A Comparative Inorganic Geochemical Analysis between the Marcellus and Utica Shales Based on XRF*

Steve Saboda[1] and Gary Lash[2]

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Abstract

A comparative chemostratigraphic analysis of a Marcellus Shale core from southwestern Pennsylvania and a Utica Shale core recovered from eastern New York using handheld XRF technology reveals significant differences in the concentration of elements that serve as proxies of detrital flux and redox conditions. Perhaps the most noticeable differences between the Marcellus and Utica is reflected in the abundances of Al, a robust proxy for clay content, and redox-sensitive elements, U and Mo, both of which are especially useful to the analysis of oxygen-deficient marine systems. Though enrichment of Mo and U in marine deposits can be ascribed to the authigenic uptake from seawater enhanced by oxygen deficient conditions, authigenic enrichment mechanisms of both elements differ from each other. The Marcellus succession illustrates a general increase of Al upsection from the TST through the RST deposits. No such trends are observed in the Utica Shale, as Al remains generally consistent throughout the most organic-rich intervals. Overall, Al is higher in the Marcellus relative to the Utica, suggesting higher clay content in the former. Impressed upon the generally increasing clastic input of the Marcellus are marked redox variations indicated by U and Mo enrichment that tell of increasingly reducing environmental conditions. These data reflect sediment accumulation in an “unrestricted marine” environment setting in which the supply of Mo to the water column was renewed at a rate that exceeded its rate of sequestration in sulfidic sediment. The concentration of redox proxies in the Utica Shale core is much less than one might expect of an organic-rich black shale. Both Mo and U values are suppressed throughout much of the core and only minimally enriched within the organic-rich sections. Chemostratigraphic analysis of the Utica core suggests that the organic-rich deposits accumulated under anoxic to intermittently euxinic conditions that would have favored

the authigenic uptake of U and Mo. However, the depleted nature of the most organic-rich deposits of the Utica Shale reflect major differences between Ordovician and Devonian worlds, possibly the result of global anoxia and consequent drawdown of the global U and Mo inventory and lack of an established land plant root system that would have favored the development of clay soil profiles.

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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.

Cornell, S.R., C.E. Brett, and C.D. Sumrall, 2003, Paleoecology and taphonomy of an edrioasteroid-dominated hardground association from tentaculitid limestones in the Early Devonian of New York; a Paleozoic rocky peritidal community: Palaios, v. 18/3, p. 212-224.

Lash, G.G., and D.R. Blood, 2014, Organic matter accumulation, redox, and diagenetic history of the Marcellus Formation, southwestern Pennsylvania, Appalachian basin: Marine and Petroleum Geology, v. 57, p. 244-263.

Website

Website accessed September 16, 2015.
http://www.mcz.harvard.edu/Departments/InvertPaleo/Trenton/Intro/GeologyPage/Geologic%20Setting/paleogeogsetting.htm#easternlaurentia

A comparative inorganic geochemical analysis between the Marcellus and Utica Shales based on XRF data

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Gary G. Lash, SUNY Fredonia

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Utica Shale Research

- **Analyzing a Utica Shale Core by use of XRF (X-ray fluorescence) and SEM (scanning electron microscope) in order to:**

    1. Generate chemostratigraphy: Higher resolution than typical well logs
    2. Asses trace element signatures to define hydrographic conditions of the ocean
    3. Work aims to produce high resolution stratigraphy that could be useful for the placement of lateral well-bores
    4. Understanding the controlling mechanisms of the formation of organic rich-deposits

- **Focus is on the lower most section defining the contact between the Utica Shale and Trenton Limestone**
    - High TOC
    - Subdued GR (unusual)
    - Why?
    - Chemostratigraphic comparison between the Utica and Marcellus

Introduction to Chemostratigraphy

- **Chemostratigraphy** – especially suited to the study of fine-grained, seemingly homogenous deposits.

- Variations in elemental concentrations, elemental ratios, and elemental enrichments relative to average shale values reflect changes in such parameters as paleoclimate, hydrographic conditions of the paleocean (including paleoredox conditions and oceanic anoxic events), and mineralogy.

- Allows for high resolution correlation of cm-scale units

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Analytical Approach

- **Handheld XRF (HHXRF) analyzer**
  - **Thermo Scientific Niton XL3t 950 GOLDD +**
  - **Equipped with a silicon drift detector & helium purge system**
  - **Hand (outcrop) samples, core, cuttings**
  - **HHXRF analysis is non-destructive and enables one to readily analyze on a cm-scale**
    - **Analysis of Utica core at 6” resolution**
  - **Provides elemental abundances with detection limits in the low ppm**

Analytical Approach

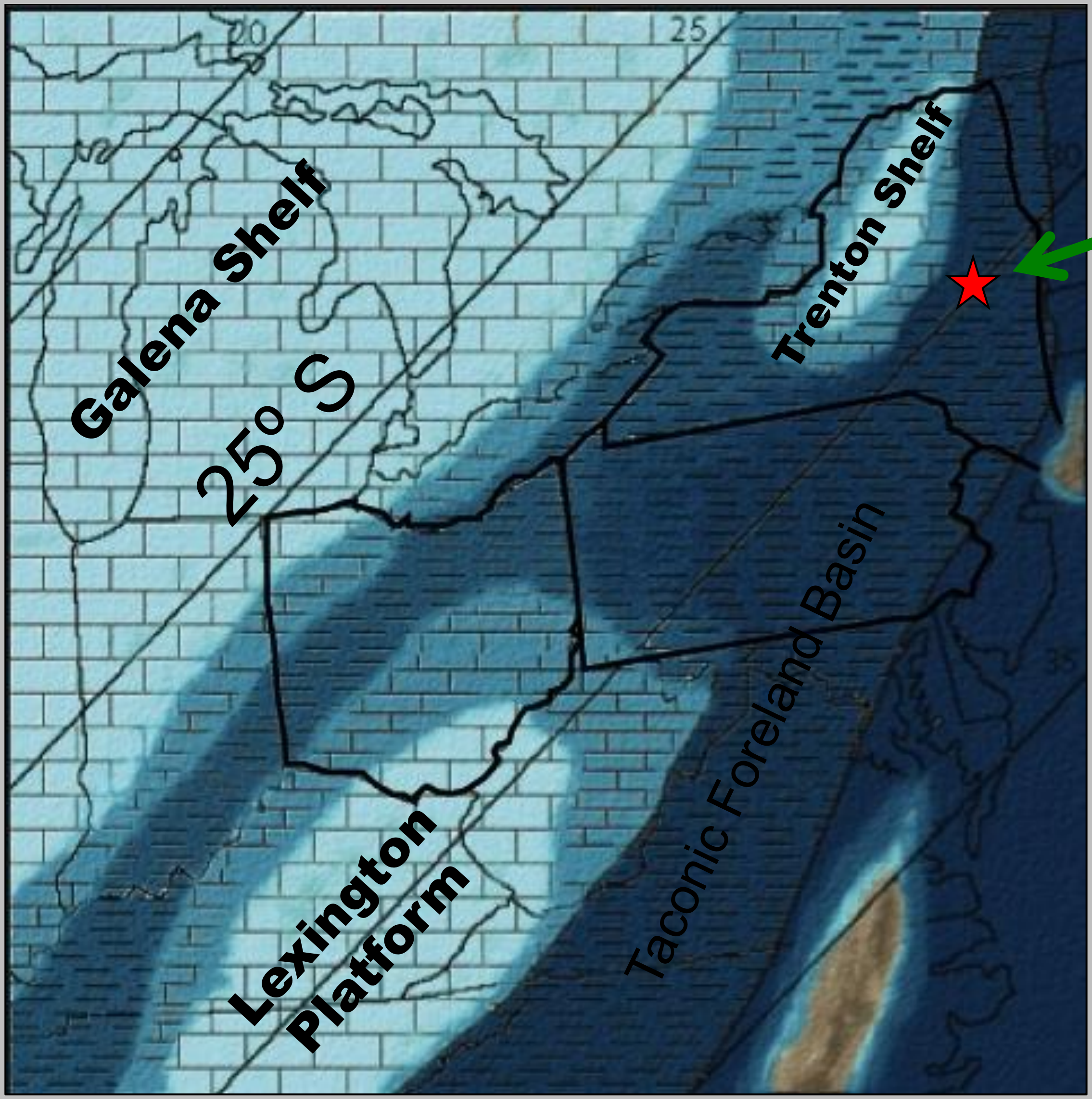
- **Smith and Malice (2010)**
  - Comparison of HHXRF technology with results of independent laboratory ICP-MS methodology
  - 160 sedimentary rock samples of mixed lithologies
- **Very strong correlations ($r^2 > 0.90$) with laboratory ICP-MS data for most major, minor and trace elements from Mg to U**
- **Repeatability (<5% relative standard deviation)**

Analytical Approach

- Differences in data sets can arise from the sample preparation procedure employed by labs versus the direct measurements *in situ* by HHXRF

- **Test Standards**
  - Certified powered samples, including U.S.G.S shale standards SGR-1b Green River Shale and SBC-1 (Brush Creek Shale)

- **Optimal Exposure Time**
  - Test exposure times ranged from 60 to 360 seconds
  - Elemental abundances of each test plotted against respective exposure times to ascertain at what point abundance-exposure time curves changed trend from one of increasing abundances with increasing exposure time to essentially constant elemental concentration with increasing exposure time
  - **150 seconds is optimal**



Modified after Cornell (2003)

http://www.mcz.harvard.edu/Departments/InvertPaleo/Trenton/Intro/GeologyPage/Geologic%20Setting/paleogeogsetting.htm#easternlaurentia

Utica Shale ("sooty" black)

Trenton

1063'

1073'

- Lithology easily identified
- Sharp contact unmistakably recognized

gray interval

Utica Shale (“sooty” black)

1044’

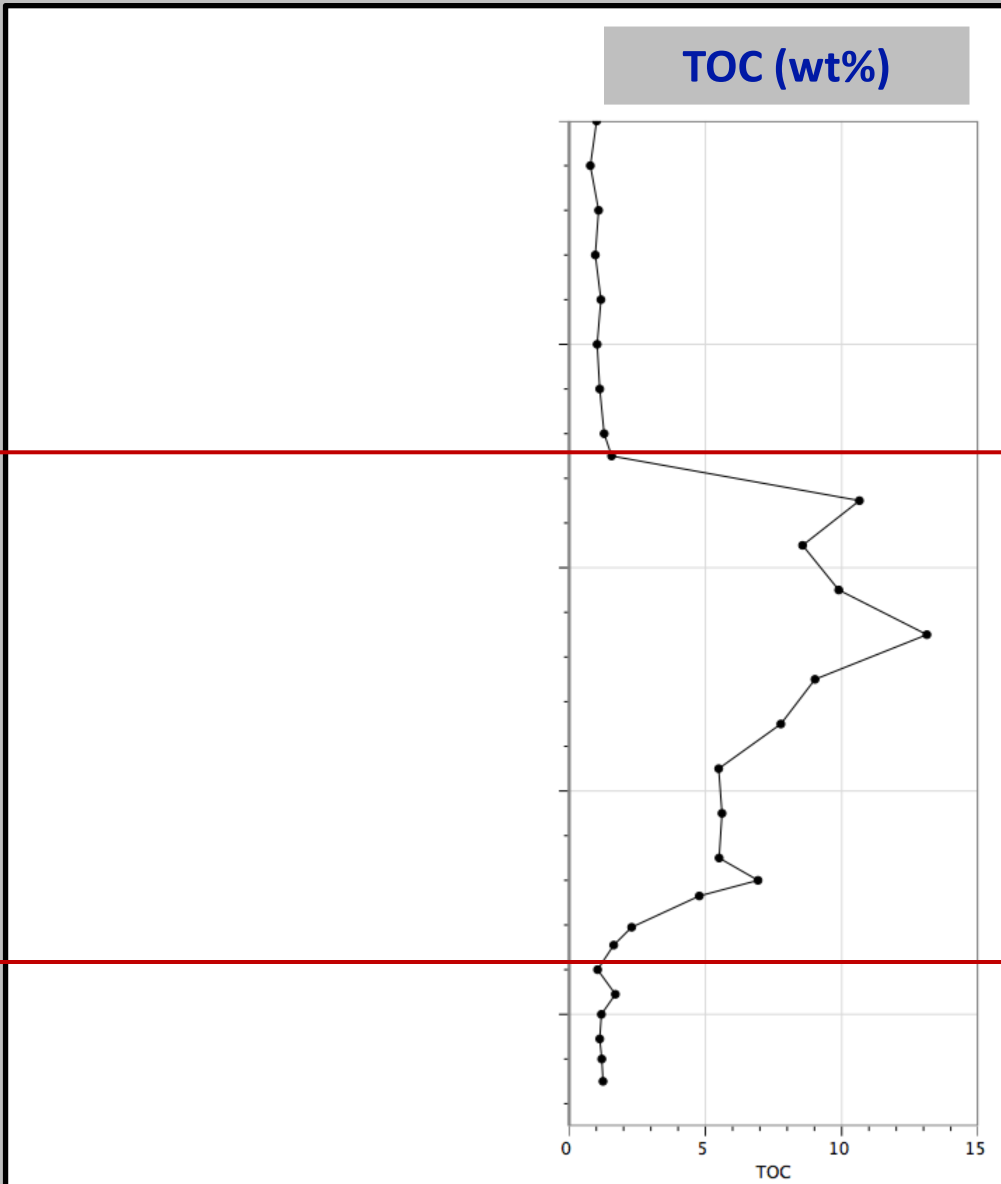
1054’

- Up-section a few meters
- Sharp contact between “sooty” black shale and black (gray) shale

