Inorganic Geochemistry of the Trenton Limestone-Utica Shale Contact Based on XRF Data*

Steve R. Saboda[1] and Gary G. Lash[2]

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[1]University at Buffalo, Buffalo, NY, USA (srsaboda@gmail.com)
[2]SUNY Fredonia, Fredonia, NY, USA

Abstract

The contact of the Upper Ordovician Utica Shale and underlying Trenton Limestone is normally recognized as a sharp increase in gamma ray (GR) response, apparently reflecting the increased abundance of organic matter from the carbonate to overlying shale. Though conventional wisdom holds that organic–rich black shales can be identified by characteristic GR log signature, this may not be the case for the Utica Shale. Chemostratigraphic analysis of the Utica Shale core 75-NY2 using handheld XRF technology in tandem with a suite TOC data indicates that the Trenton–Utica contact based on GR response actually falls within the Utica Shale. Gamma–ray response principally reflects the abundance of K, Th, and especially U. Indeed, it is enrichment of the latter above crustal levels in the presence of abundant organic matter and related bacterial sulfate reduction typical of those environments in which black shale accumulates. However, U values of the lower carbonaceous interval of the Utica Shale remain close to or even depleted relative to crustal values, essentially unchanged from those concentrations of the underlying Trenton Limestone. Of particular interest is the roughly 6m thick interval of calcareous dark black shale devoid of graptolites containing > 10% TOC at the bottom of the Utica Shale. The apparent dichotomy of elevated TOC and minimal U concentration is obvious from an artificial GR log generated from our chemostratigraphic data that displays a profile similar to GR signatures documented from Utica wells. These results suggest that the sharp increase in GR response normally recognized as the Trenton/Utica contact actually delimits the top of the organic–rich interval within the bottom of the Utica. The level at which the GR increases is observed to be the boundary of organic–rich shale and overlying organic-lean (TOC ~ 1%) grayish black shale. The contact of the organic–rich and organic–lean shale correlates with an increase of U somewhat in excess of crustal levels. Although authigenic U concentrations can be

diluted by increased clastic flux, measured abundances of detrital proxies, including Al, Si, Ti, and Zr, are inconsistent with such an explanation. The U–depleted nature of the most organic–rich deposits of the Utica Shale may reflect the impress of Middle Ordovician global anoxia and consequent of drawdown of the global aqueous U inventory.

Selected References

Cross, G.E., 2004, Fault related mineralization and fracturing in the Mohawk Valley, Eastern New York: Master's thesis, State University of New York, Buffalo, New York (SUNY), 238 p.

Jacobi, R.D. and C.E. Mitchell, 2002, Geodynamical interpretation of a major unconformity in the Taconic Foredeep; slide scar or onlap unconformity?: Physics and Chemistry of the Earth, v. 27/1-3, p. 169-201.

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.

Smith, C.N., and A. Malicse, 2010, Rapid Handheld X-Ray Flourescence (HHXRF) Analysis of Gas Shales: AAPG Search and Discovery Abstract #90108. Web accessed 24 October 2011, http://www.searchanddiscovery.com/abstracts/pdf/2010/intl/abstracts/ndx_smith.pdf.

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Steve Saboda, American Energy Utica, LLC
Gary G. Lash, SUNY Fredonia

MS Thesis 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 placement of lateral well-bores
    4. Understanding the controlling mechanisms of the formation of organic rich-deposits

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

Analytical Approach

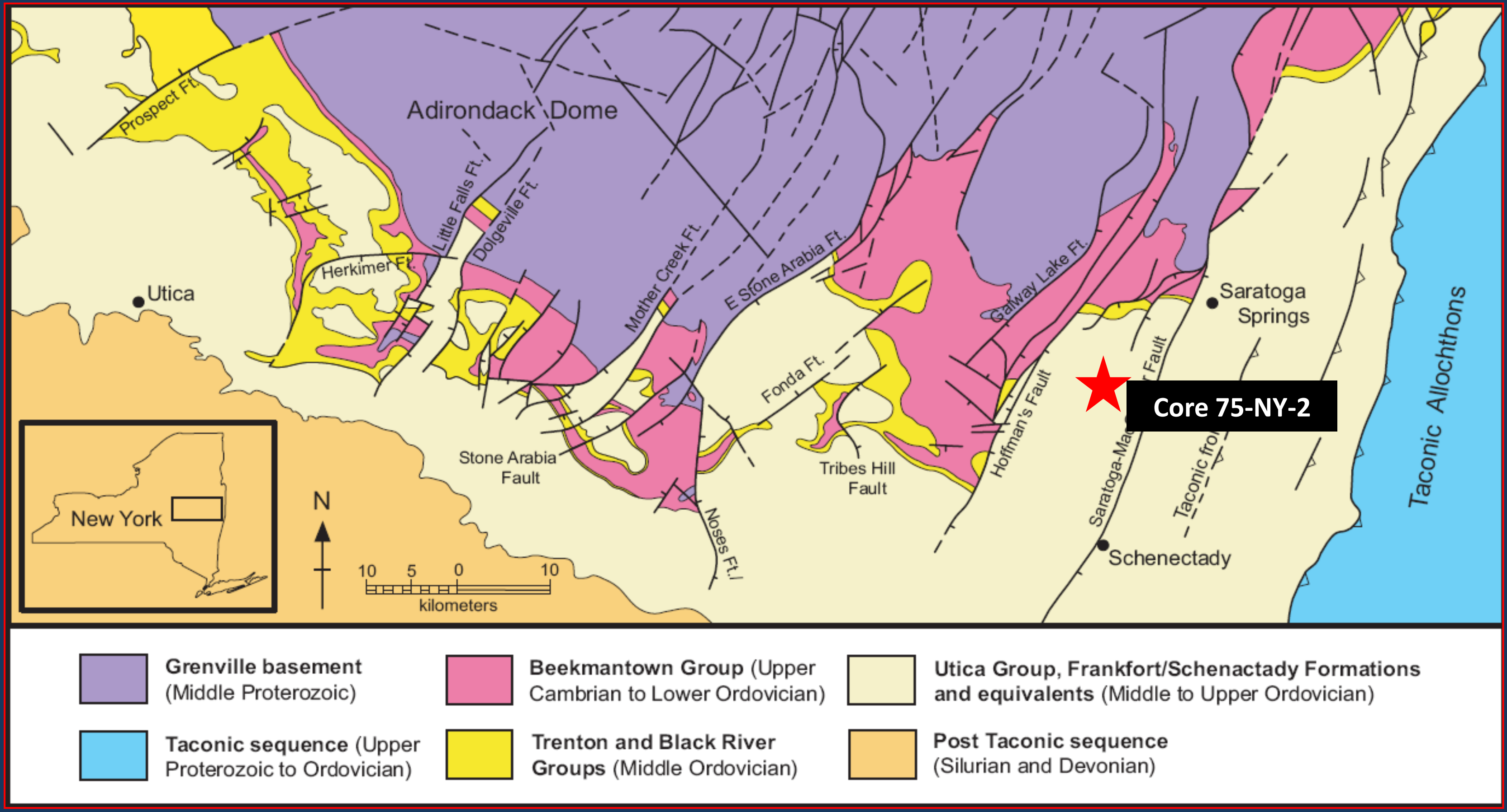
Handheld XRF (HHXRF) analyzer …

Thermo Scientific Niton XL3t 950 GOLDD+…
…hand (outcrop) samples, core, cuttings…

…very strong correlations ($r^2 > 0.90$) with laboratory ICP-MS (inductively coupled plasma mass spectrometry) data for most major, minor and trace elements from Mg to U (Smith and Malicse, 2010)…

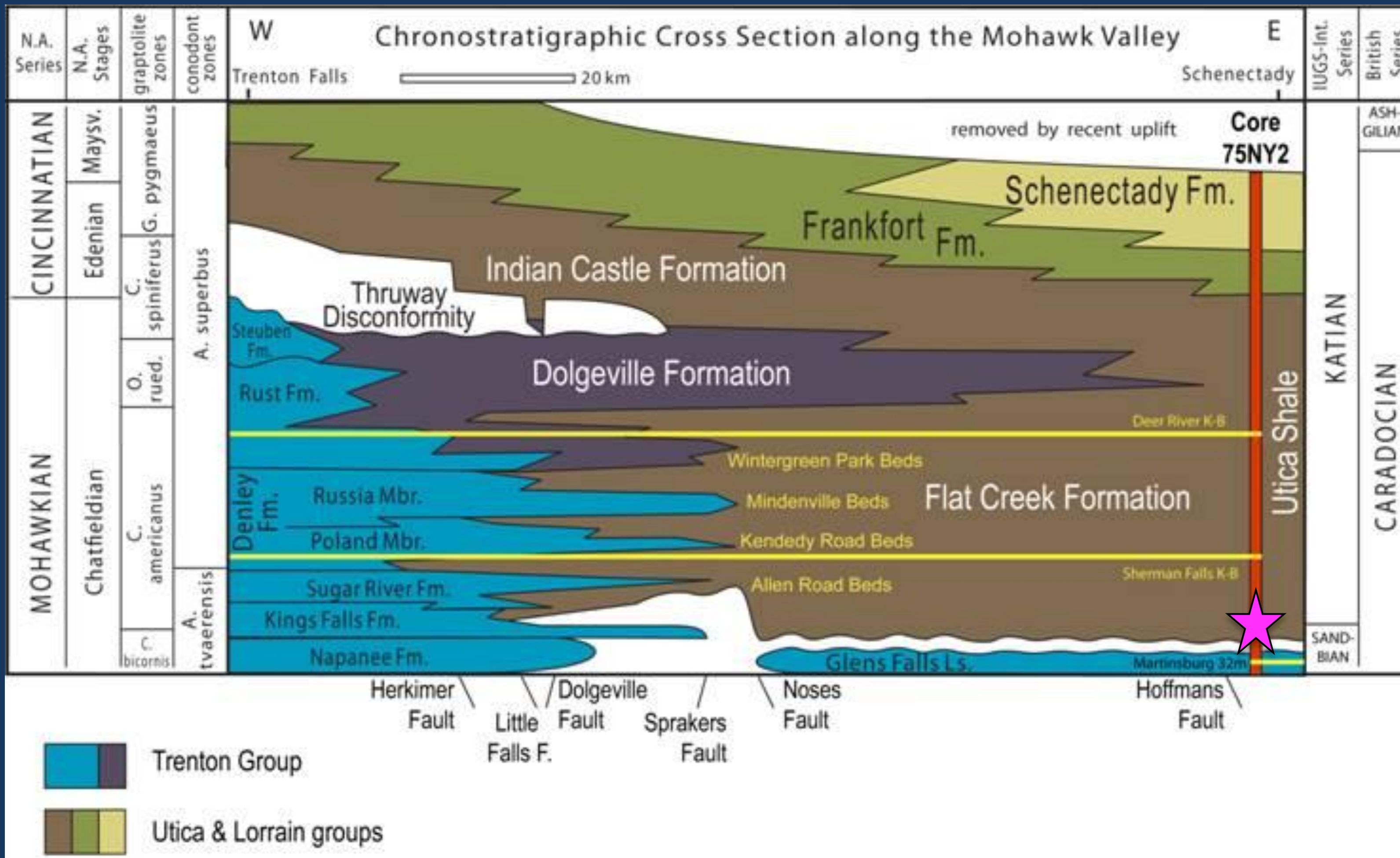
…shale can be analyzed at cm scale resolution…

Mohawk Valley Area
Core 75-NY-2



after Cross, 2004

Mohawk Valley Stratigraphy



Revised from Jacobi and Mitchell, 2002, based on new data from core 75NY2, pers. com. C. E. Mitchell and M. Roloson, 2010

1063’

Utica Shale (“sooty” black)

Trenton Ls. (Glens Falls Ls.)

