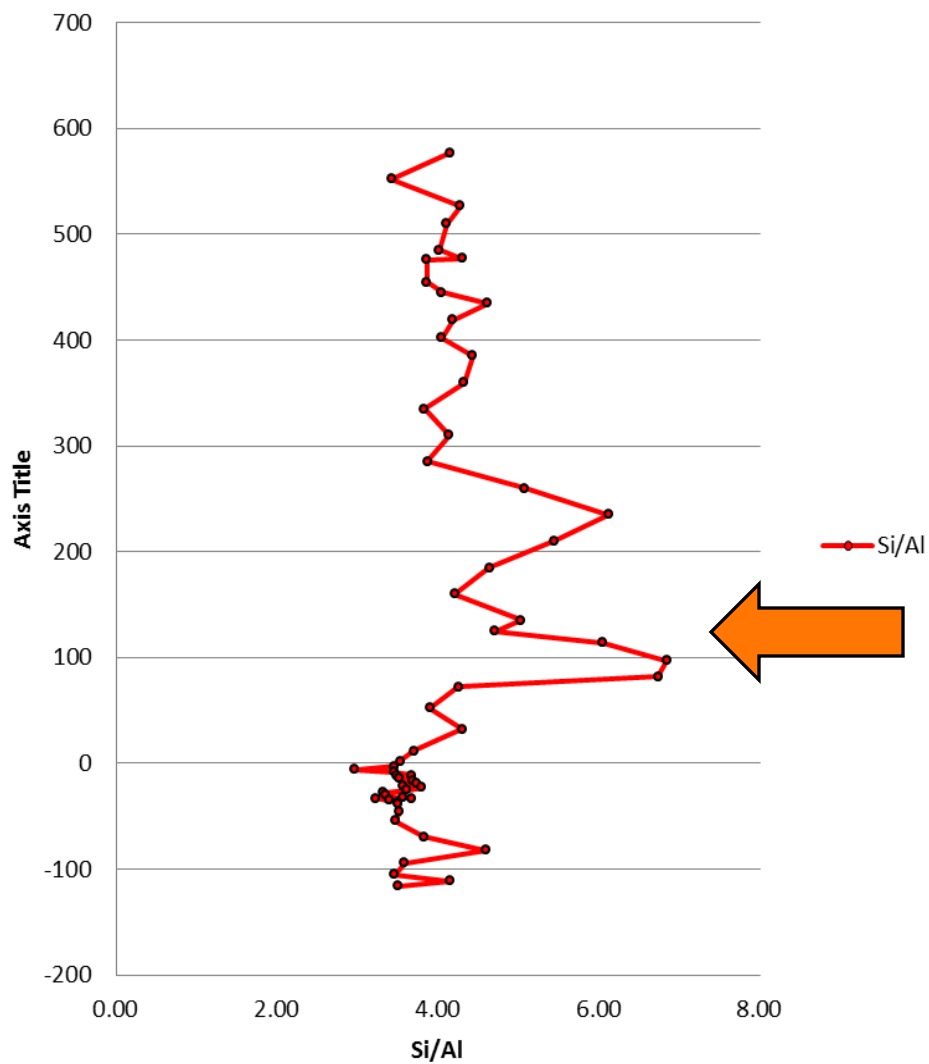


- As with the Marcellus example, Si/Al, Mo/TOC, and TOC all co-vary in the Dunkirk Shale, suggesting that renewal of basin water that supplied Mo may also have supplied the nutrients needed to stimulate primary productivity



