Inorganic Elemental Data 101: Evaluating Redox Conditions in Mudstones

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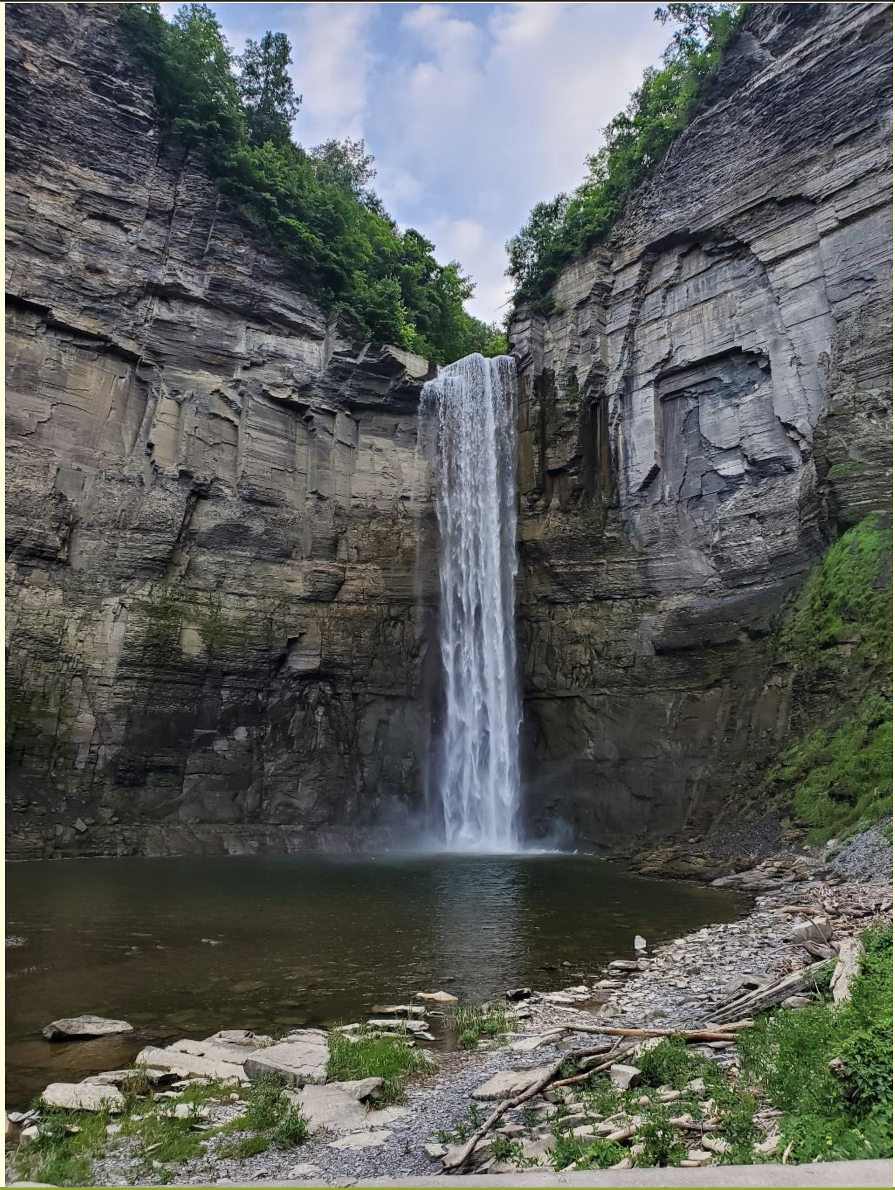
3 Main Points

- **Not all black shales accumulate under the same depositional conditions (applies to the basin and stratigraphic scale for a particular mudstone as well)**
  - **Deep stratified basins, shallow energetic environments, coastal upwelling, restricted lagoon, lacustrine**
- **Not all elemental interpretations are straight forward and they should be used in the context of the entire data set**
- **Likewise elemental data sets should be combined with other data sets to understand and predict reservoir facies distribution**
  - **Standard core analysis, sedimentological analysis, field studies**