1073’

- Lithology easily identified
- Sharp contact unmistakably recognized

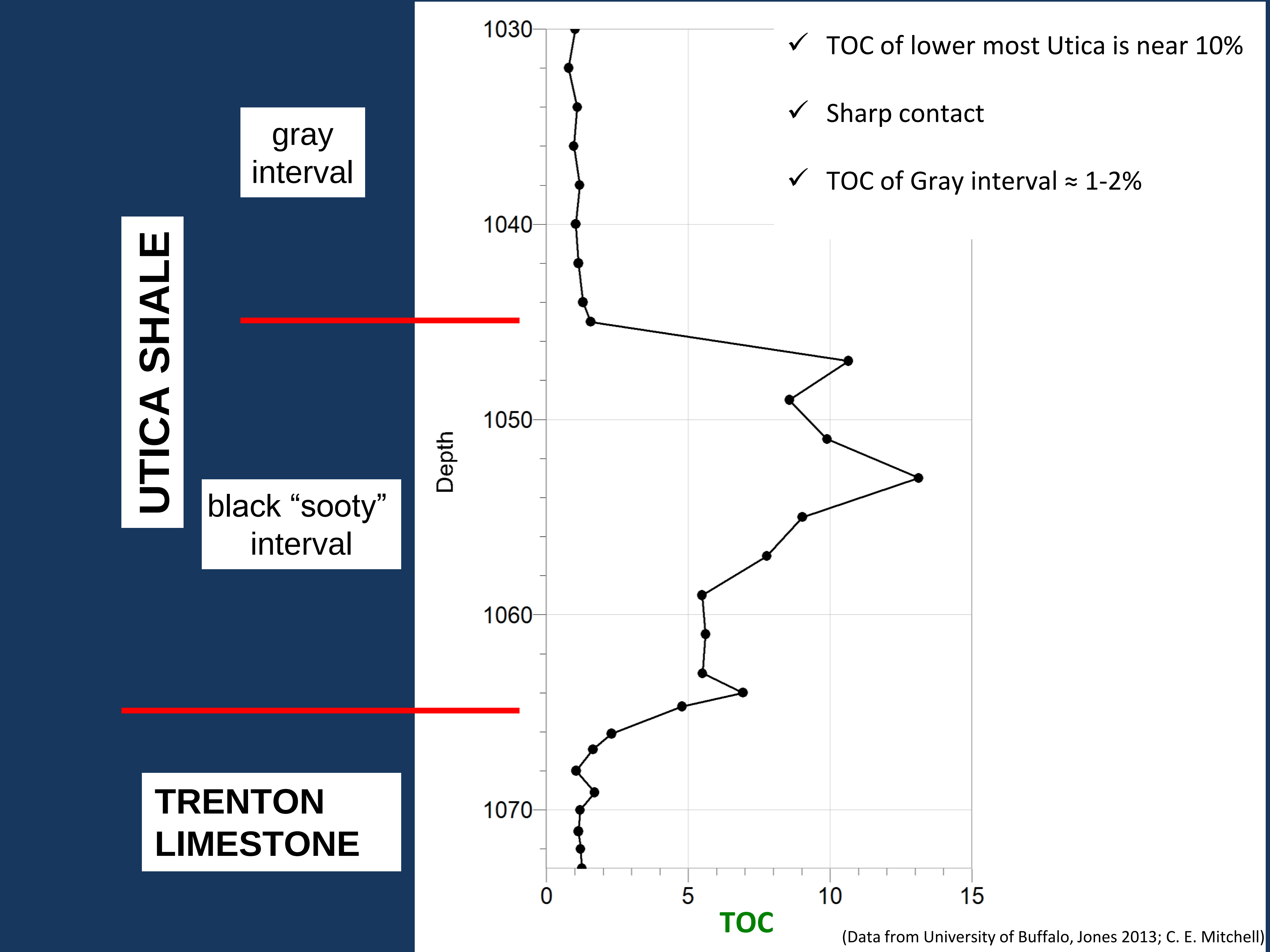
1054’

Utica Shale (“sooty” black)

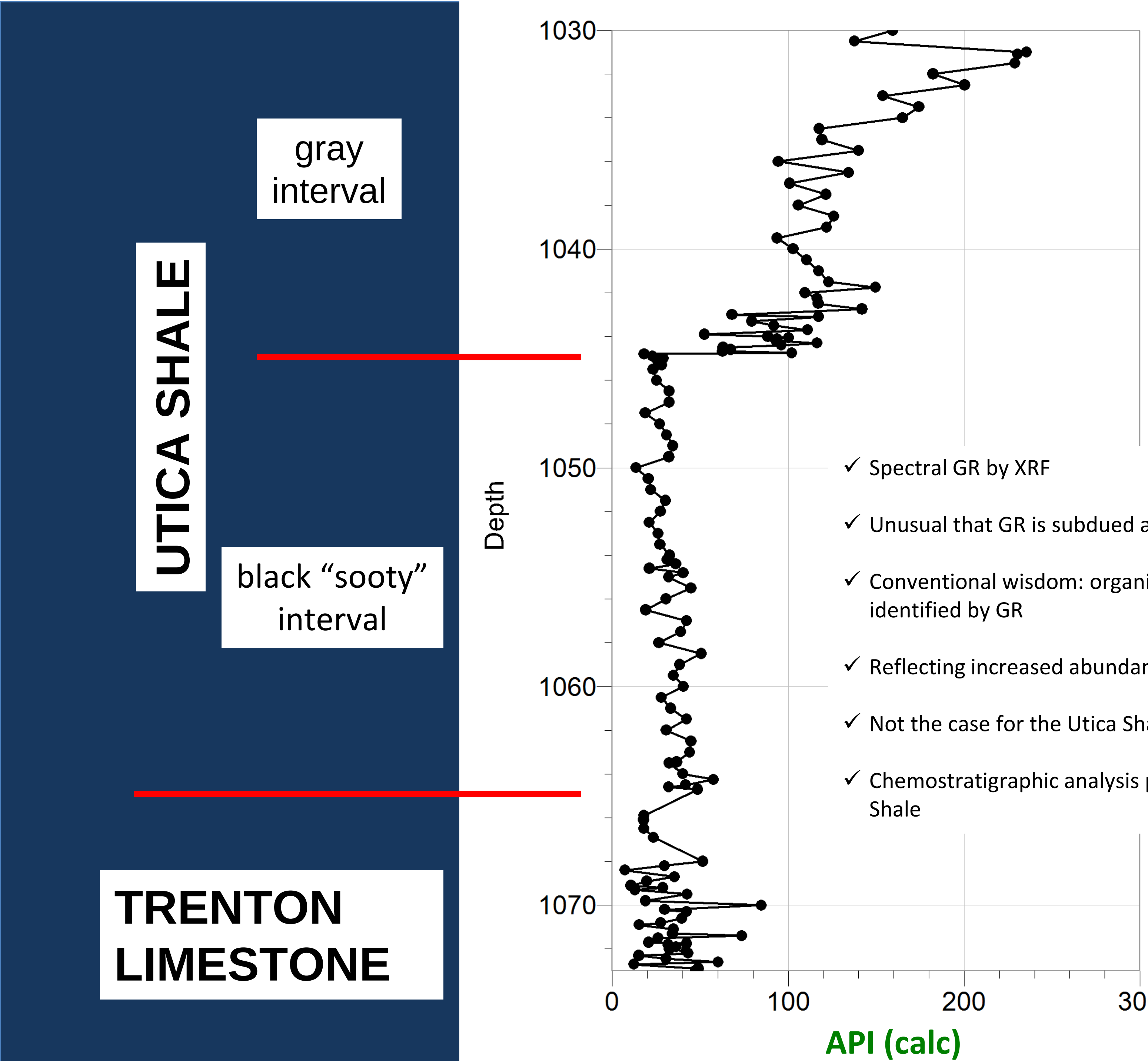
gray interval

1044’

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



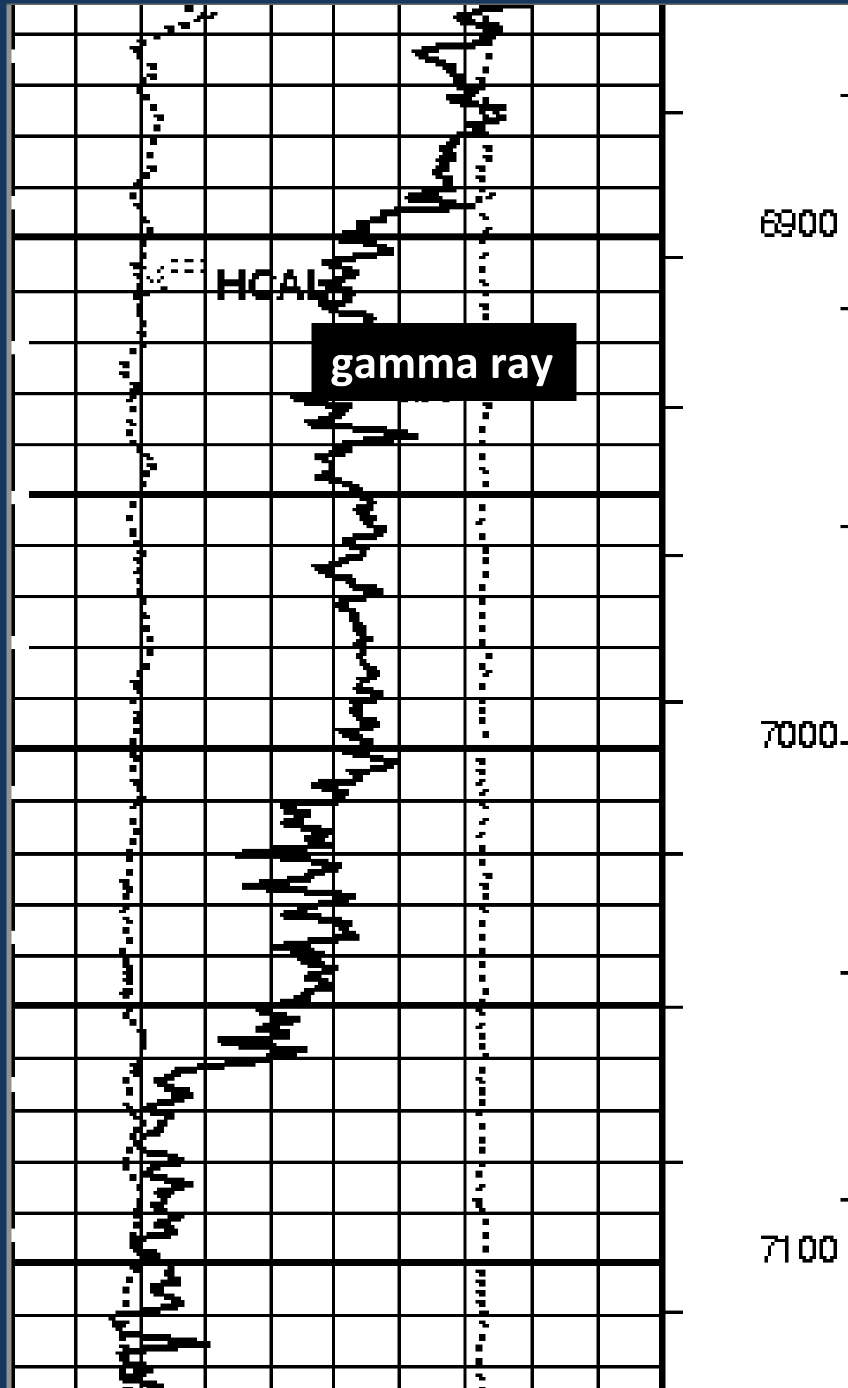
✓ TOC of lower most Utica is near 10%
✓ Sharp contact
✓ TOC of Gray interval ≈ 1-2%
gray interval
UTICA SHALE
black “sooty” interval
TRENTON LIMESTONE
Depth
1030
1040
1050
1060
1070
0
5
10
15
TOC
(Data from University of Buffalo, Jones 2013; C. E. Mitchell)



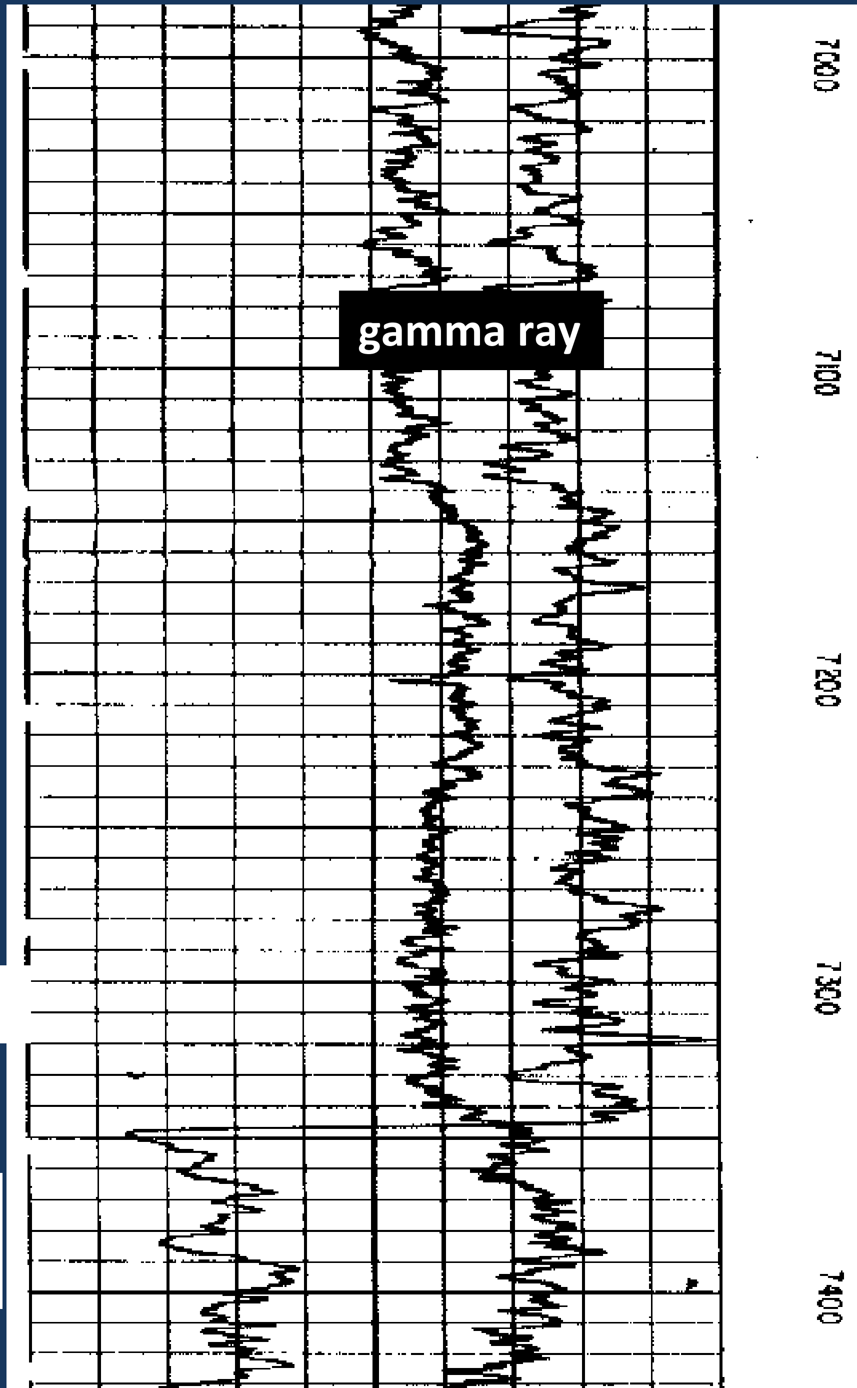
- ✓ Spectral GR by XRF
- ✓ Unusual that GR is subdued although TOC is high
- ✓ Conventional wisdom: organic-rich shale can be identified by GR
- ✓ Reflecting increased abundance of TOC
- ✓ Not the case for the Utica Shale
- ✓ Chemostratigraphic analysis places contact within Utica Shale