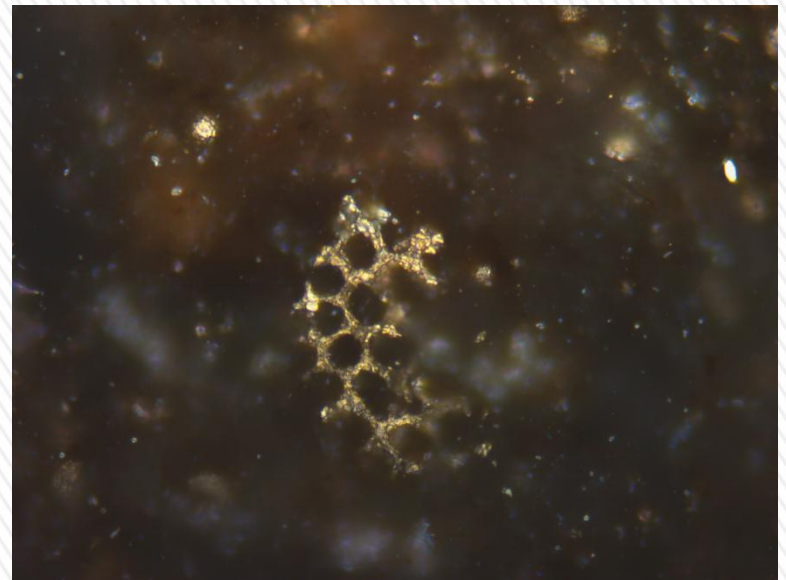
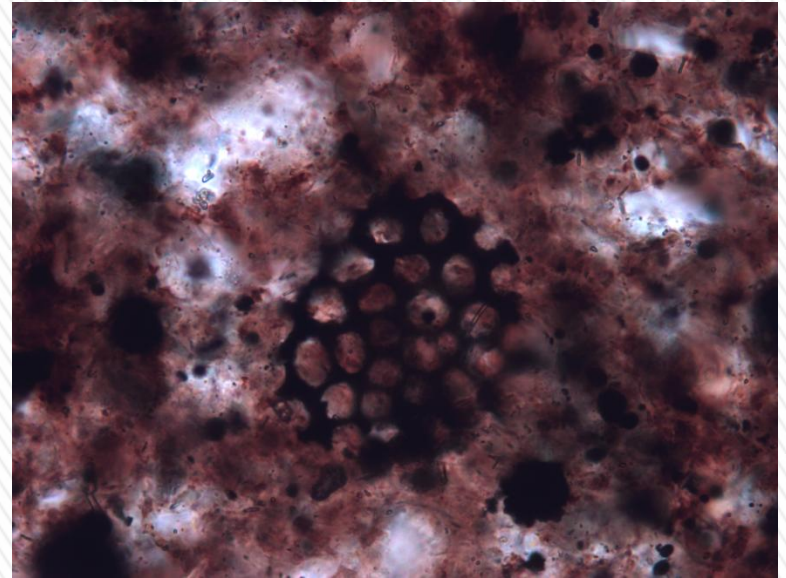
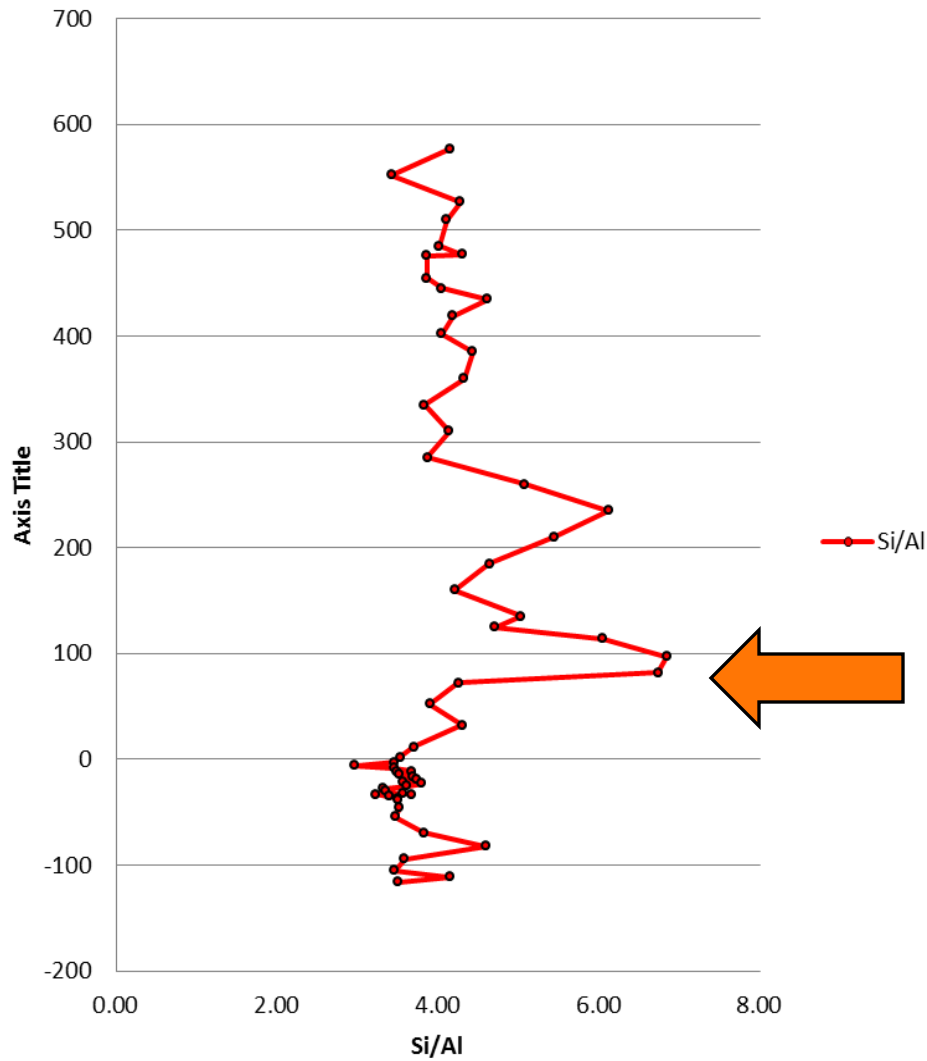
SILICA IN THE DUNKIRK SHALE