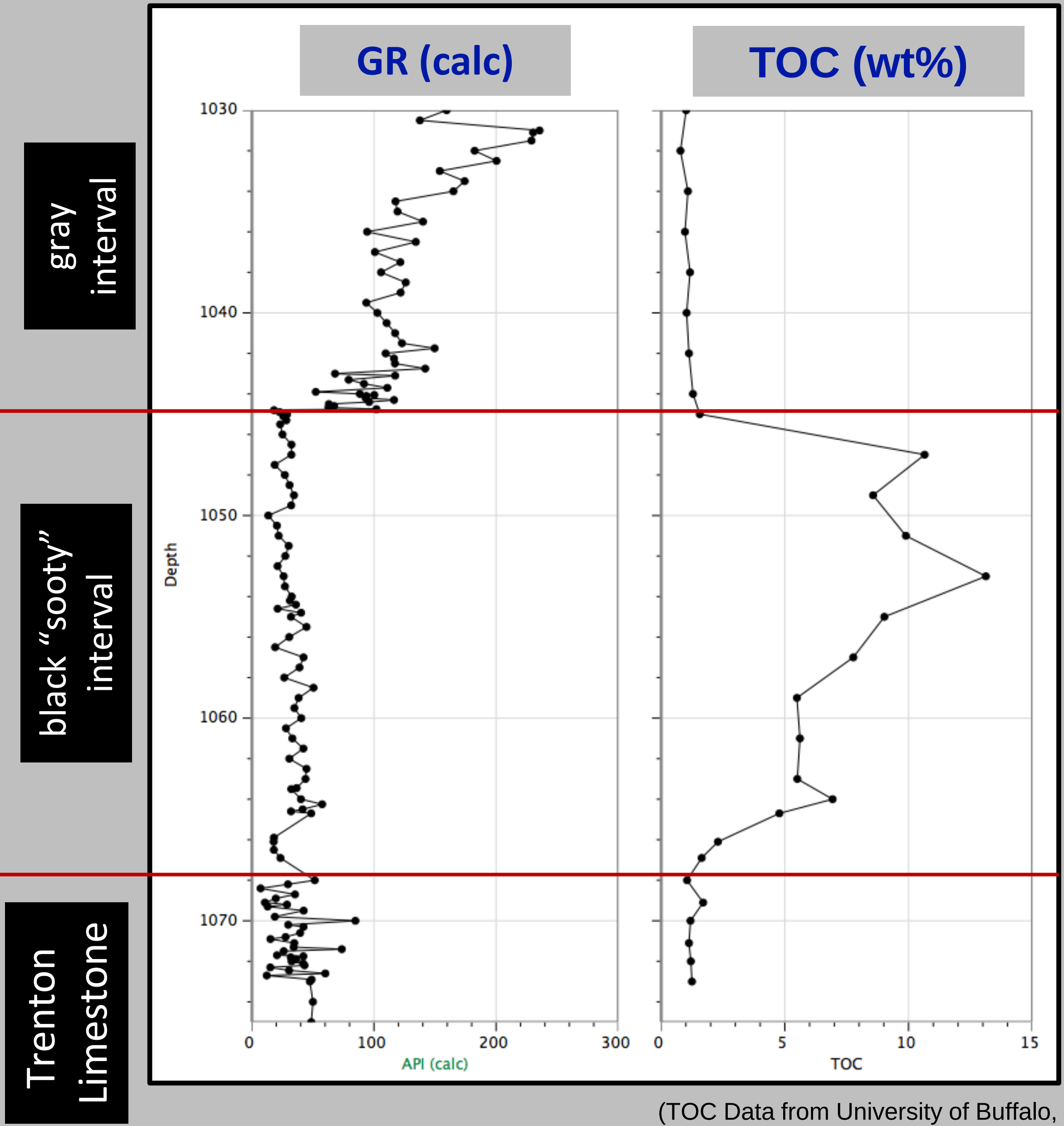
gray interval

black “sooty” interval

Trenton Limestone



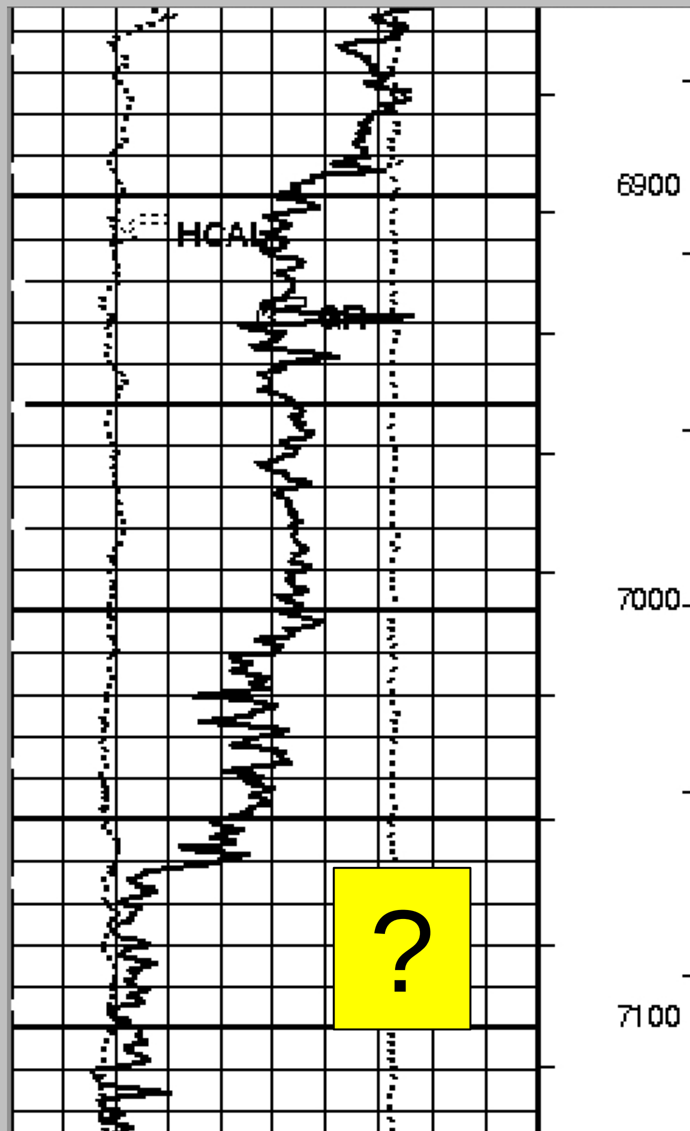
(TOC Data from University of Buffalo, Jones 2013; C. E. Mitchell)



- Unusual that GR is subdued although TOC is high
- Spectral GR by XRF (U,K,Th)
- Conventional wisdom: organic-rich shale can be identified by GR
- Reflecting increased abundance of TOC
- Not the case for the Utica Shale
- Chemostratigraphic analysis places contact within Utica Shale

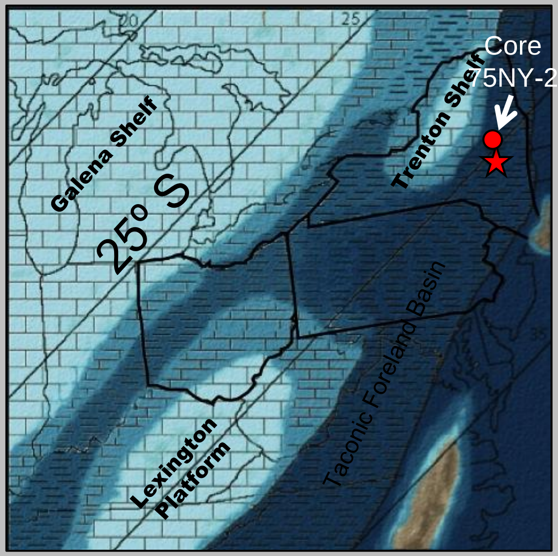
(TOC Data from University of Buffalo, Jones 2013; C. E. Mitchell)

gamma ray



Utica Shale

Trenton Limestone



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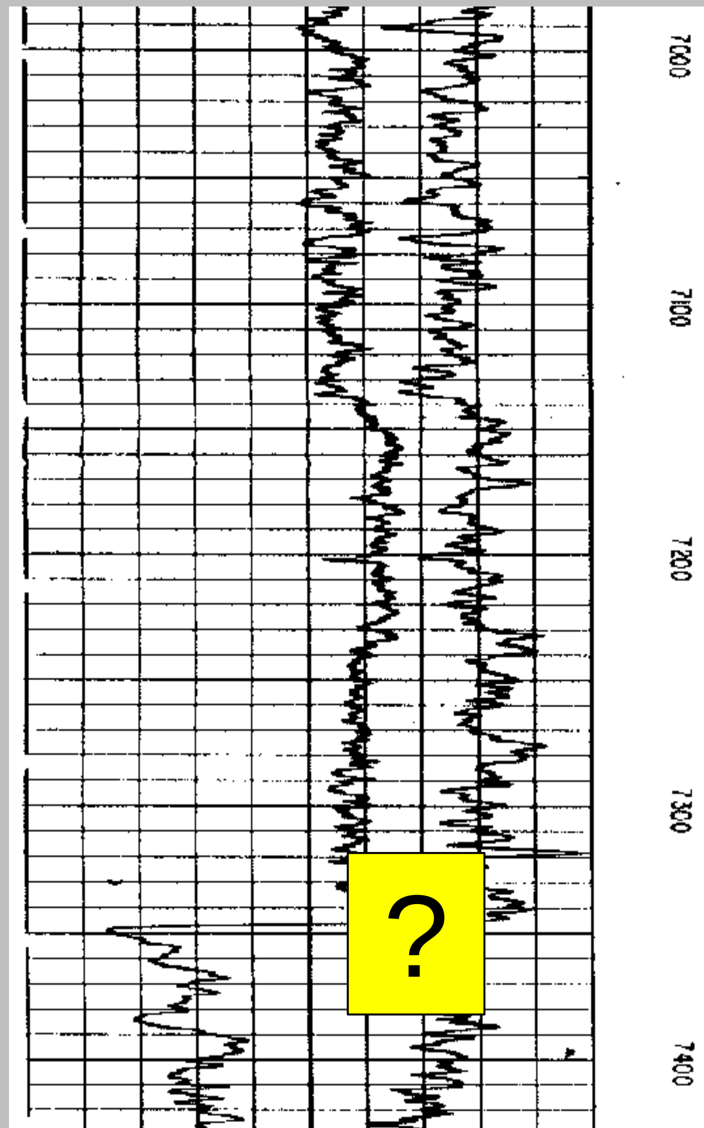
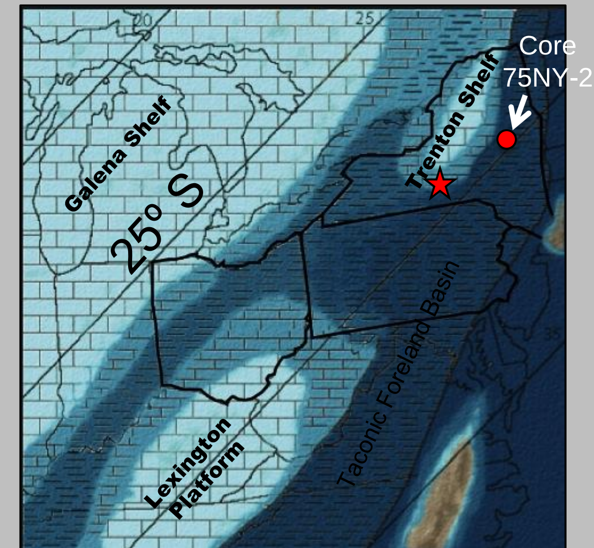
- eastern NY
- Near core 75NY-2

gamma ray



Utica Shale

Trenton Limestone



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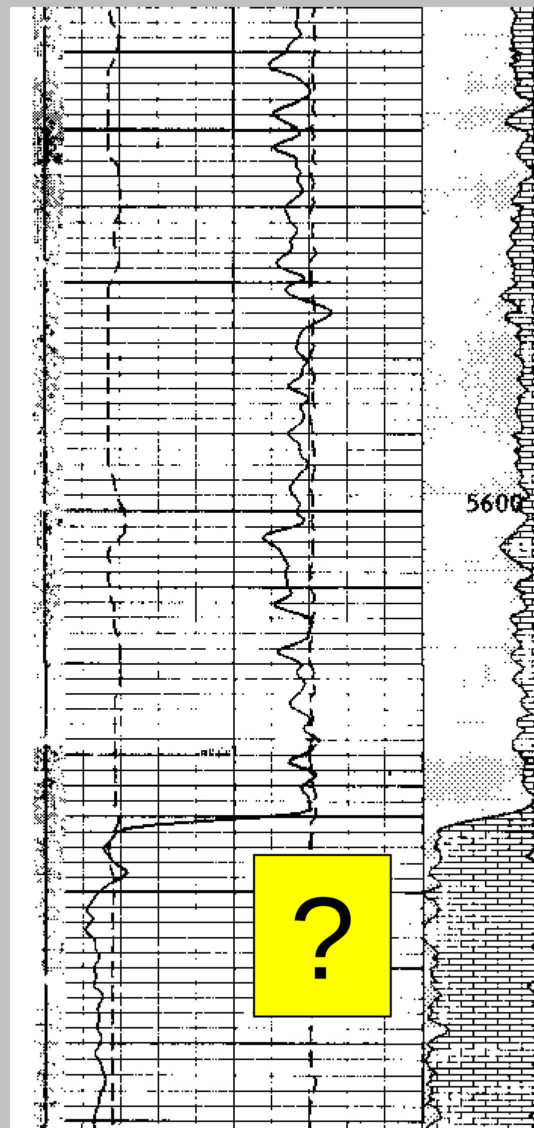
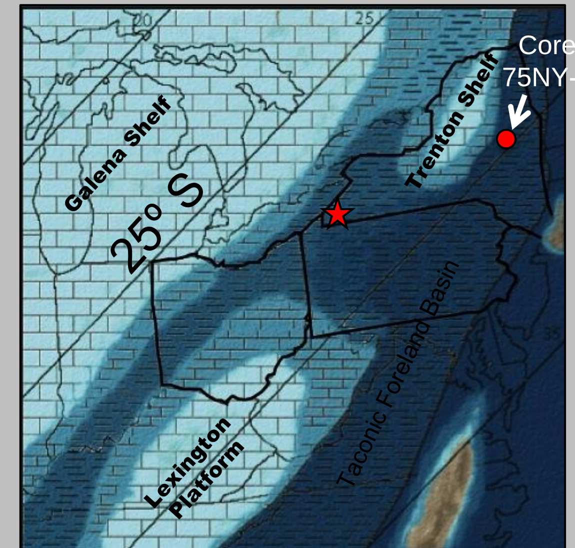
Tompkins County, NY