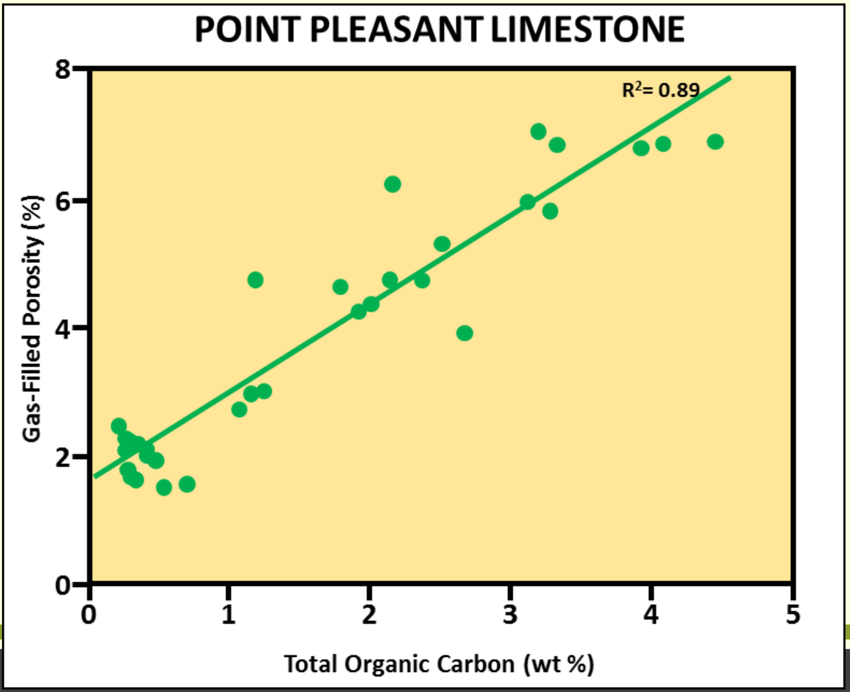
Purpose of the Work

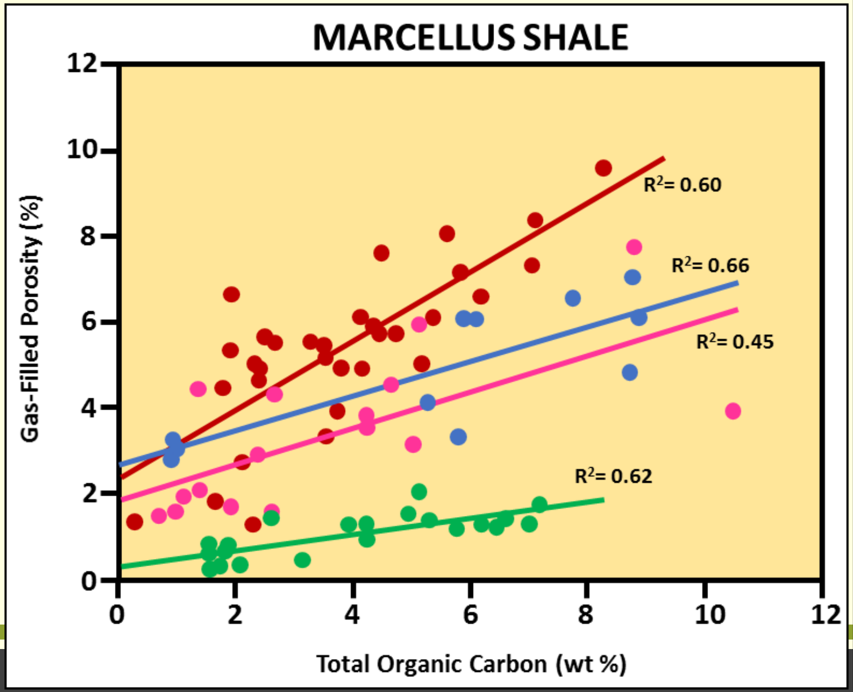
Production Mechanisms

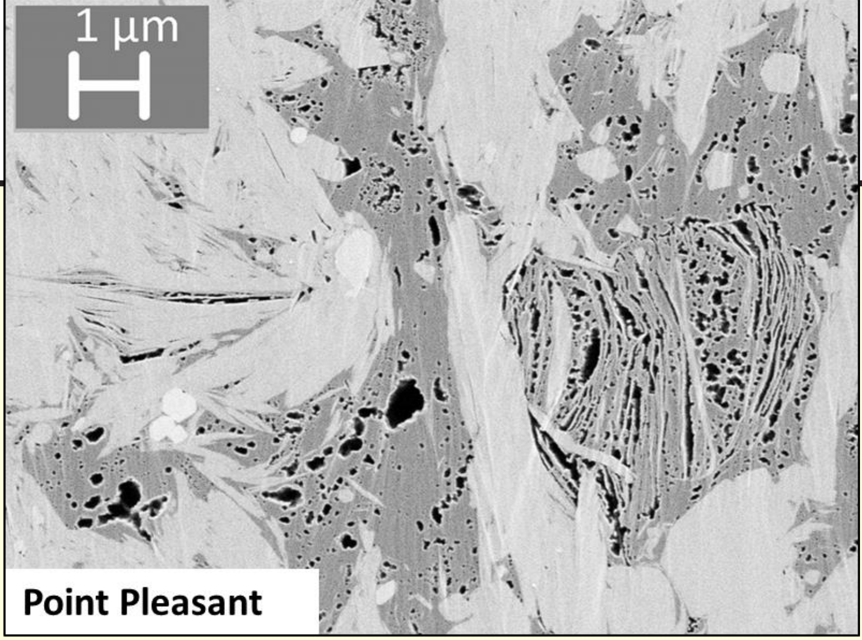
- In many unconventional reservoirs, organic matter hosts the majority of porosity.