Dunkirk Shale-Pt Gratiot Section



SILICA IN THE DUNKIRK SHALE

Dunkirk Shale-Pt Gratiot Section



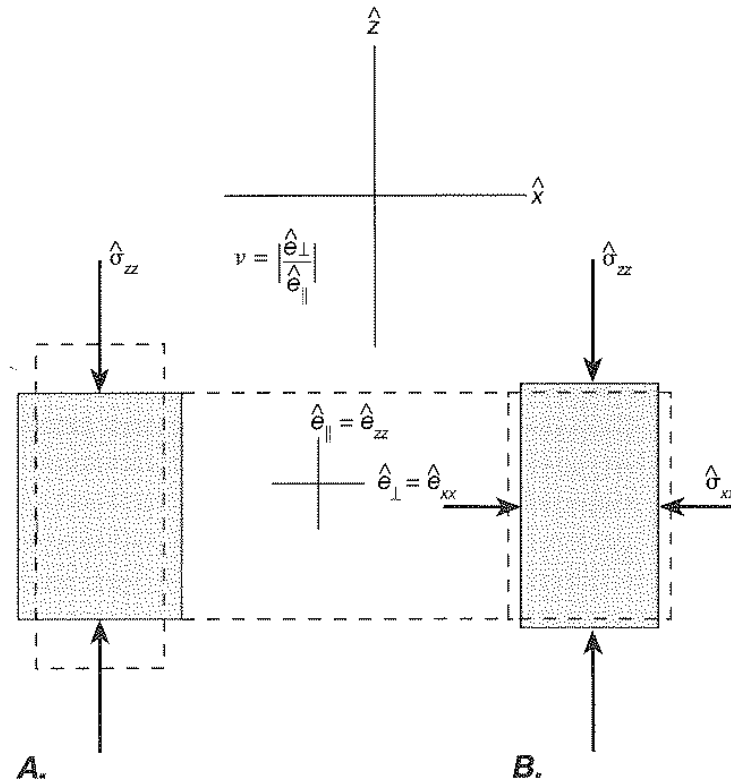
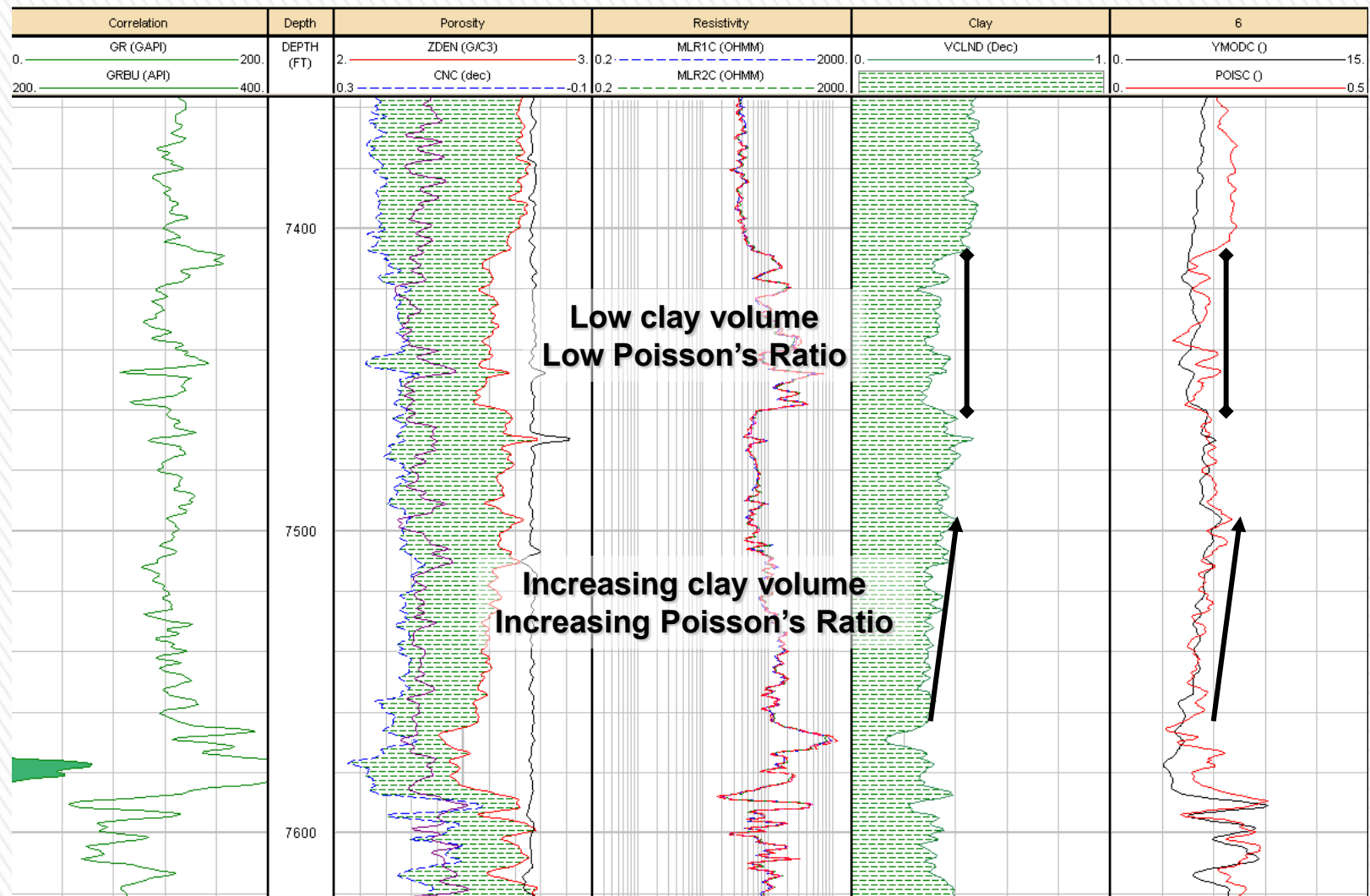


Figure 9.1 The Poisson effect. Dimensional changes are exaggerated for clarity. A. Comparing the unstressed shape (dashed rectangle) with the shape caused by uniaxial compression $\hat{\sigma}_{zz}$ (shaded rectangle) illustrates the Poisson expansion. B. If a radial pressure $p = \hat{\sigma}_{xx} = \hat{\sigma}_{yy}$ is added to the uniaxial stress in part A, the Poisson effect decreases the amount of shortening parallel to $\hat{\sigma}_{zz}$.

