Inorganic Geochemistry of the Middle-Upper Ordovician Utica Shale Defining Clastic Trends Including a Change of Source Provenance Based on XRF Data*

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Abstract

The Middle-Upper Ordovician Utica Shale was deposited during a time when atmospheric conditions did not favor the establishment of land plants resulting in clastic input different from what conventional wisdom holds for organic-rich shales. A chemostratigraphic analysis of a Utica Shale core from eastern New York using handheld XRF technology reveals two organic-rich intervals depleted in detrital elements including Al, Si, Ti, and K reflecting the lack of clastic input including the abundance of clay. Perhaps the most noticeable feature of both organic-rich intervals is the enrichment of calcium, which is thought to be detrital as opposed to authigenic or biogenic calcium carbonate. Not only are the two organic-rich intervals enriched in Ca, however, the Ca profile displays a steady increase from the lower organic-rich interval to the upper 33m thick interval. Calcium's steady increase, including the 33m calcareous interval, may be due to a change in the tectonic stress regime resulting in an increase in the amount of carbonate sediment shed from a peripheral forebulge into the basin. Above both organic-rich intervals a sharp increase of detrital elements Al, Si, Ti, and K reflect pulses of sediment delivered to the basin indicating a change of environment and dilution of organic matter. Al, which is a robust proxy for clay displays cyclicity throughout much of the core influenced by sea level fluctuations and may reveal 3rd or 4th order cycles. Superimposed on to the cyclic deposition of the Utica is a change of source provenance indicated by a sharp contact of zirconium, nickel, and vanadium. The lack of a land plant root system during the Ordovician may have resulted in lower sediment input including clay and resulting low algal productivity.

Selected References

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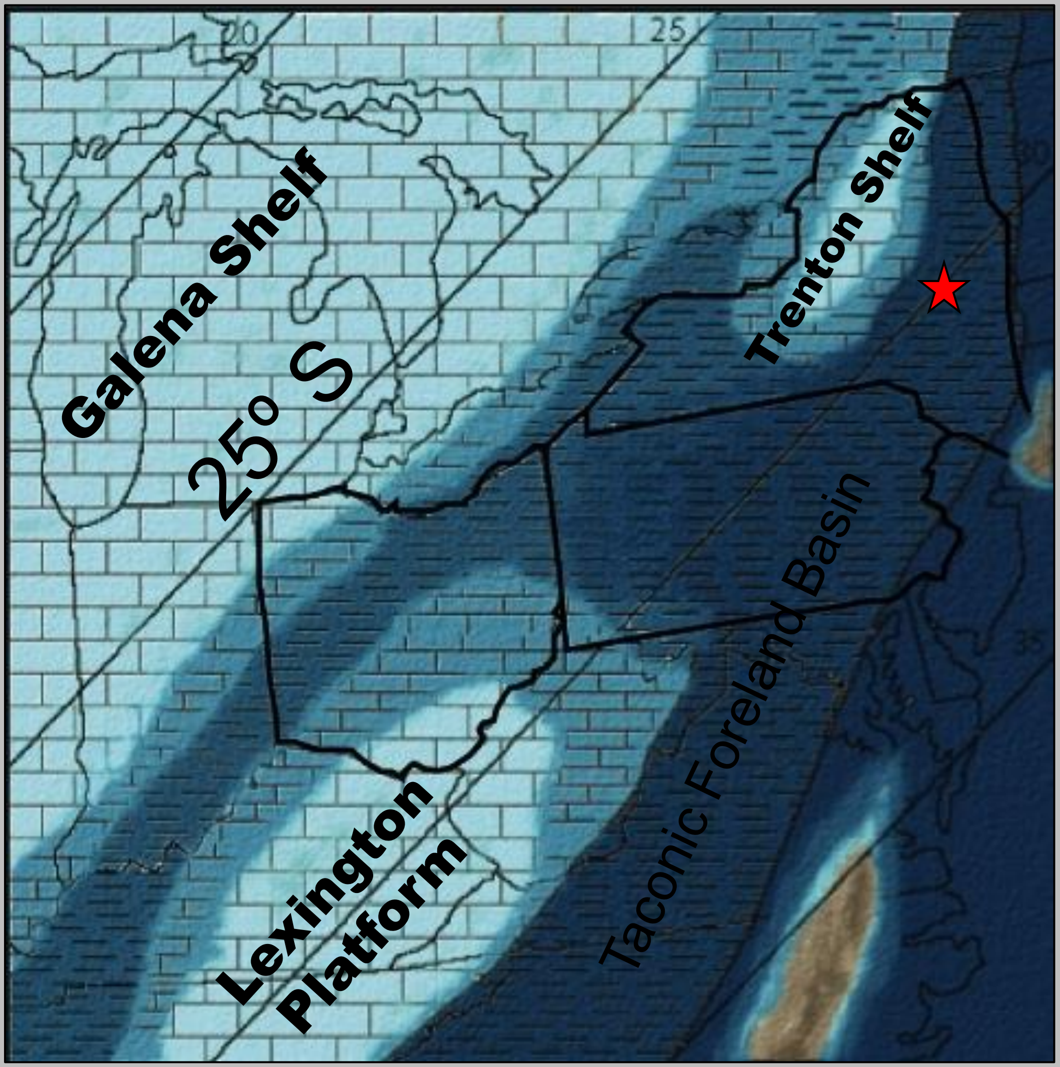
Gary G. Lash, SUNY Fredonia

Introduction to Chemostratigraphy

Analyzing a Utica Shale Core by use of XRF (X-ray fluorescence) 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
5. Reservoir Quality

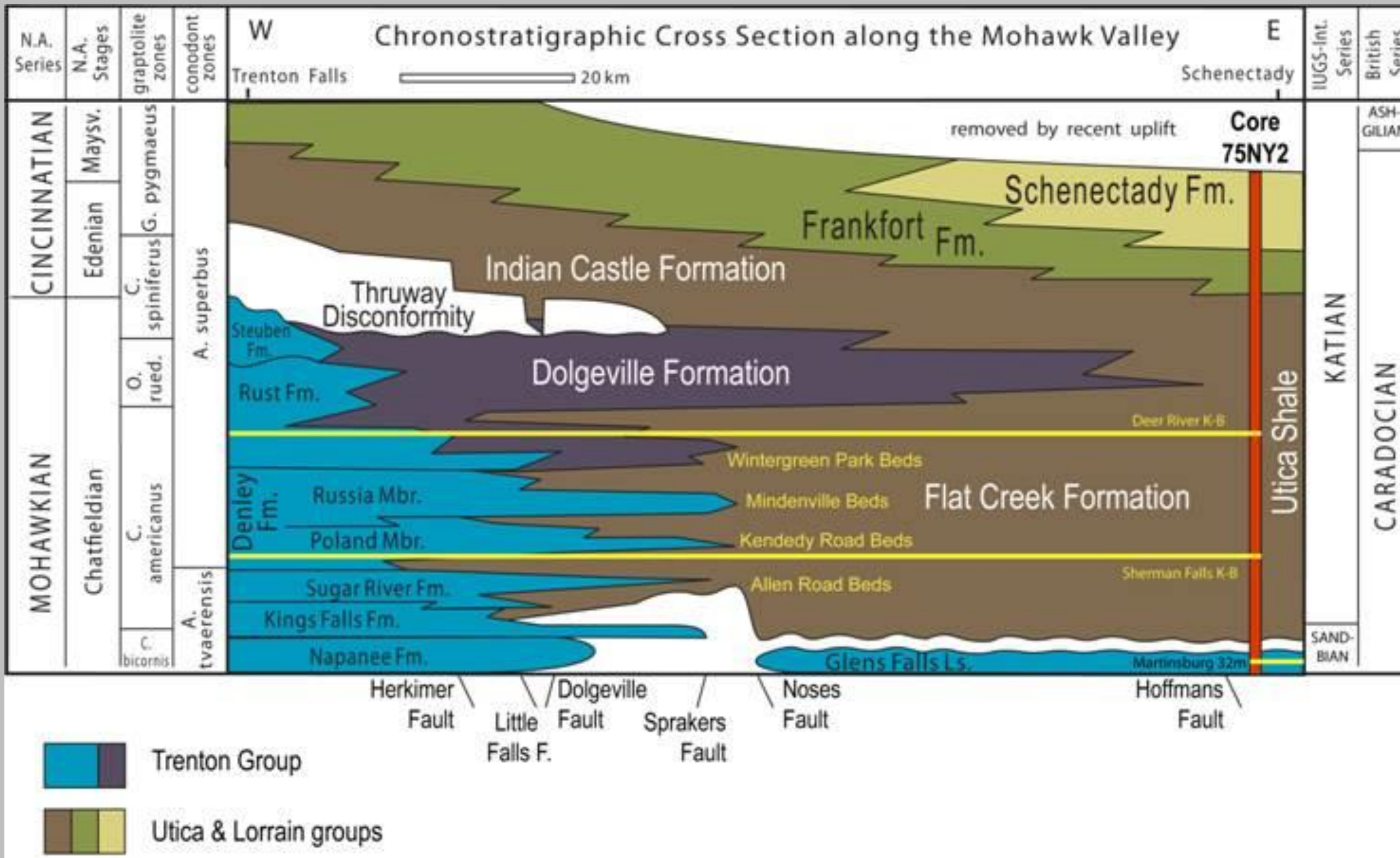
Core 75NY-2 Location



Modified after Cornell (2003)

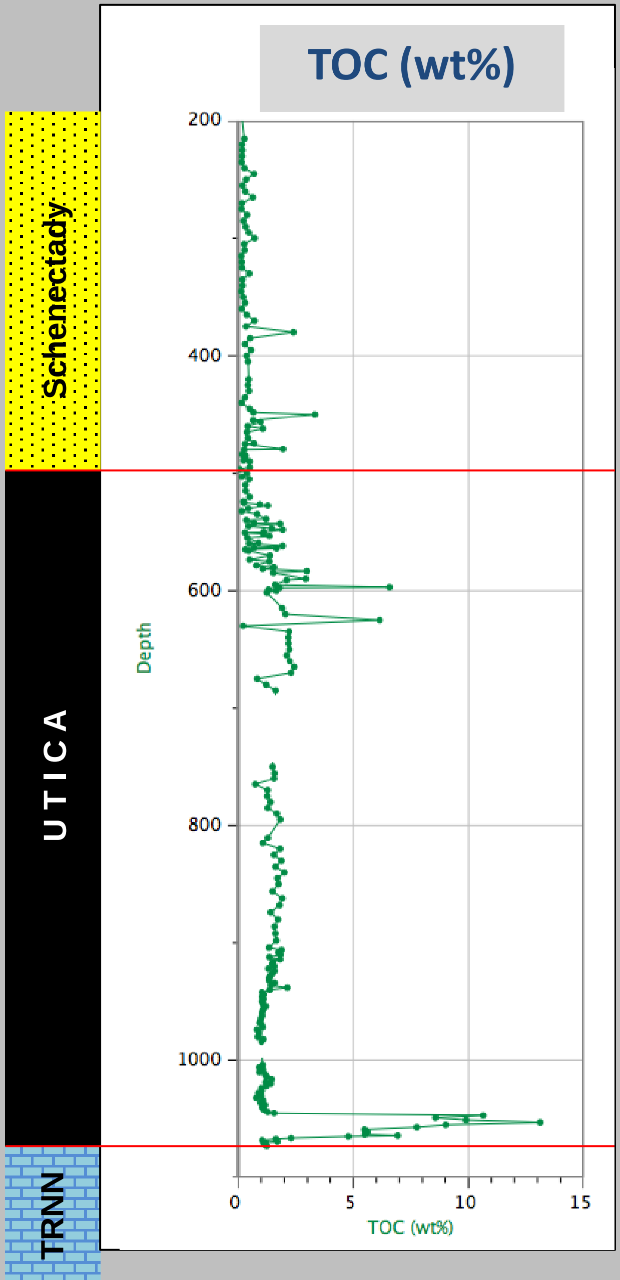
http://www.mcz.harvard.edu/Departments/InvertPaleo/Trenton/Intro/GeologyPage/Geologic%20Setting/paleogeogsetting.htm#easternla urentia