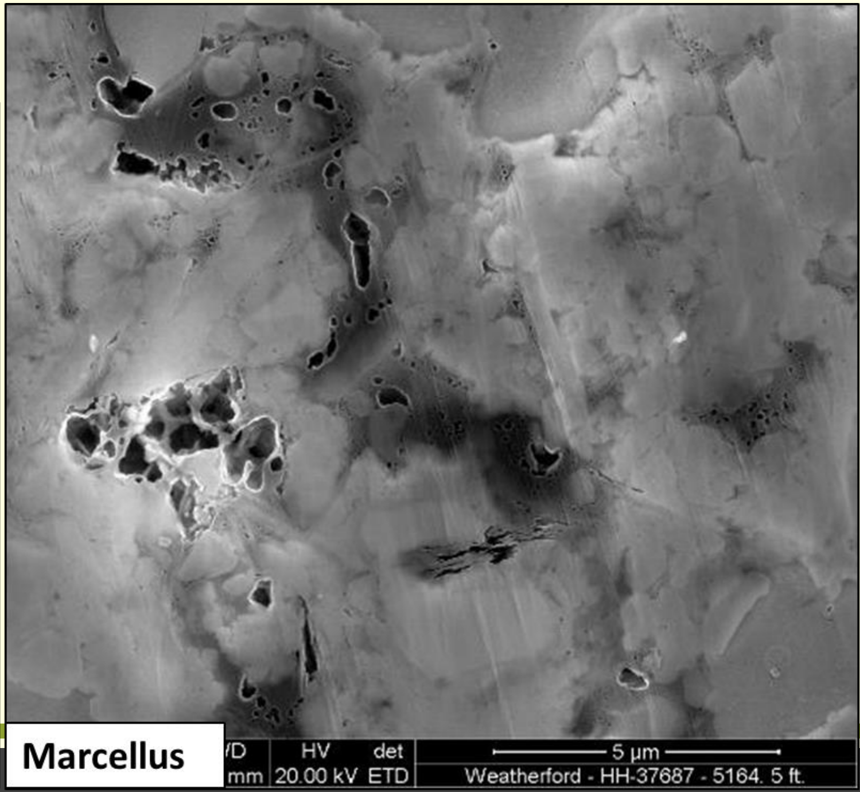
- Indeed, some reservoirs depict a strong correlation between gas-filled porosity and TOC.

- Reservoirs are self sourcing, the original TOC represents the starting material for hydrocarbon generation.