gamma ray



Utica Shale

Trenton Limestone



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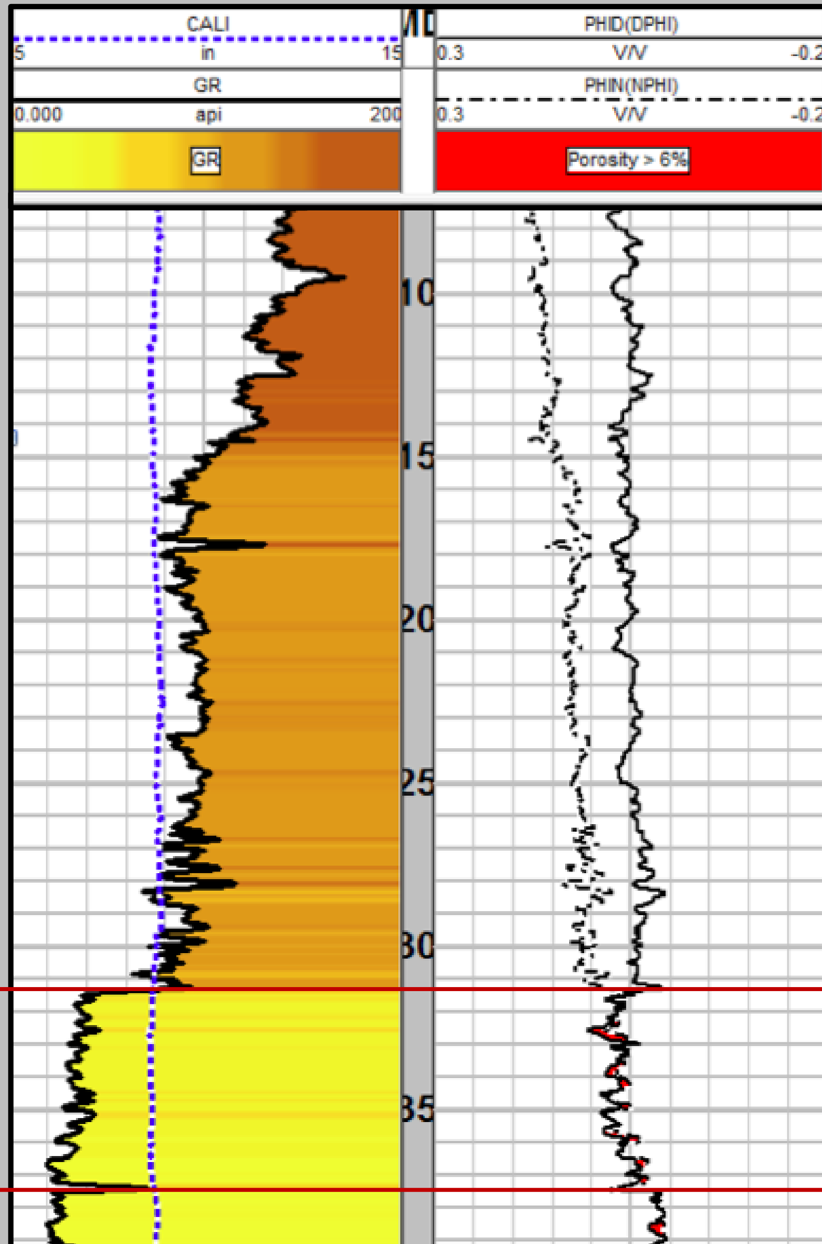
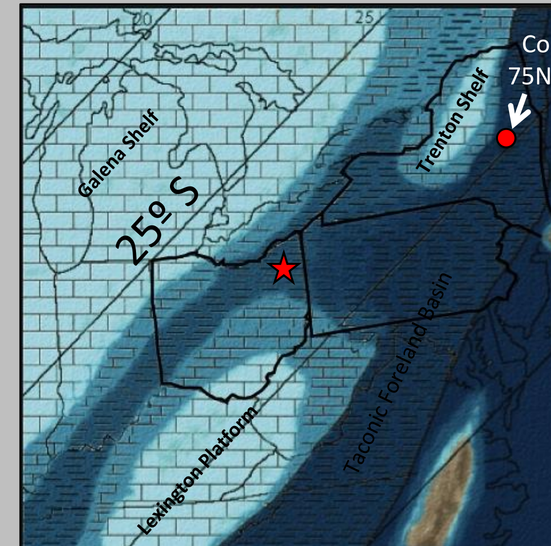
Chautauqua County, NY



Utica Shale

Point Pleasant

Trenton Limestone



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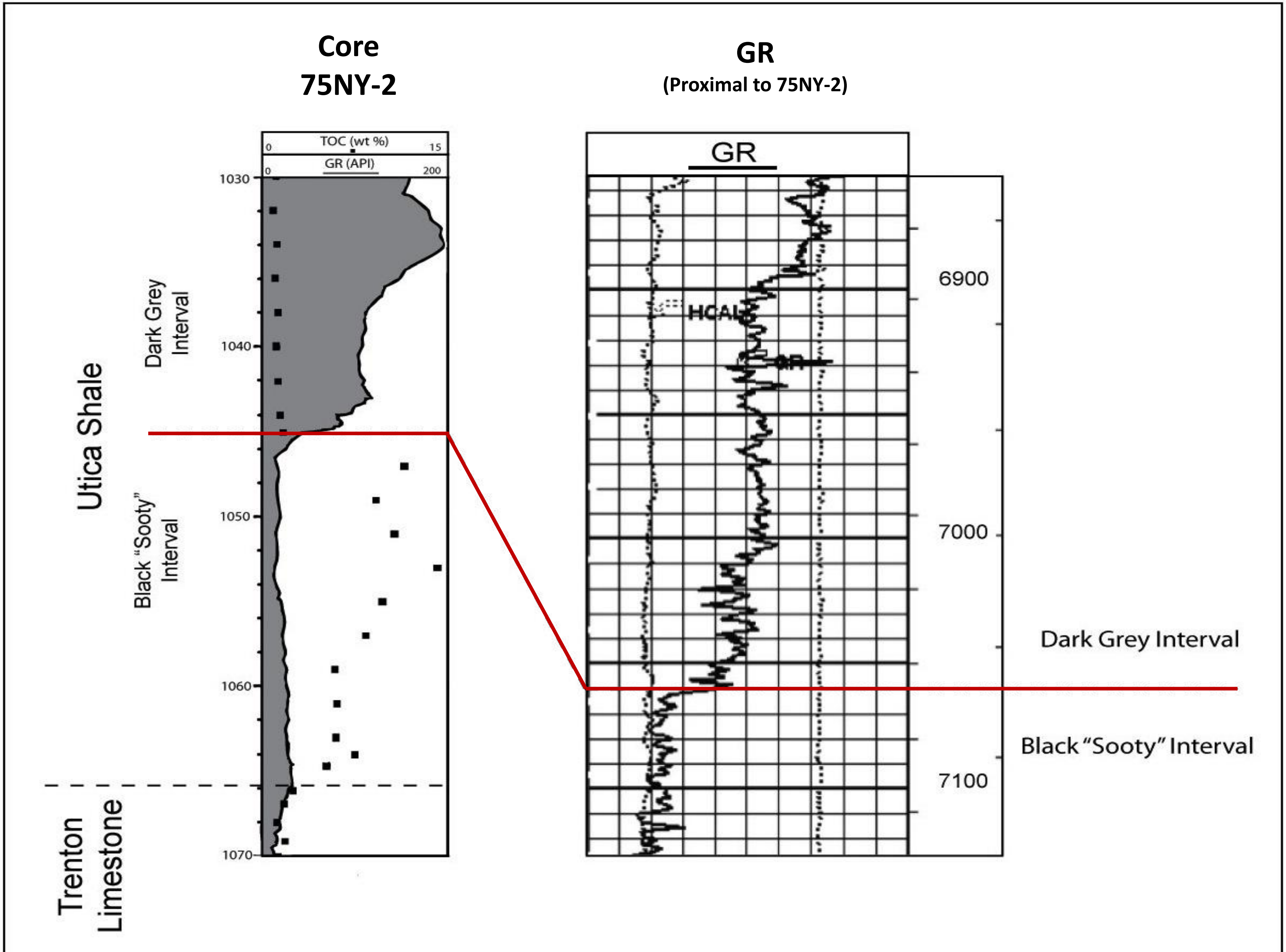
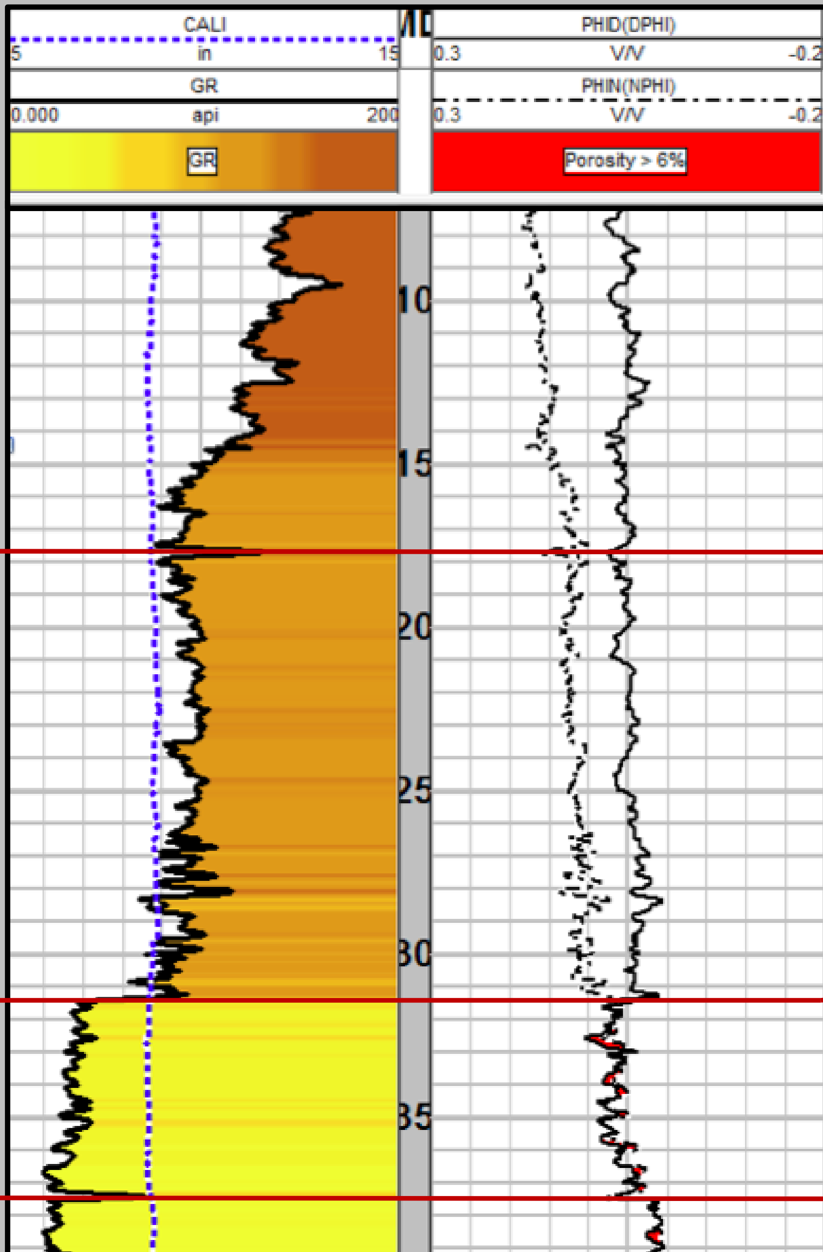
Ohio

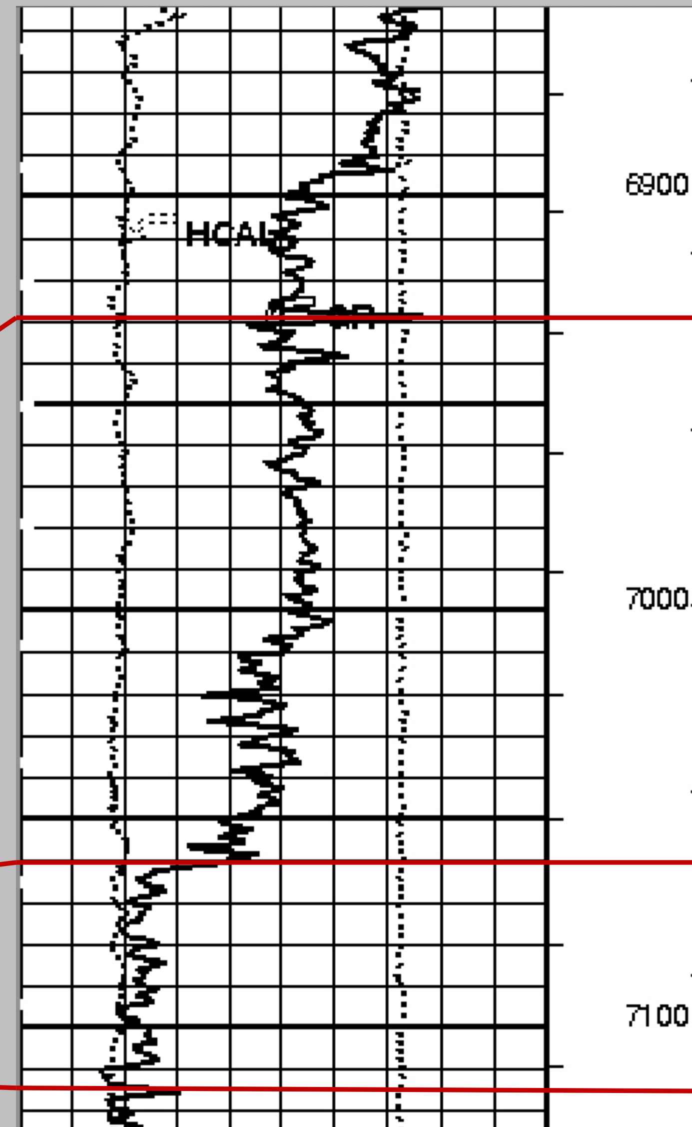


Core
75NY-2
GR
(Proximal to 75NY-2)
TOC (wt %)
0
15
GR (API)
0
200
1030
1040
1050
1060
1070
Utica Shale
Dark Grey Interval
Black "Sooty" Interval
Trenton Limestone
GR
HCAL
GR
6900
7000
7100
Dark Grey Interval
Black "Sooty" Interval

Ohio



New York
(Proximal to 75NY-2)