Mohawk Valley Stratigraphy

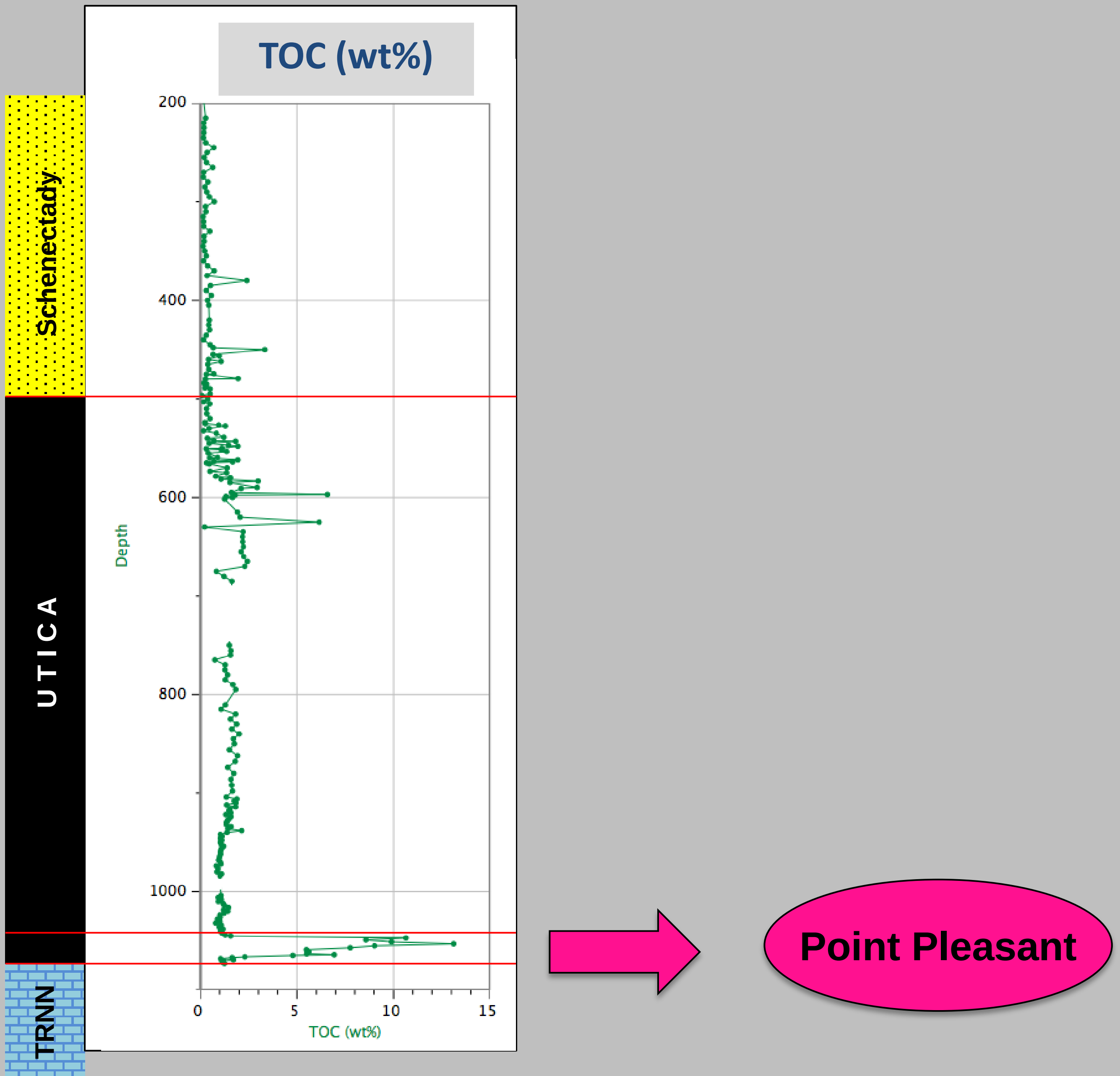


Jacobi and Mitchell, 2002

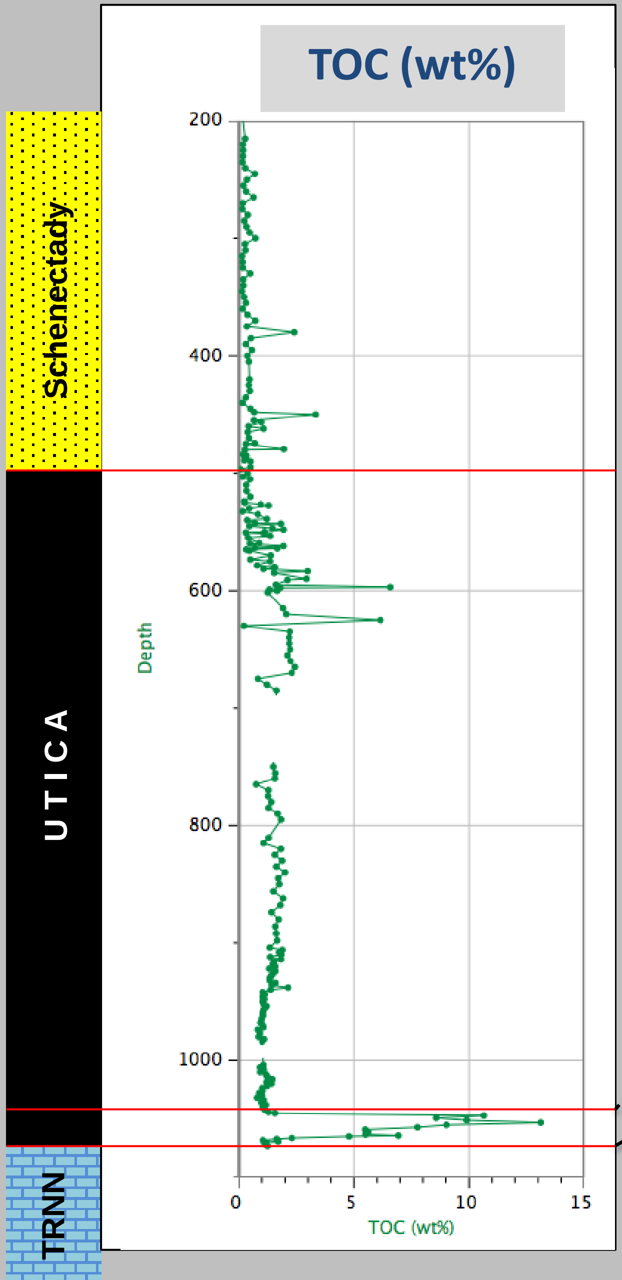
Stratigraphy

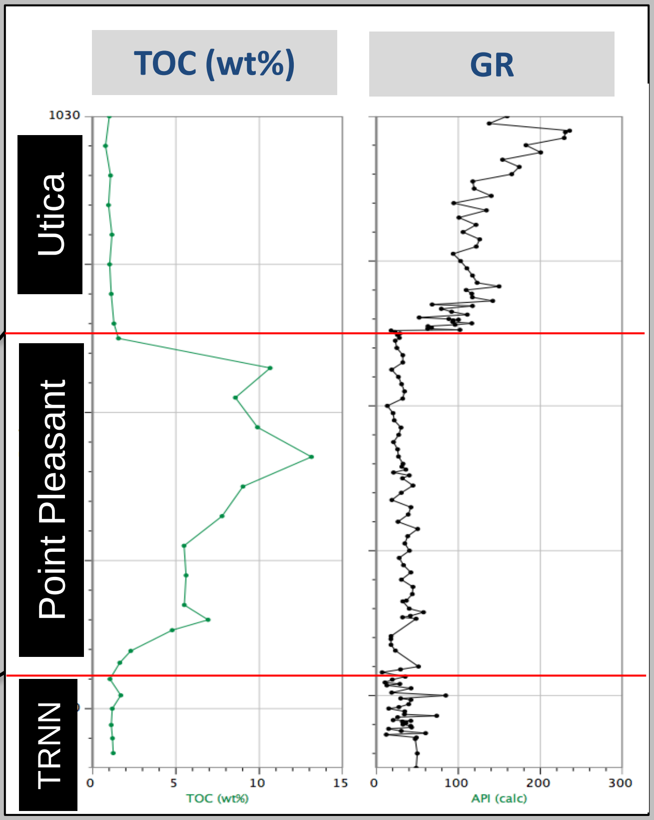


Stratigraphy



Stratigraphy



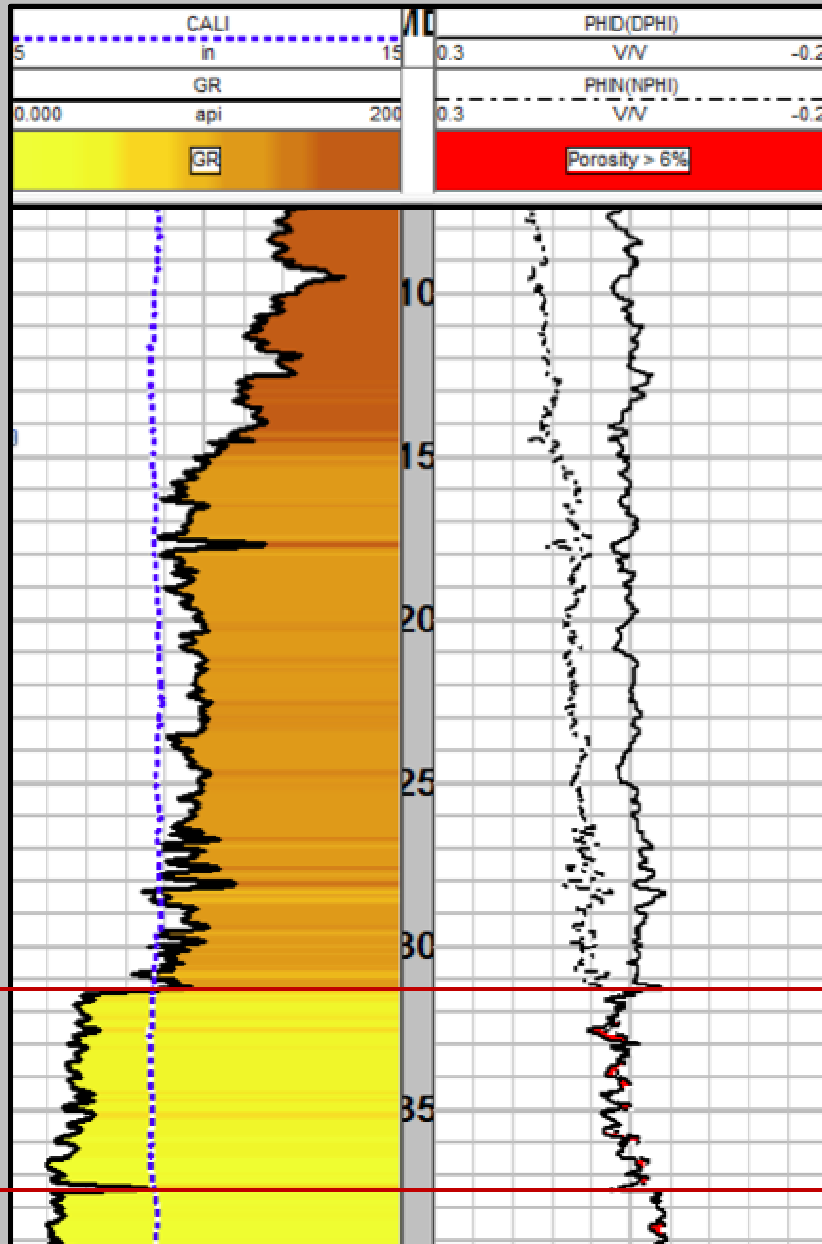


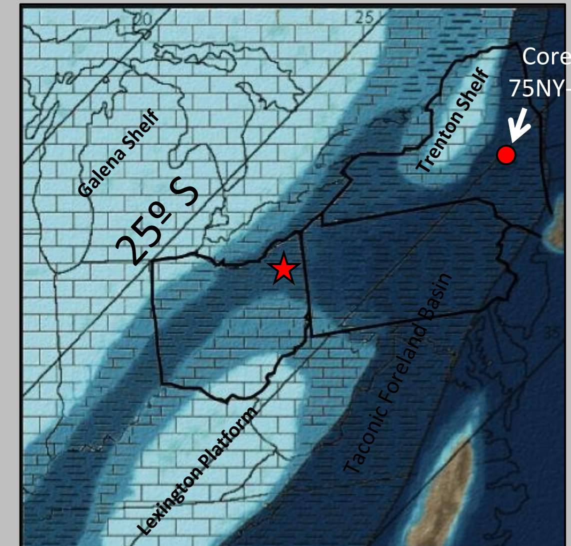
Point Pleasant

Utica Shale

Point Pleasant

Trenton Limestone

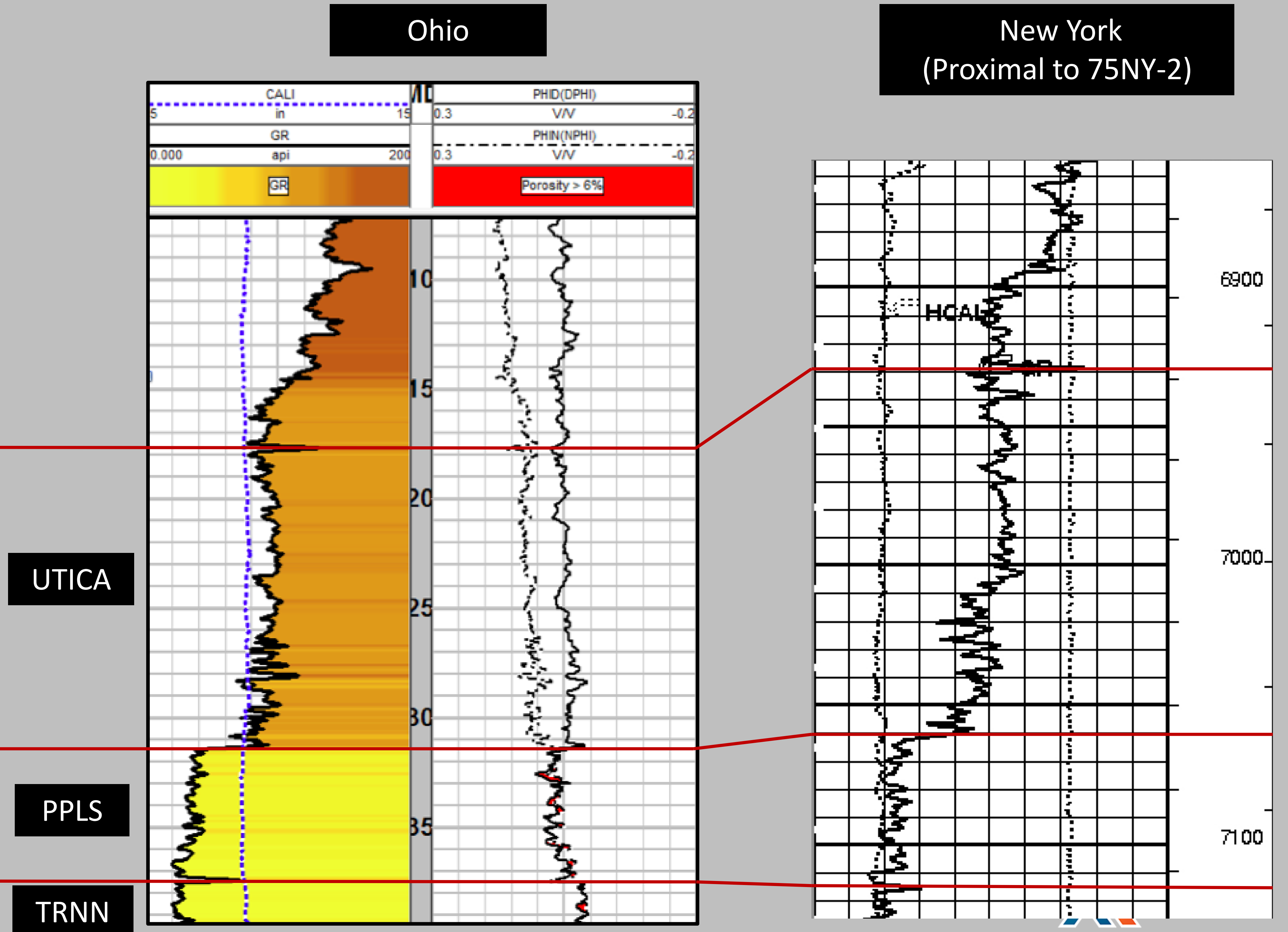


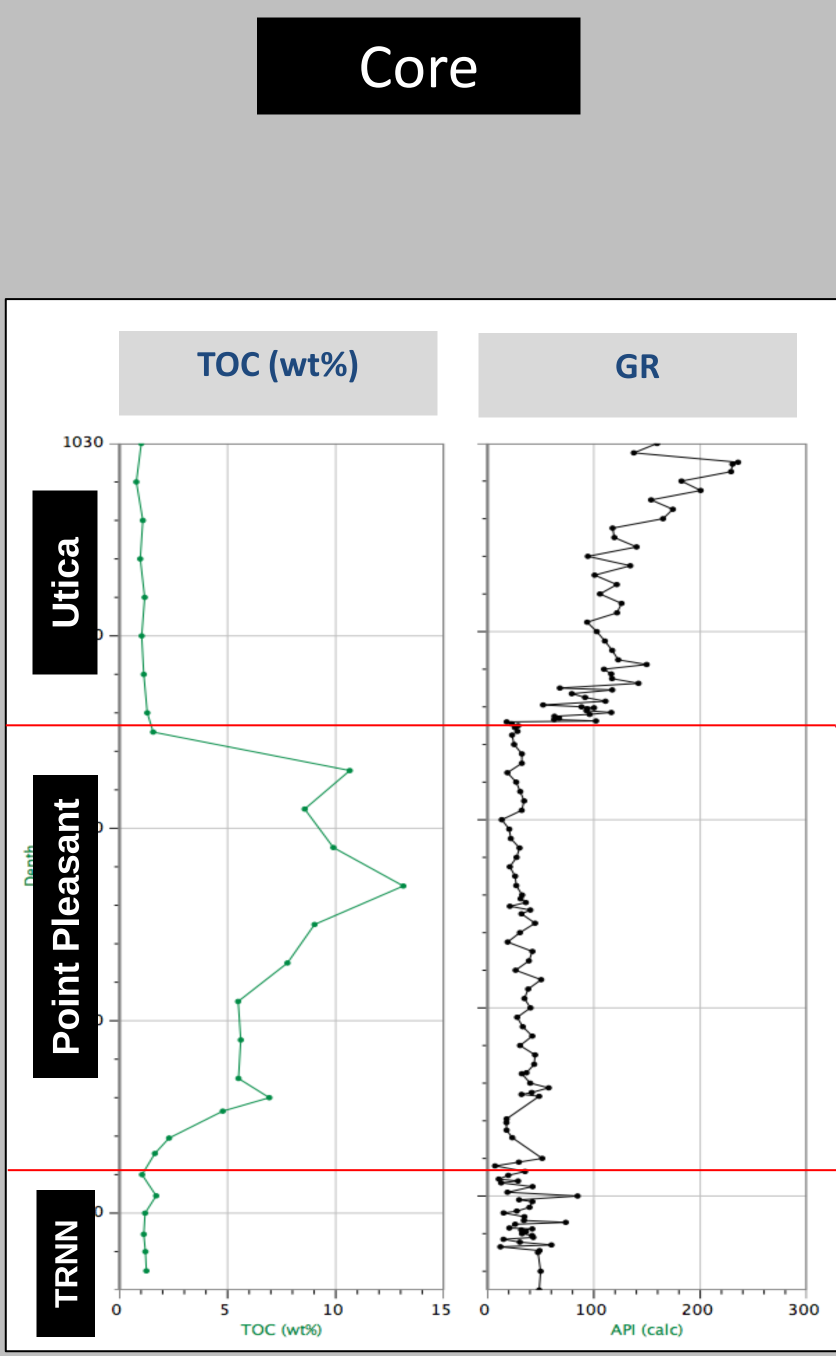


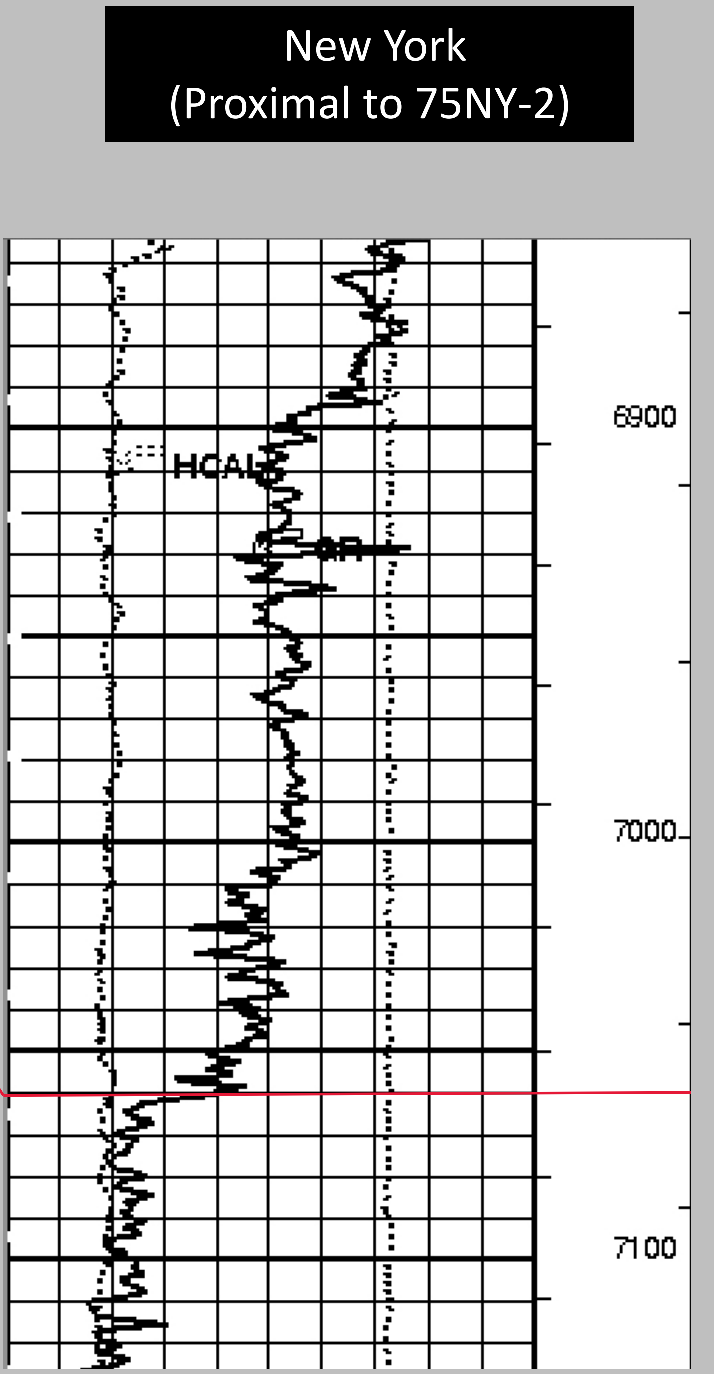
Modified after Cornell (2003)

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

Ohio

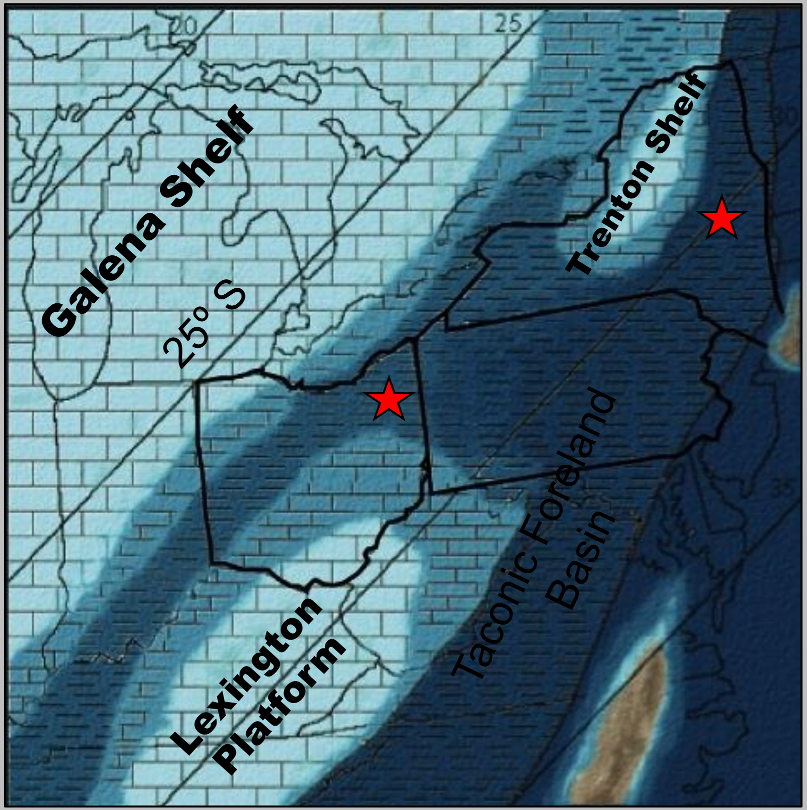

Ohio
New York
(Proximal to 75NY-2)
CALI
5
in
15
GR
0.000
api
200
GR
PHID(DPHI)
0.3
V/V
-0.2
PHIN(NPHI)
0.3
V/V
-0.2
Porosity > 6%
10
15
20
25
30
35
HCAL
6900
7000
7100
UTICA
PPLS
TRNN


Core
TOC (wt%)
GR
1030
Utica
Point Pleasant
TRNN
0
5
10
15
TOC (wt%)
0
100
200
300
API (calc)


New York
(Proximal to 75NY-2)
HCAL
6900
7000
7100

Core 75NY-2 Location

- Core from New York State shares similar log characteristics to well in northern Ohio
  - At least Point Pleasant facies equivalent
  - Likely there are depositional differences throughout the basin
- What can we learn from depositional trends seen in core from eastern New York state ?