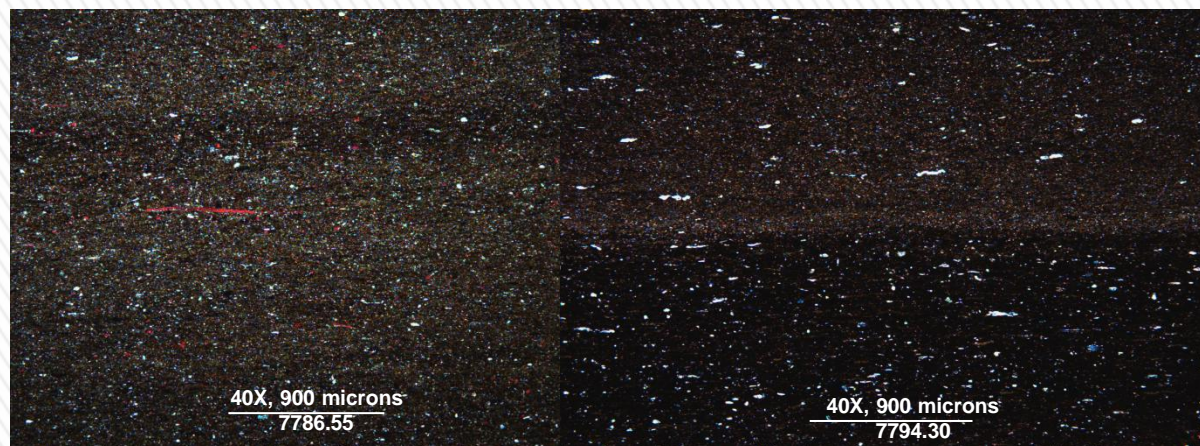
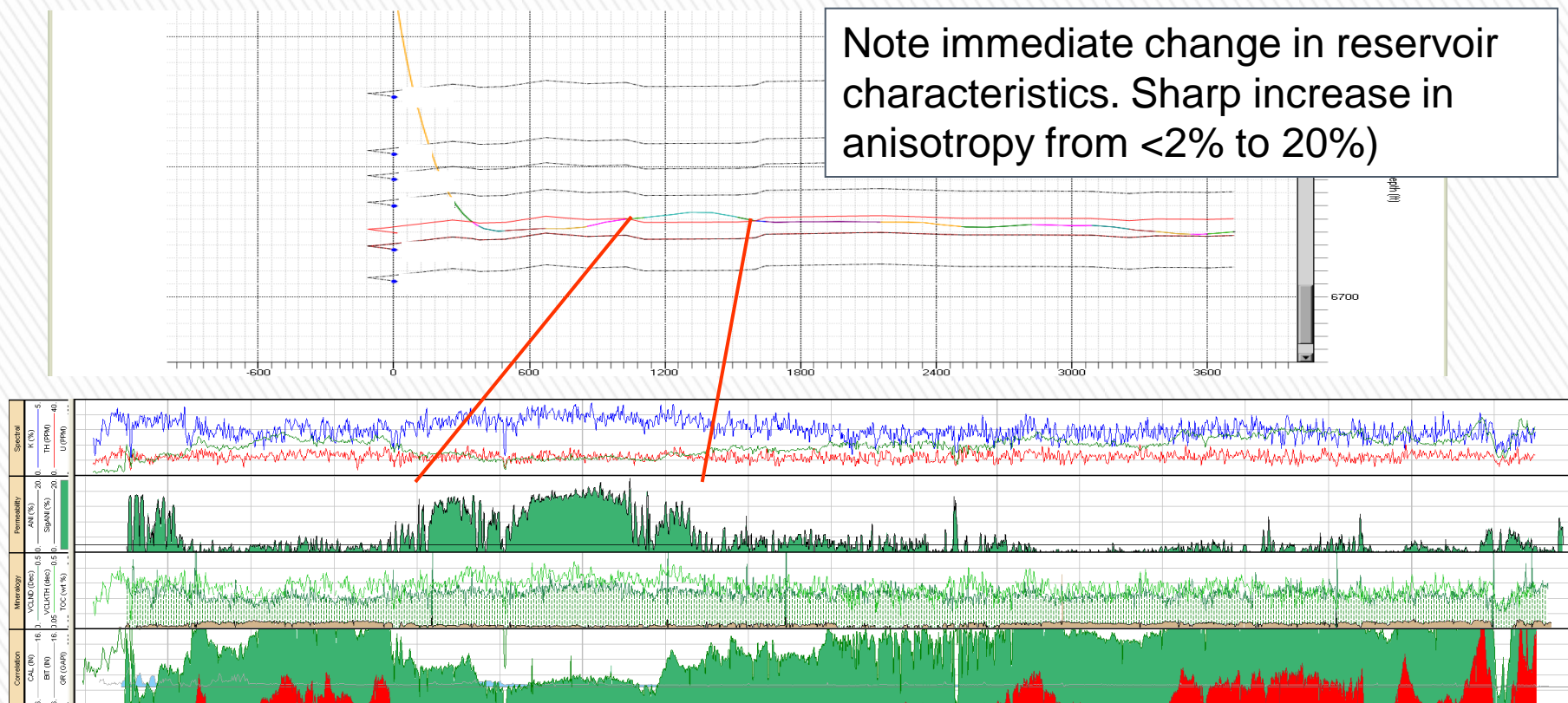
- ▶ Biogenic silica in the system limits the drilling, completion, and production issues associated with high clay volume
- ▶ The Marcellus represents the first major, and most distal black shale of the Acadian foreland basin
- ▶ Clay is the dominant detrital component
- ▶ Poisson's Ratio: a measure of the expansion of a material perpendicular to the direction of the applied force.
- ▶ Under radial stress conditions the Poisson effect is reduced (i.e. poisson expansion would be least under isotropic stress conditions)