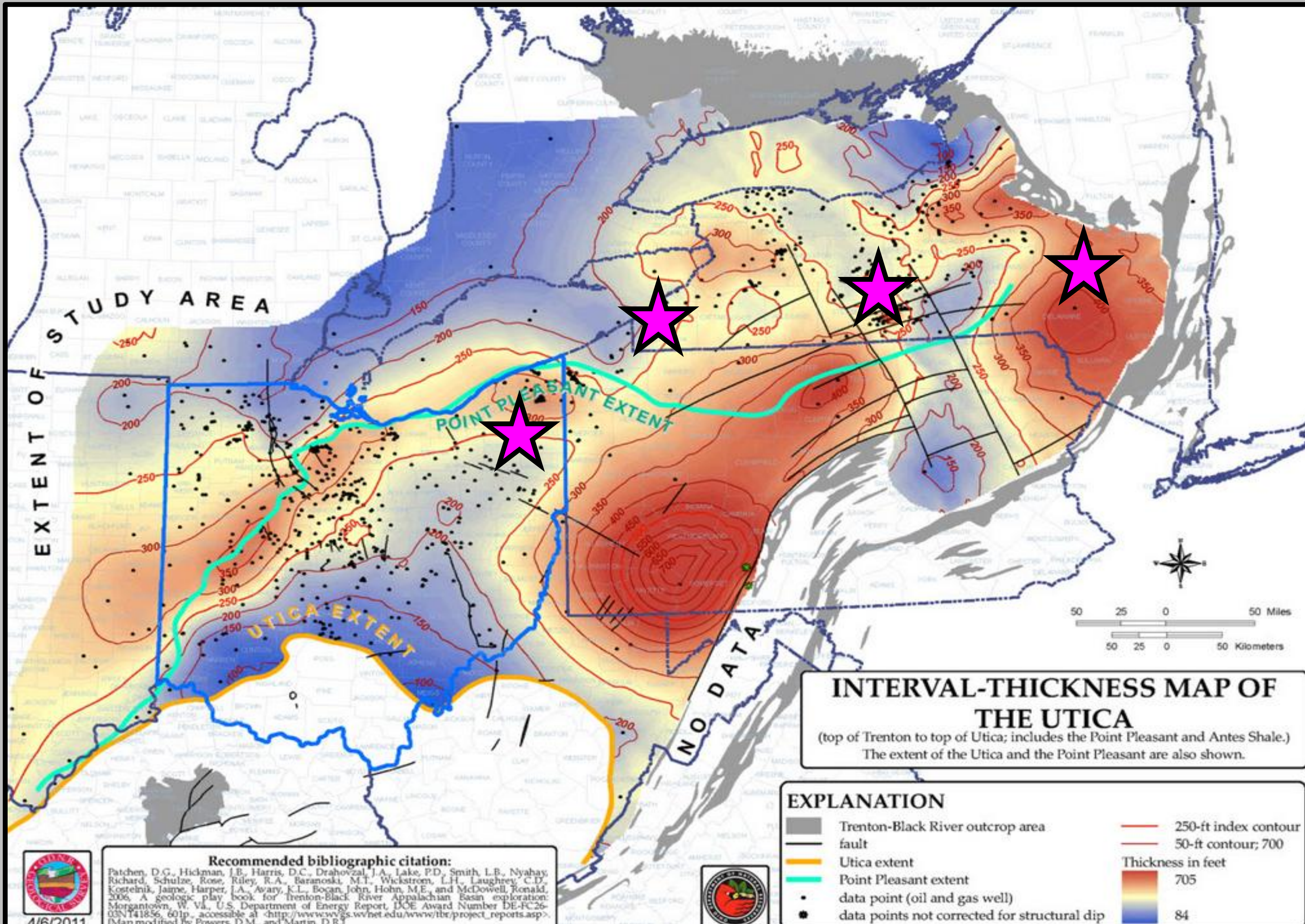


UTICA

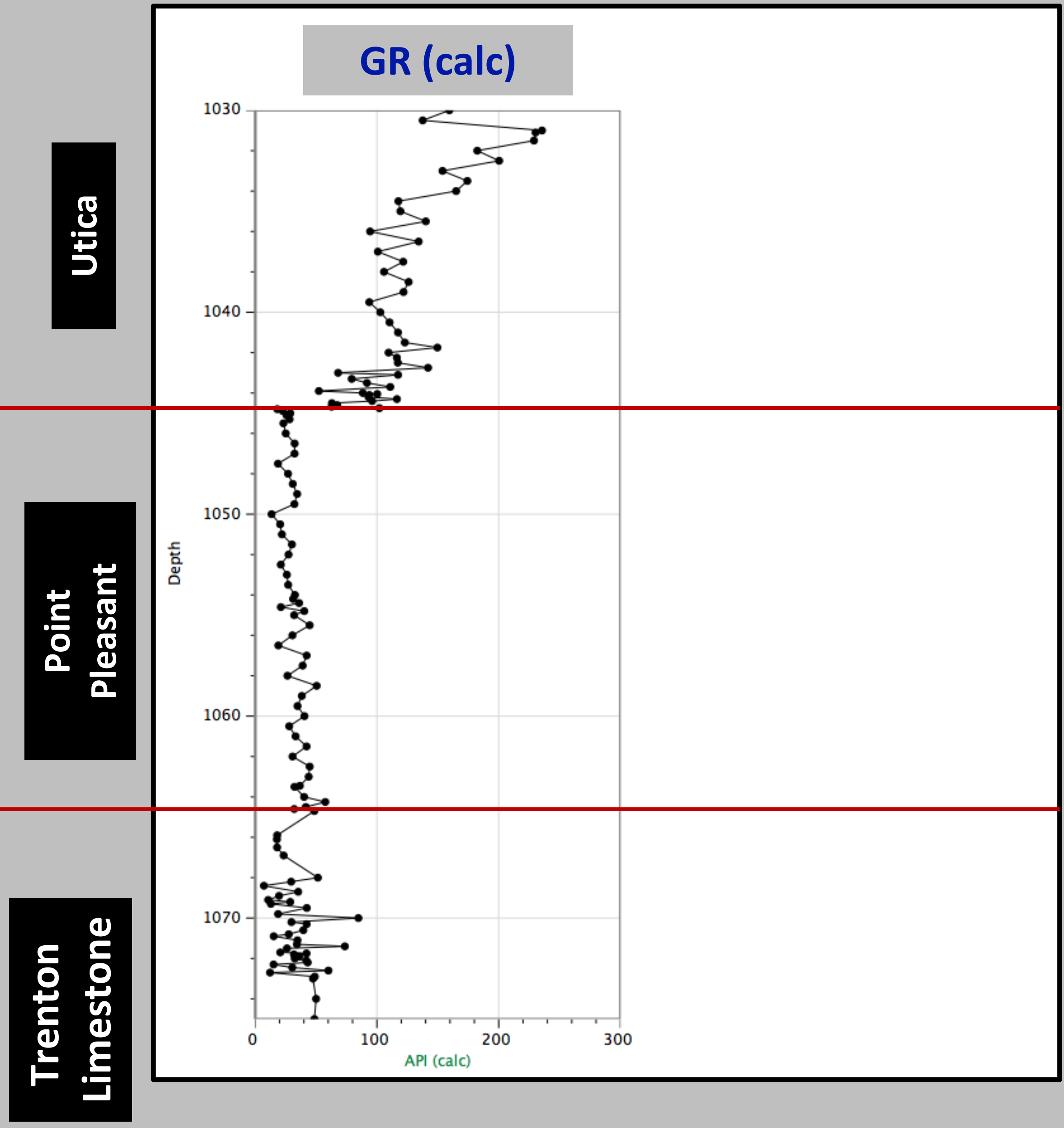
PPLS

TRNN

What is the extent of the Point Pleasant ?

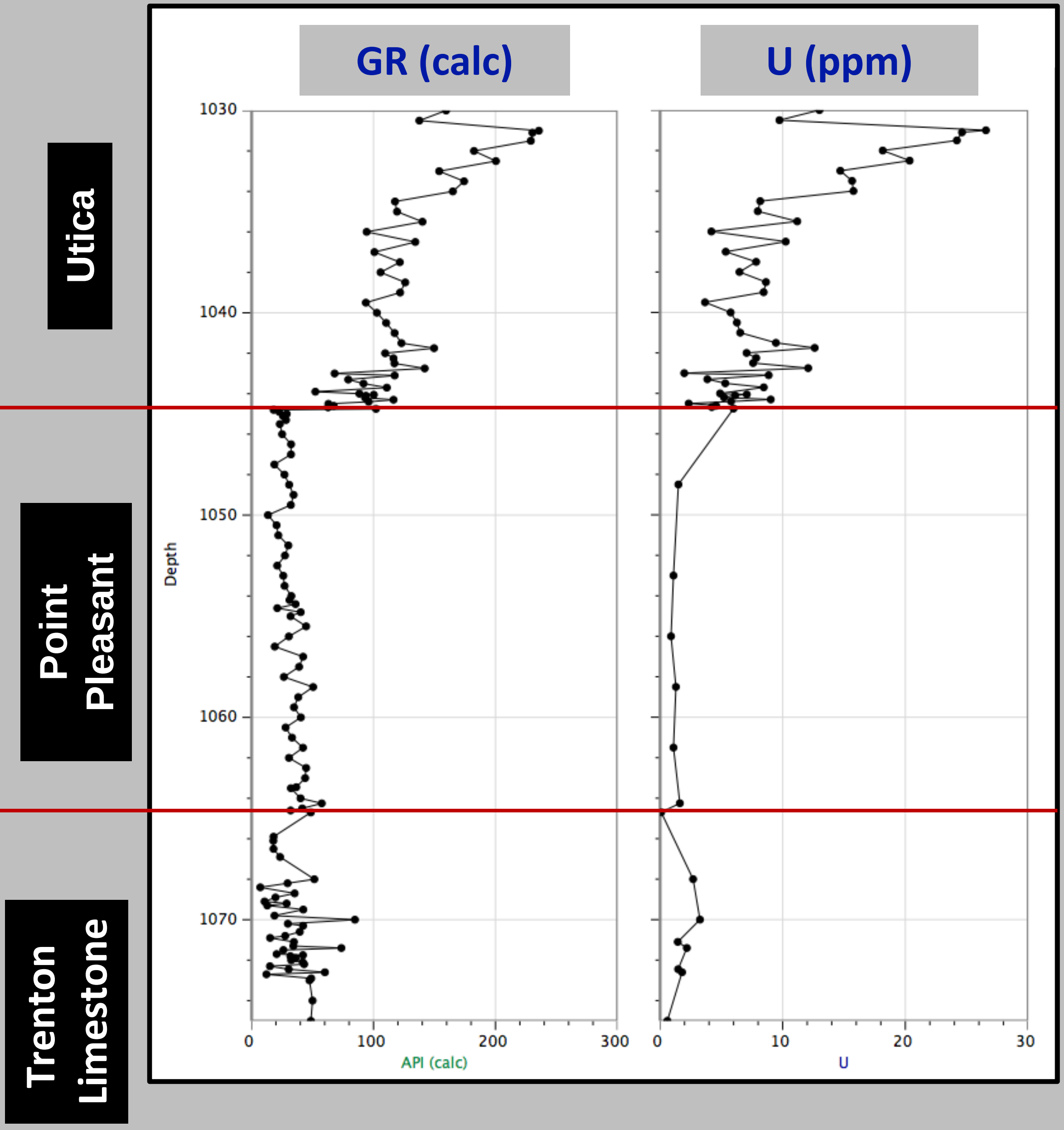


Low Gamma Ray ?



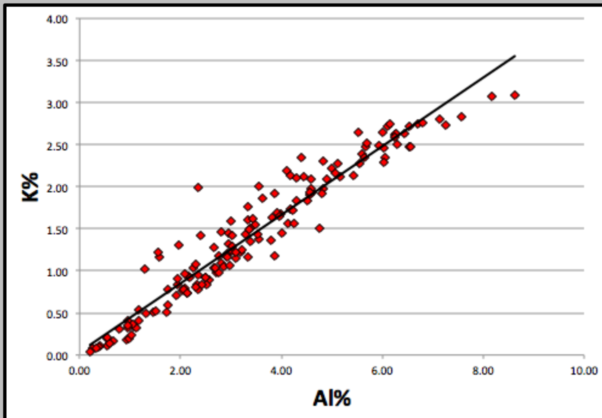
Why ?

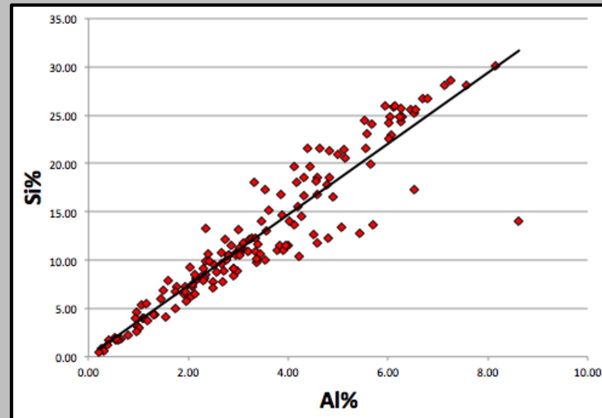
Low Uranium



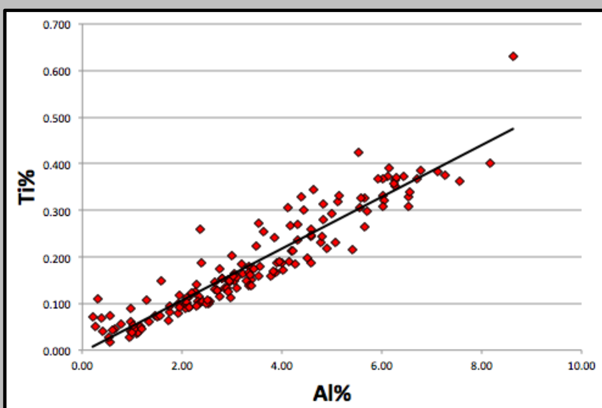
- U profile indicates values close to or even depleted to crustal values (U = 2.7 ppm)
- Contact organic-rich & organic-lean correlates to an increase of:
  - Somewhat in excess
  - Values not as expected (both intervals)
- What controls U precipitation?
  - rate of sedimentation (dilution)
  - authigenic carbonate
  - redox conditions