Modified after Cornell (2003)
http://www.mcz.harvard.edu/Departments/InvertPaleo/Trenton/Intro/GeologyPage/Geologic%20Setting/paleogeogsetting.htm#easternlaurentia

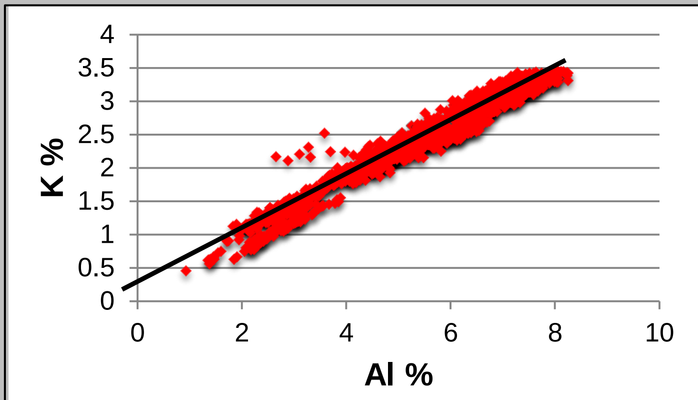
Utica Shale and Clastic Trends

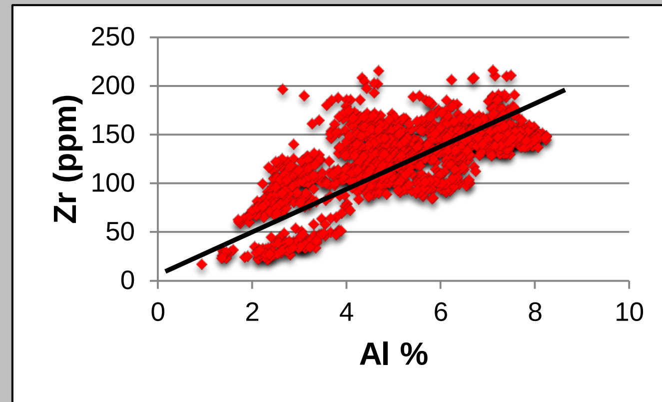
Detrital Proxies: Al, Si, Ti, K, Zr

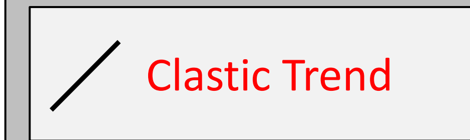
Aluminum Normalization

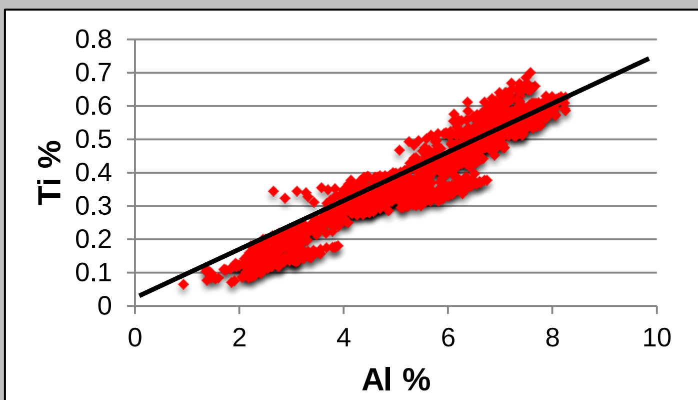
- Aluminum (Al) is a robust proxy for clay
- Aluminum is used:
    - To establish the total lithogenous content of sediment as it is considered to be a proxy for clay mineral flux in fine grained clastic deposits.
    - As a normalization parameter by which authigenic enrichment of redox sensitive elements can be assessed.
- Strong correlations between Al and other elements is indicative of the detrital flux.
- Data points that are decoupled from the detrital trend must be accounted for.

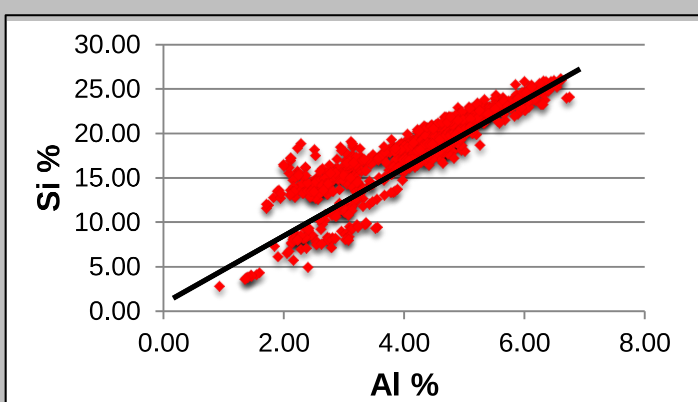
Detrital Proxies









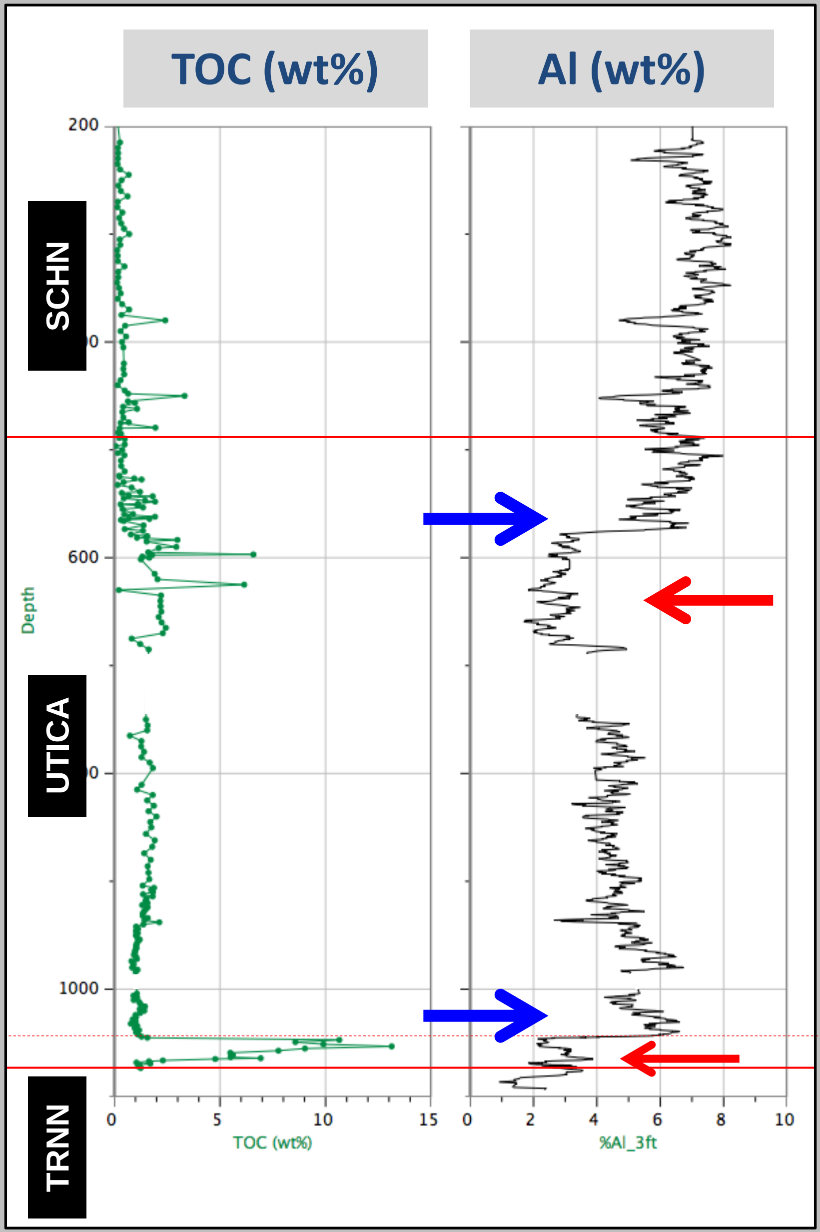


- Aluminum is a robust proxy for clay
- Any deviation from the clastic trend may have resulted from:

  Eolian input
  Biogenic sources
  Increased energy
  Weathering
  Change of source provenance

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

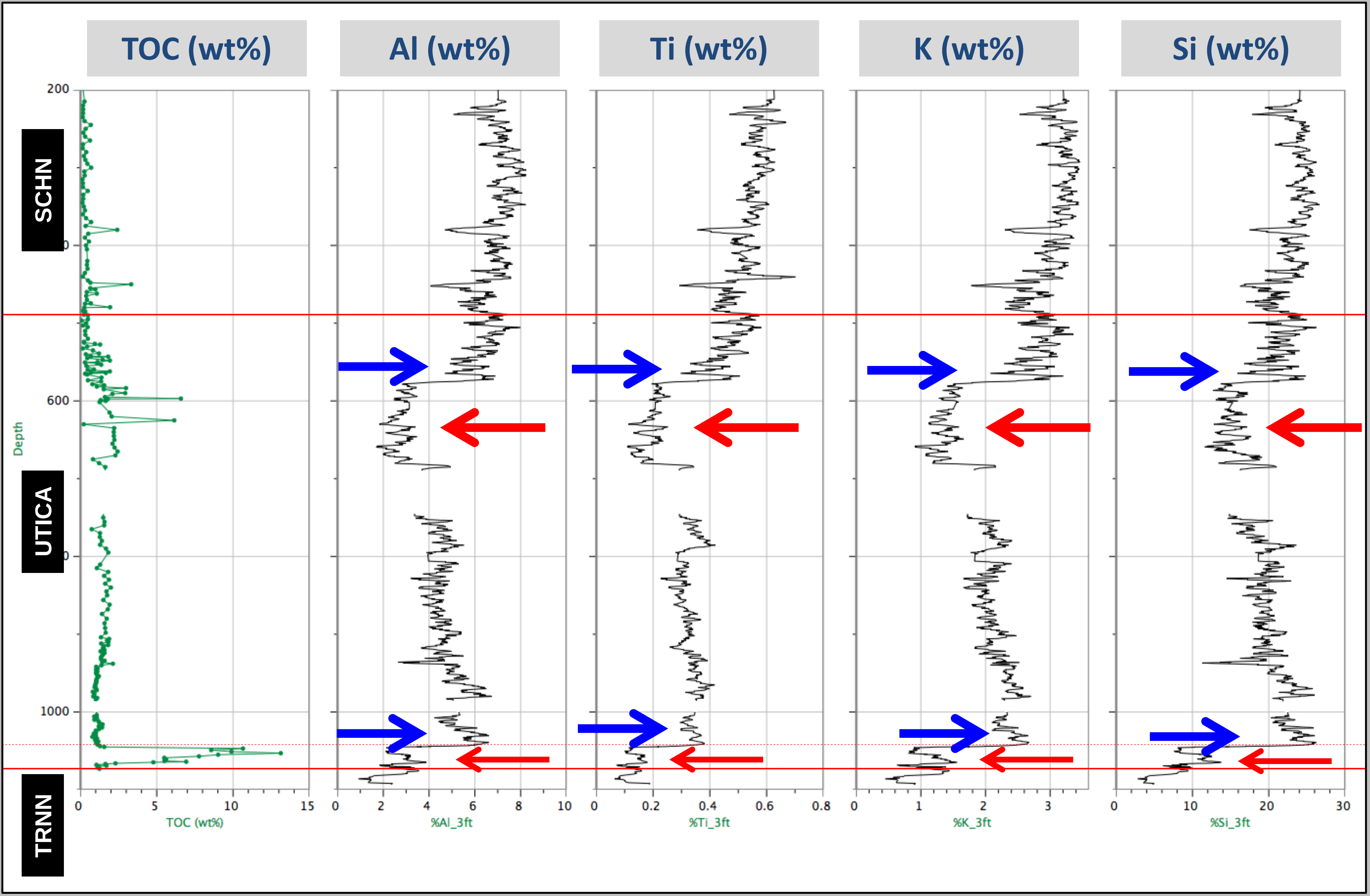
Clastic Trends



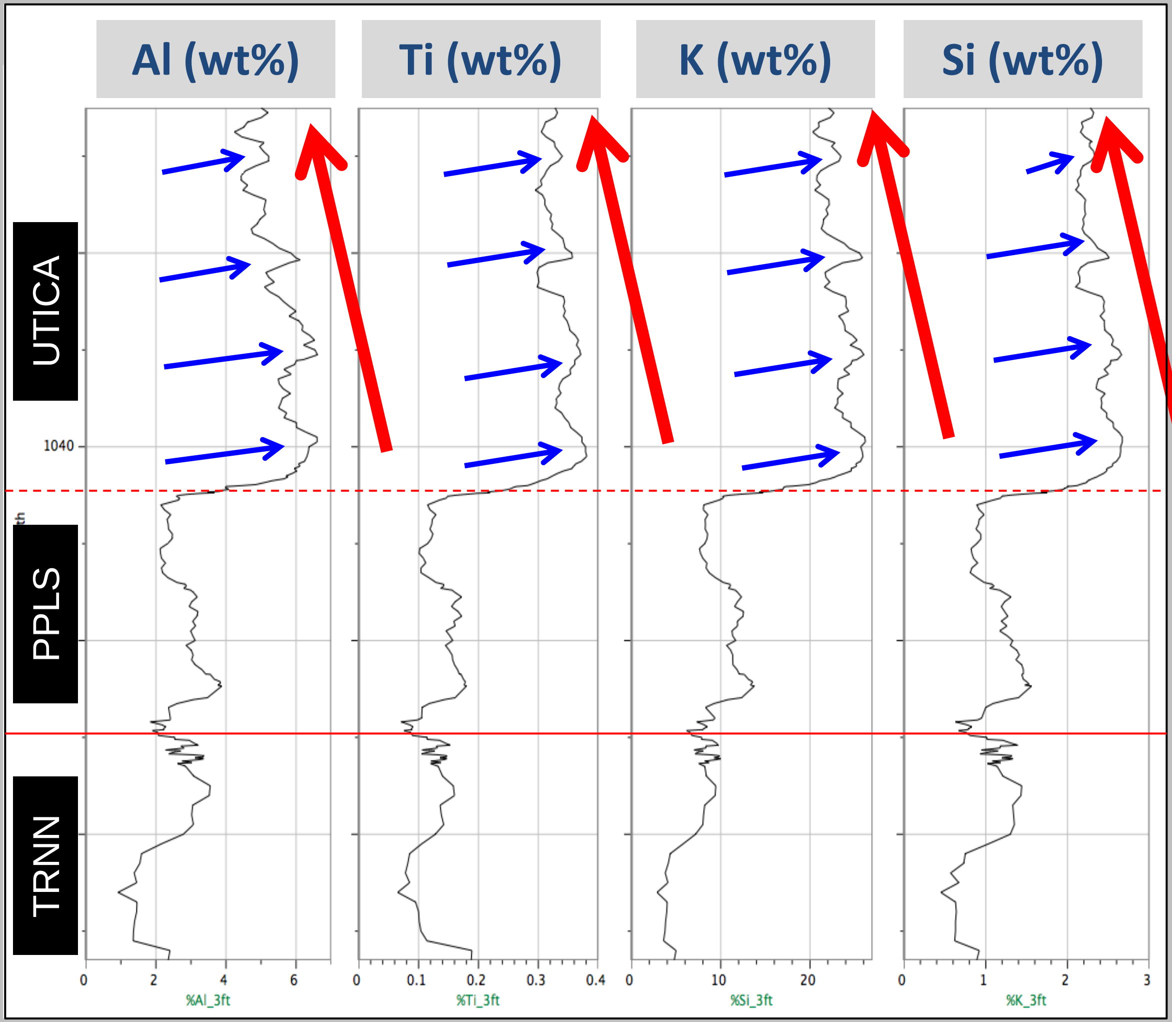
Both organic-rich sections depleted of detrital elements

- Indicative of low sedimentation rate during organic matter deposition
- Both organic-rich sections followed by sharp increase of sedimentation rate