Utica Shale

Trenton Limestone



eastern NY

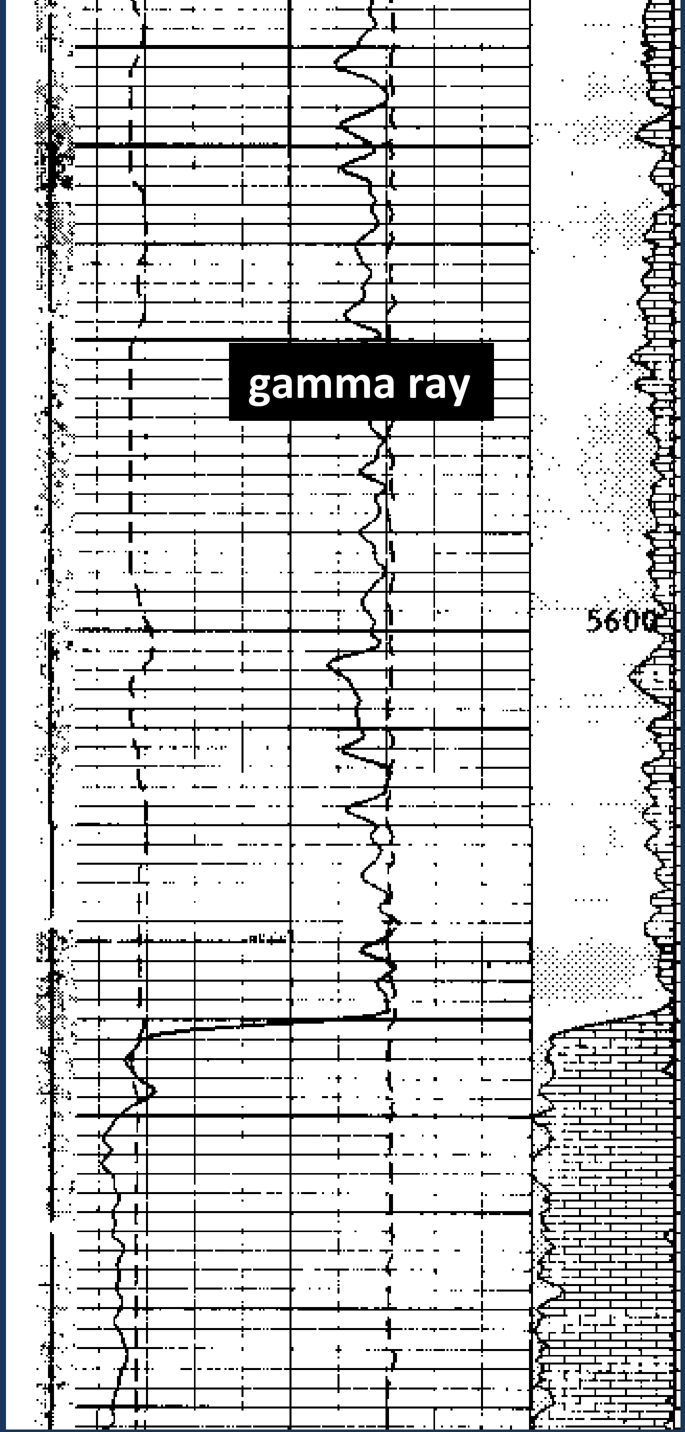


Utica Shale

Trenton Limestone

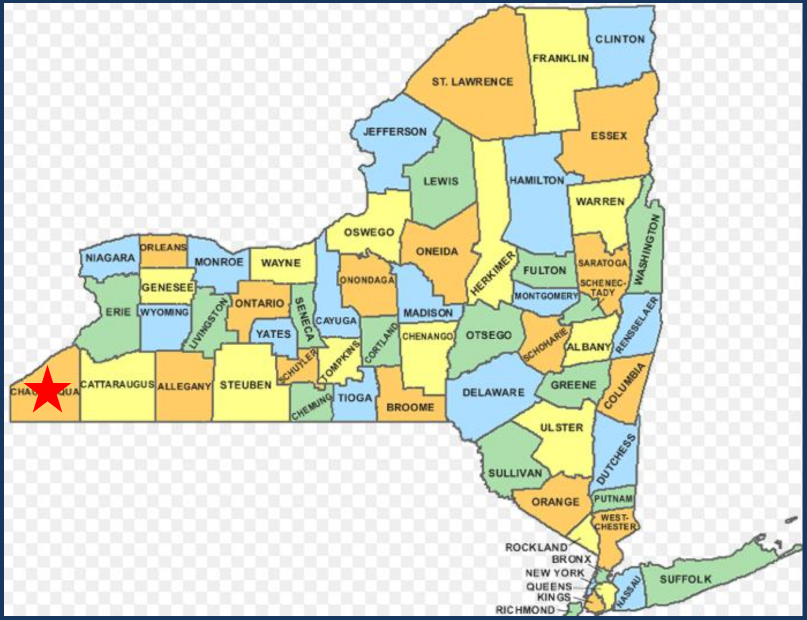
Tompkins County, NY

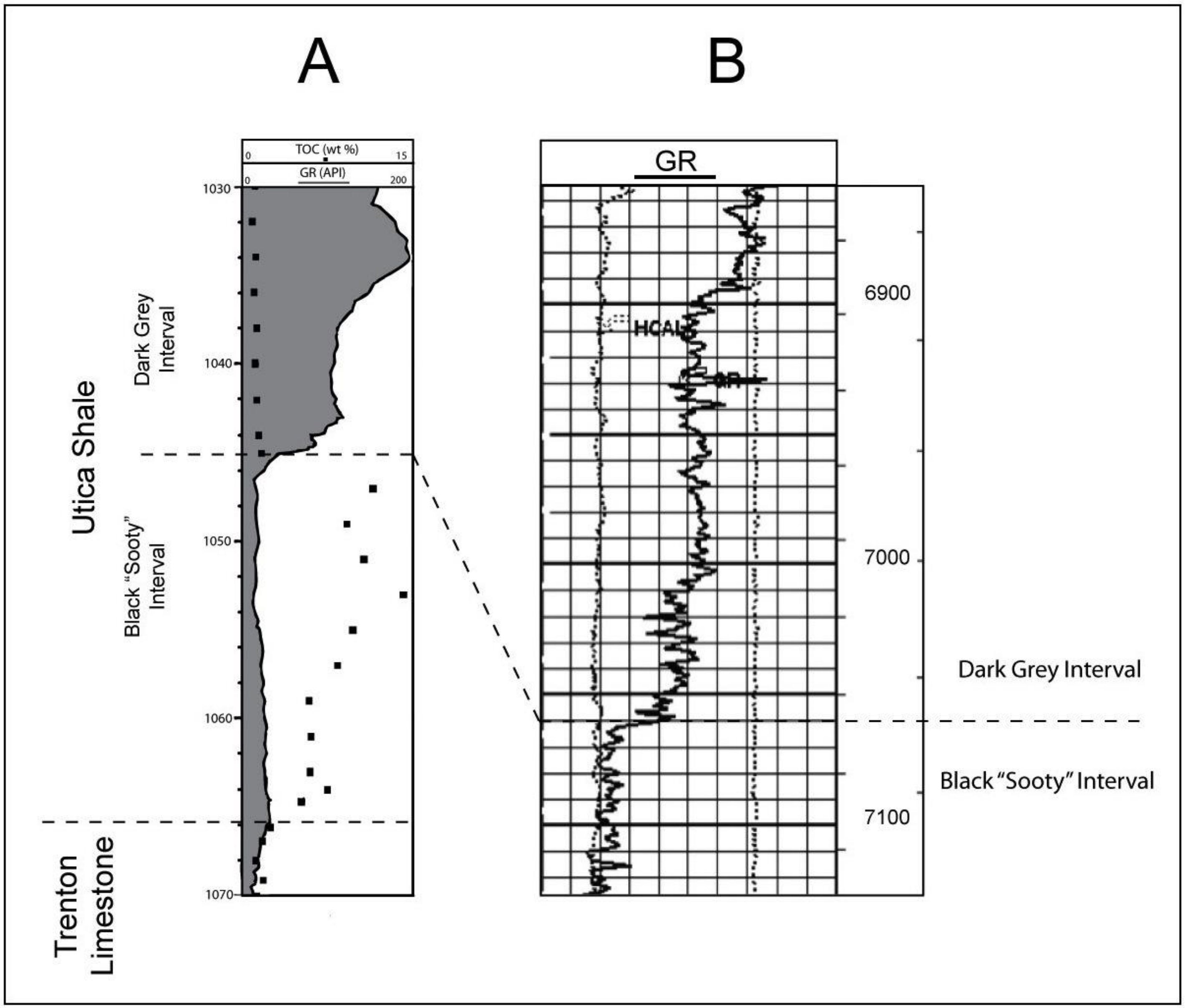
22531; Chautauqua County, NY



Utica Shale

Trenton Limestone





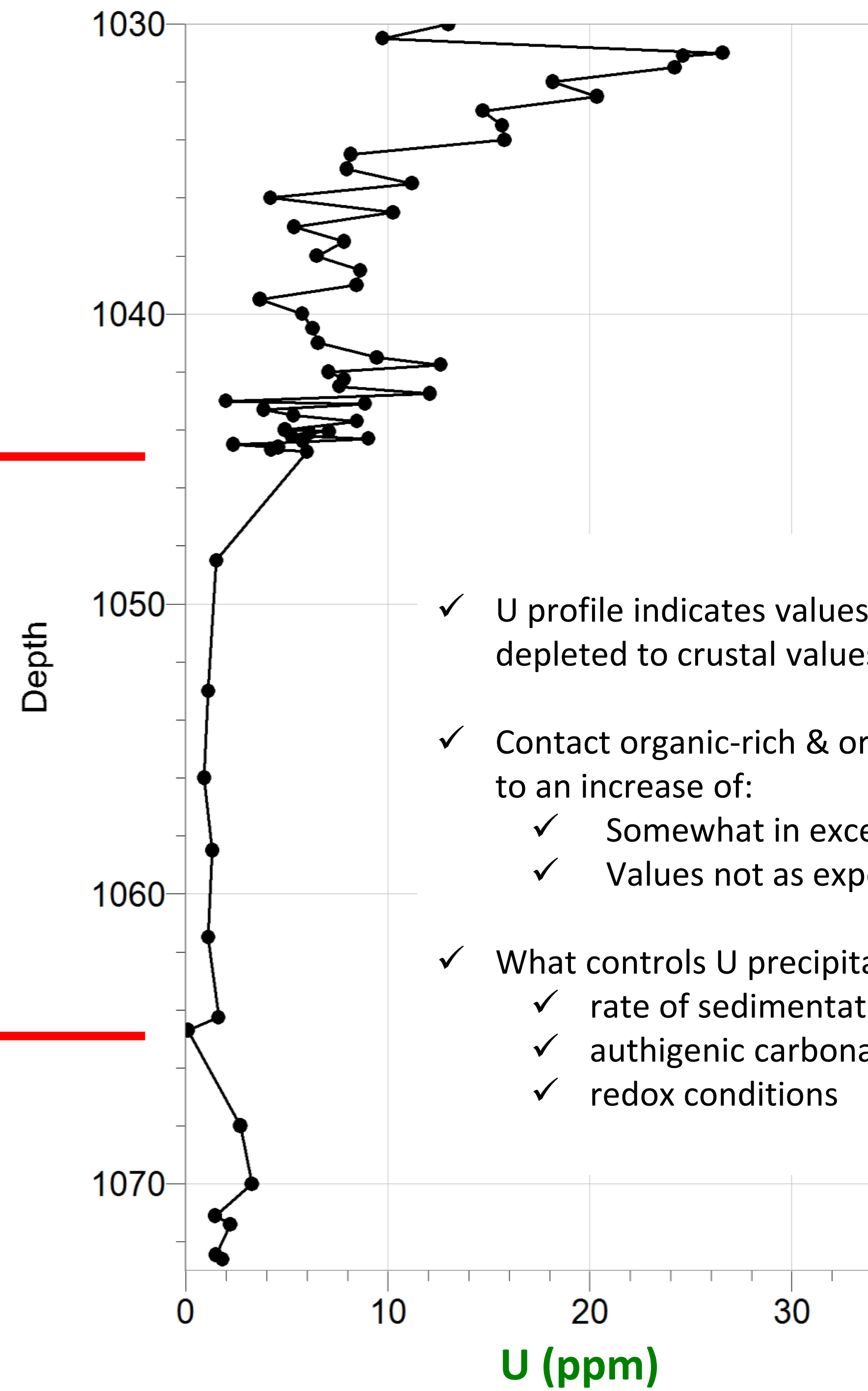
- Spectral GR similar to GR logs throughout NYS
- To understand why GR is subdued; must understand how GR is derived
- GR relies on 3 radio active elements (**U**, K, Th)