Detrital Proxies

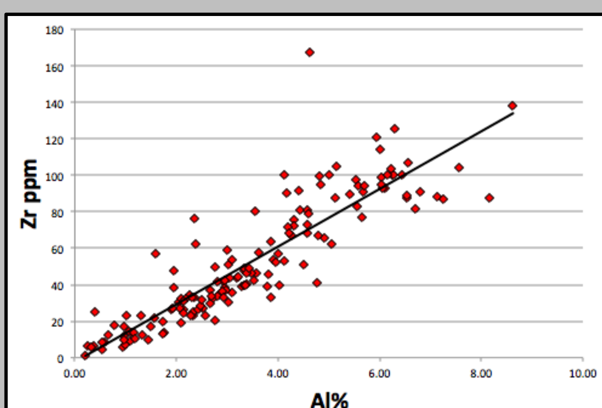




Scatter plot interval



Clastic Trend

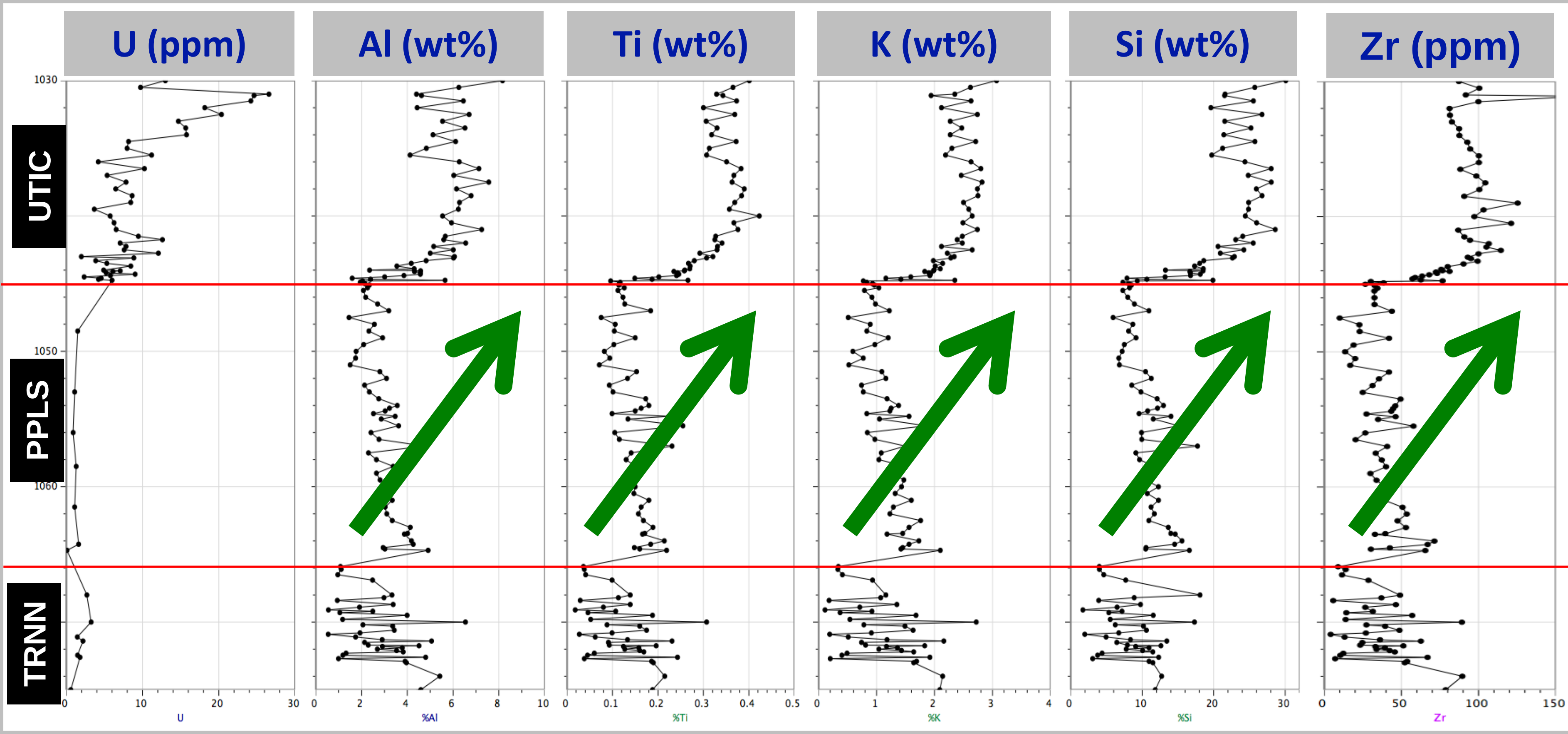


- Aluminum is a robust proxy for clay
- Any deviation from the clastic trend may have resulted from:

  Eolian input
  Biogenic sources
  Increased energy
  Weathering
  Change of source provenance

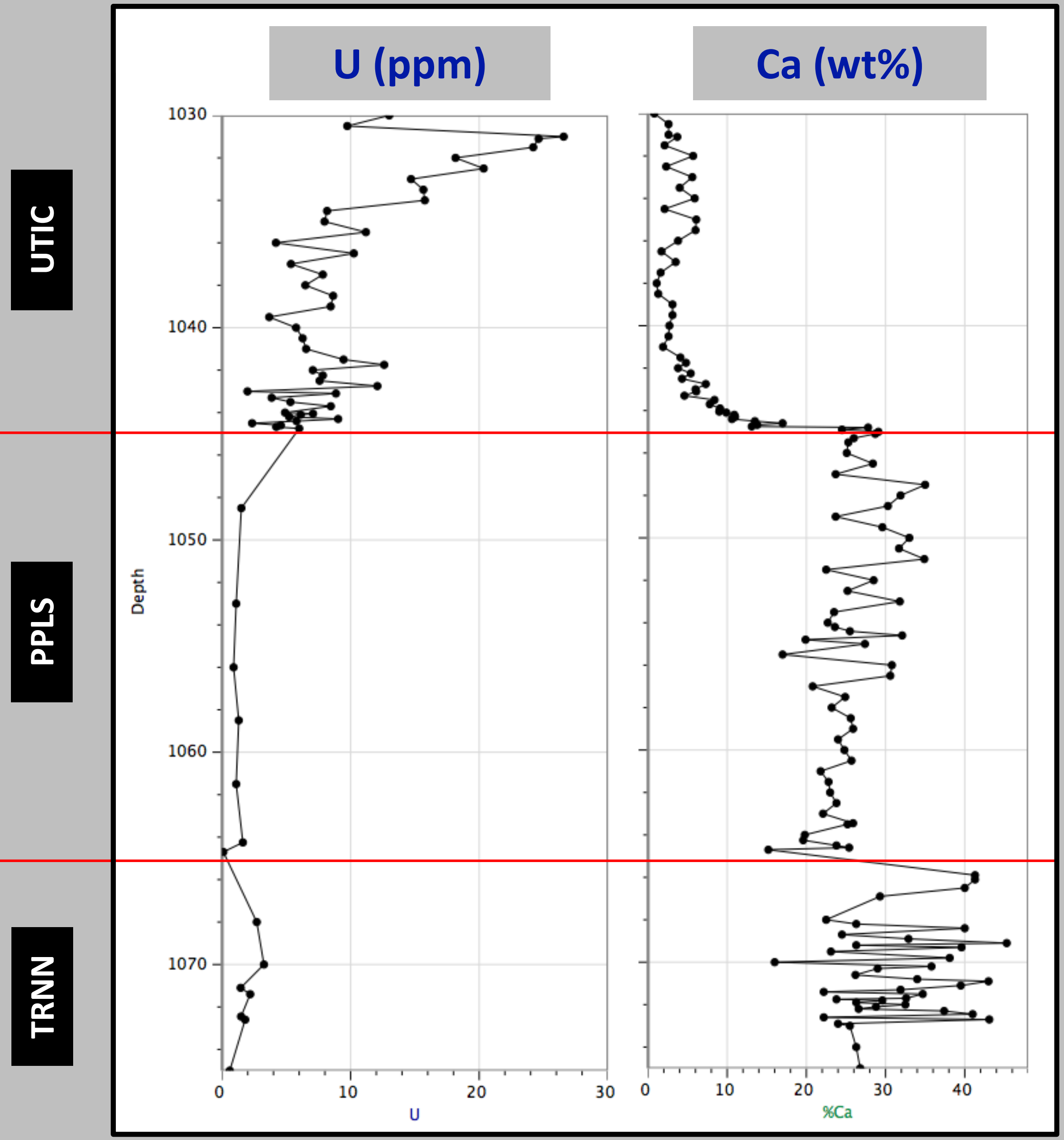
- A strong correlation exist between well known detrital proxies K, Ti, Si, Zr and Al

Dilution of Uranium ?



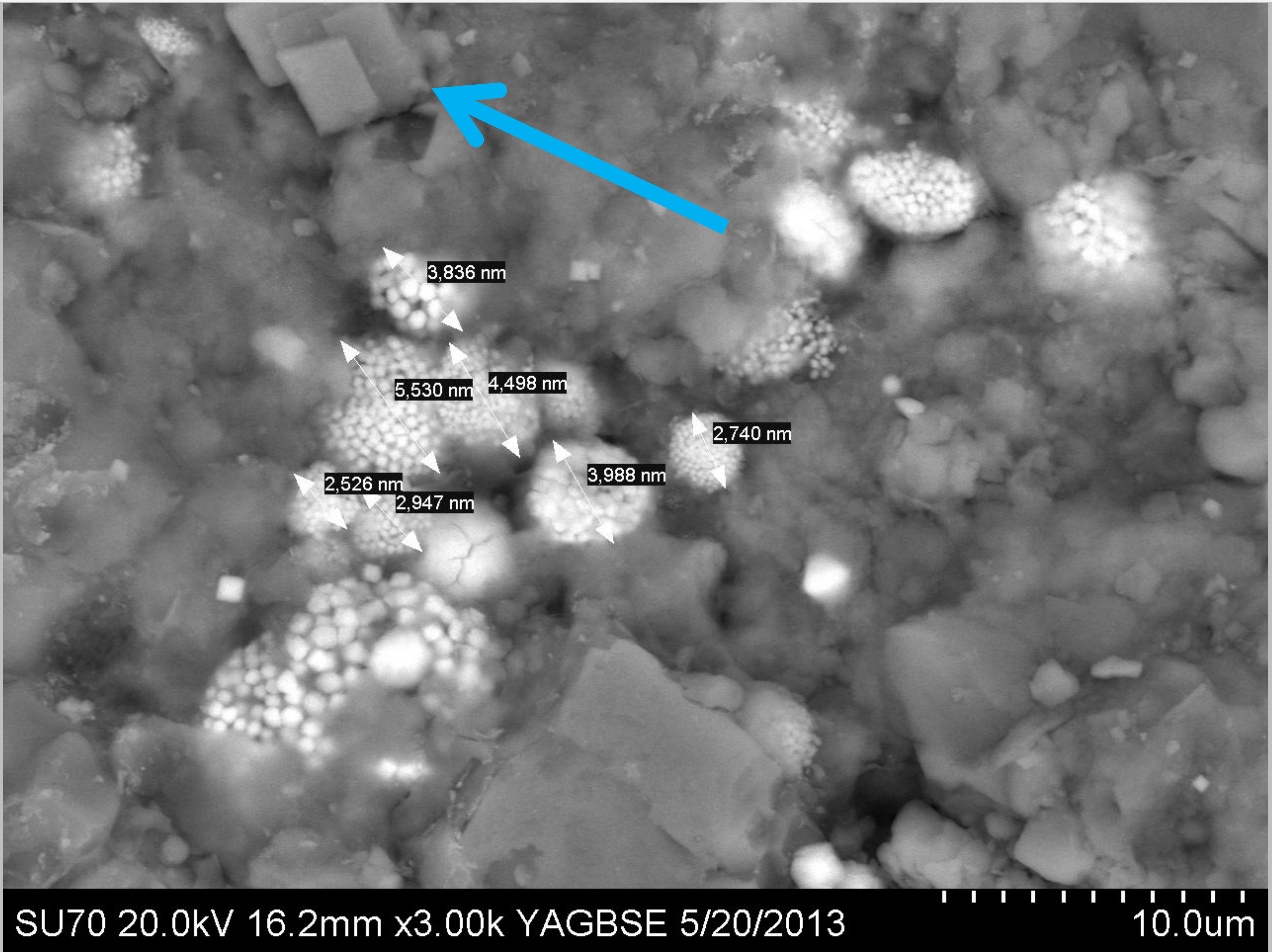
Uranium needs a sufficient amount of time to adhere to OM and or clay particles.

Authigenic Carbonate inhibiting U precipitation?