Clastic Trends



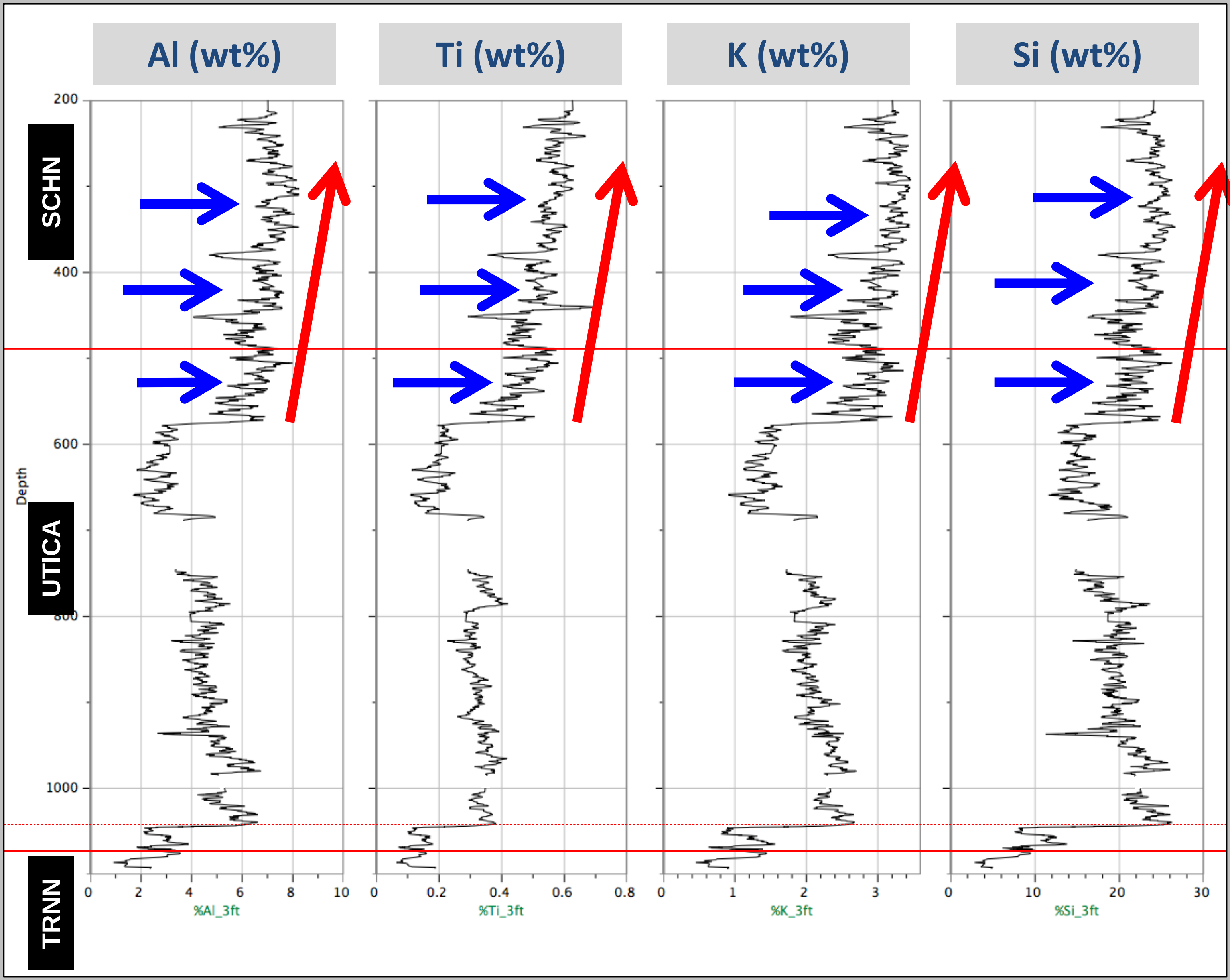
Clastic Trends



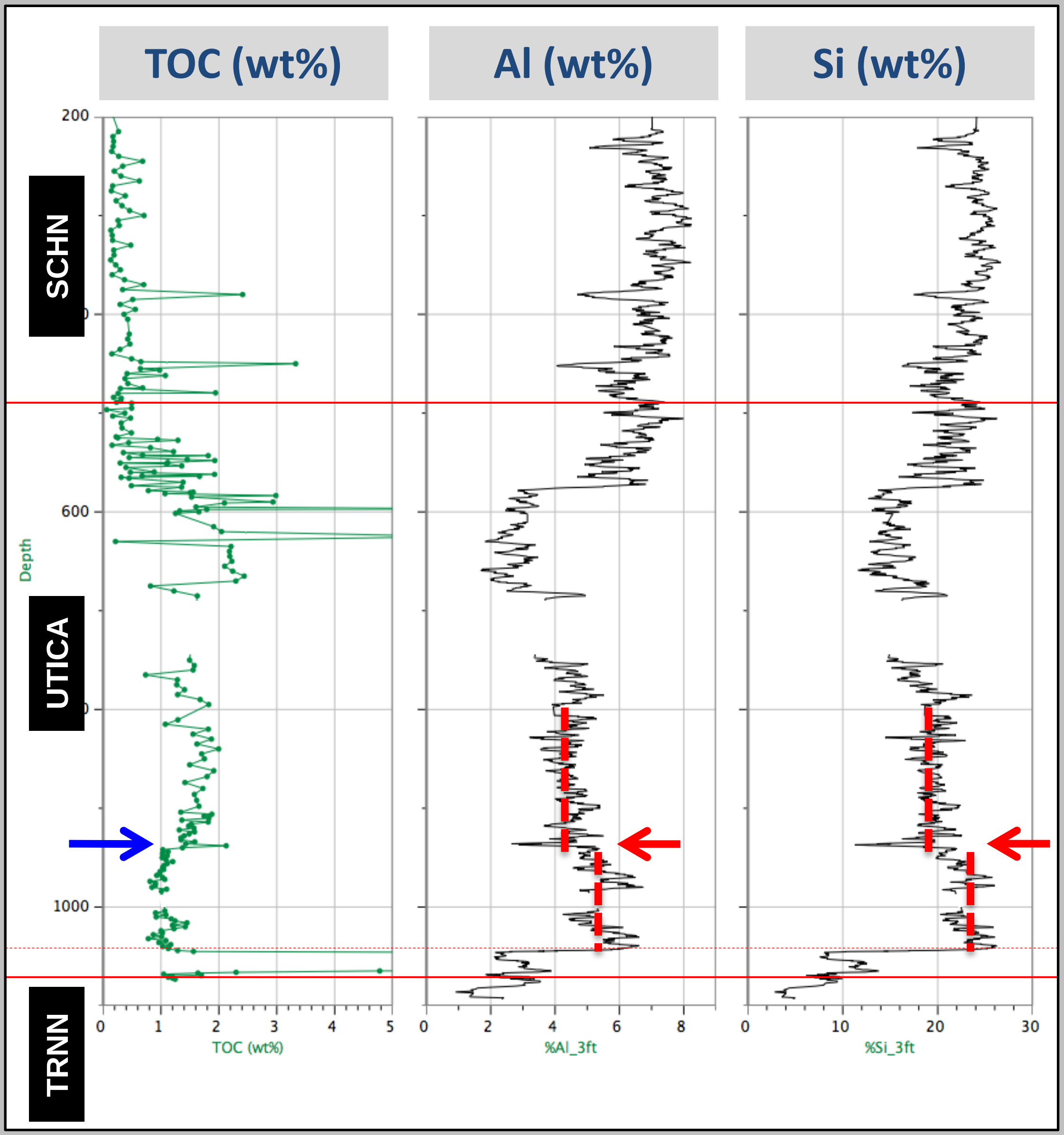
Example of high resolution deposition Sequences within the Utica Shale

- General decrease of clastic input
- depositional cycles superimposed on to the decreasing trend

Clastic Trends



Dilution



Not only do we see lack of deposition in both organic-rich section

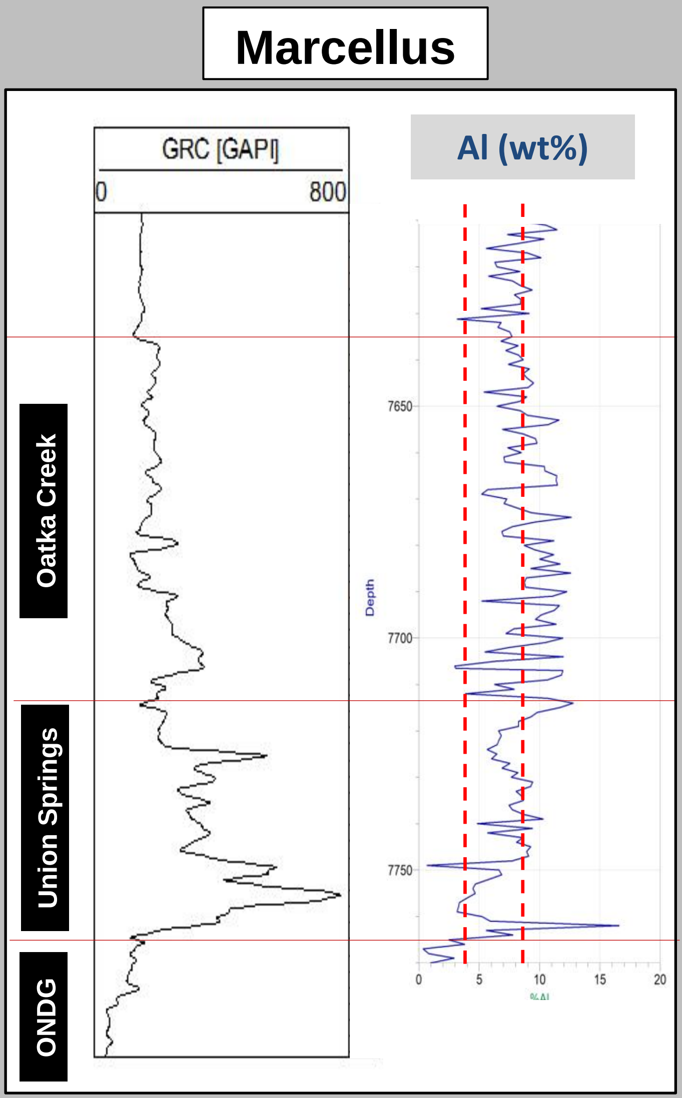
Subtle decrease in clastic input results in subtle, but noticeable increase of TOC

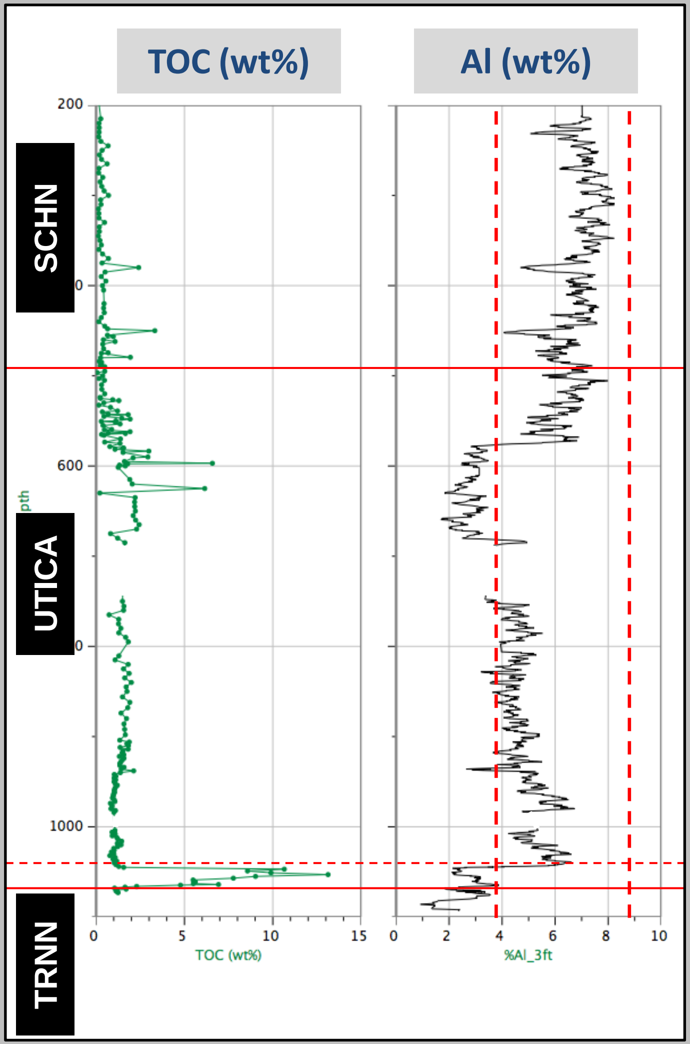
- It appears sedimentation rate/dilution largely control the presence of TOC in the Utica Shale
- At least in core 75-NY2

Clay

Maximum Al values within Utica/Point Pleasant organic rich section: > 4%

Average Shale Al% value = 8.8% (Wedepohl, 1971)





Clay

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

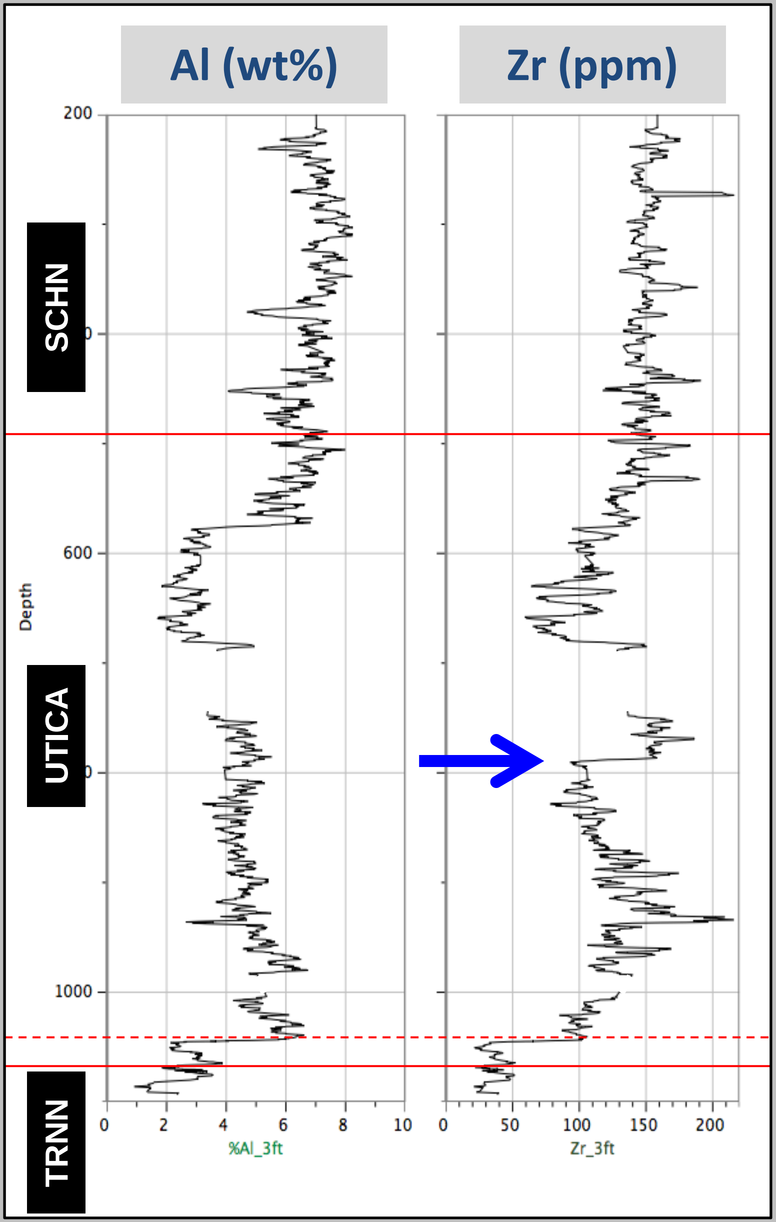
- Establishment of land plant root system during the Devonian
    - Atmospheric conditions
        - Ordovician: CO_2 6000 ppm
        - Early Devonian: CO_2 4000 ppm
        - Late Devonian: CO_2 400 ppm
- **Lack of land plant root system during Ordovician**

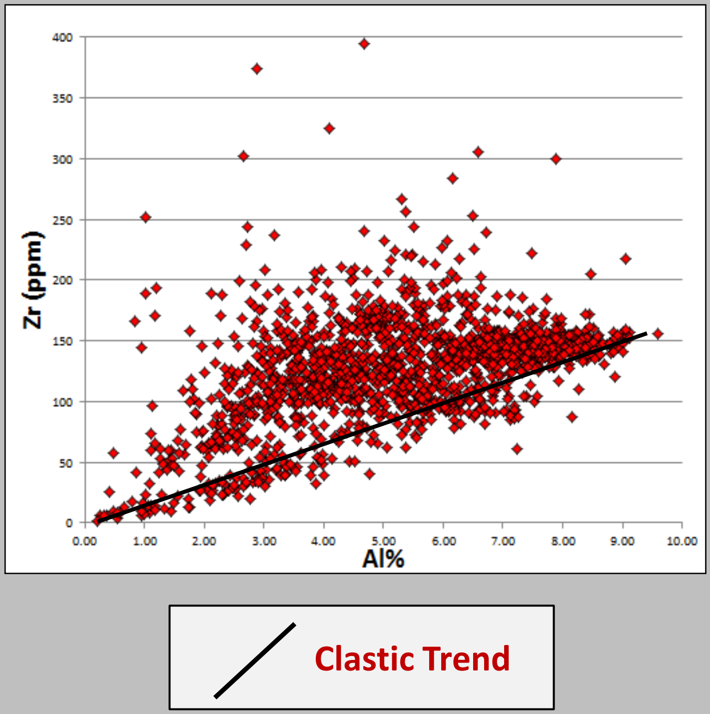
http://www.devoniantimes.org

Lack of algal productivity during Ordovician?