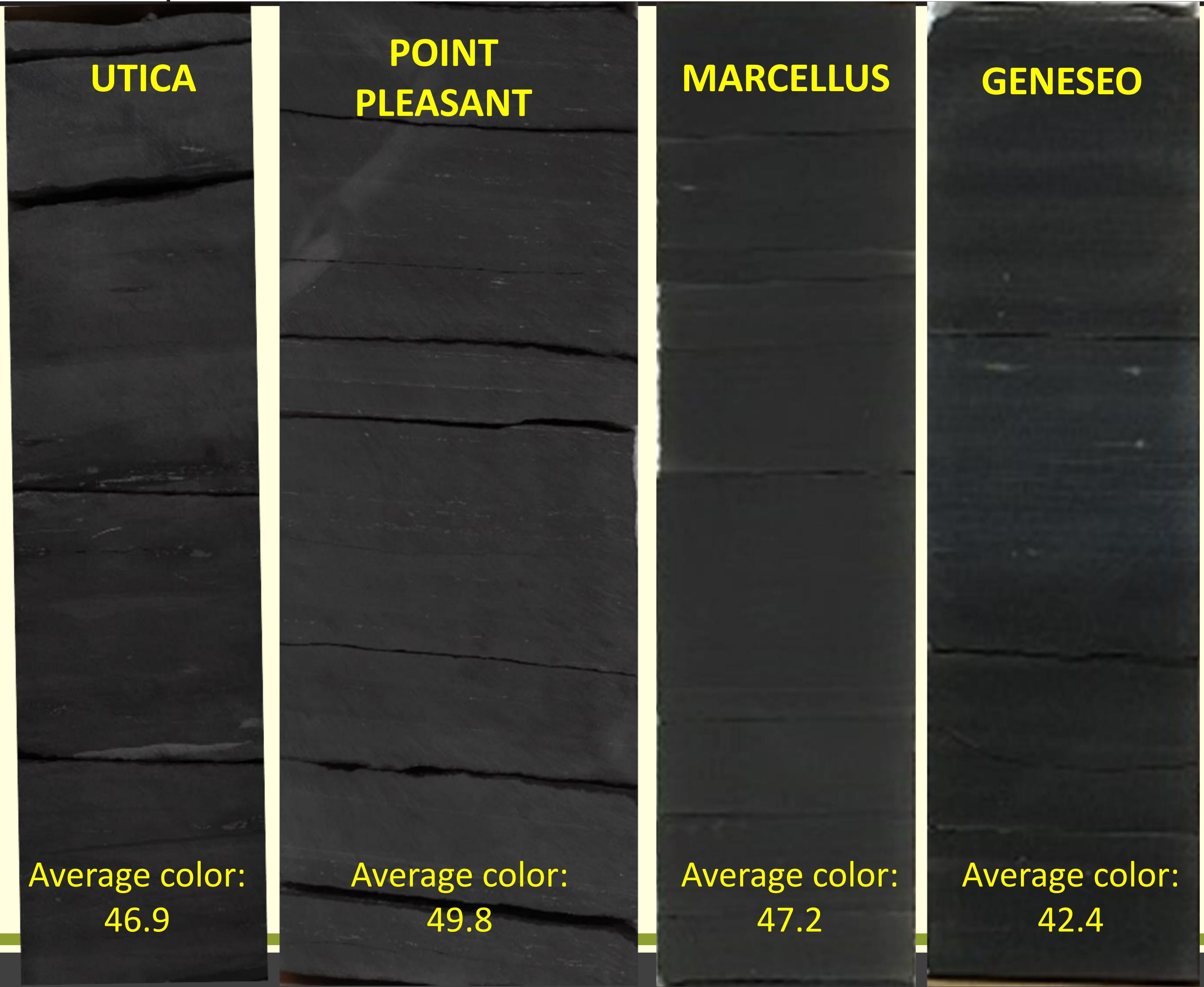


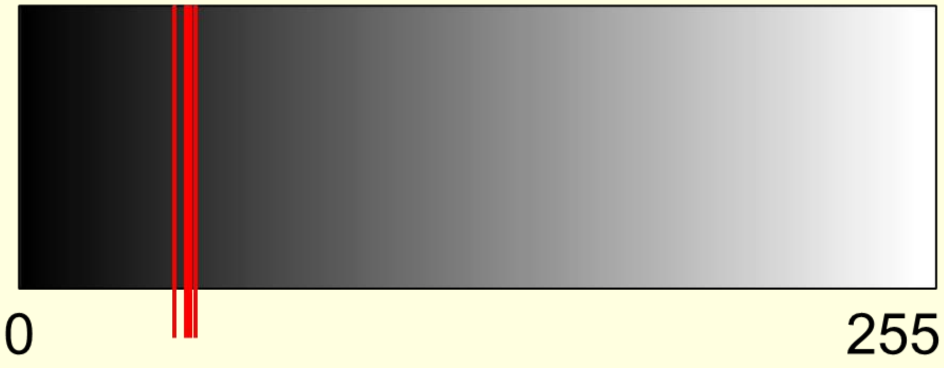




Purpose of the Work

Visual Characterization of Organic-rich Mudstone





Quantitatively there is a <3% difference in the color of these formations.

These rocks range from oxic/dysoxic to anoxic/euxinic.

Visual inspection alone is not enough to understand the depositional environment.

While extremely useful, even sedimentary structures (bedding laminae, erosion surfaces, fossils, etc.) cannot definitively inform on the redox state of rocks.