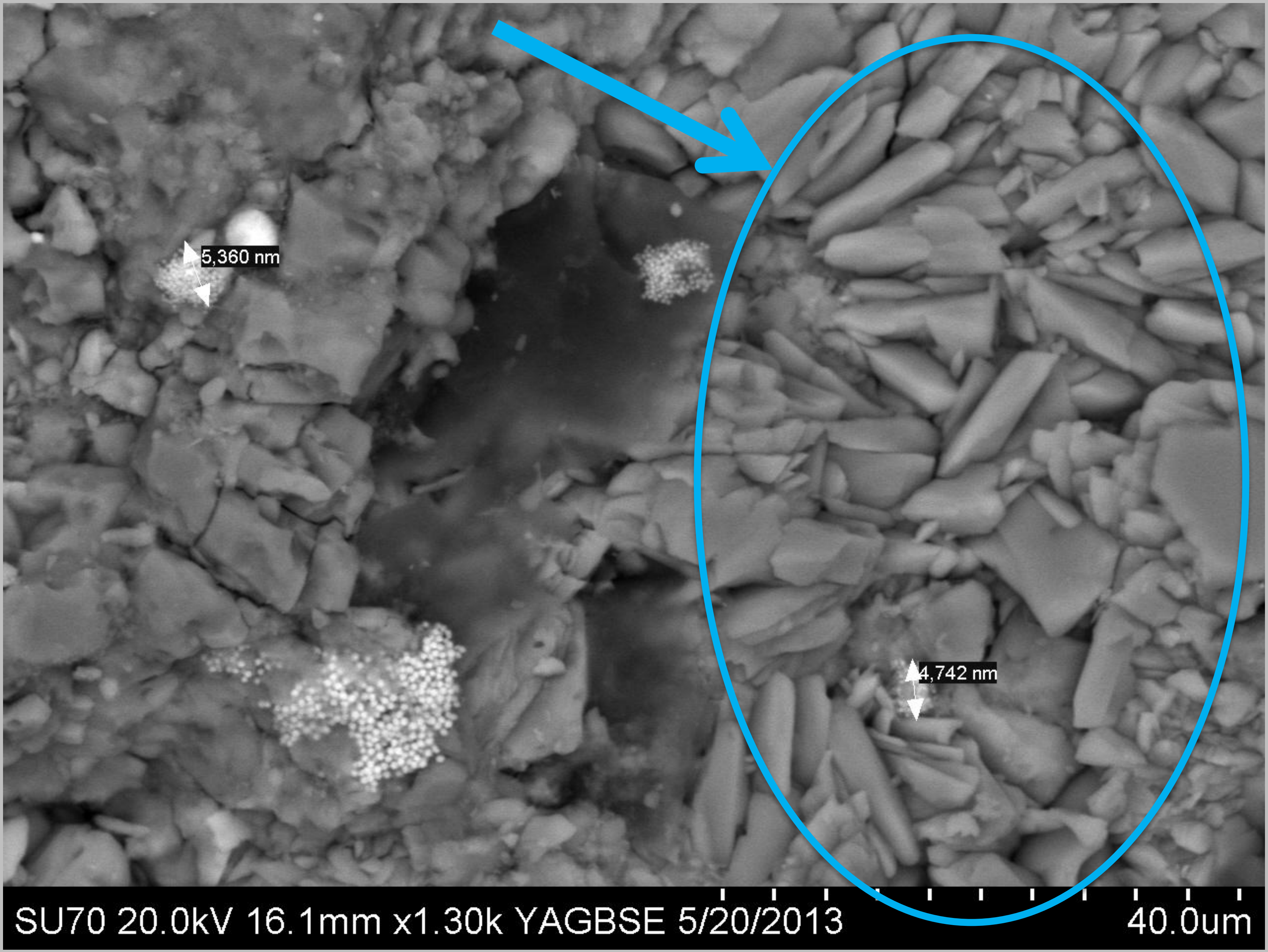


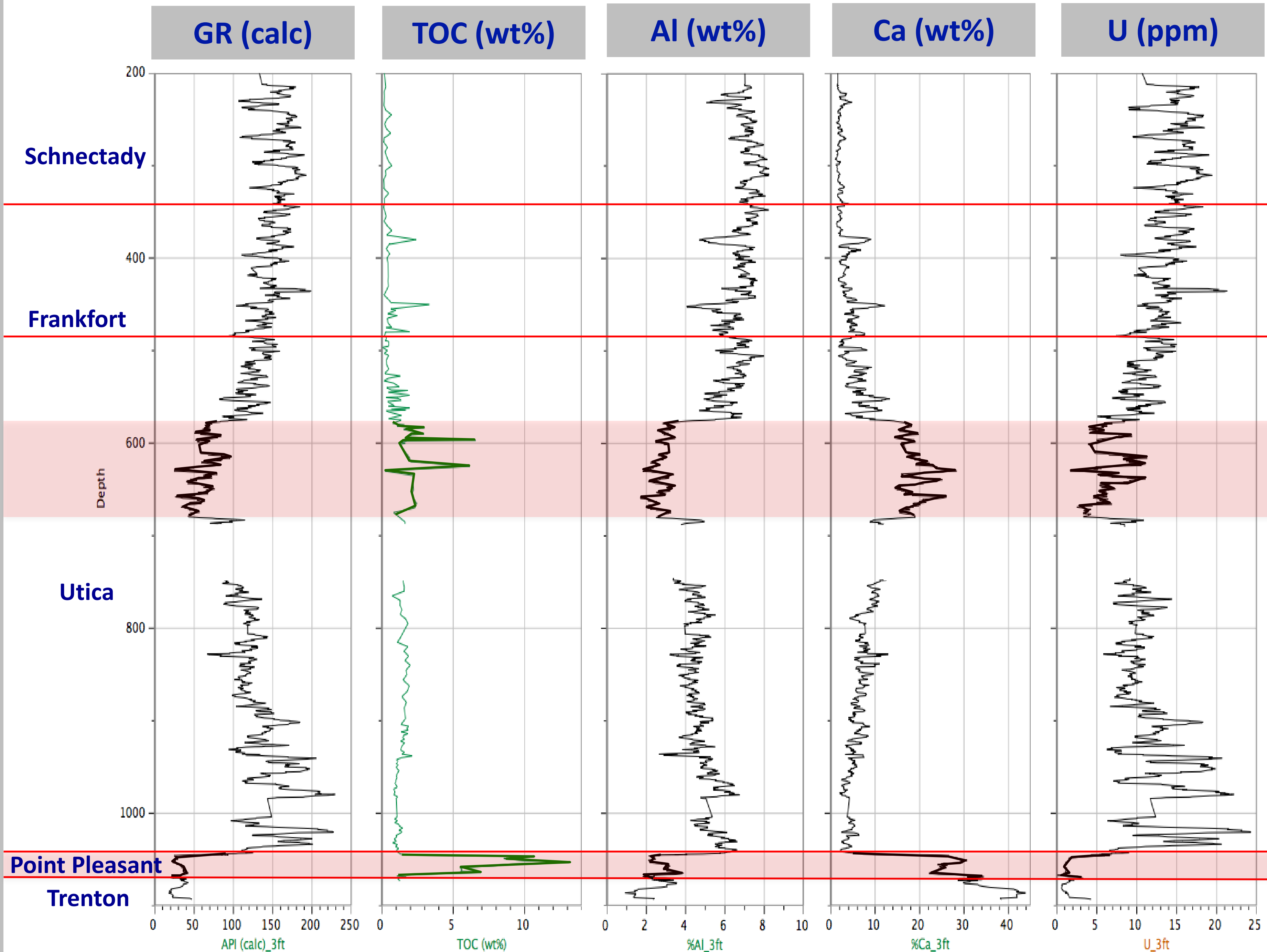
- Authigenic CaCO3 precipitation inhibits U precipitation
- Ca precipitates in limestone as calcium carbonate (CaCO3)
- Elevated in the Point Pleasant
- Sharp contact at Utica
- Ca is thought to be detrital not authigenic

Authigenic Carbonate inhibiting U precipitation?



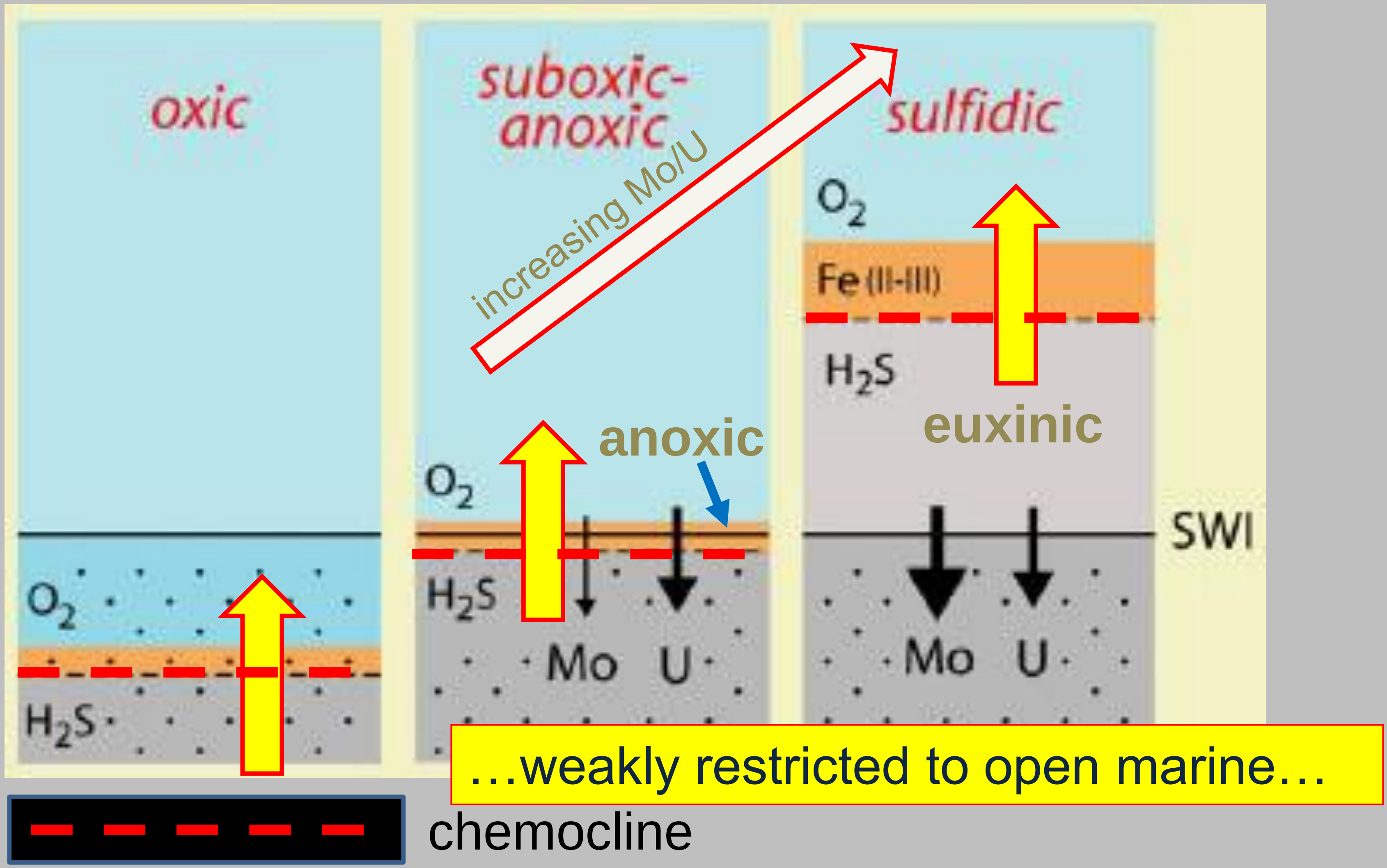
Authigenic Carbonate inhibiting U precipitation?





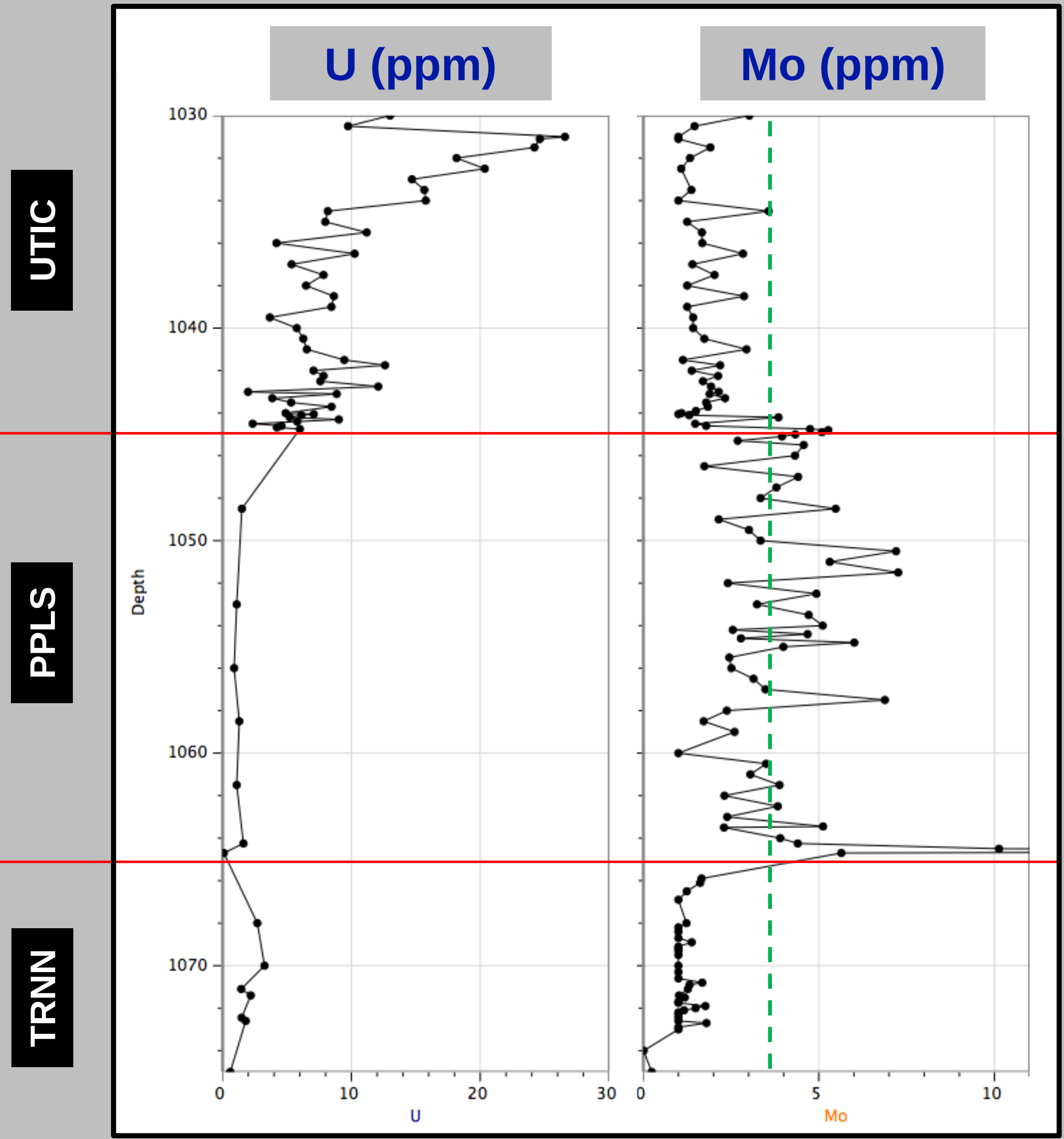
GR (calc)
TOC (wt%)
Al (wt%)
Ca (wt%)
U (ppm)
Schnectady
Frankfort
Utica
Point Pleasant
Trenton
Depth
200
400
600
800
1000
0 50 100 150 200 250
API (calc)_3ft
0 5 10
TOC (wt%)
0 2 4 6 8 10
%Al_3ft
0 10 20 30 40
%Ca_3ft
0 5 10 15 20 25
U_3ft

…increasingly reducing conditions…



Algeo and Tribovillard, 2009

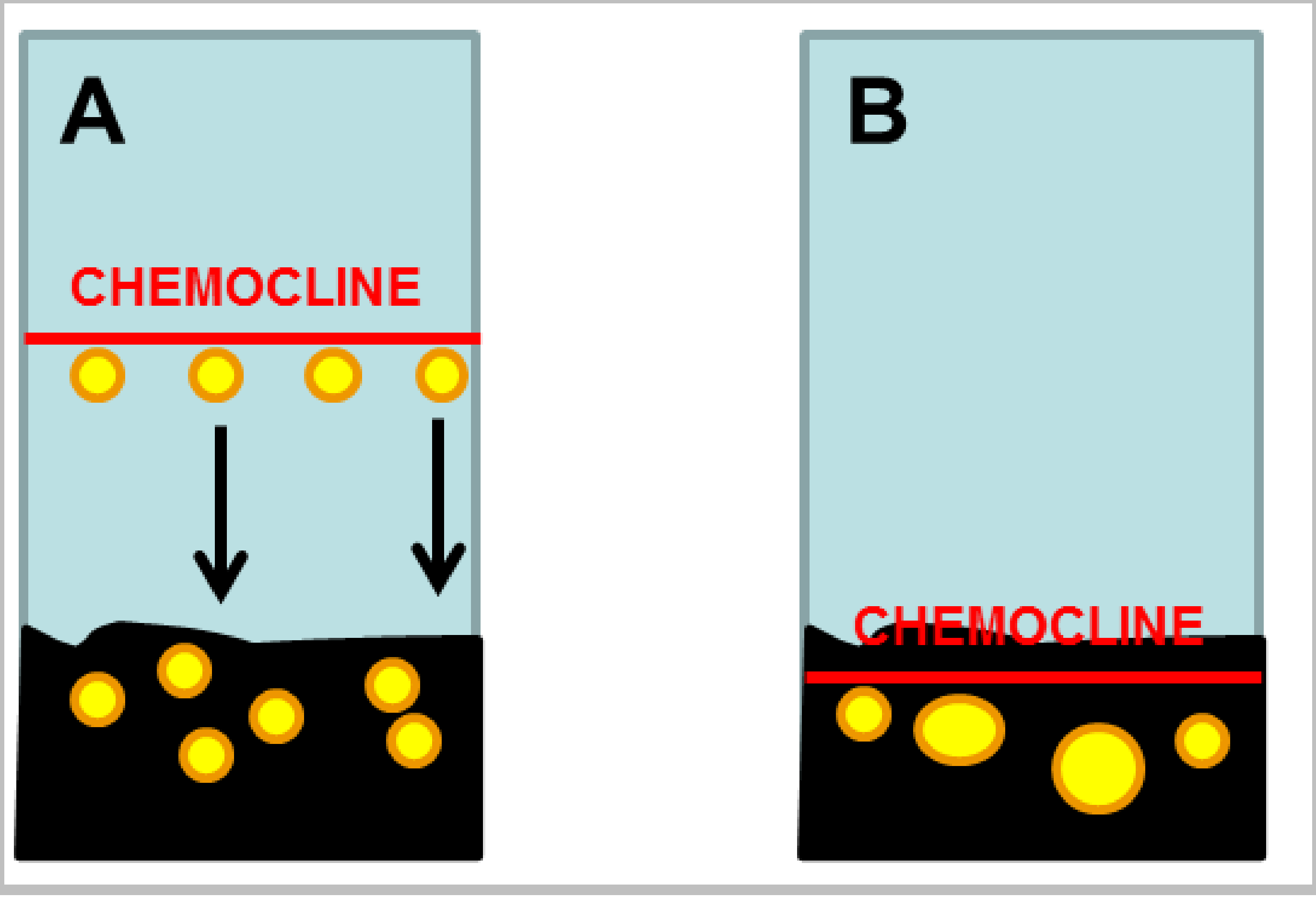
What were the redox conditions of the sediment ?