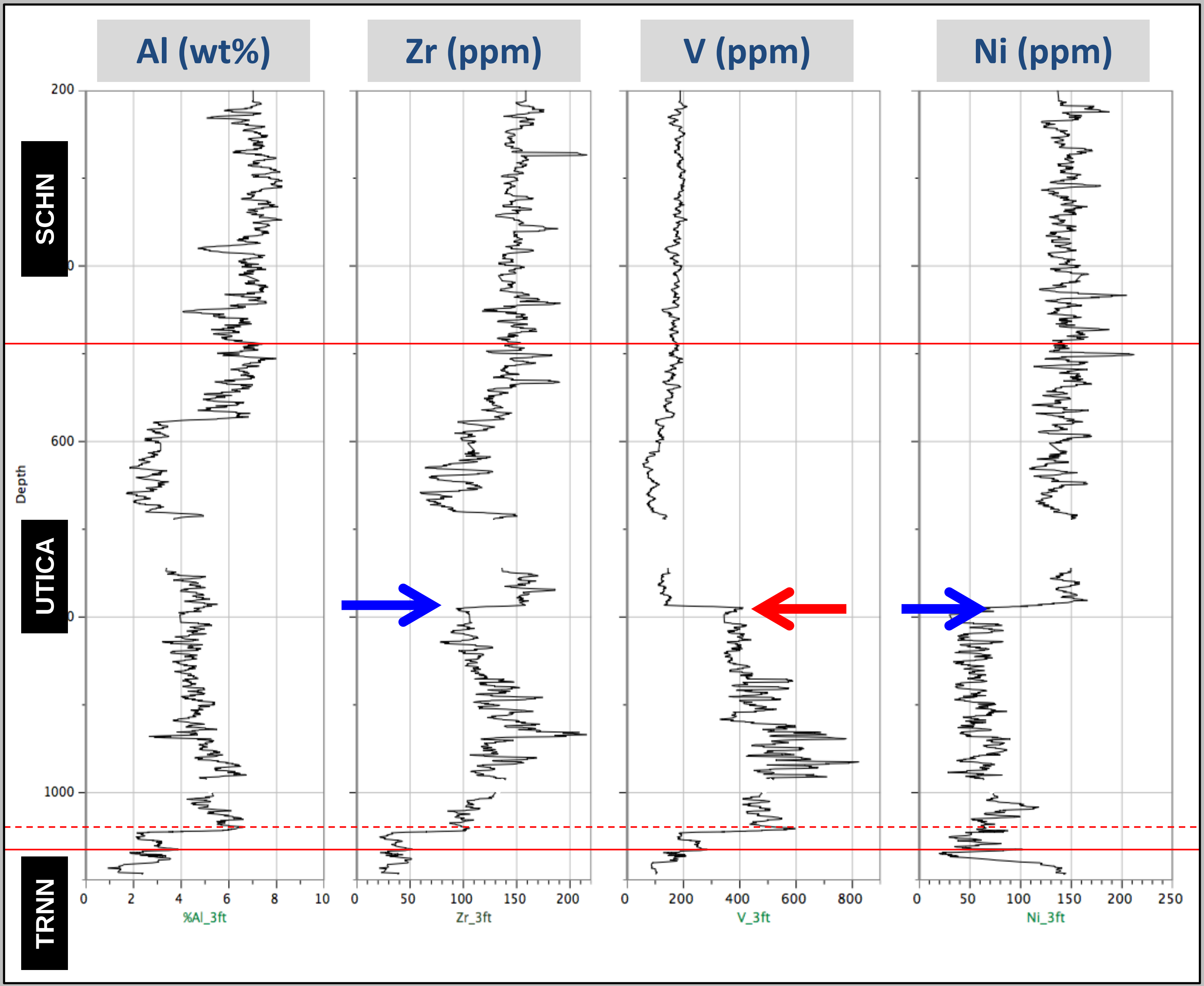
- Less TOC compared to Marcellus Shale

Source Provenance

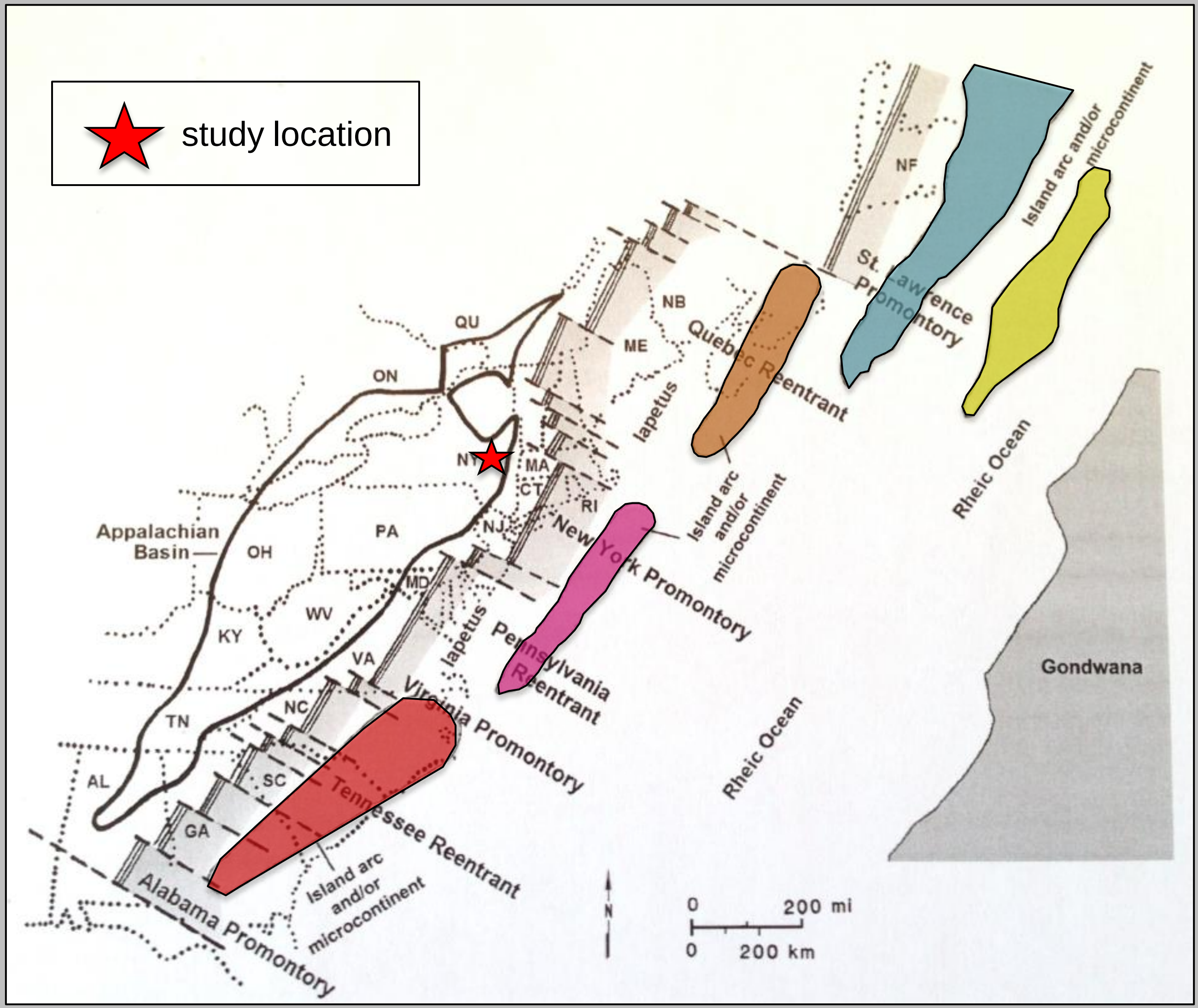




Source Provenance

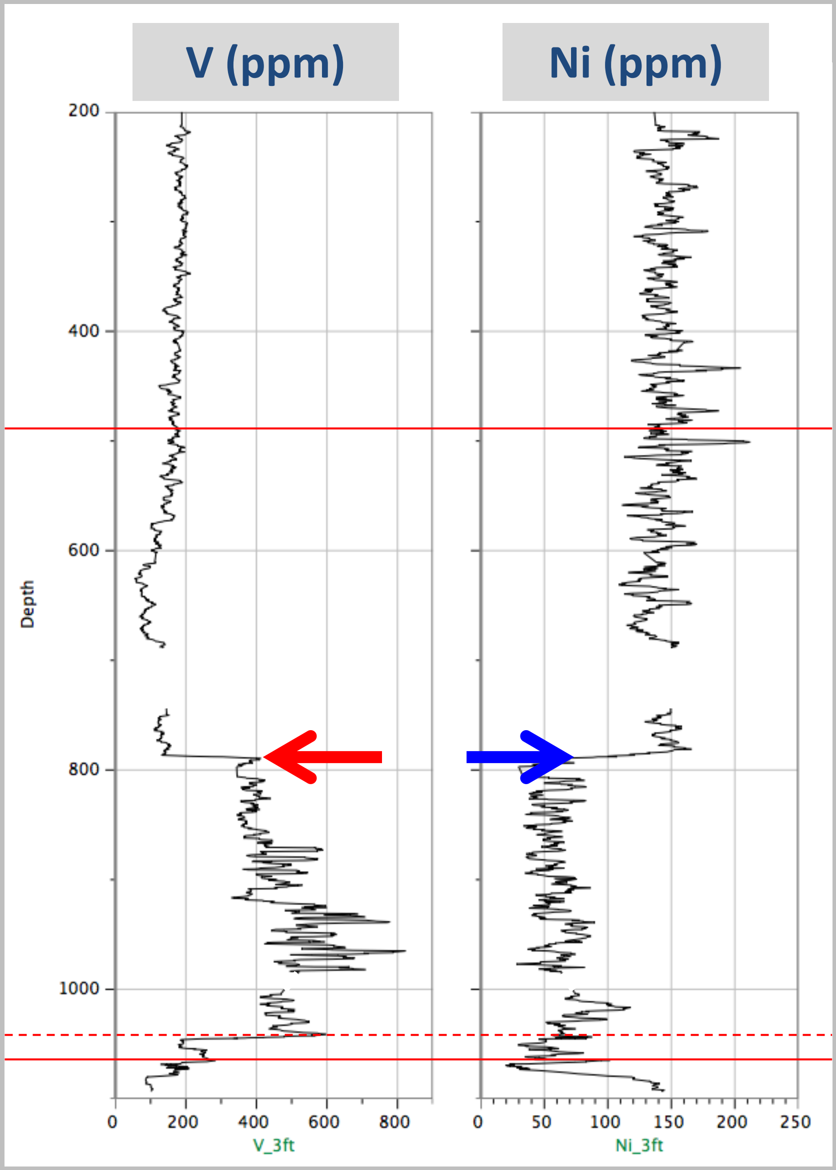


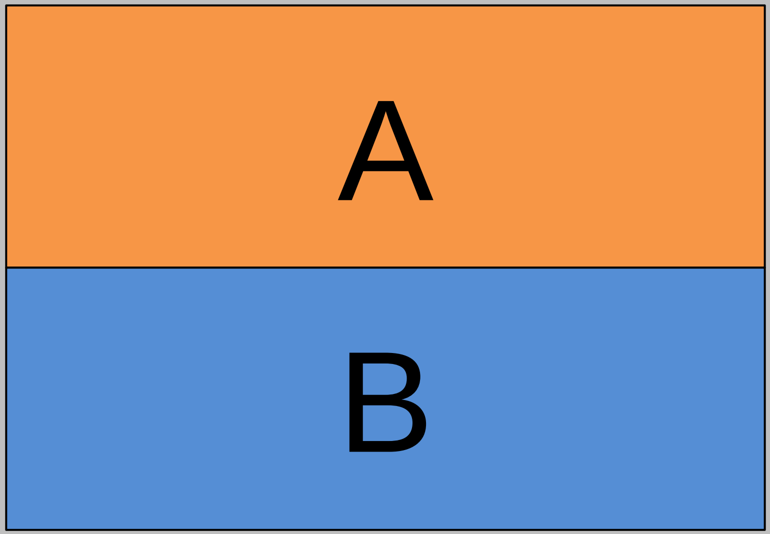
Source Provenance



(After Ettensohn and Lierman, 2012)