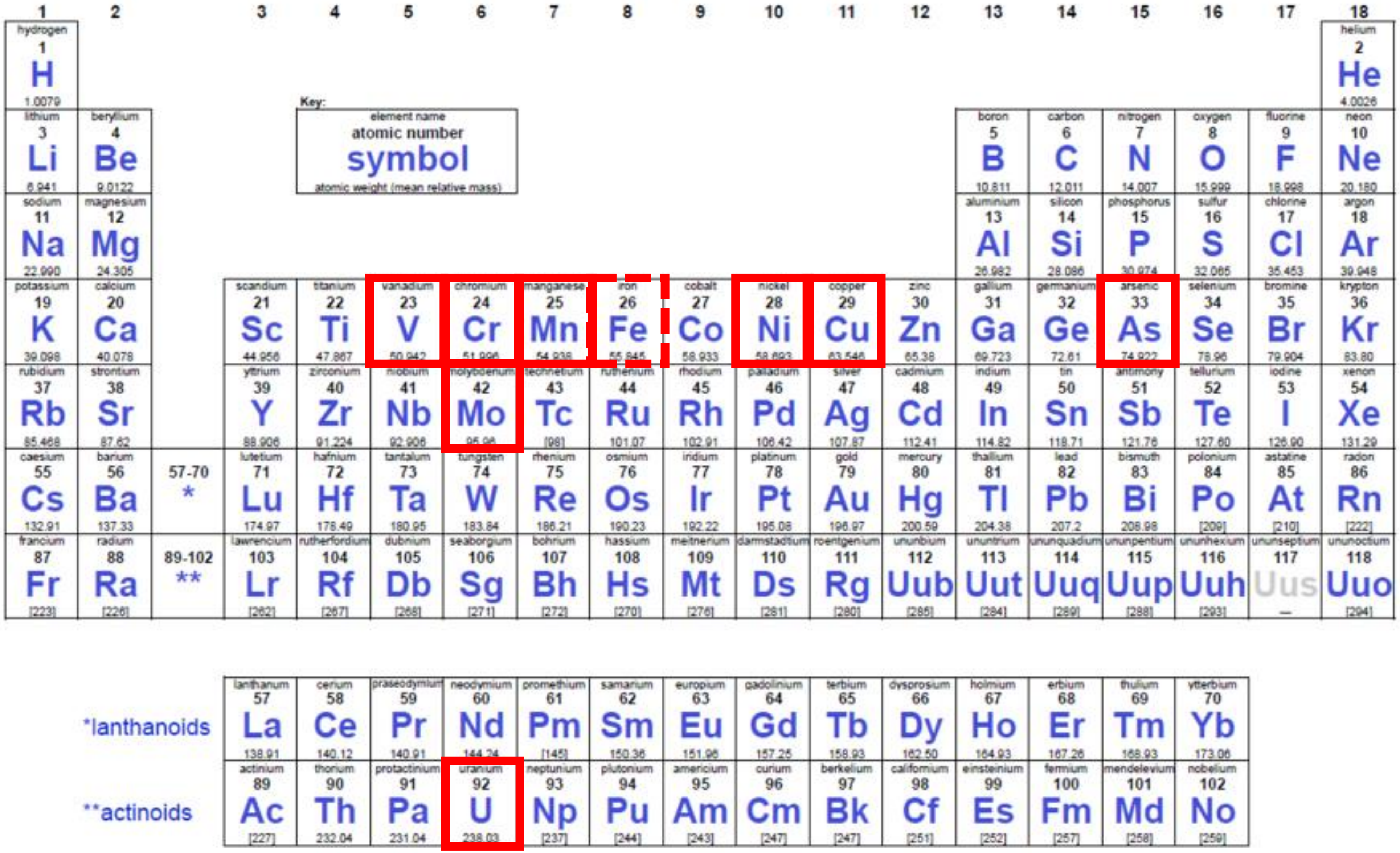
Water oxygenation conditions

Oxygen (ml/l)	Oxygenation regime environments facies	Biofacies
>2.0	Oxic	Aerobic
2.0-0.2	Dysoxic	Dysaerobic
2.0-1.0	moderate	
1.0-0.5	severe	
0.5-0.2	extreme	
0.2-0.0	Suboxic	Quasi-anaerobic
0.0	Anoxic	Anaerobic
0.0 (H2S)	Euxinic	