UTICA SHALE

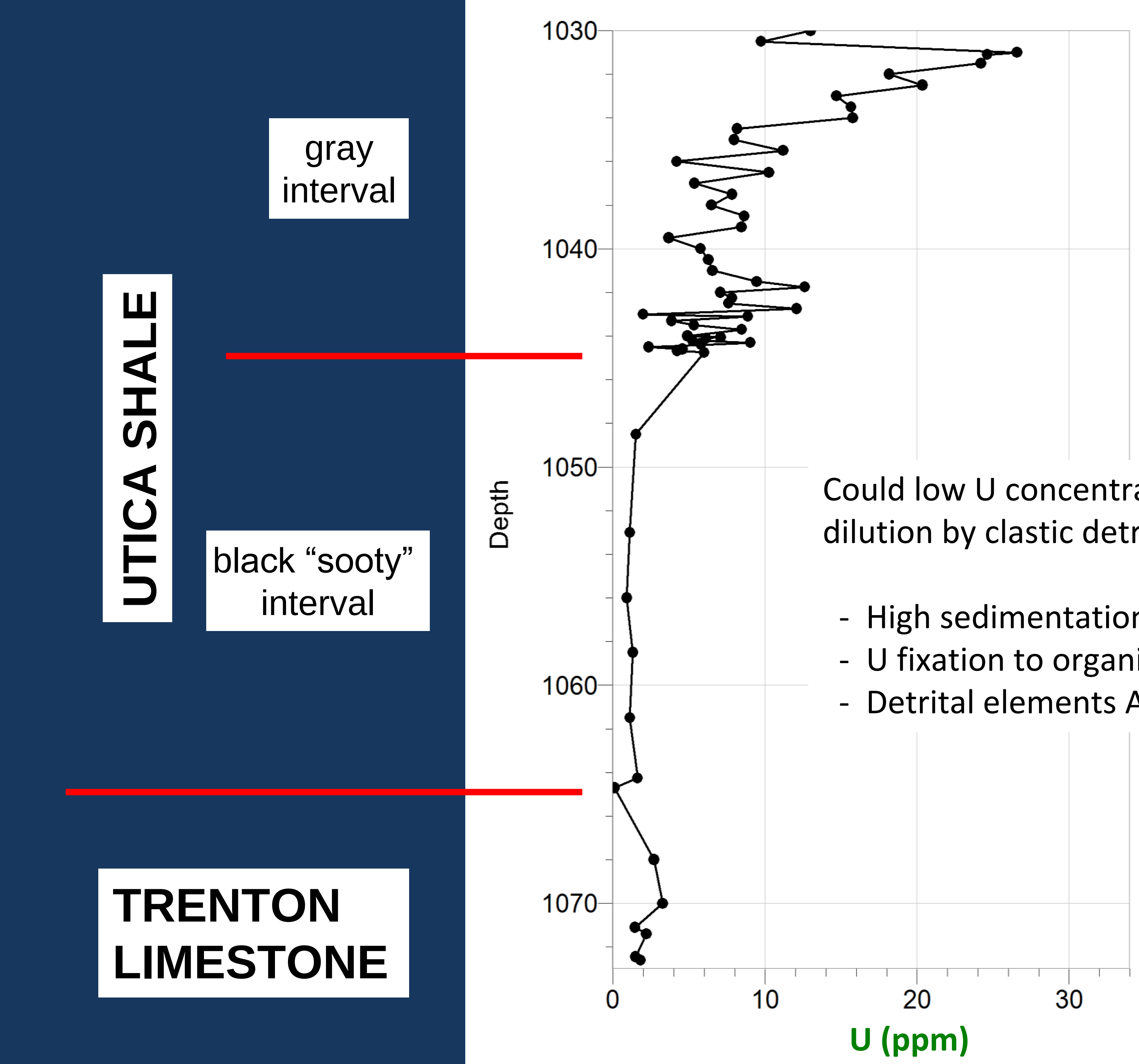
gray interval

black “sooty” interval

TRENTON LIMESTONE

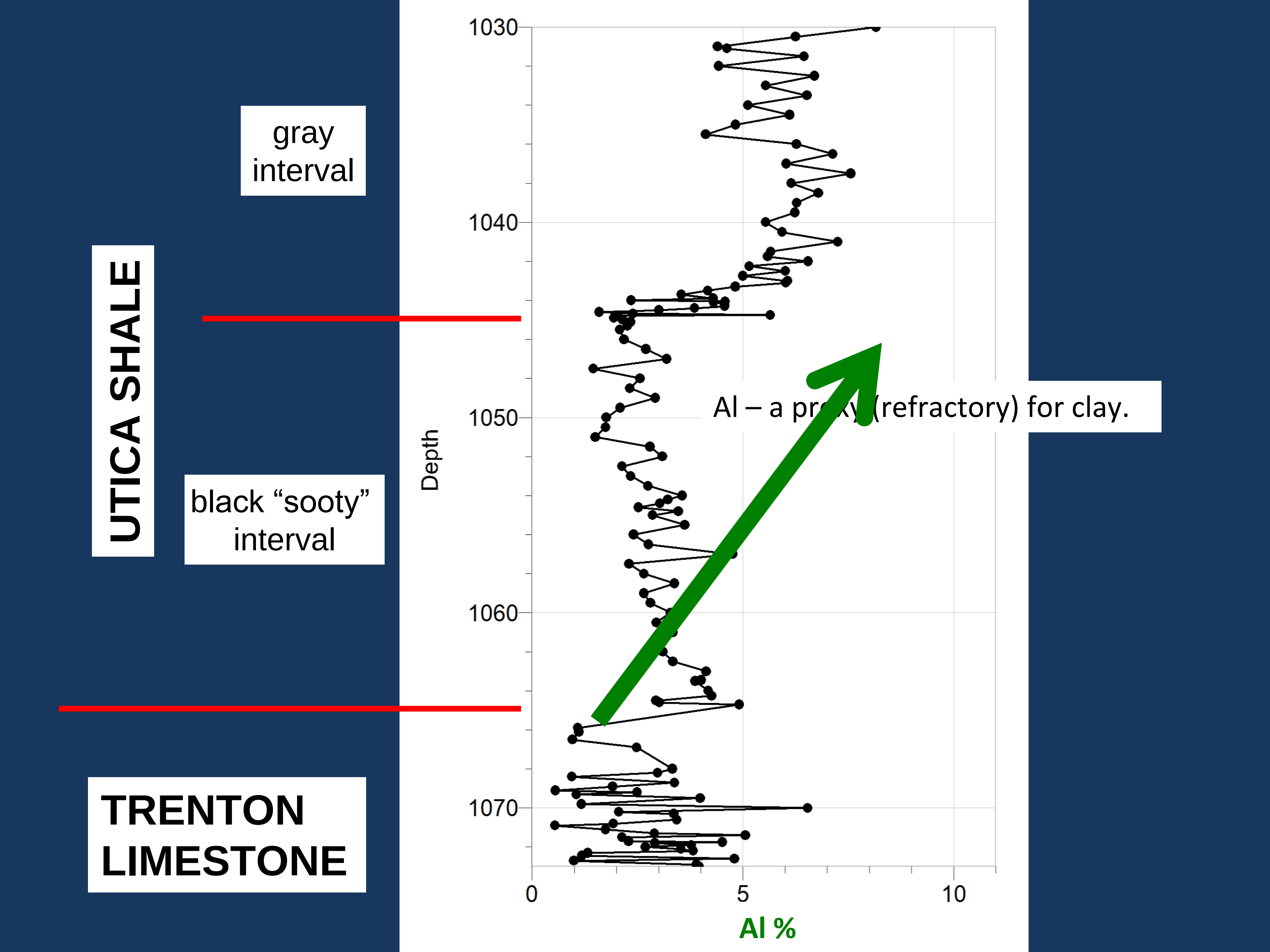


- ✓ U profile indicates values close to or even depleted to crustal values (U = 2.7 ppm)
- ✓ Contact organic-rich & organic-lean correlates to an increase of:
  - ✓ Somewhat in excess
  - ✓ Values not as expected (both intervals)
- ✓ What controls U precipitation?
  - ✓ rate of sedimentation
  - ✓ authigenic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



Could low U concentrations reflect dilution by clastic detritus?

- High sedimentation rate?
- U fixation to organics and sediment
- Detrital elements Al, Si, Zr, Ti



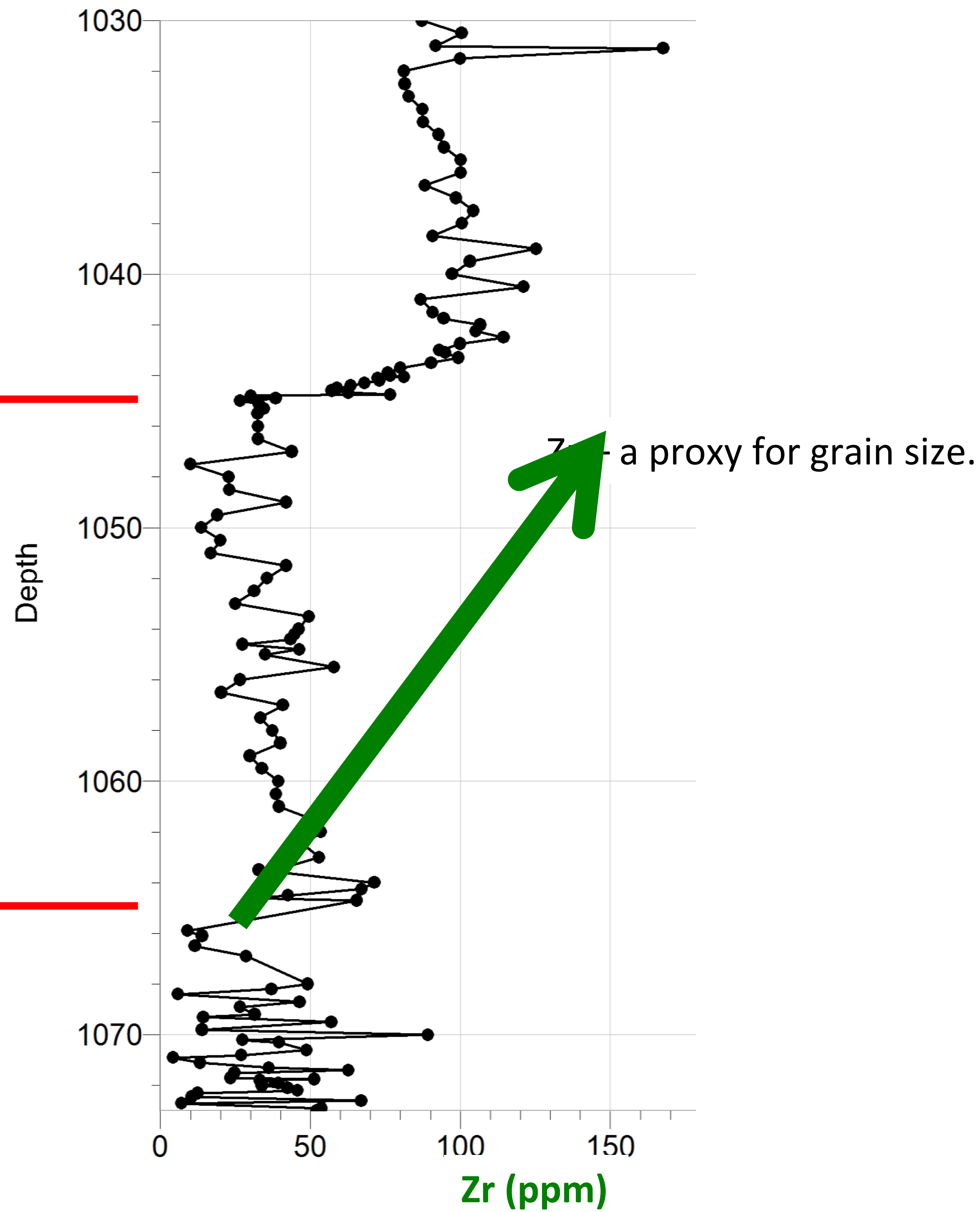
gray interval
UTICA SHALE
black “sooty” interval
TRENTON LIMESTONE
1030
1040
1050
1060
1070
Depth
0
5
10
Al %
Al – a proxy (refractory) for clay.