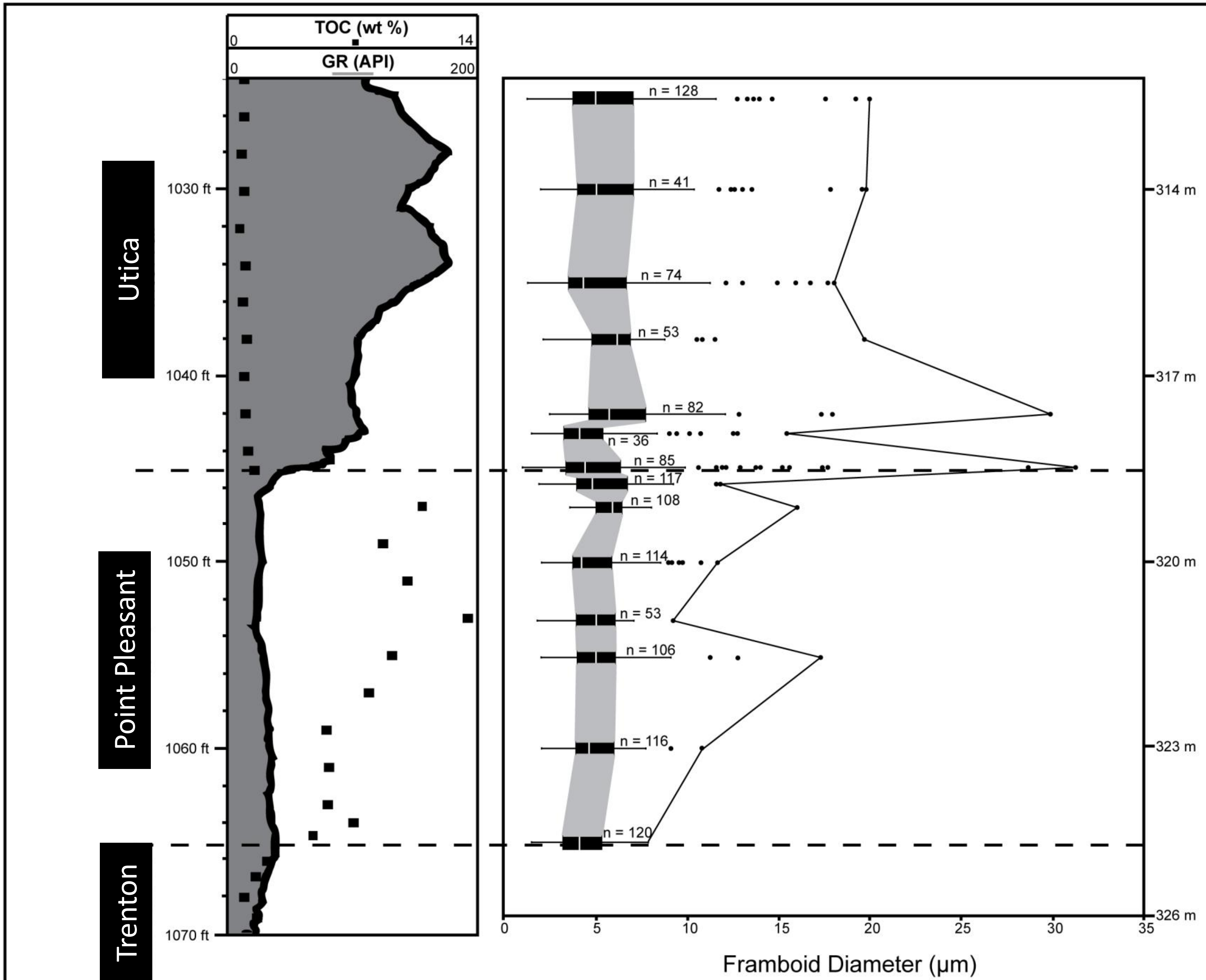
crustal values

- Slight enrichment of Mo suggest conditions were at least intermittently euxinic.
- Mo values, while not all that high, do exceed crustal values (3.7 ppm);
- However, still lower than expected for highly reducing conditions
- Both U and Mo should be more enriched

Redox conditions and Pyrite Framboids

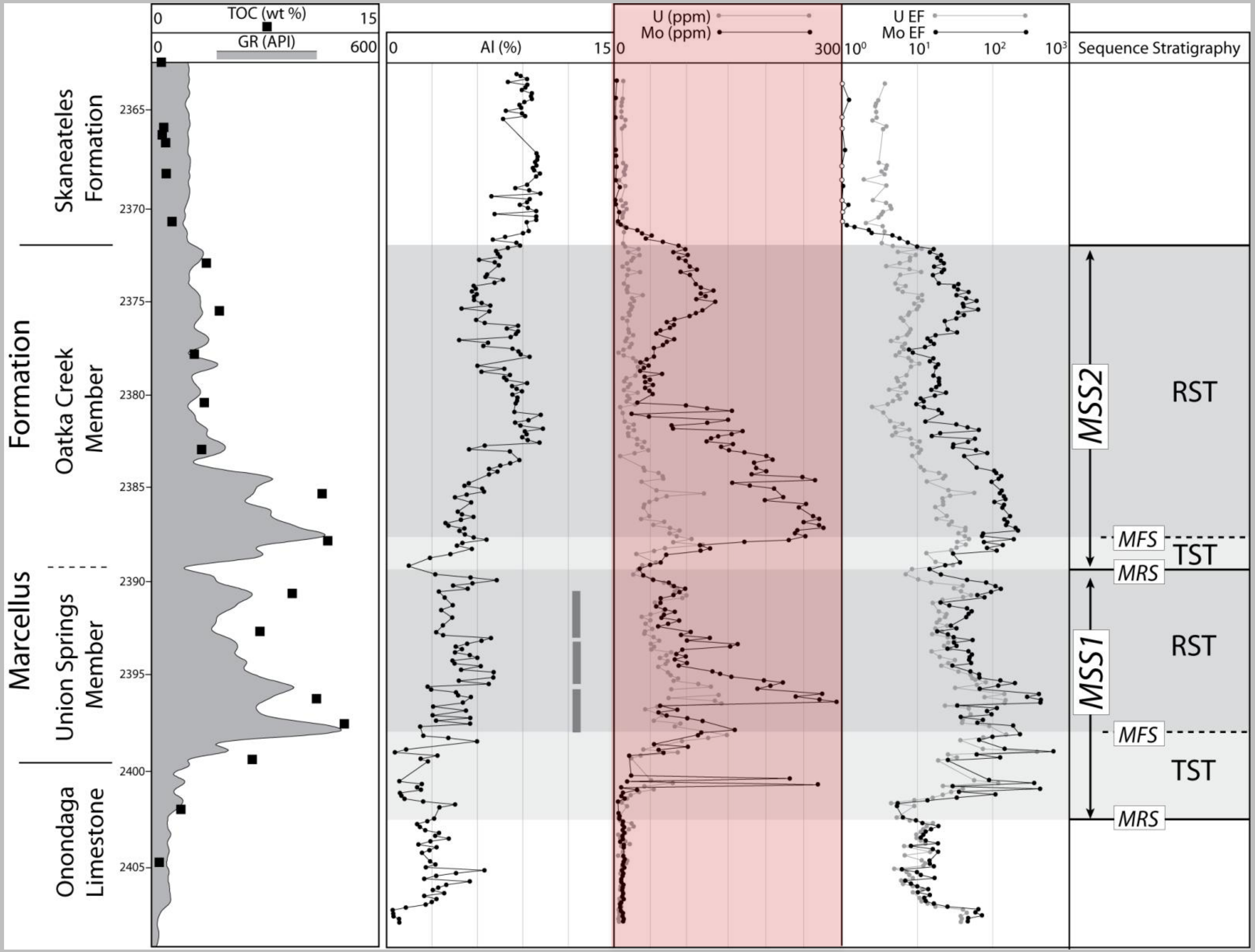


- Pyrite framboids form at the chemocline (small amount of O_2 is necessary);
- Framboids that form in the water column can grow to ***~5um*** before the water cannot support their weight and they sink
    - Statistical analysis of the framboid diameters show that under these conditions mean diameter is ~5um, with a ***narrow range***
- Framboids and euhedrlal grains forming in anoxic (near the redox boundary) sediment are limited by availability of reactants and can grow to much larger and diverse sizes.



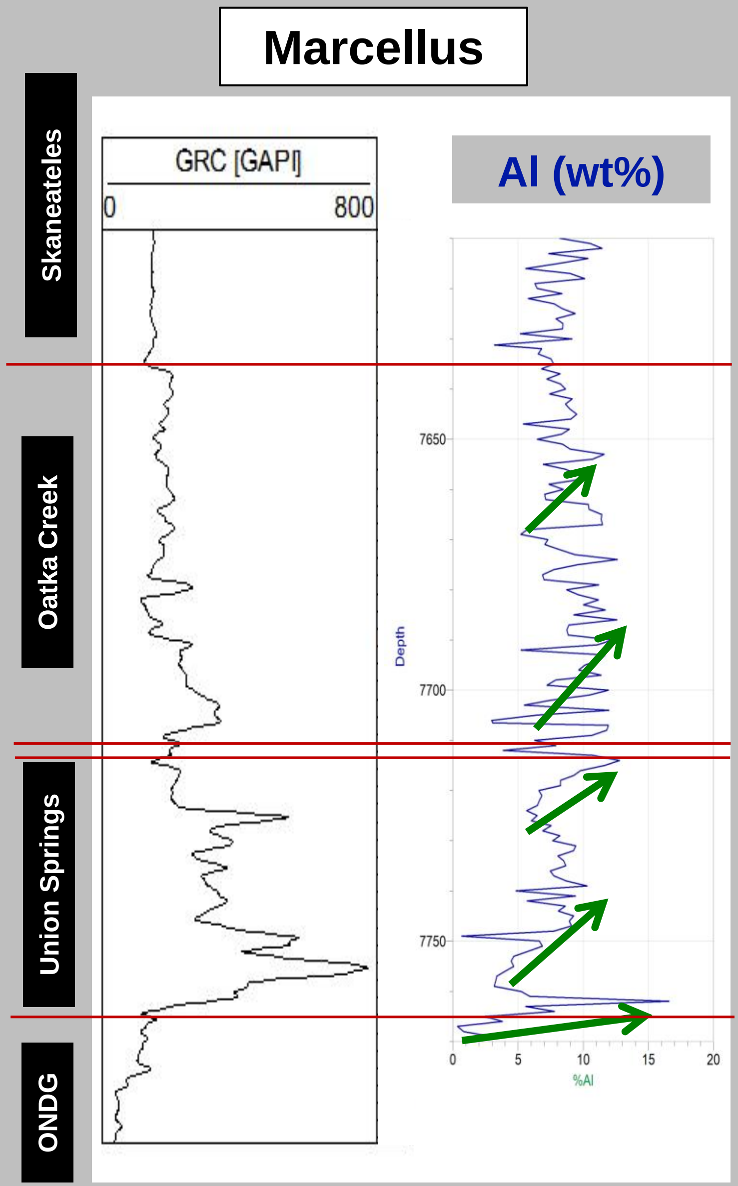
TOC (wt %)
0
14
GR (API)
0
200
Utica
Point Pleasant
Trenton
1030 ft
1040 ft
1050 ft
1060 ft
1070 ft
n = 128
n = 41
n = 74
n = 53
n = 82
n = 36
n = 85
n = 117
n = 108
n = 114
n = 53
n = 106
n = 116
n = 120
314 m
317 m
320 m
323 m
326 m
0
5
10
15
20
25
30
35
Framboid Diameter (µm)