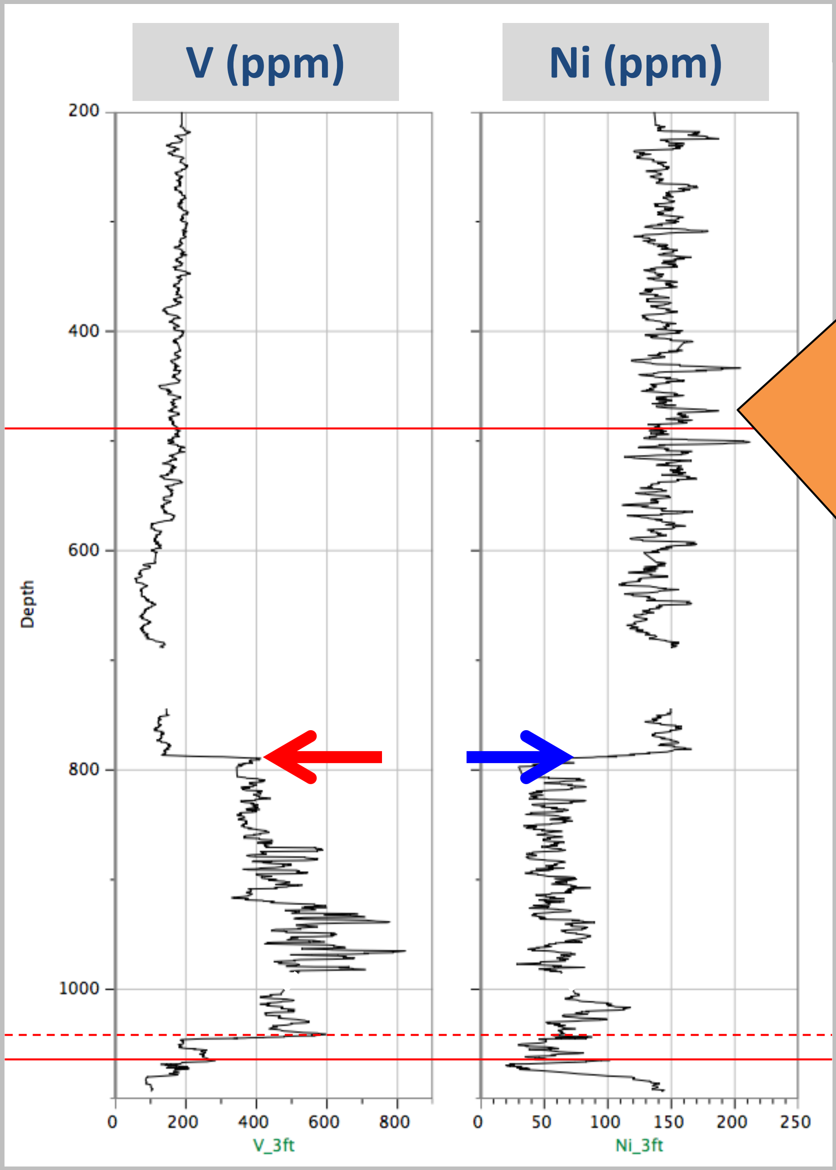
Source Provenance

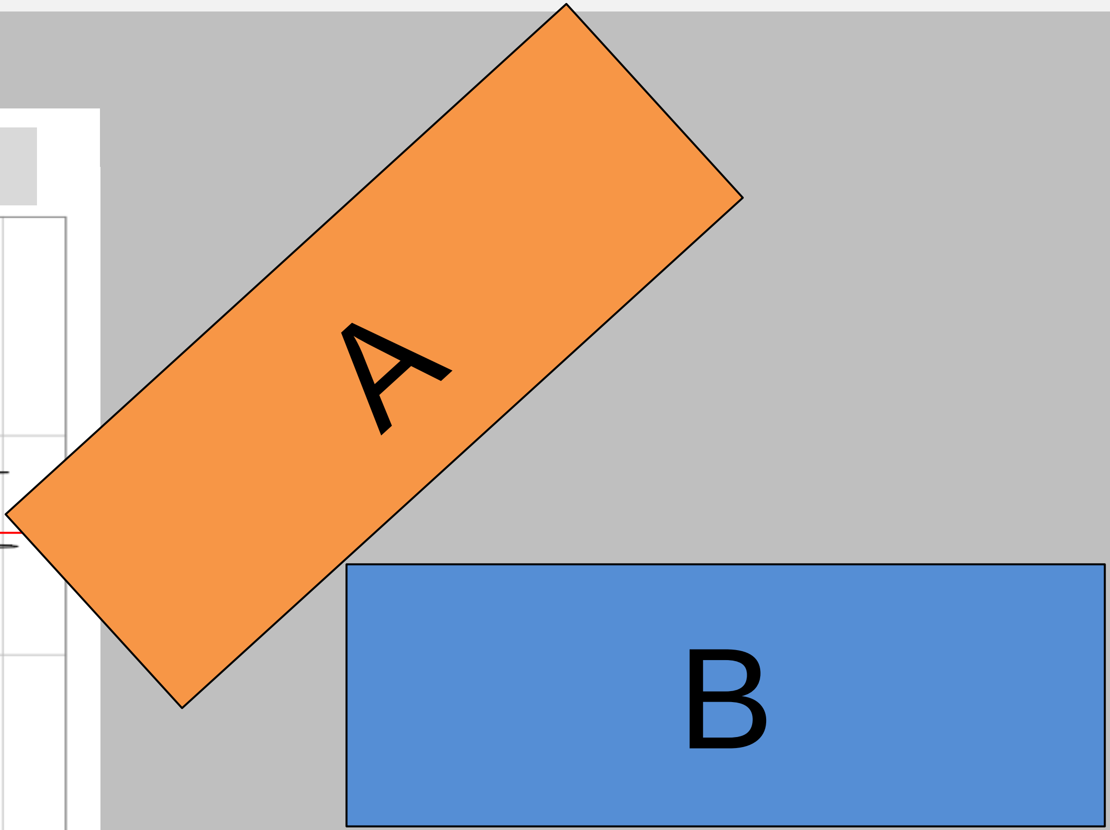




sediment source unroofing

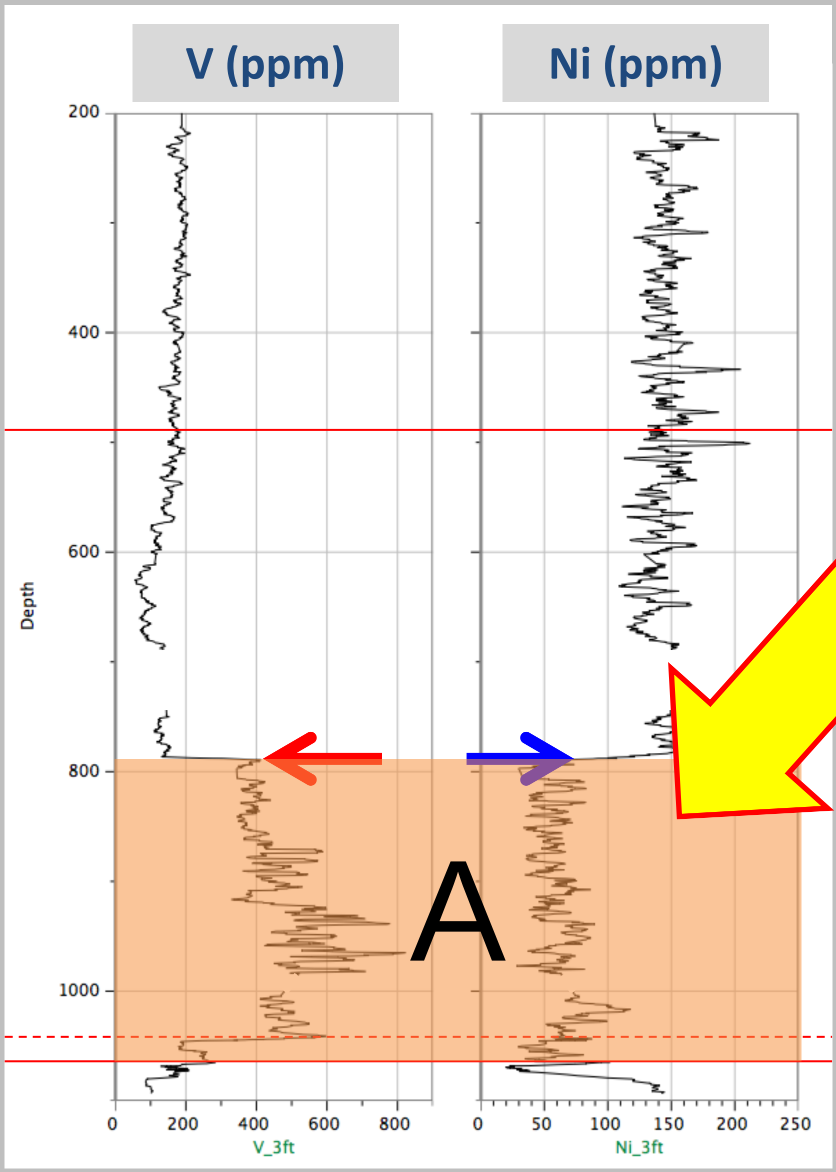
Source Provenance





sediment source unroofing

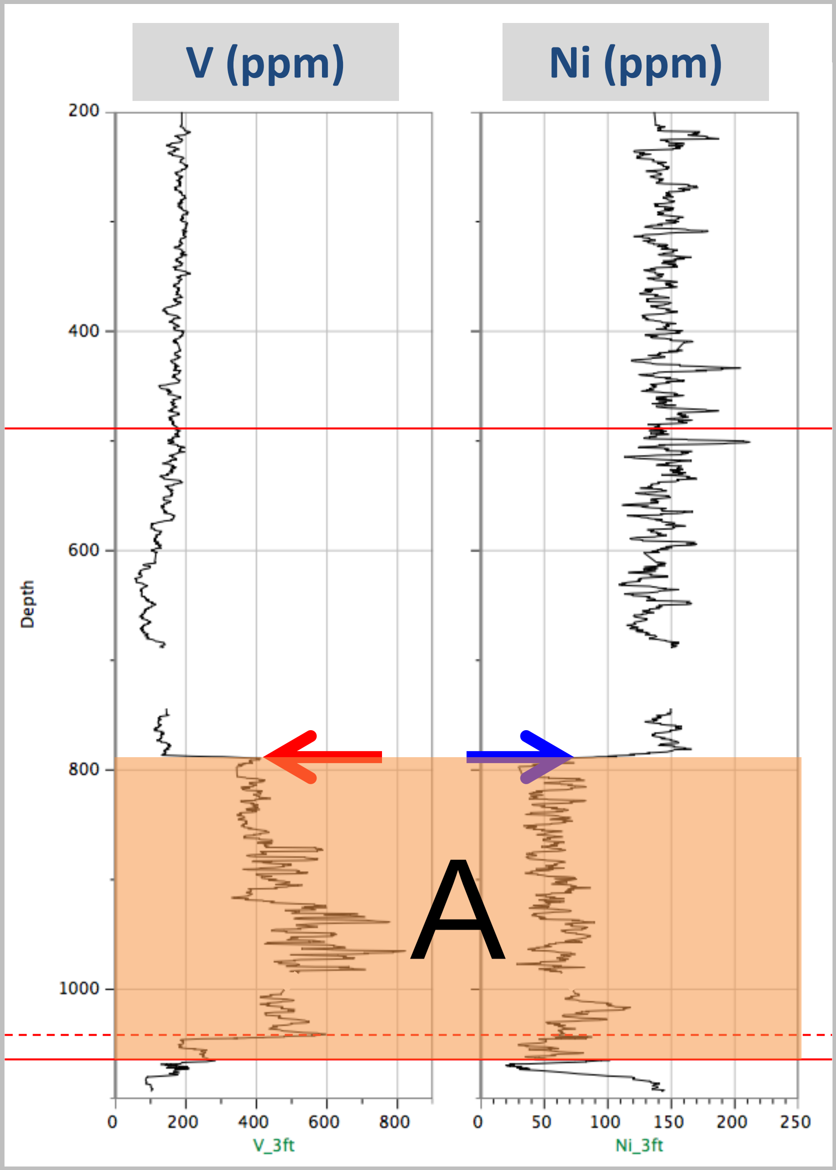
Source Provenance

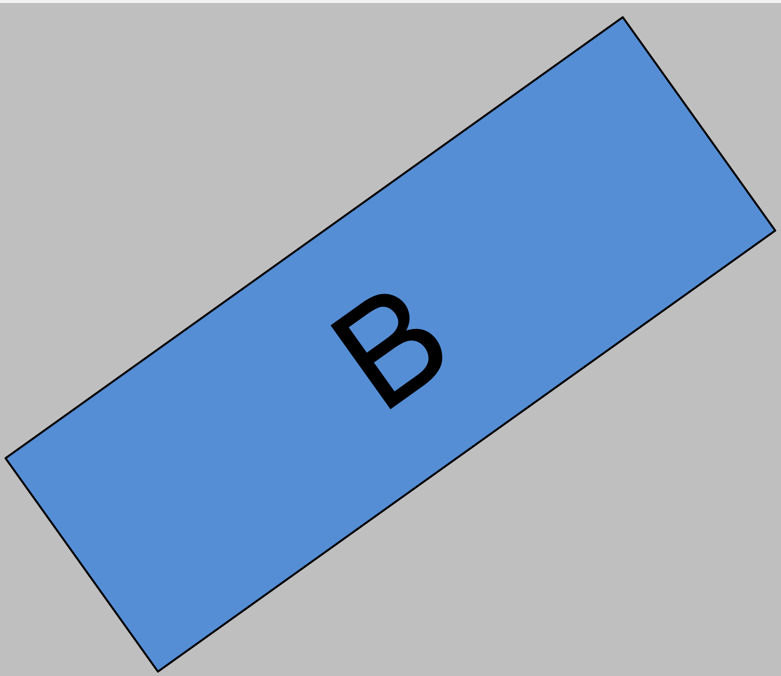


B

sediment source unroofing

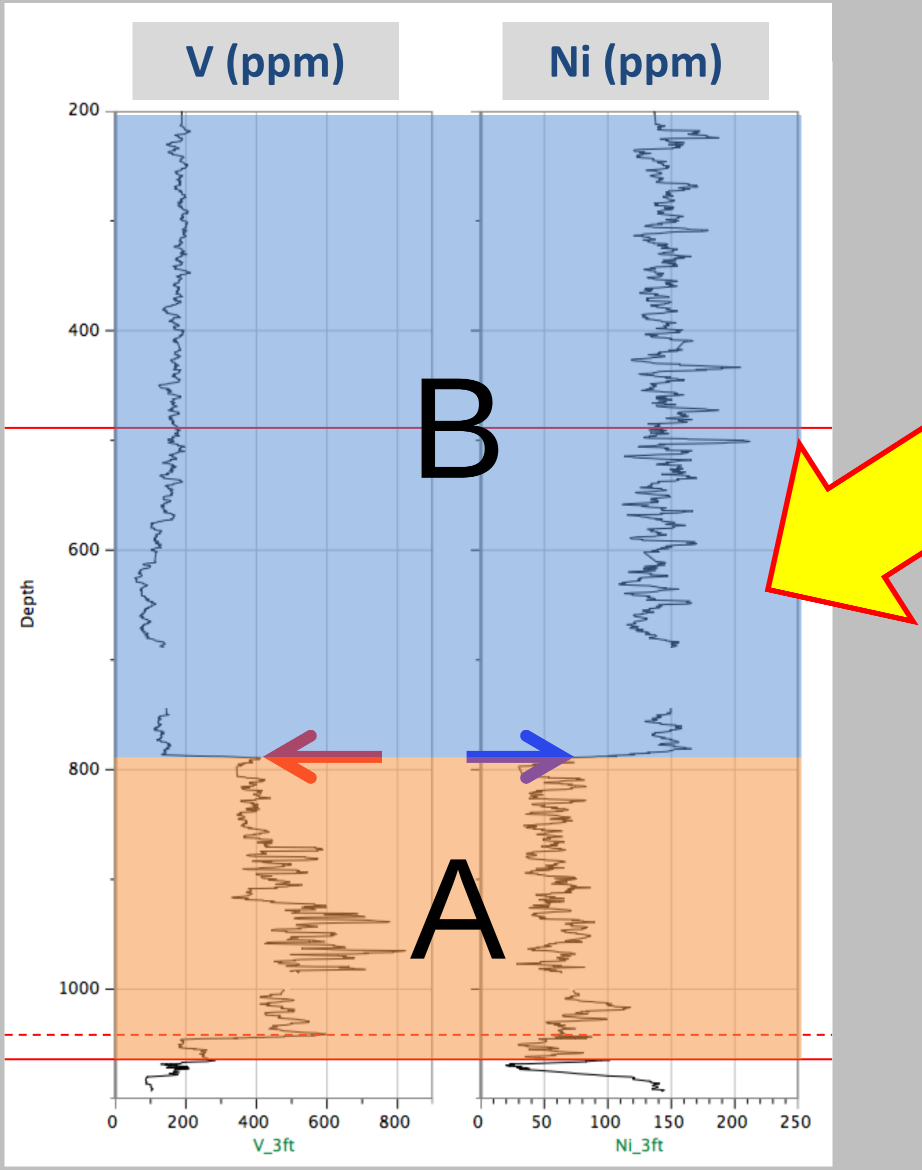
Source Provenance





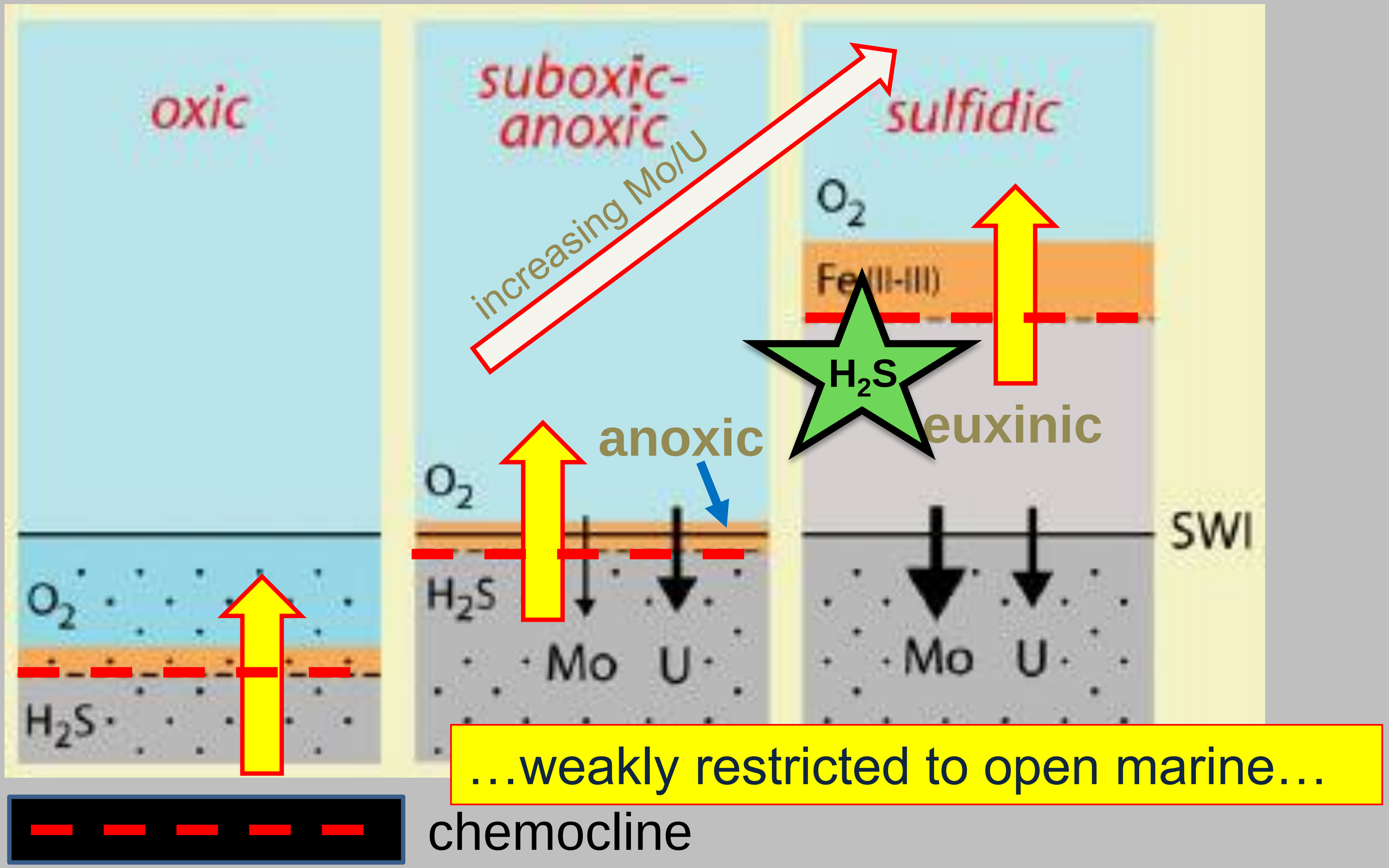
sediment source unroofing

Source Provenance



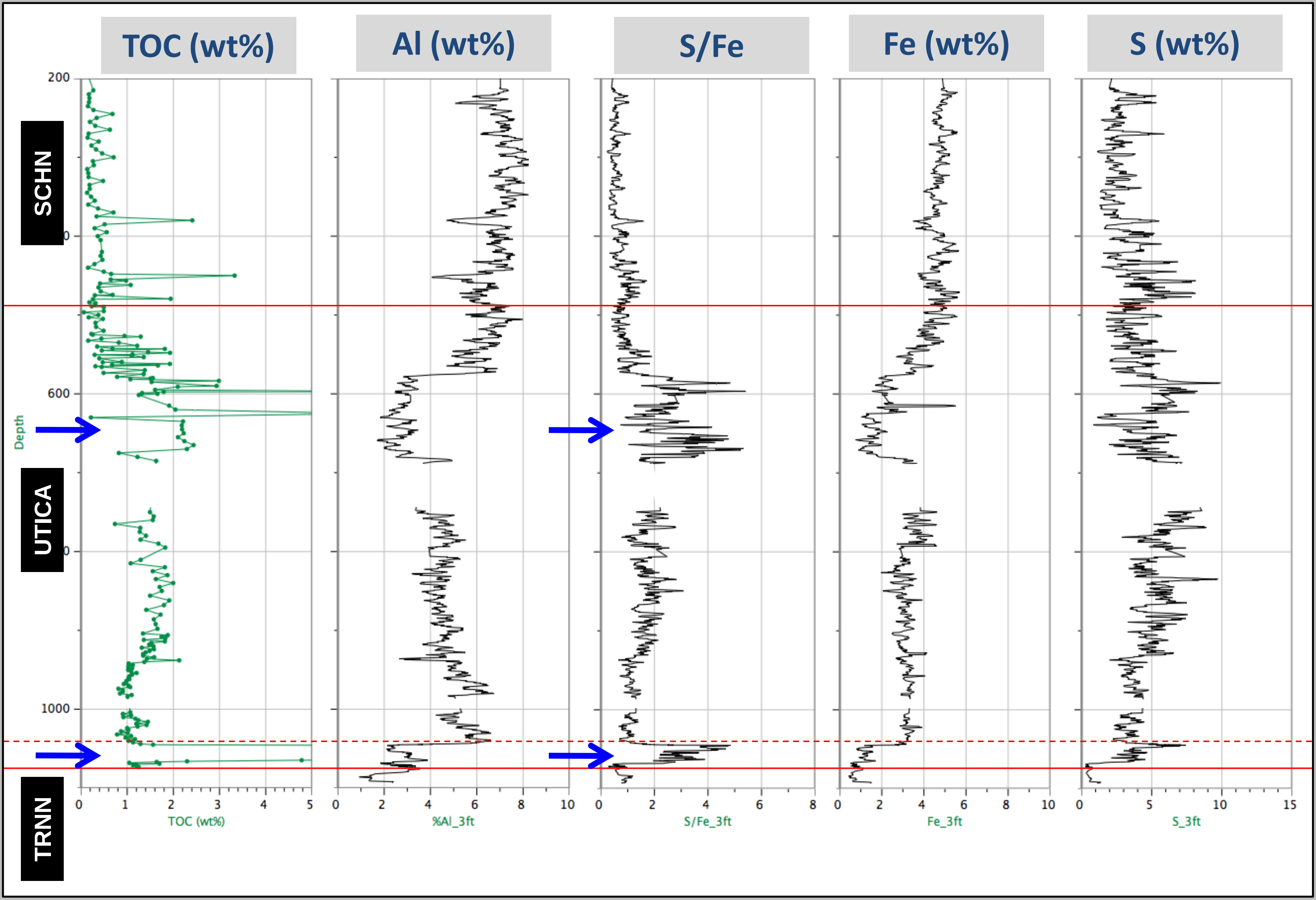
sediment source unroofing

…increasingly reducing conditions…

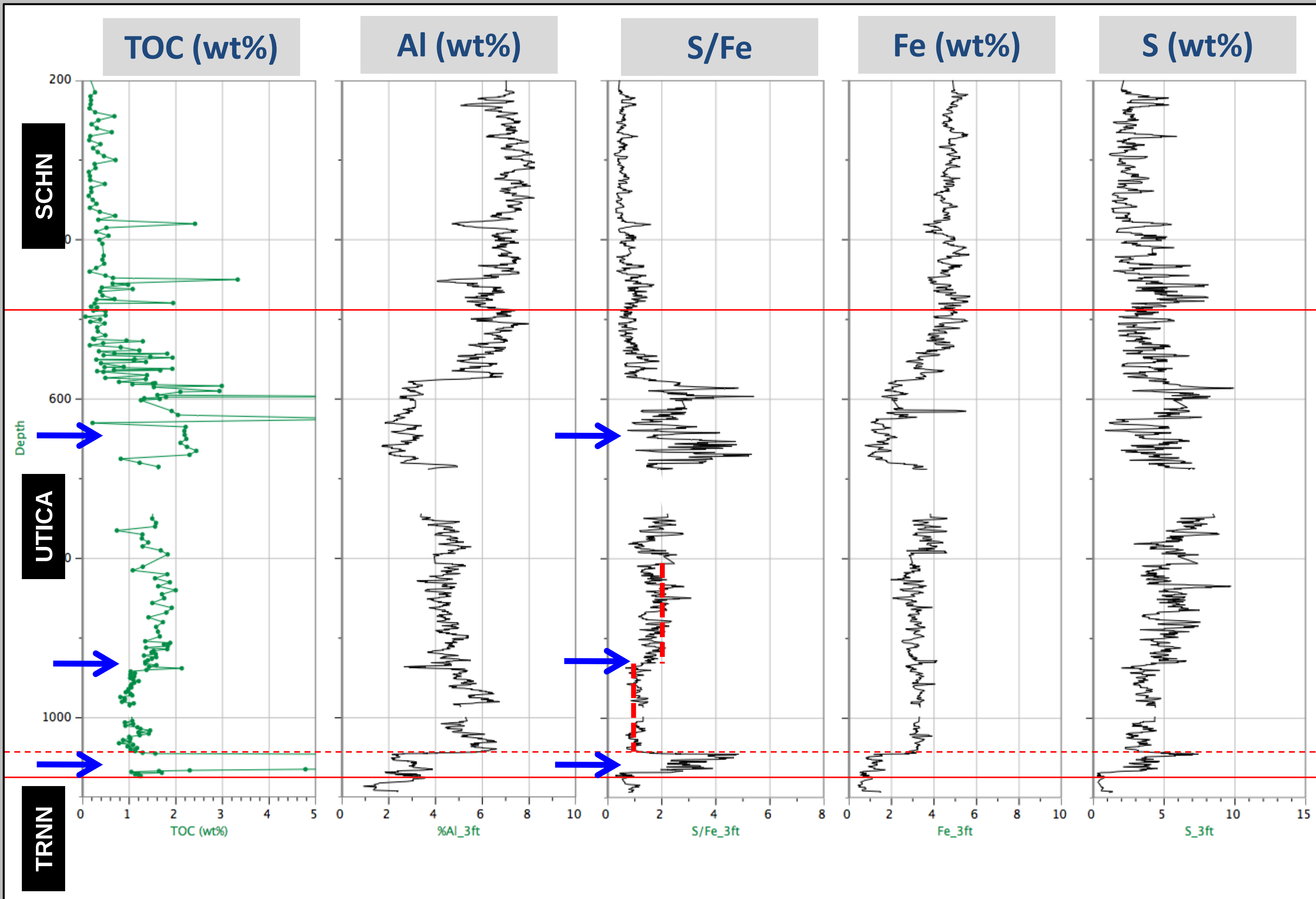


Algeo and Tribovillard, 2009

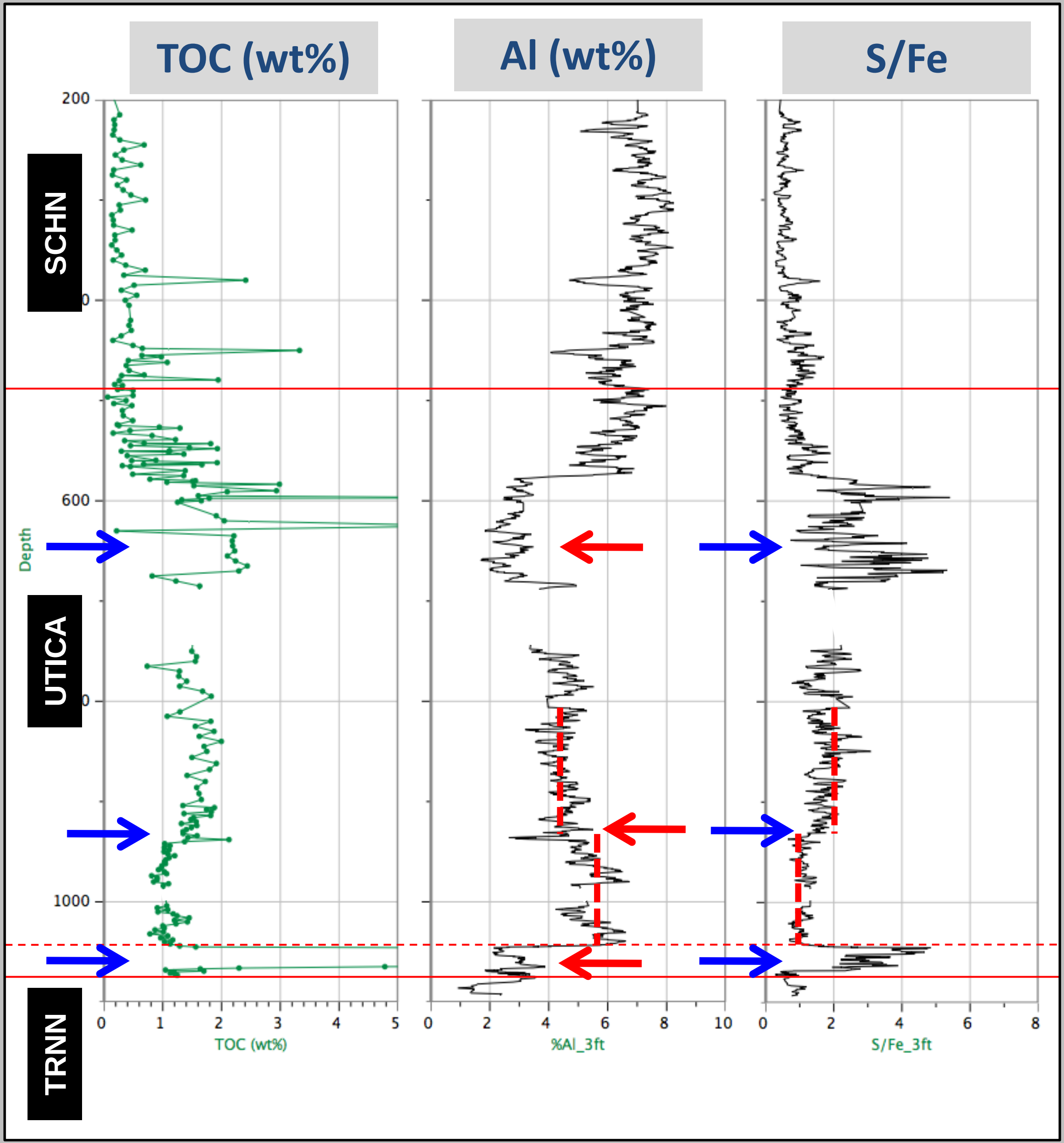
Organic Matter and Preservation



Organic Matter and Preservation

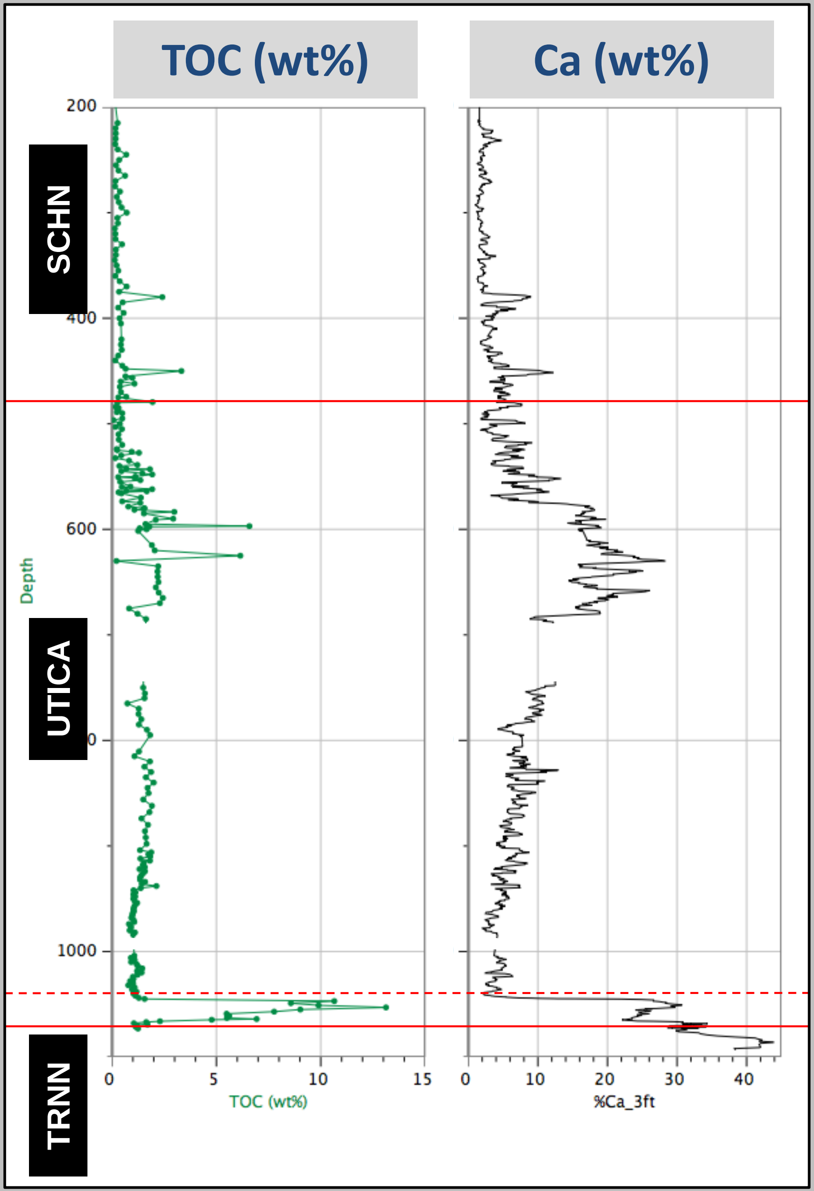


Organic Matter and Preservation / Dilution



TOC largely controlled by dilution and preservation