gray interval

UTICA SHALE

black “sooty” interval

TRENTON LIMESTONE

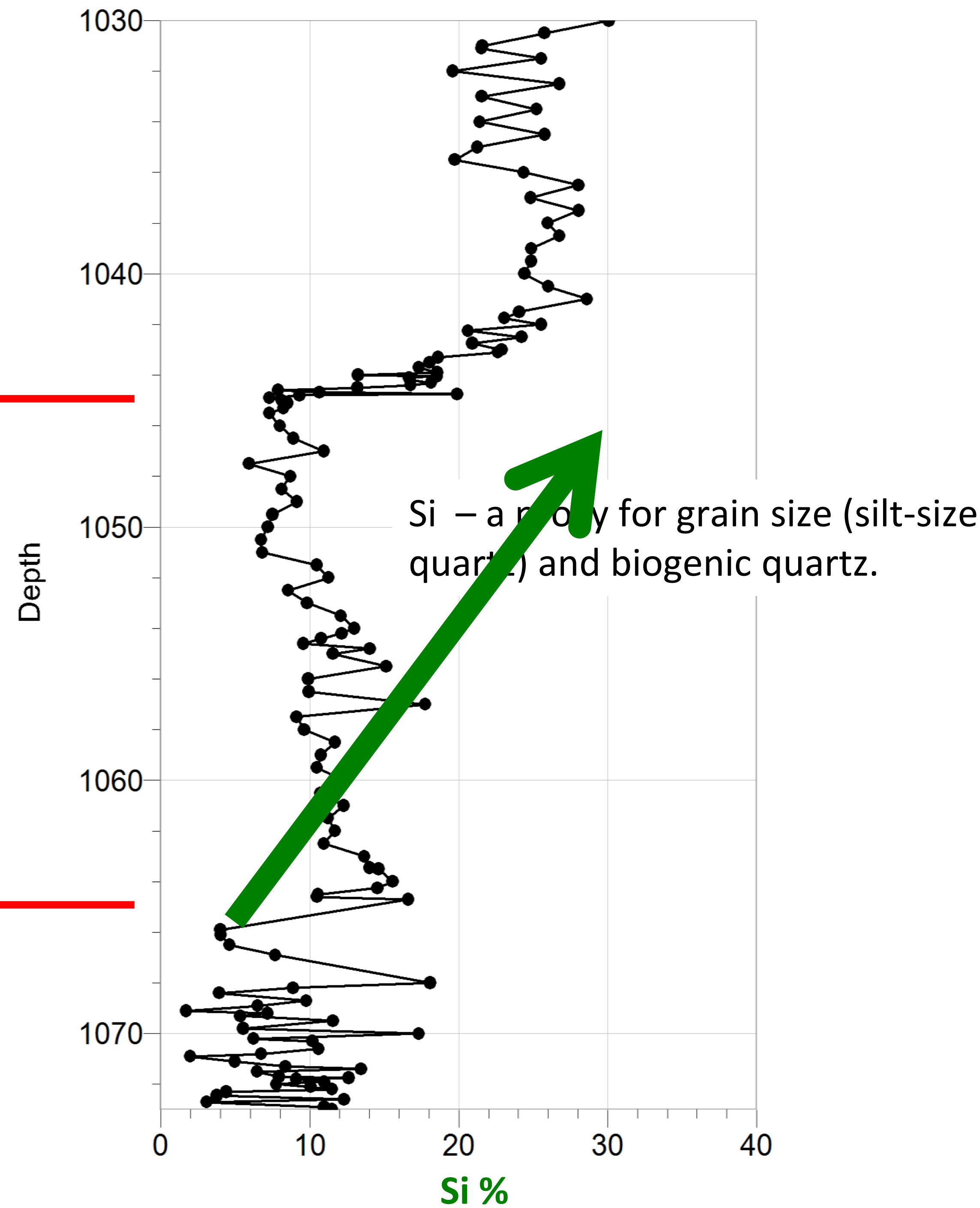


gray interval

UTICA SHALE

black “sooty” interval

TRENTON LIMESTONE

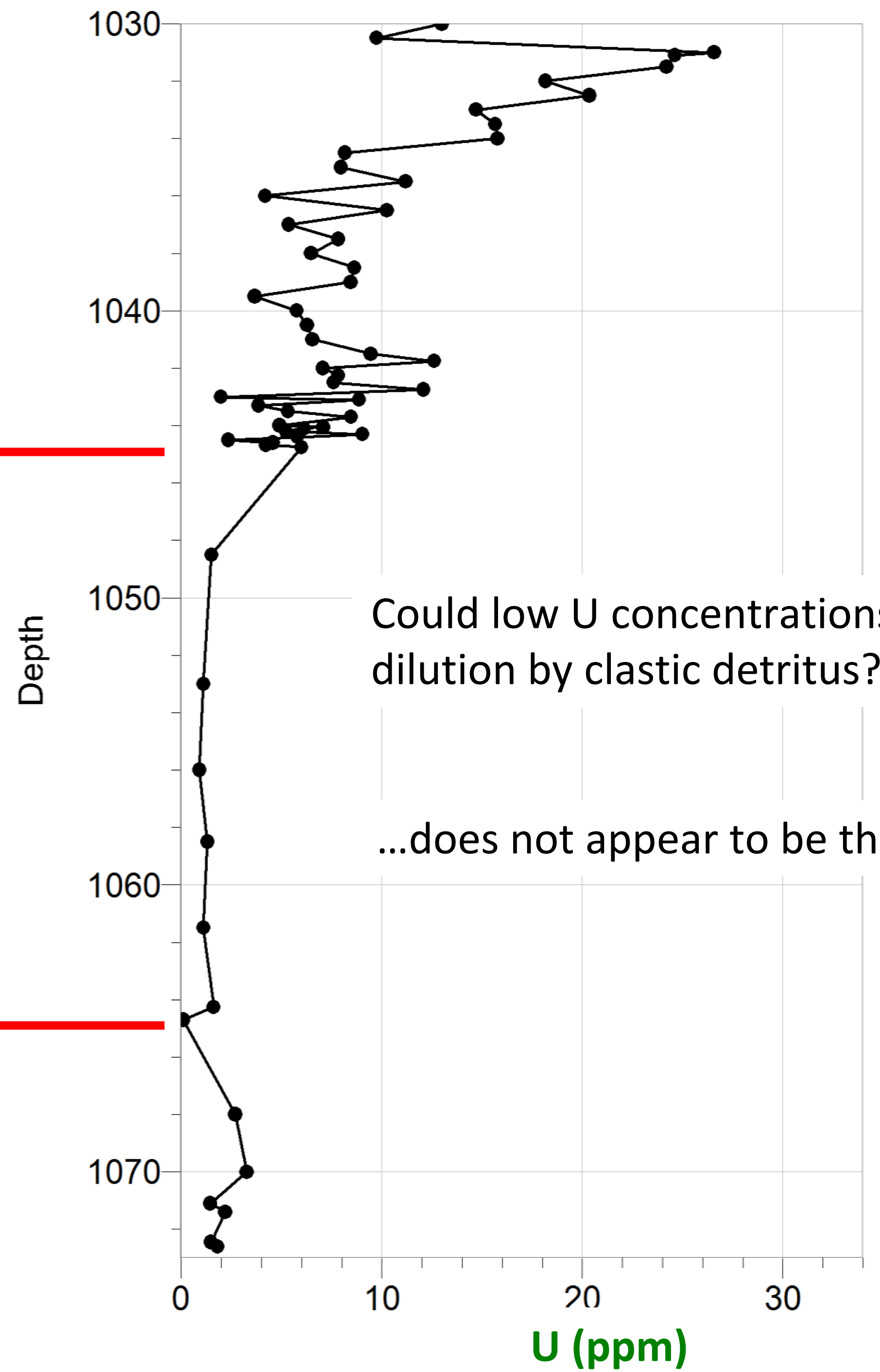


UTICA SHALE

gray interval

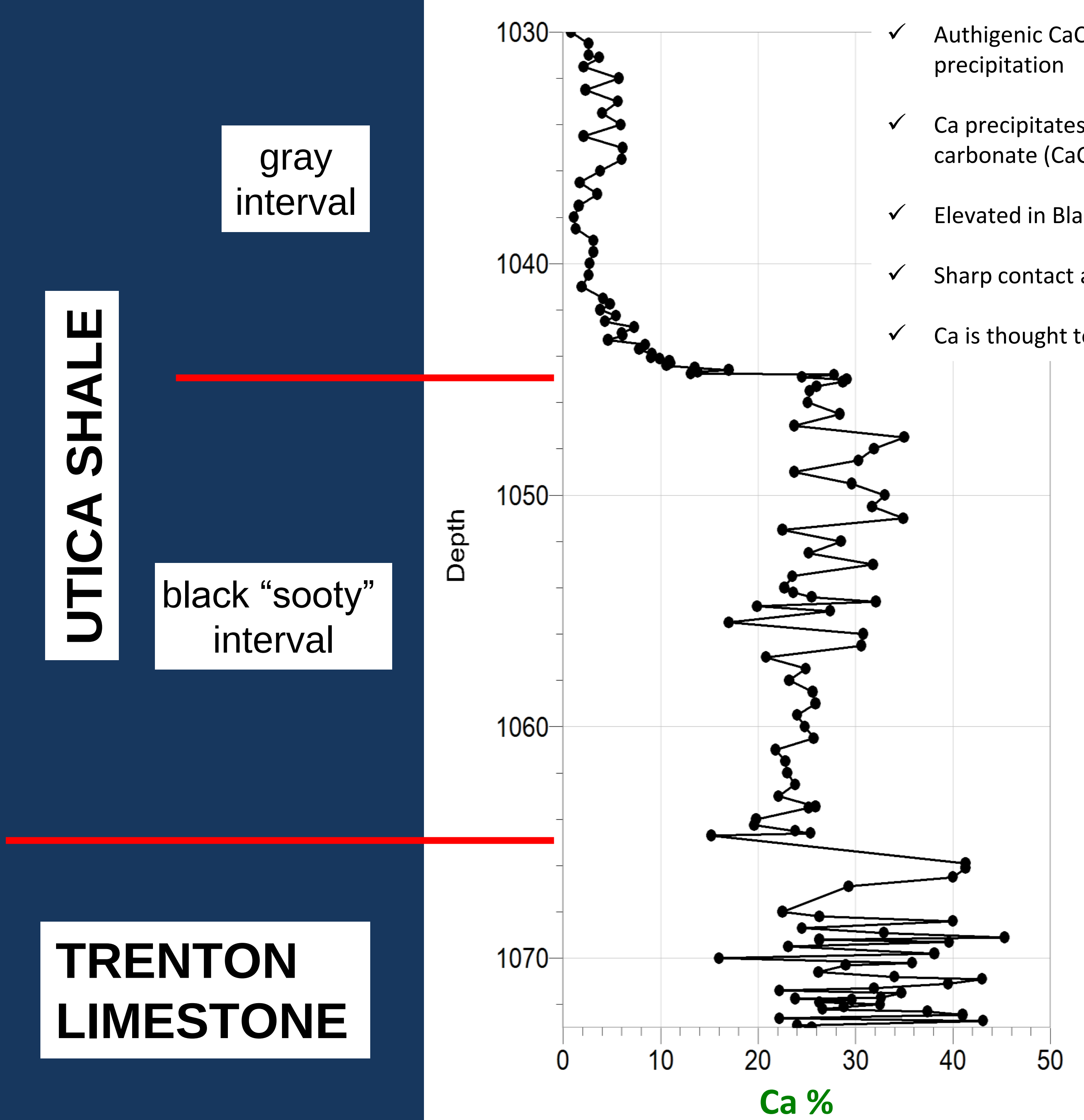
black “sooty” interval

TRENTON LIMESTONE

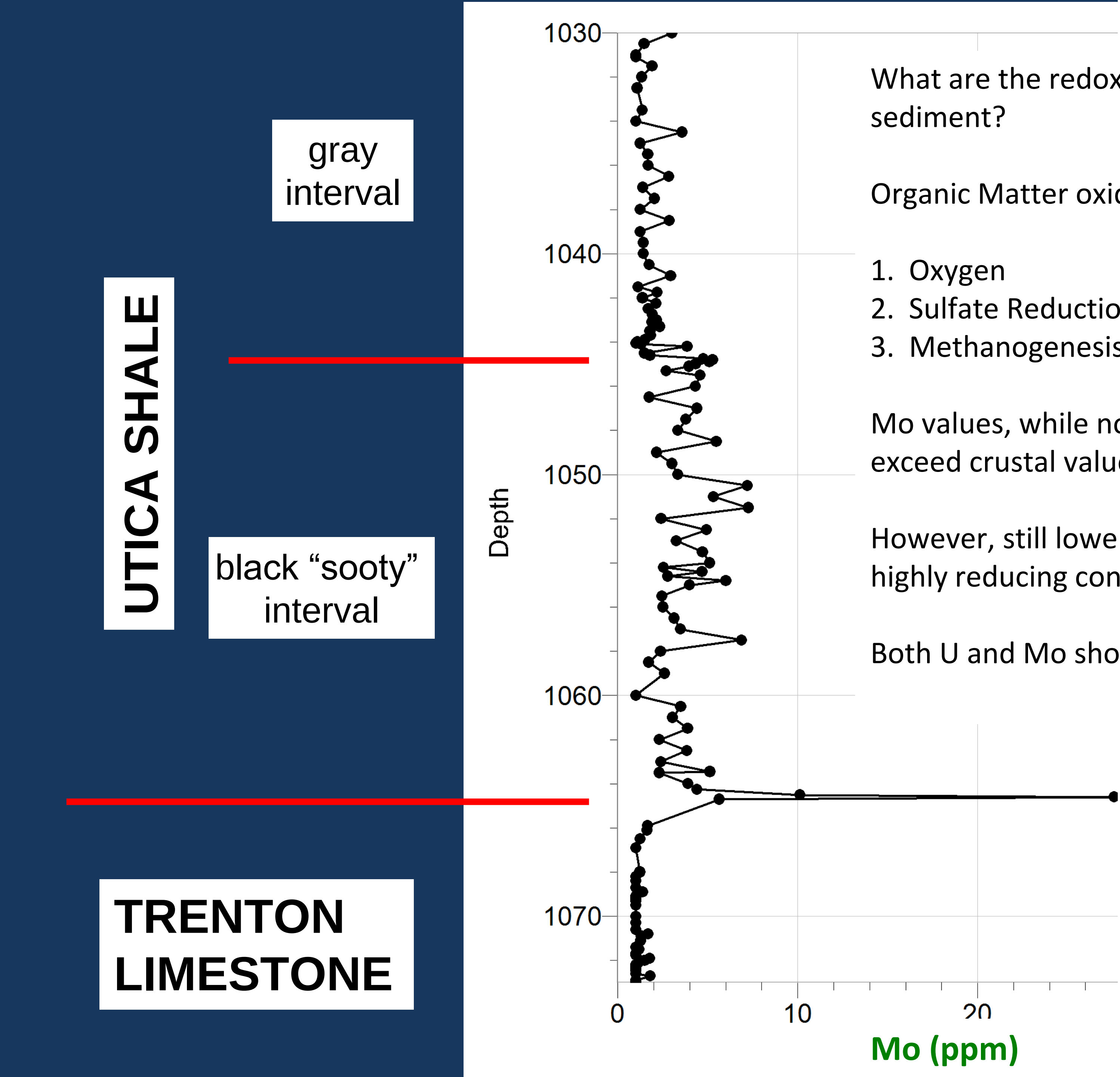


Could low U concentrations reflect dilution by clastic detritus?