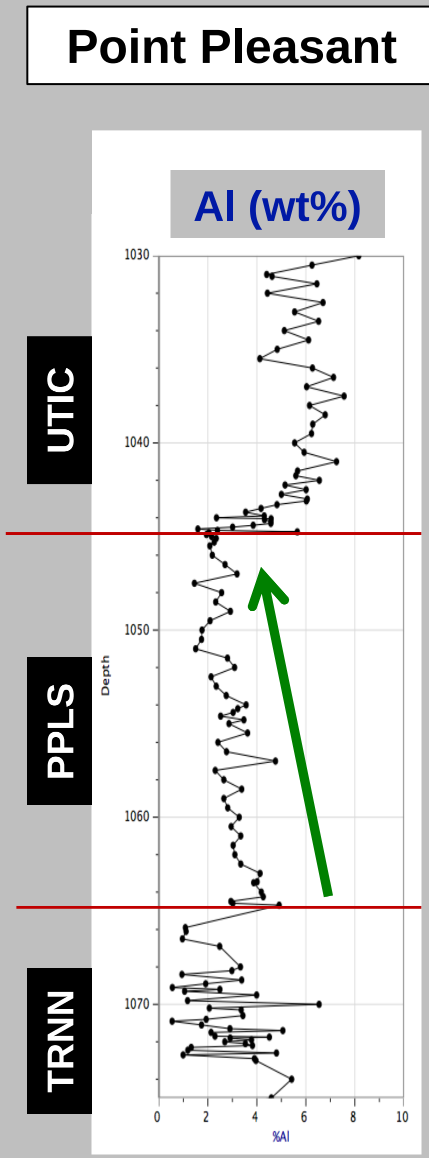
Marcellus Shale: Redox Conditions



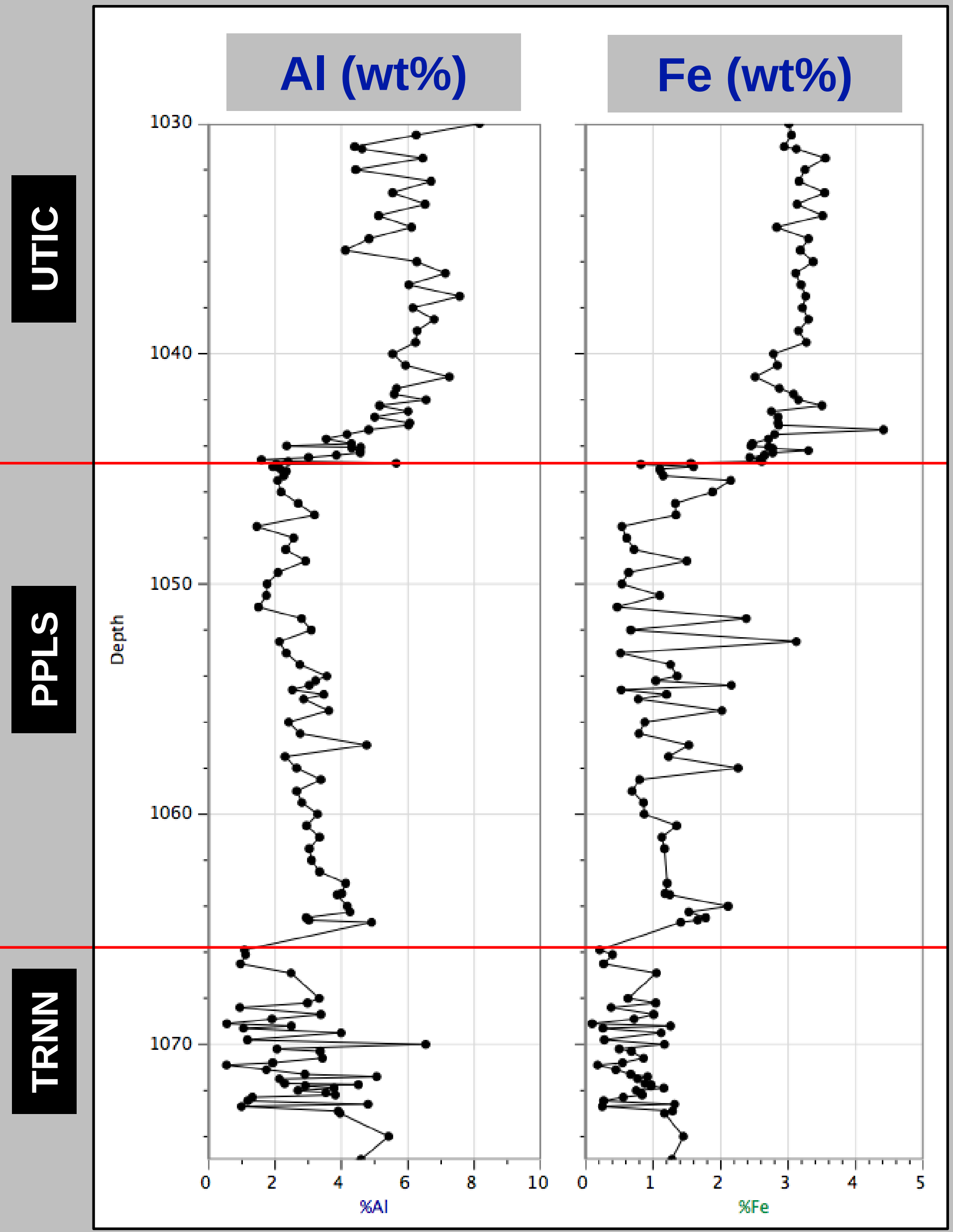
Lash and Blood, 2014. Organic matter accumulation, redox, and diagenetic history of the Marcellus Formation, southwestern Pennsylvania, Appalachian basin: Marine and Petroleum Geology.

Detrital Input



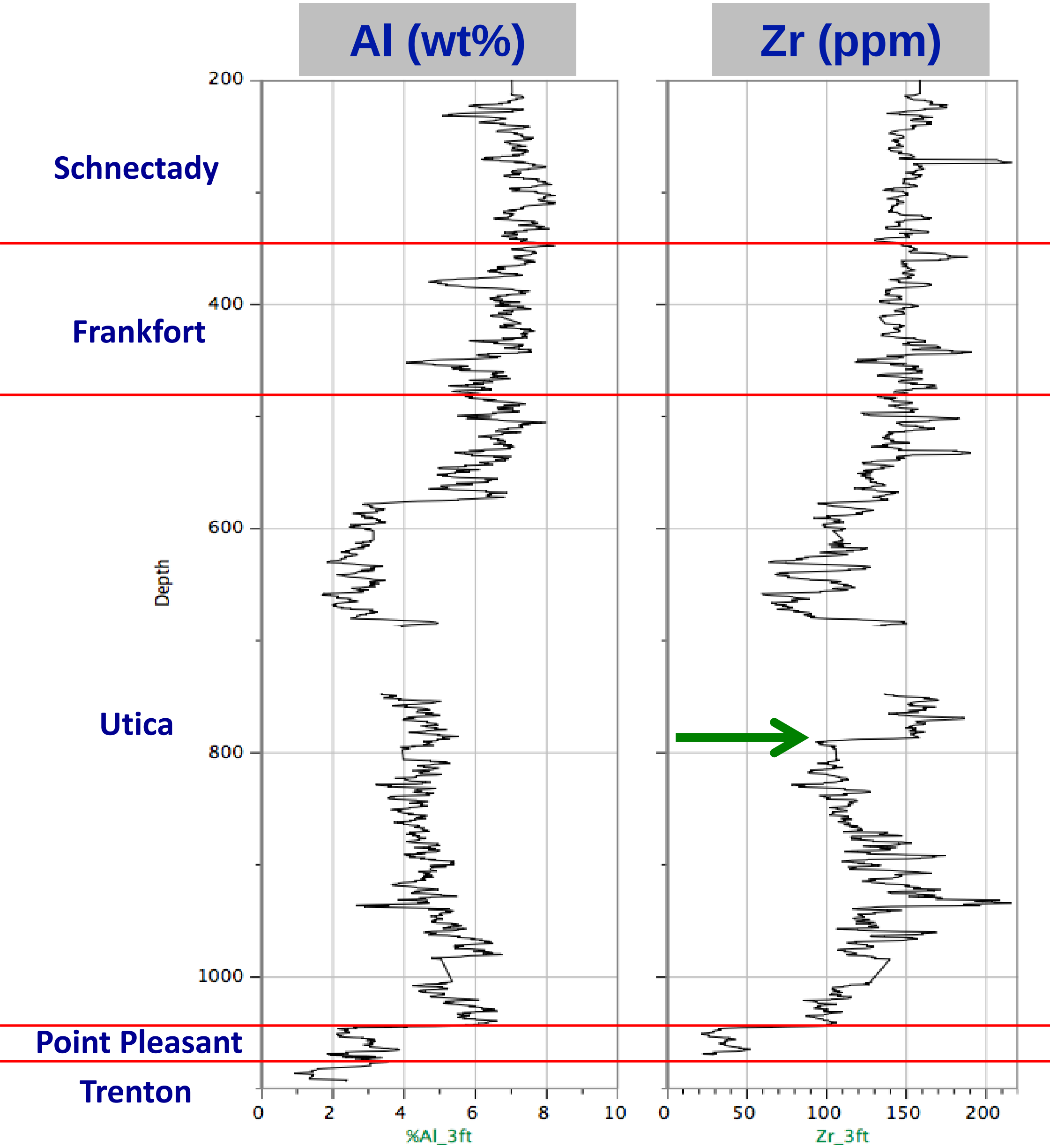


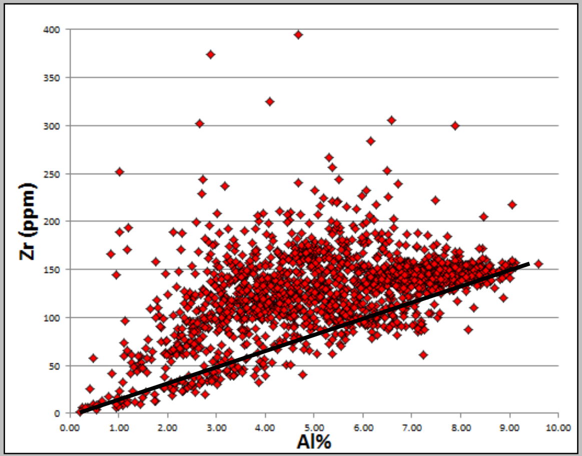
Clay Inhibiting Redox Proxies ?



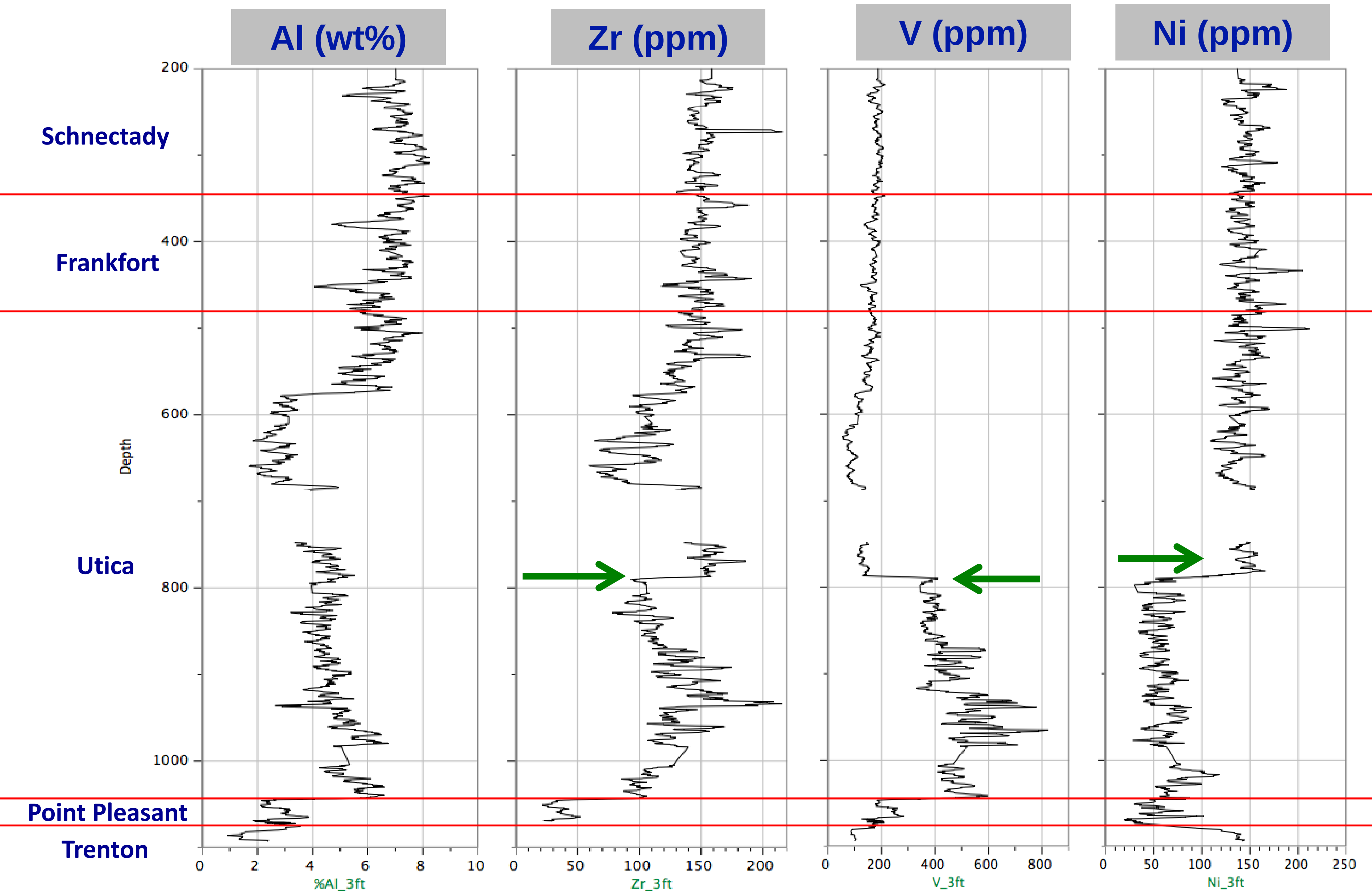
- Two forms of iron:
  - Detrital
  - Reactive
- Enrichment of Fe with pyrite formation (FeS_2)
  - Process require H_2S
  - Unrelated to cation exchange
- Fe and Al profile almost identical
- **Fe Limited**

Source Provenance





Source Provenance



Conclusion

Why is there a difference of clay between the Marcellus and Point Pleasant Utica Shale ?

- Establishment of land plant root system during the Devonian
  - Atmospheric conditions
    - Ordovician: CO_2 6000 ppm
    - Early Devonian: CO_2 4000 ppm
    - Late Devonian: CO_2 400 ppm
- **Lack of land plant root system during Ordovician**

Conclusion

Why is there a difference of redox proxies between the Marcellus and Point Pleasant Utica Shale ?

- Pyrite morphology and Mo enrichment suggest the Point Pleasant Utica Shale accumulated under reducing to intermittently euxinic, Fe limited conditions
- Rule Out: dilution, authigenic carbonate, cation exchange

Ocean Chemistry of the Ordovician appears to be different from the Devonian

- **Lack of land plant root system *may have* resulted in the lack of trace elements delivered to the ocean**
- **Middle (Late) Ordovician (Caradocian) Oceanic Anoxic Event**
  - Black shale deposited on pelagic sediment found in the Southern Uplands of Scotland
  - *may have* depleted global inventory of redox elements

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