RELATIONSHIP BETWEEN PR AND CLAY VOLUME



ANISOTROPY AND SEQUENCE STRATIGRAPHY



- Planarity of platey clay grains produces anisotropic fabric in regressive systems tract sections.



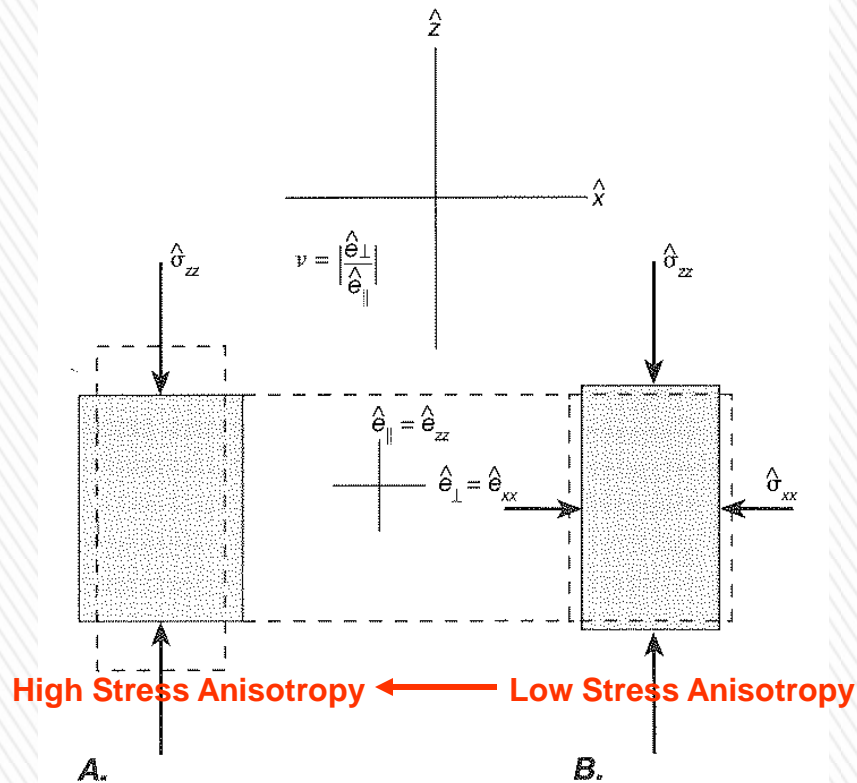


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- Poisson's Ratio: a measure of the expansion of a material perpendicular to the direction of the applied force.
- Increasing anisotropy will create conditions that are closer to the uniaxial model.
- Poisson effect will be more apparent.



$$\mathbf{E}^{\sigma_n} = \sigma_n - P_f$$

Where:

\mathbf{E}^{σ_n} is the effective normal stress

σ_n is the total normal stress

P_f is the pore fluid stress

- ▶ As the reservoir pressure is reduced via production the effective stress on the rock increases. This will result in an increase in Poisson expansion and proppant embedment in high PR (i.e. high clay) rock.



- ▶ Si/Al, Si/Zr, Ti/Al in the Marcellus suggest enrichment of biogenic silica in portions of the Marcellus shale
- ▶ Transgression and intermittent connectivity to the global ocean may have been one of the supplies for nutrients in the basin that stimulated primary productivity
- ▶ Observations in the Upper Devonian Dunkirk Shale are consistent with the presence of biogenic silica enrichment in the lower part of the section
- ▶ Biogenic silica creates a rigid high modulus framework which mitigates the adverse effects of clays with respect to completions and production.