…does not appear to be the case…



- ✓ Authigenic CaCO3 precipitation inhibits U precipitation
- ✓ Ca precipitates in limestone as calcium carbonate (CaCO3)
- ✓ Elevated in Black "sooty interval"
- ✓ Sharp contact at black grey interval
- ✓ Ca is thought to be detrital not authigenic



What are the redox conditions of the sediment?

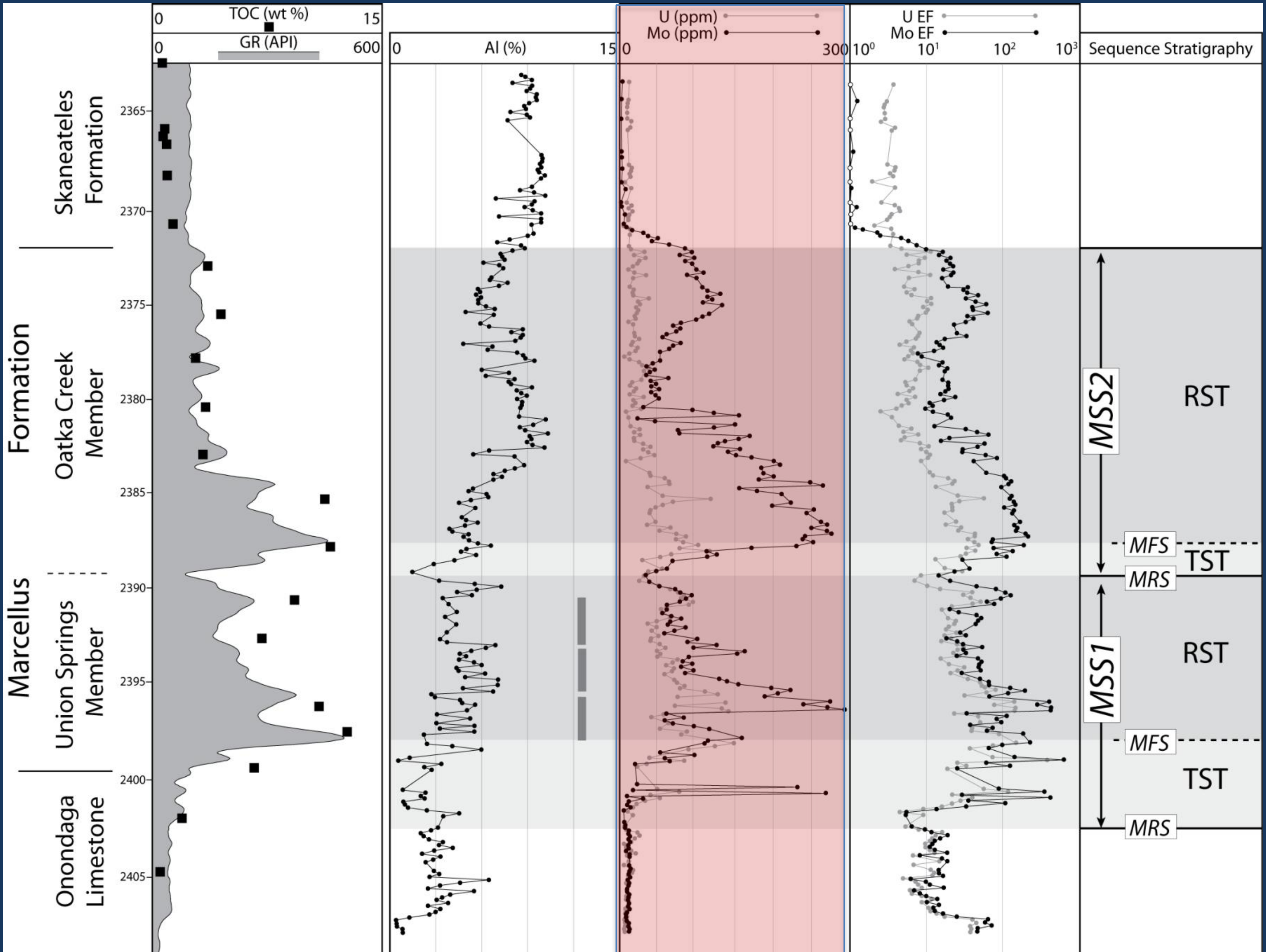
Organic Matter oxidation process:

1. Oxygen
2. Sulfate Reduction (H_2S)
3. Methanogenesis

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

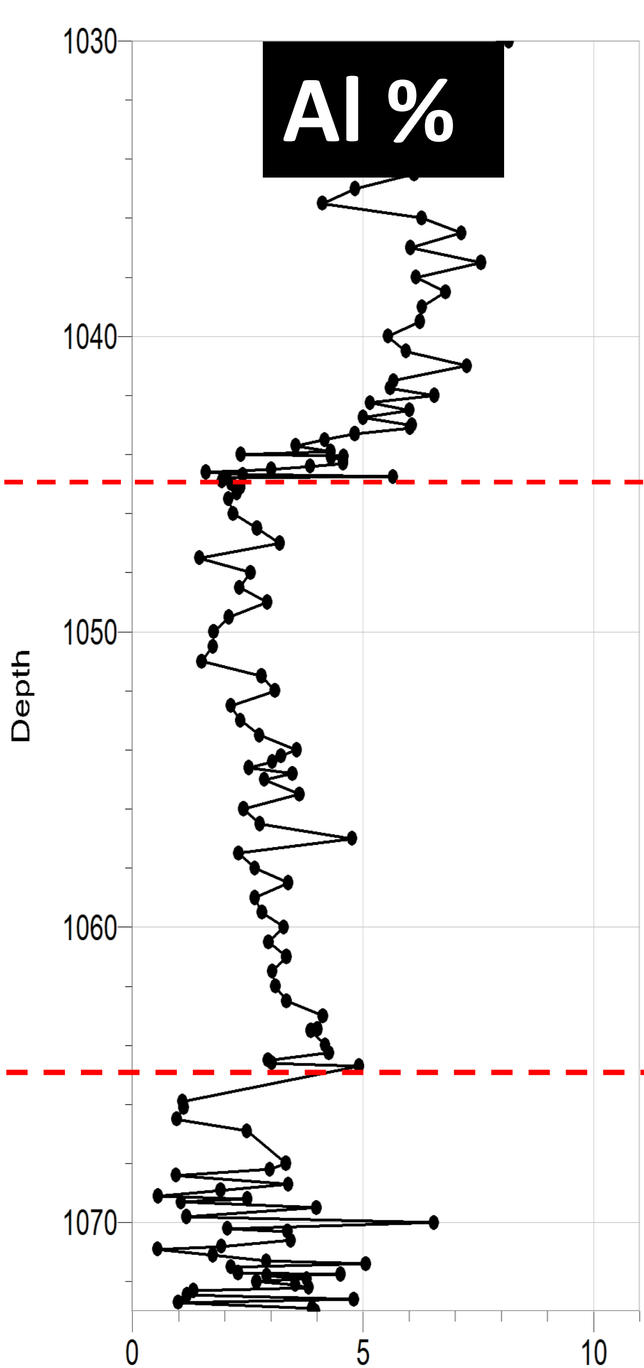


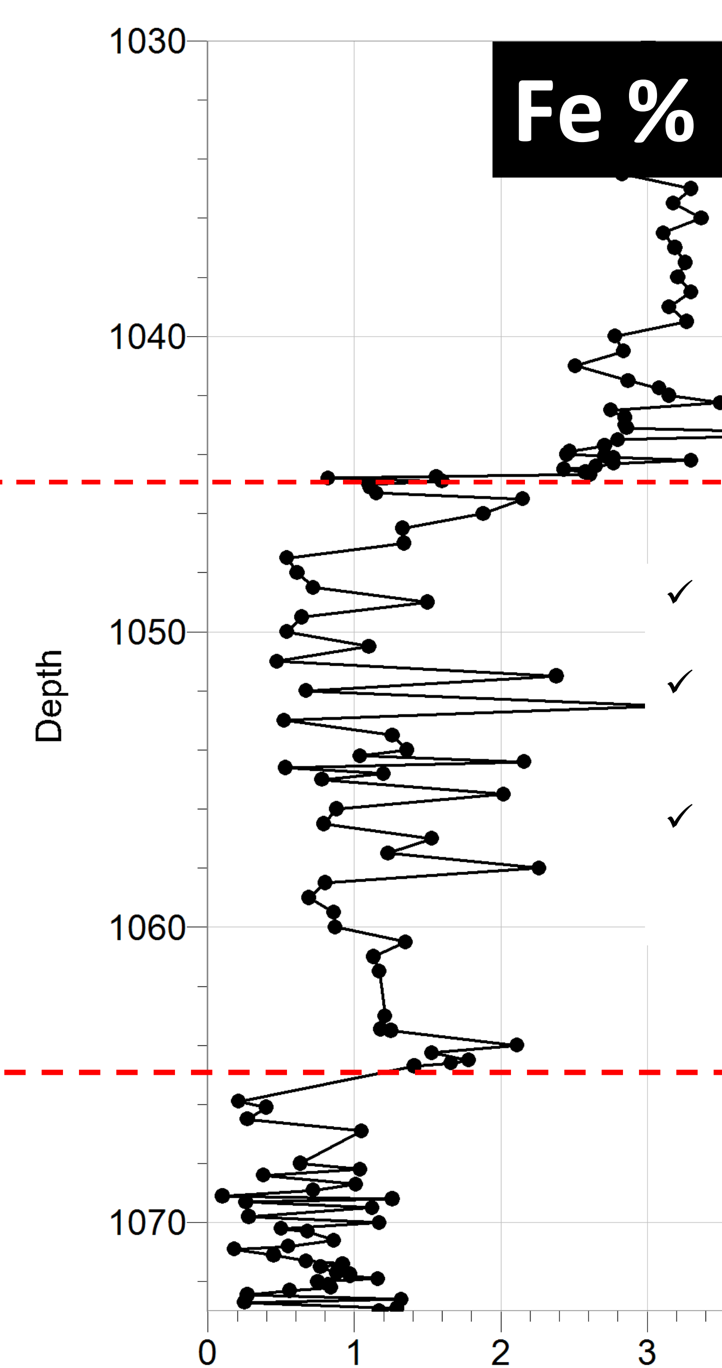
Lash and Blood, 2014. Organic matter accumulation, redox, and diagenetic history of the Marcellus Formation, southwestern Pennsylvania, Appalachian basin: Marine and Petroleum Geology.