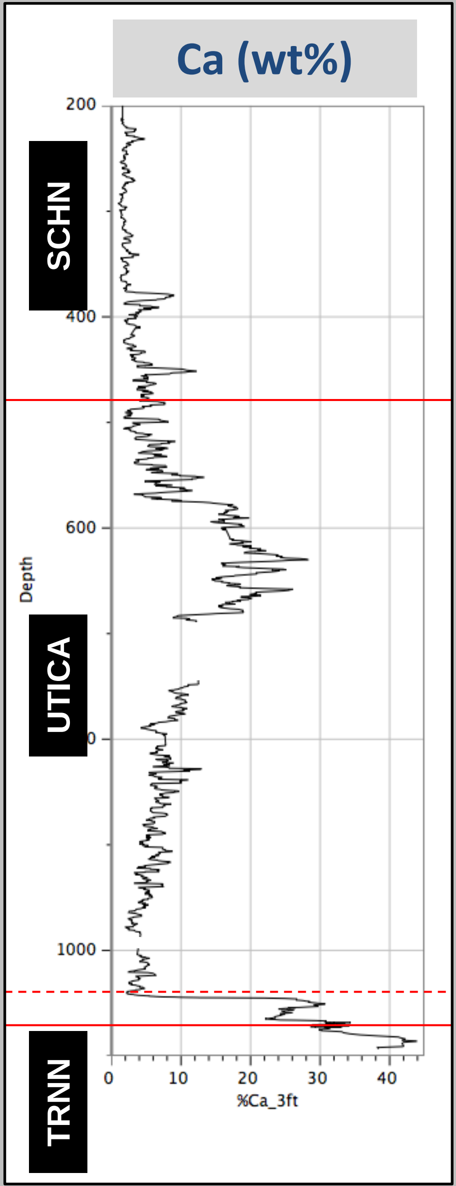
Source of Carbonate

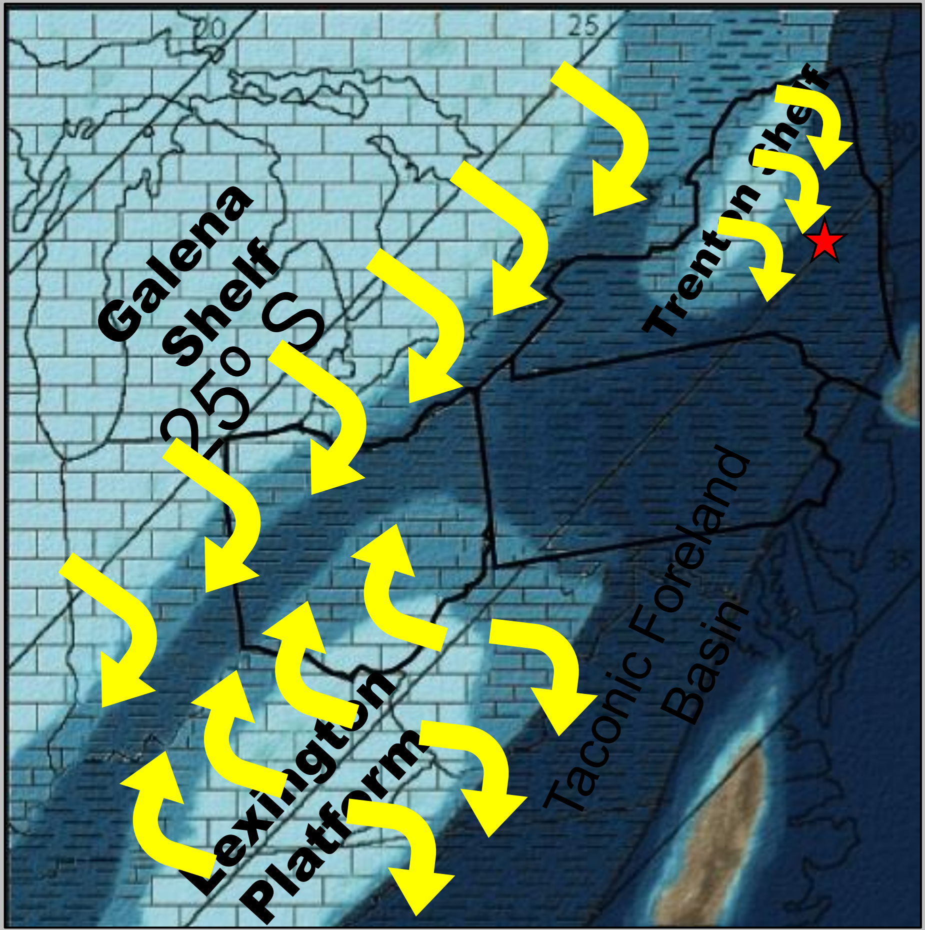


What is the source of carbonate in the Utica/Point Pleasant Shale?

- Much of the Utica Shale displays elevated values of Ca
- Ca is a proxy for calcium carbonate ($CaCO_3$)
- Both organic-rich sections contain elevated values of Ca
- detrital or authigenic ?

Source of Carbonate





Modified after Cornell (2003)

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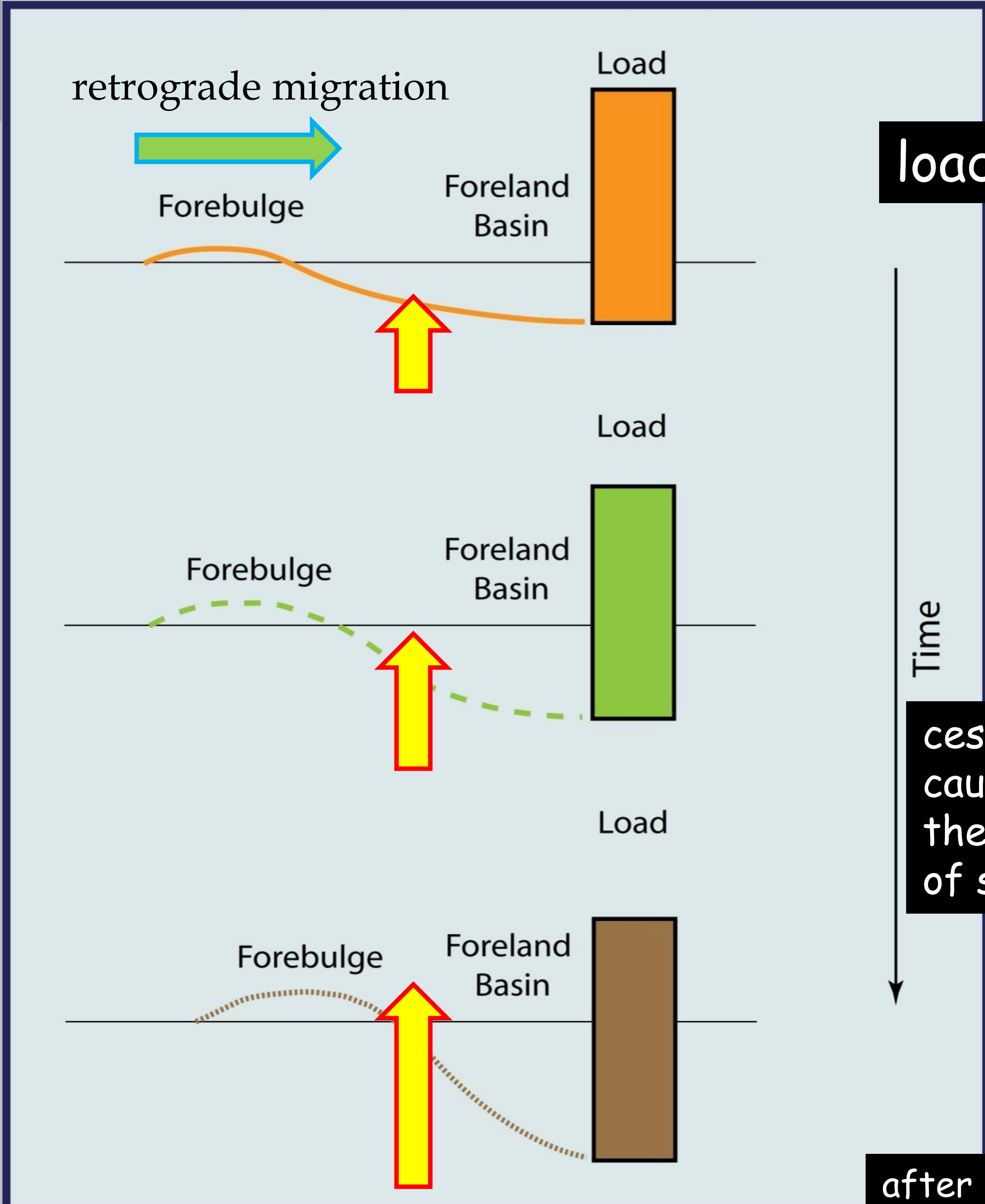
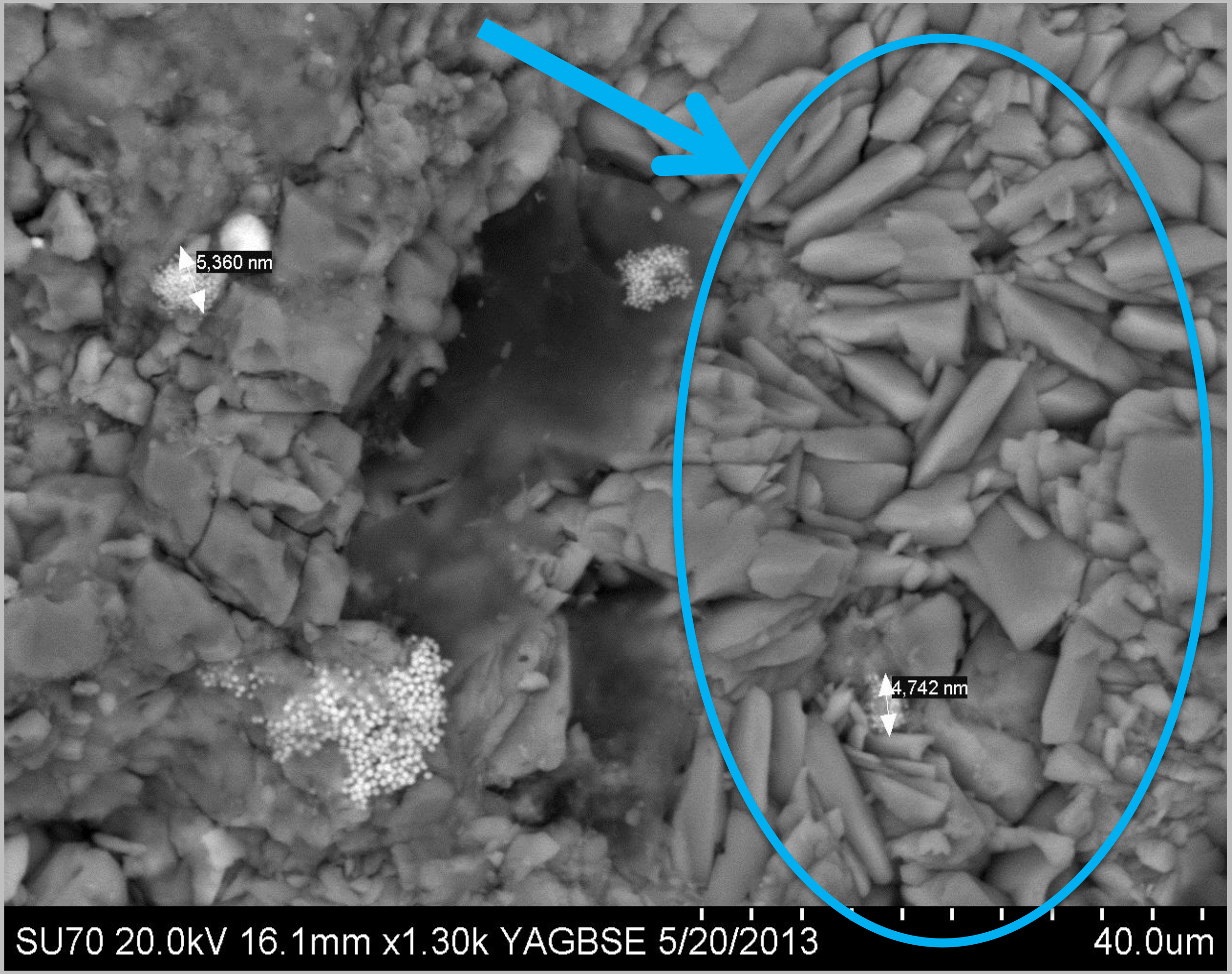
loading-type “relaxation



cessation of thrust migration causes retrograde migration of the forebulge and accumulation of shallow-water carbonates

after Ettensohn (1994)

Evidence of Authigenic Carbonate



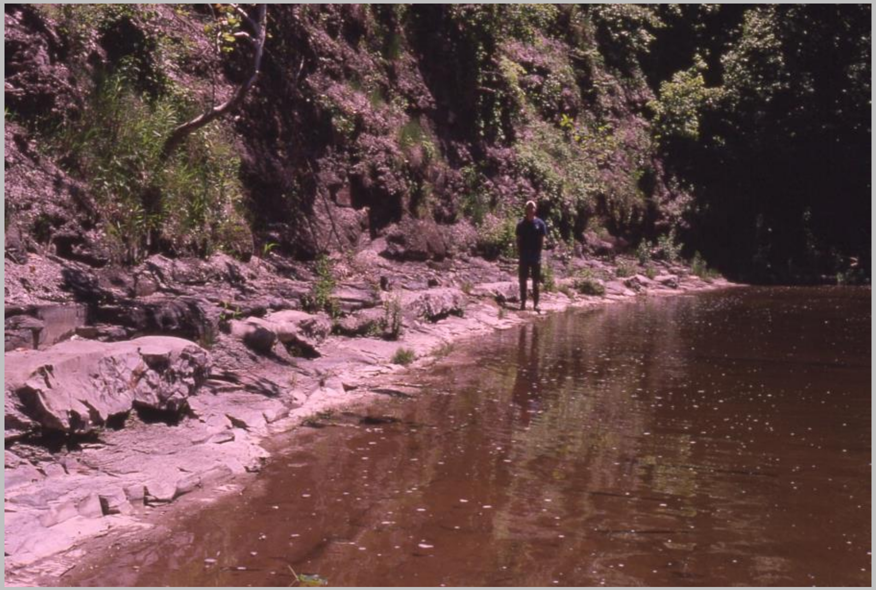
Carbonate Concretions

Carbonate concretions form from authigenic carbonate produced by the early diagenetic process anaerobic oxidation of methane