gray interval

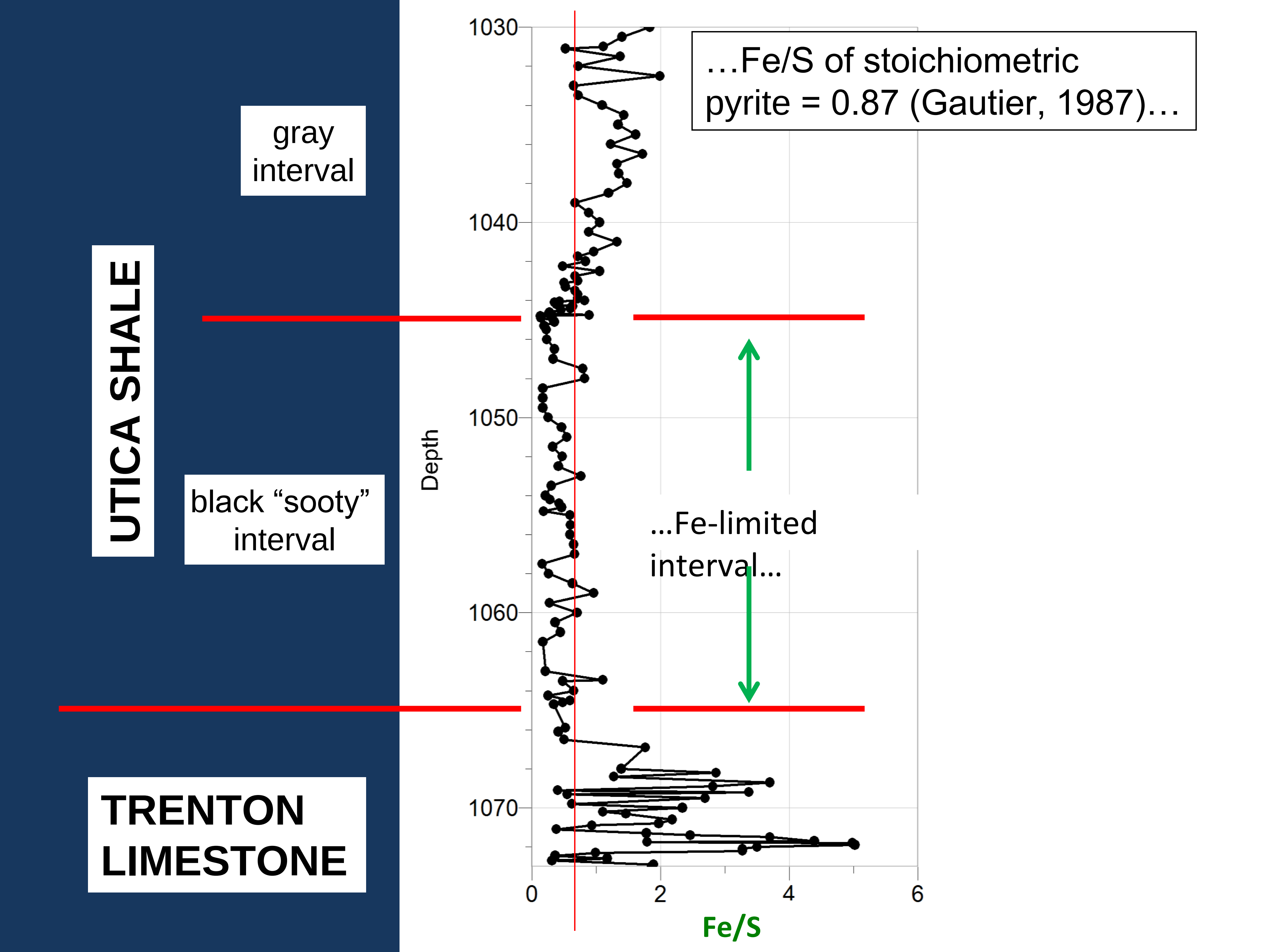
black interval

Trenton

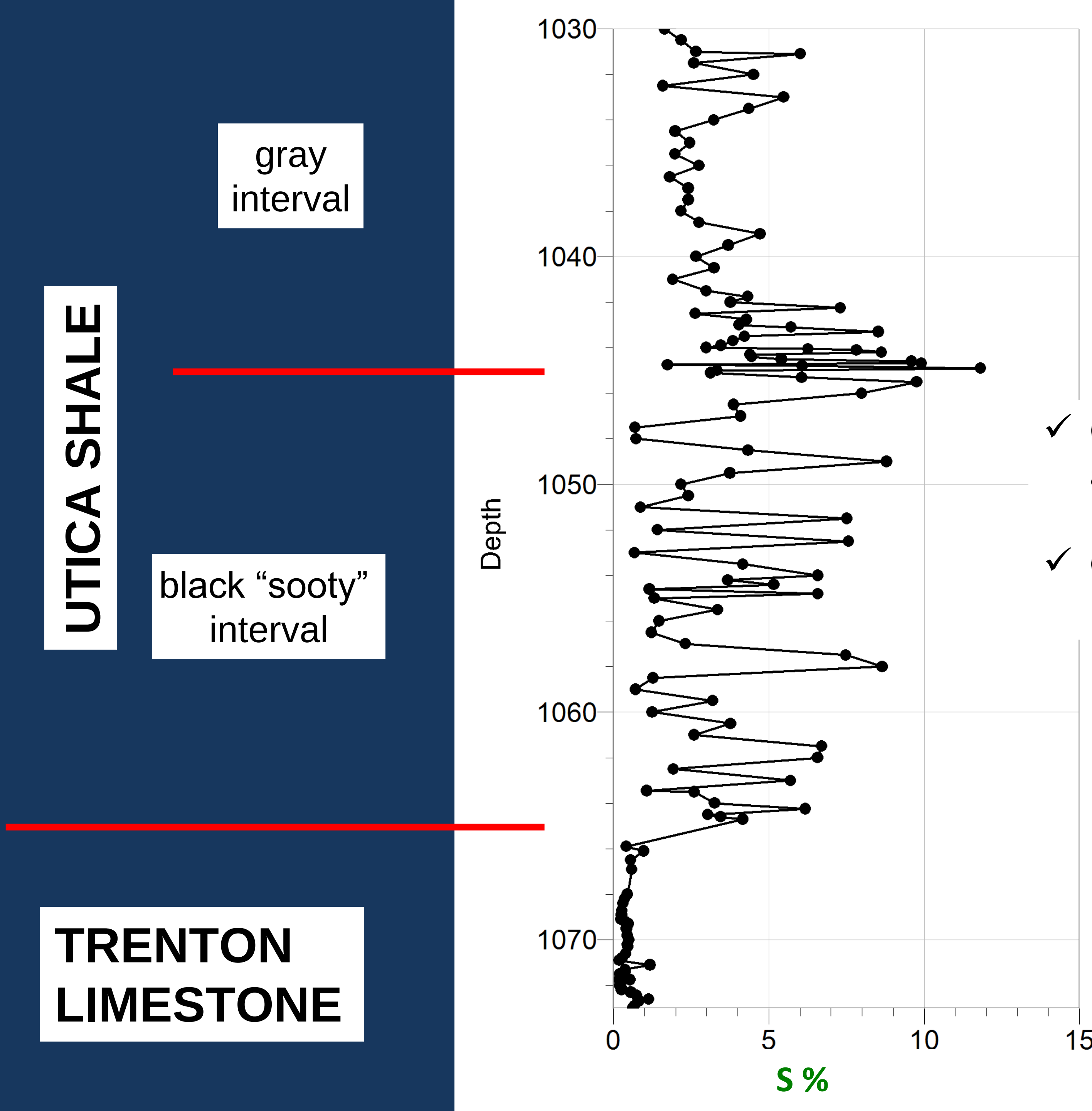




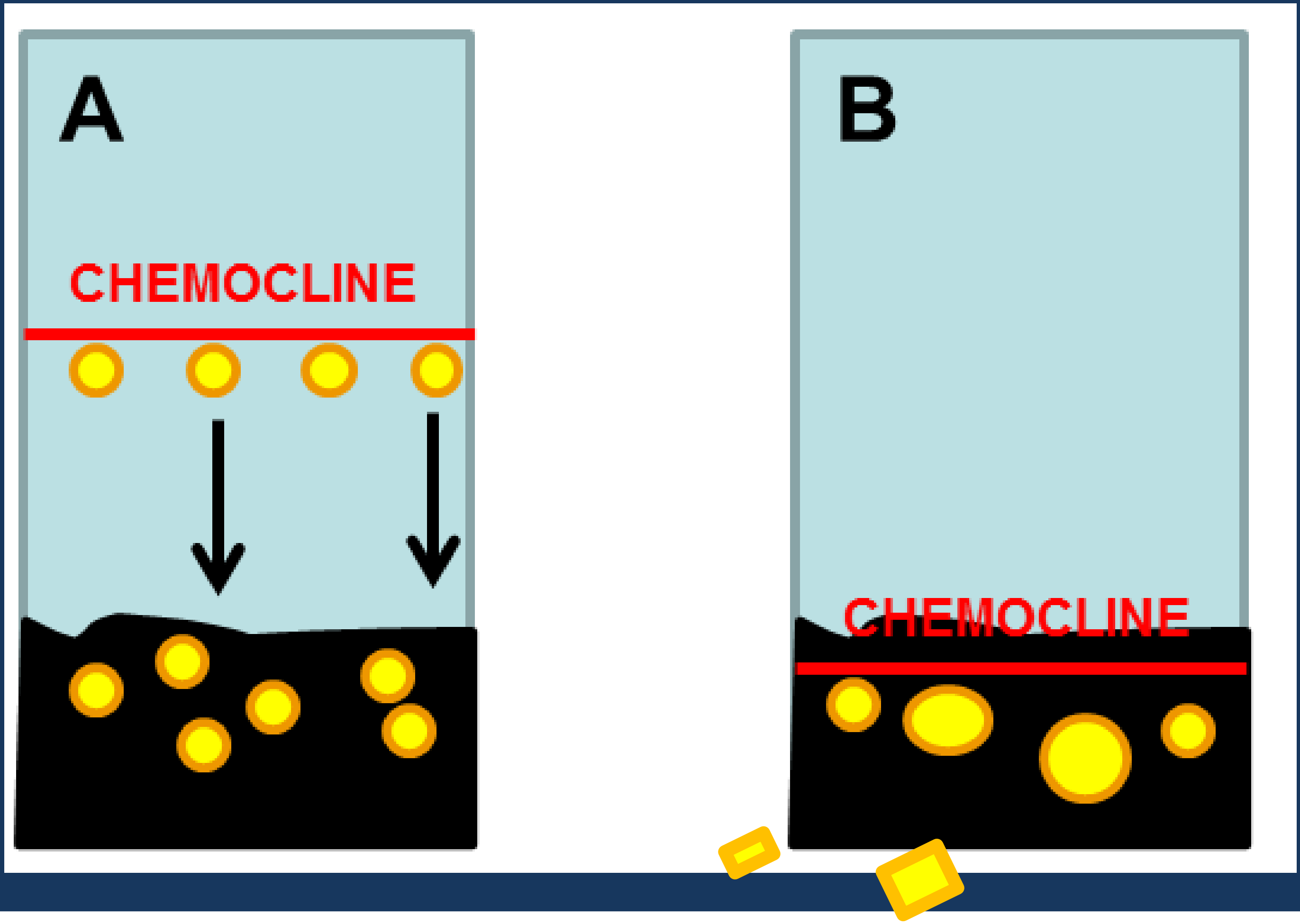
- ✓ Pyrite (FeS_2)
- ✓ Need Reducing condition (H_2S) & reactive Fe
- ✓ Two forms of iron:
  - detrital
  - reactive



gray interval
UTICA SHALE
black “sooty” interval
TRENTON LIMESTONE
…Fe/S of stoichiometric pyrite = 0.87 (Gautier, 1987)…
…Fe-limited interval…
Depth
1030
1040
1050
1060
1070
0
2
4
6
Fe/S

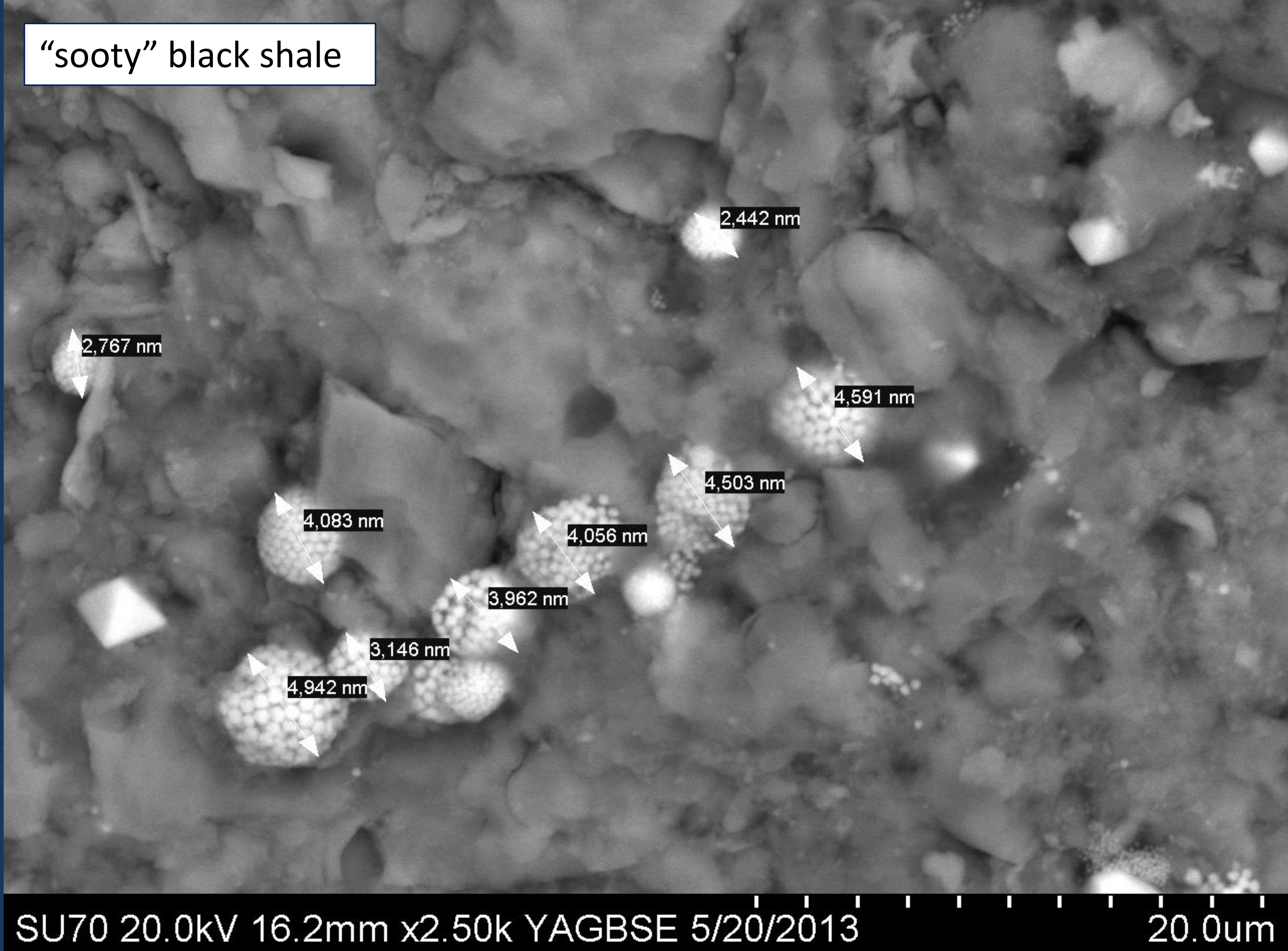


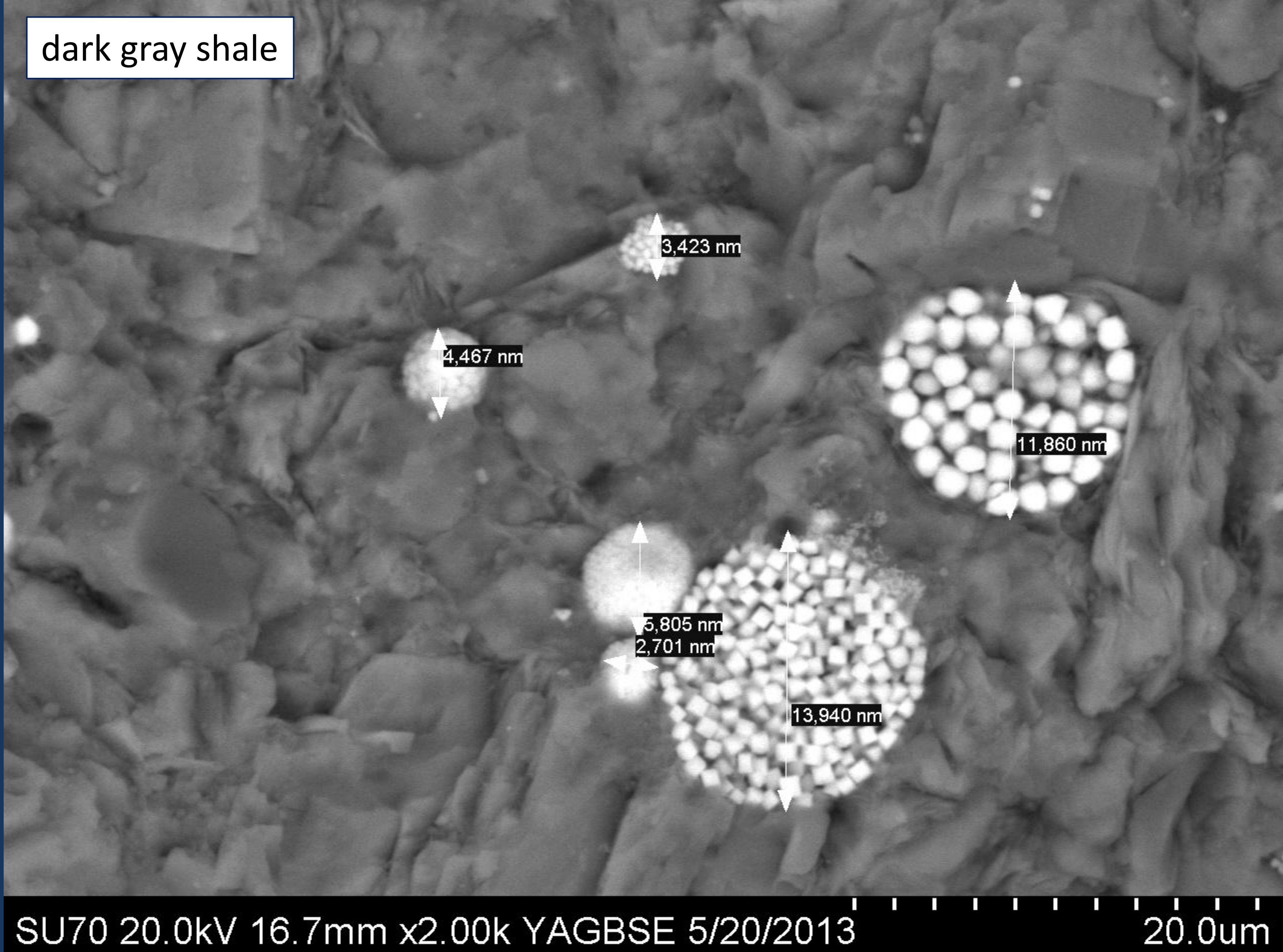
- ✓ Overwhelming amount of Sulfur
- ✓ Conditions must have been reducing

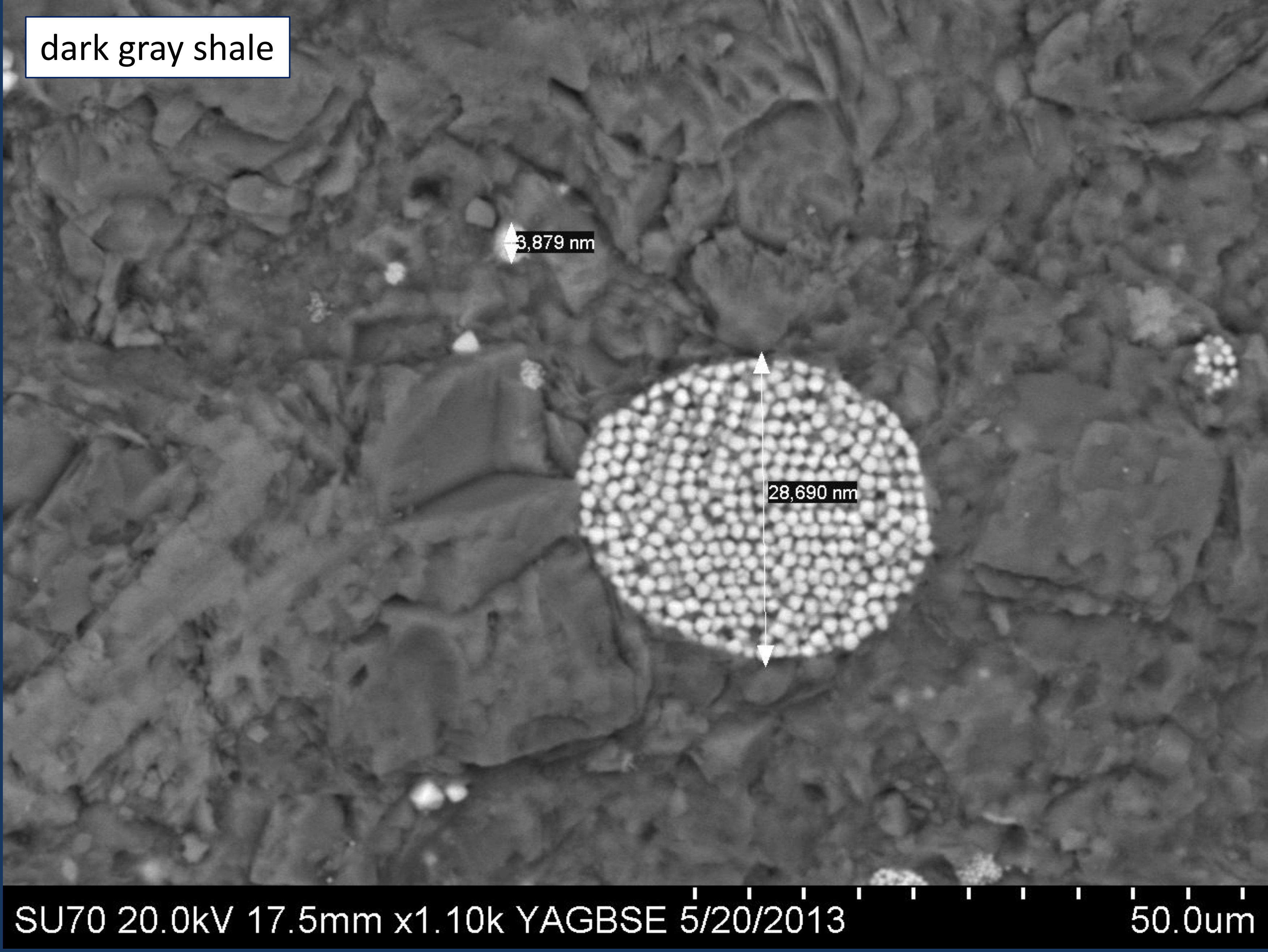


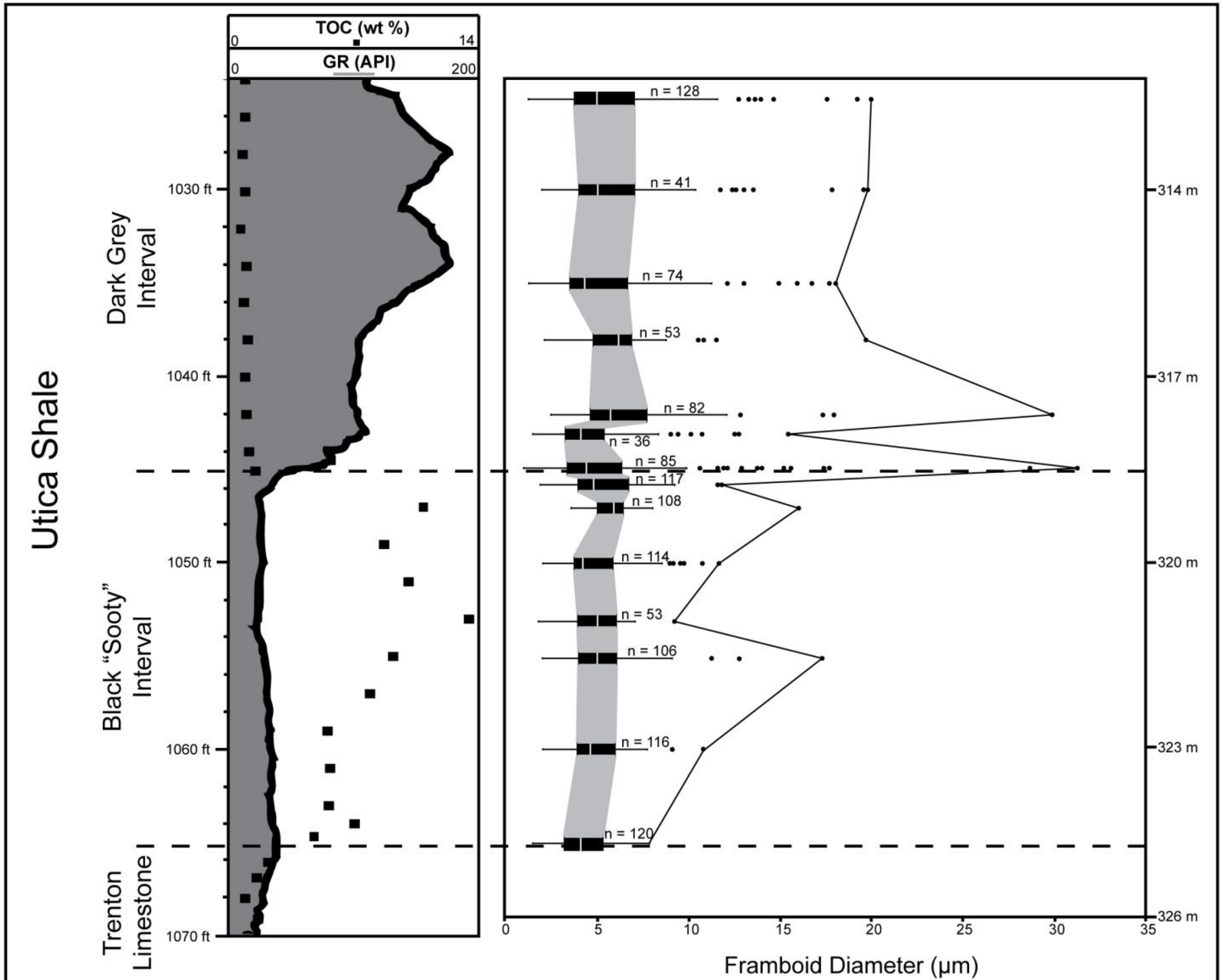
- Pyrite framboids form at the chemocline (small amount of O_2 is necessary);
- Framboids that form in the water column can grow to ~5um before the water cannot support their weight and they sink
  - Statistical analysis of the framboid diameters show that under these conditions mean diameter is ~5um, 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.

“sooty” black shale




dark gray shale
3,423 nm
4,467 nm
11,860 nm
5,805 nm
2,701 nm
13,940 nm
SU70 20.0kV 16.7mm x2.00k YAGBSE 5/20/2013
20.0um


dark gray shale
3,879 nm
28,690 nm
SU70 20.0kV 17.5mm x1.10k YAGBSE 5/20/2013
50.0um



Utica Shale
Dark Grey Interval
Black "Sooty" Interval
Trenton Limestone
TOC (wt %)
0
14
GR (API)
0
200
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)

Remaining Questions

-the “sooty” black shale, the most organic-rich interval, is defined by sub-crustal values of U;

-pyrite morphologies, Mo enrichment, and Fe/S suggest that the “sooty” black shale accumulated under reducing to intermittently euxinic, Fe-limited conditions;

-explanation for the seemingly U-depleted nature of the most organic-rich deposits;

-Middle (Late) Ordovician (Caradocian) Oceanic Anoxic Event;

Questions

Steve Saboda,
Geologist,
American Energy Utica, LLC
steve.saboda@aep-lp.com

Gary G. Lash,
Dept. of Geosciences,
SUNY Fredonia,
Fredonia, NY, 14063