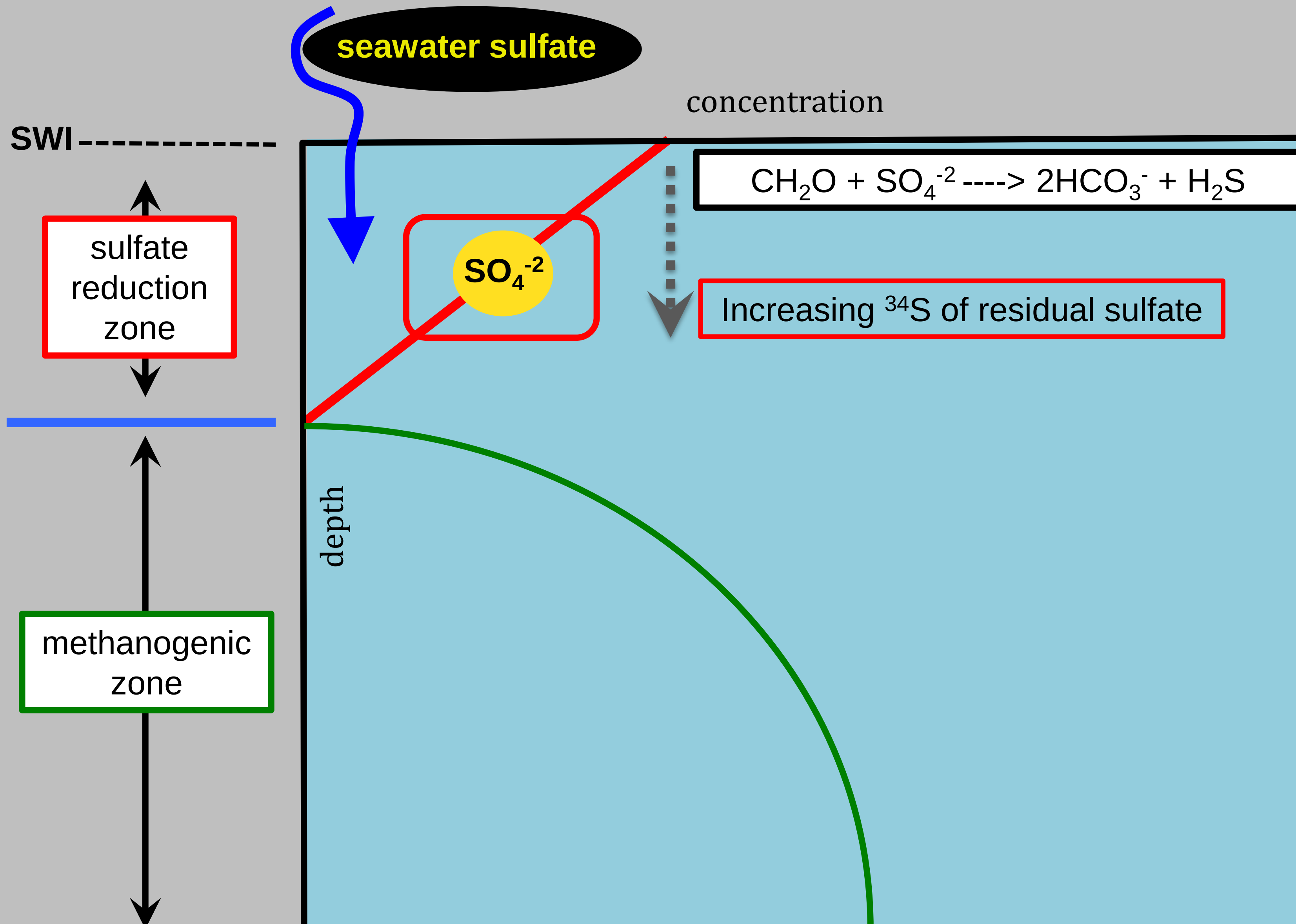
- know to form ~ 1 m beneath the seafloor
- along stratigraphic intervals

- Abundance of carbonate concretions seen in Devonian shales

- Lack of concretions in the Utica Shale



Anaerobic Oxidation of Methane (AOM)



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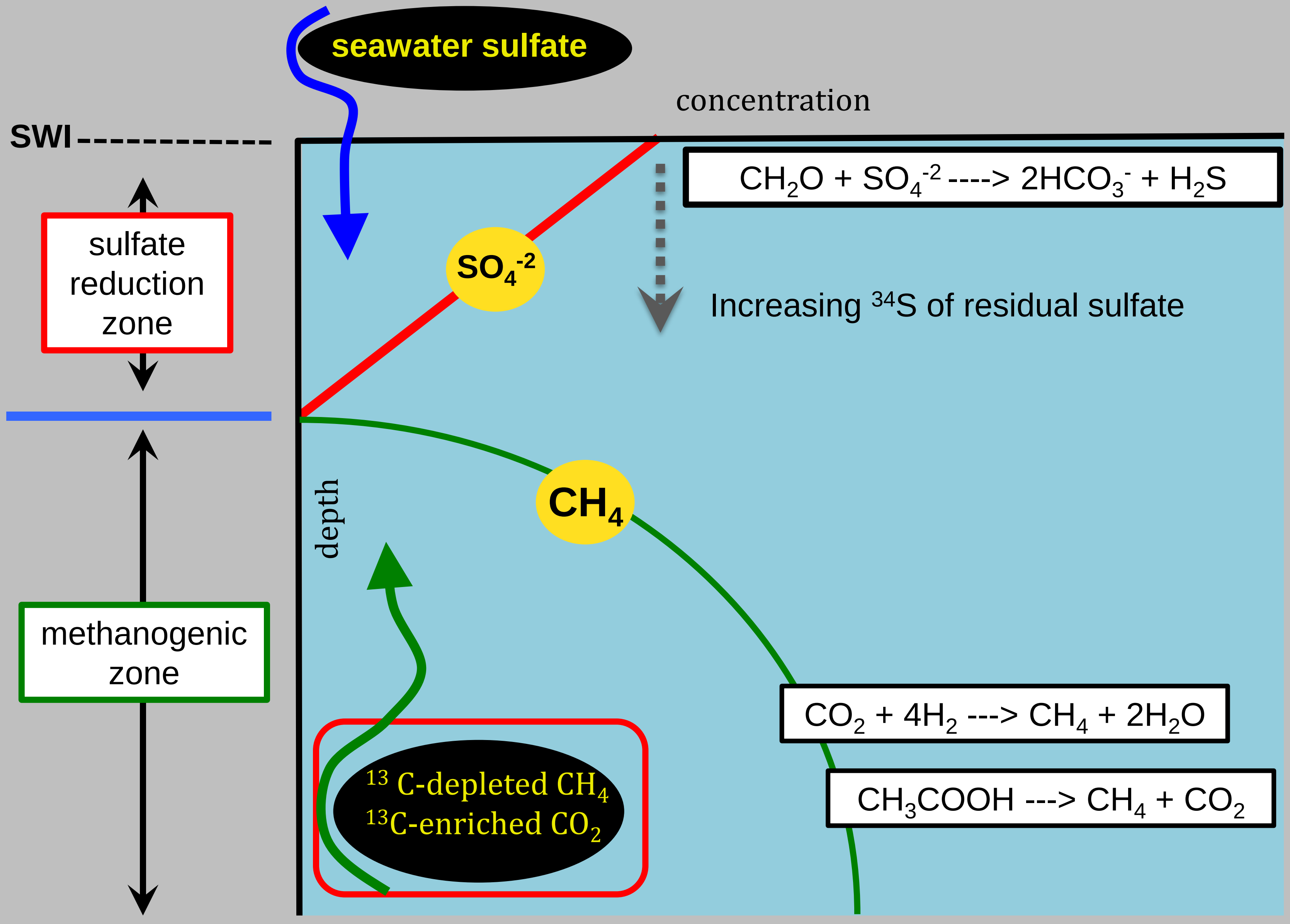

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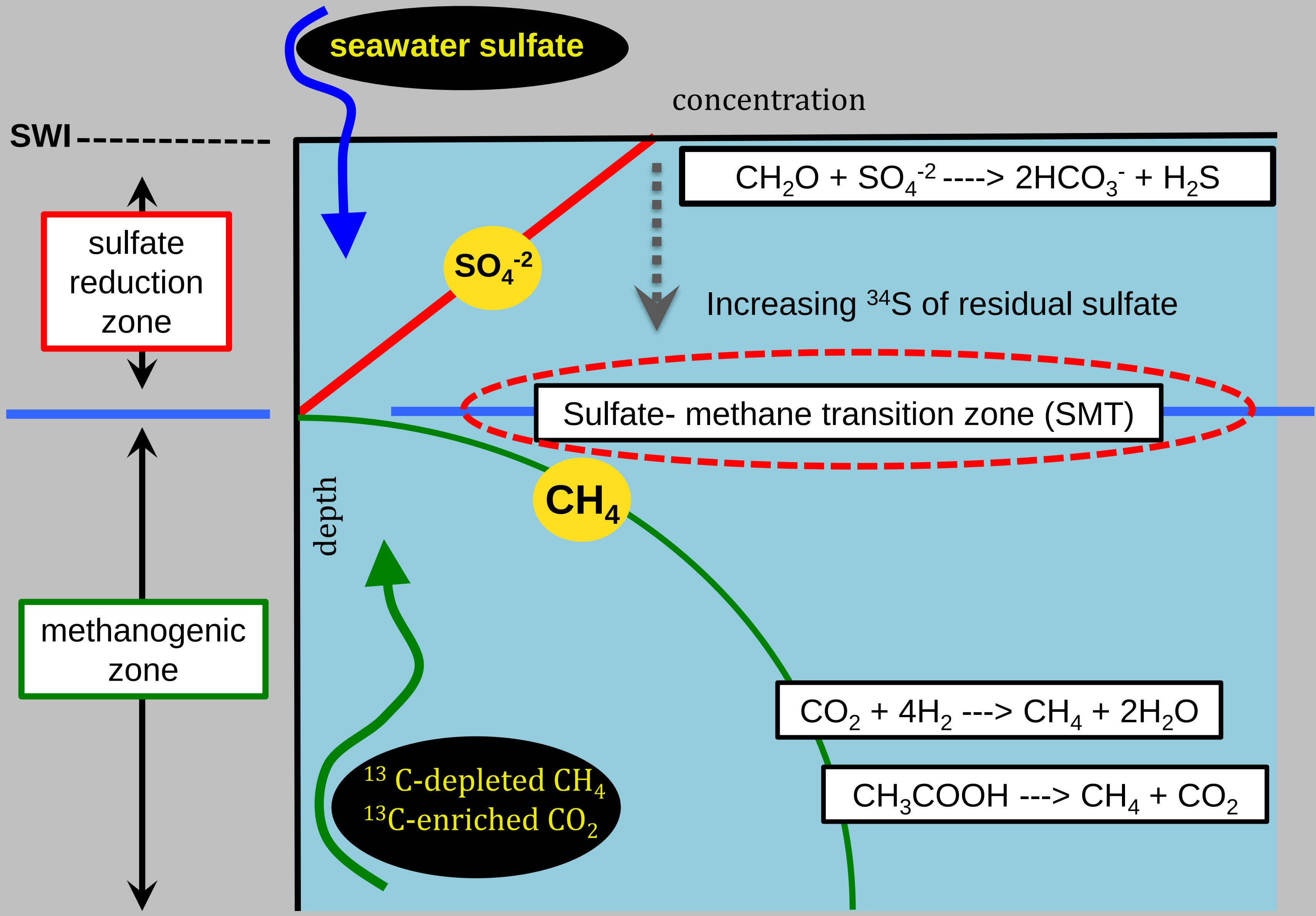

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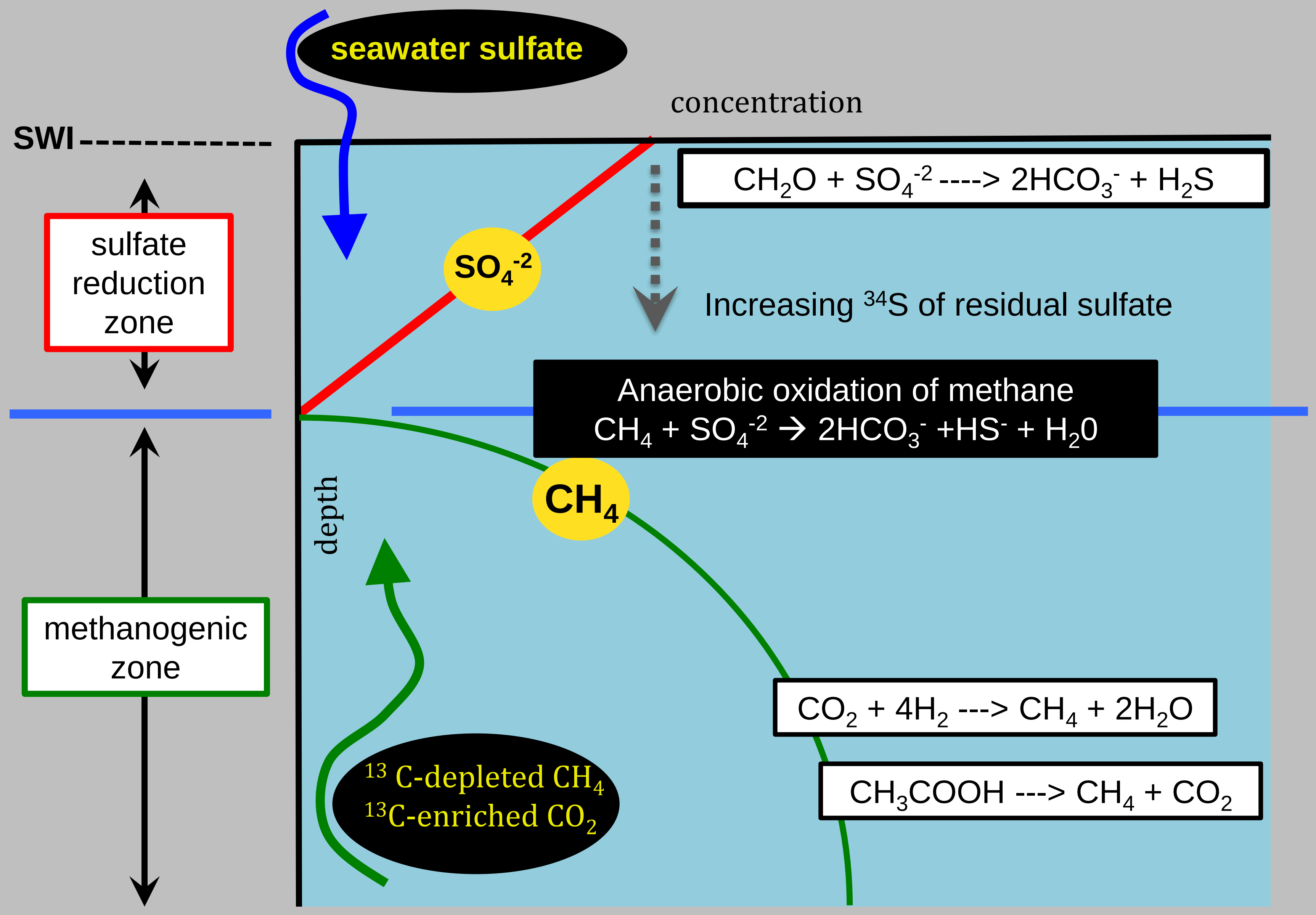
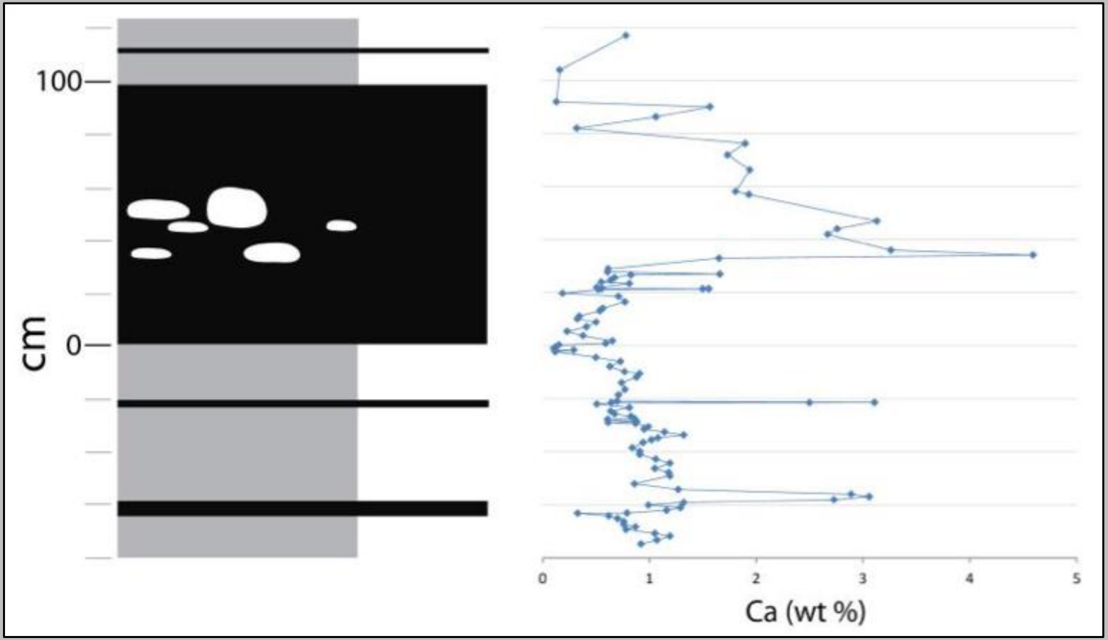
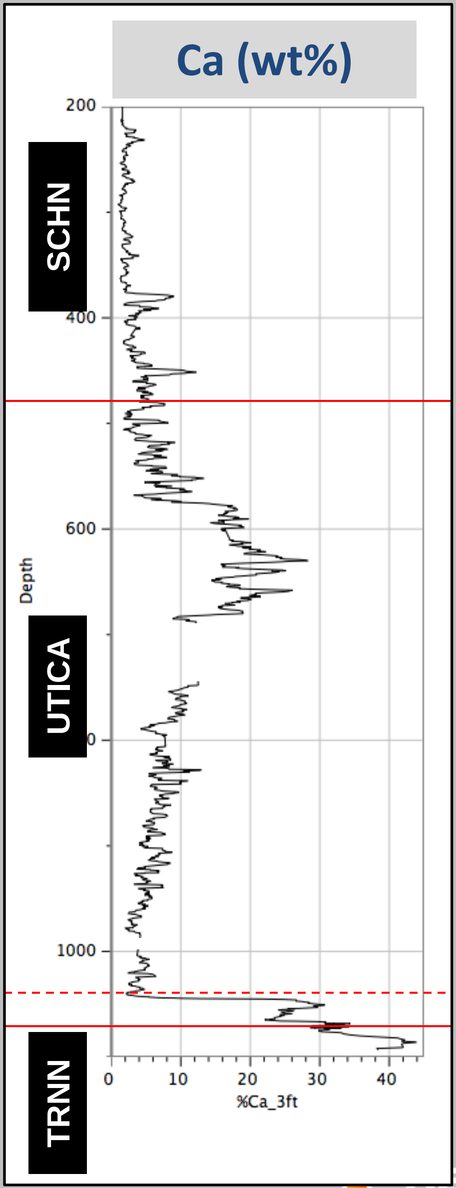


Authigenic Carbonate





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Questions

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