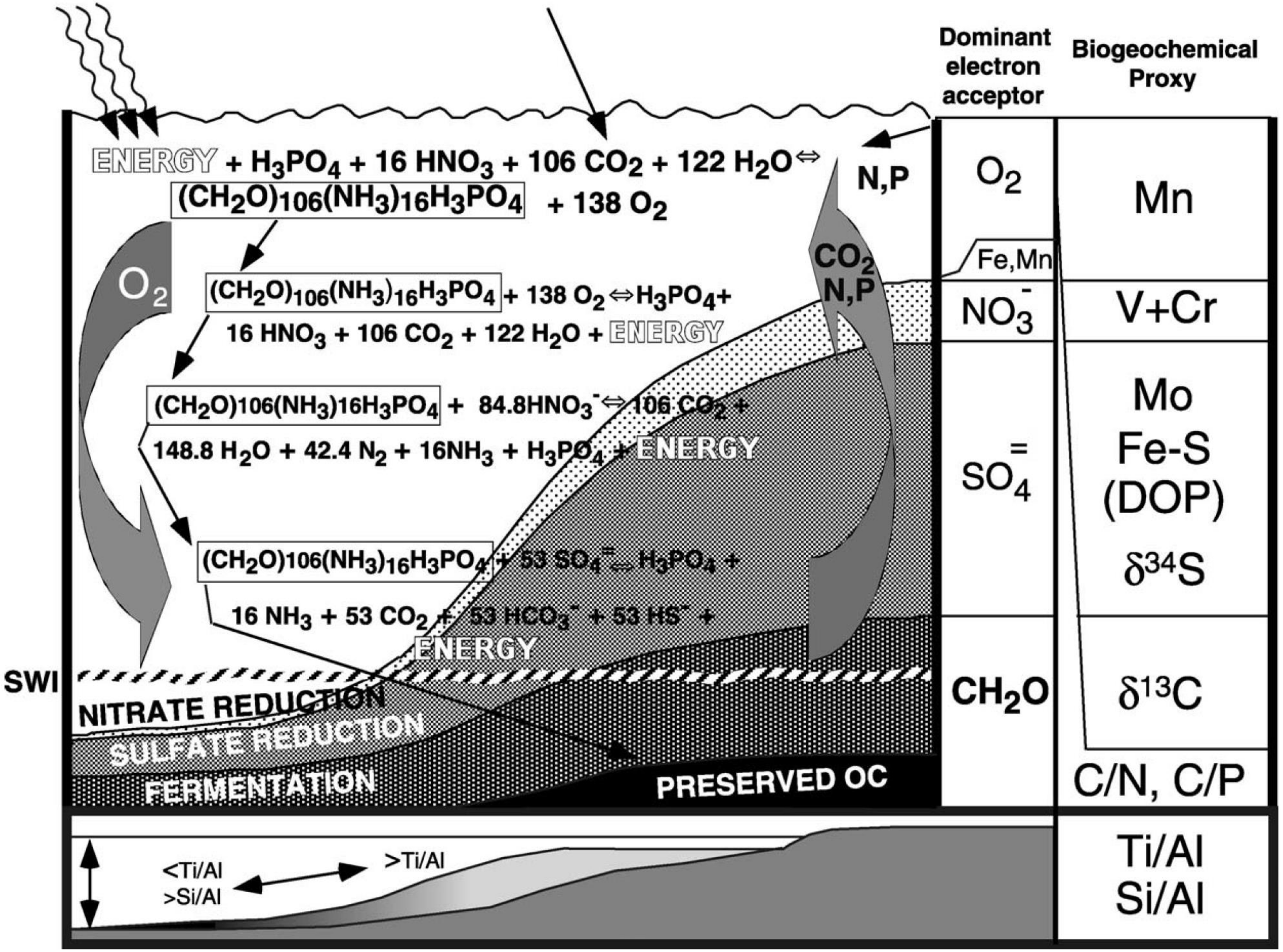
Modified from Tyson and Pearson, 1991

- Three chemical species play a role in the oxidization of organic matter:
  - Oxygen
  - Nitrate
  - Sulfate
- Eukaryote and prokaryote communities use oxygen to oxidize organic material until the supply of oxygen is dissolved.
- Denitrifying bacteria then consume nitrate until it is dissolved.
- The reservoir of sulfate is used to oxidize organic matter by sulfate-reducing bacteria.
- Finally, organic matter can undergo fermentation before preservation.
- These processes further influence the degree to which certain elements remain in the water or accumulate in sediment.
- These are know as Redox Sensitive Trace Elements (RSTE).

Redox sensitive trace elements



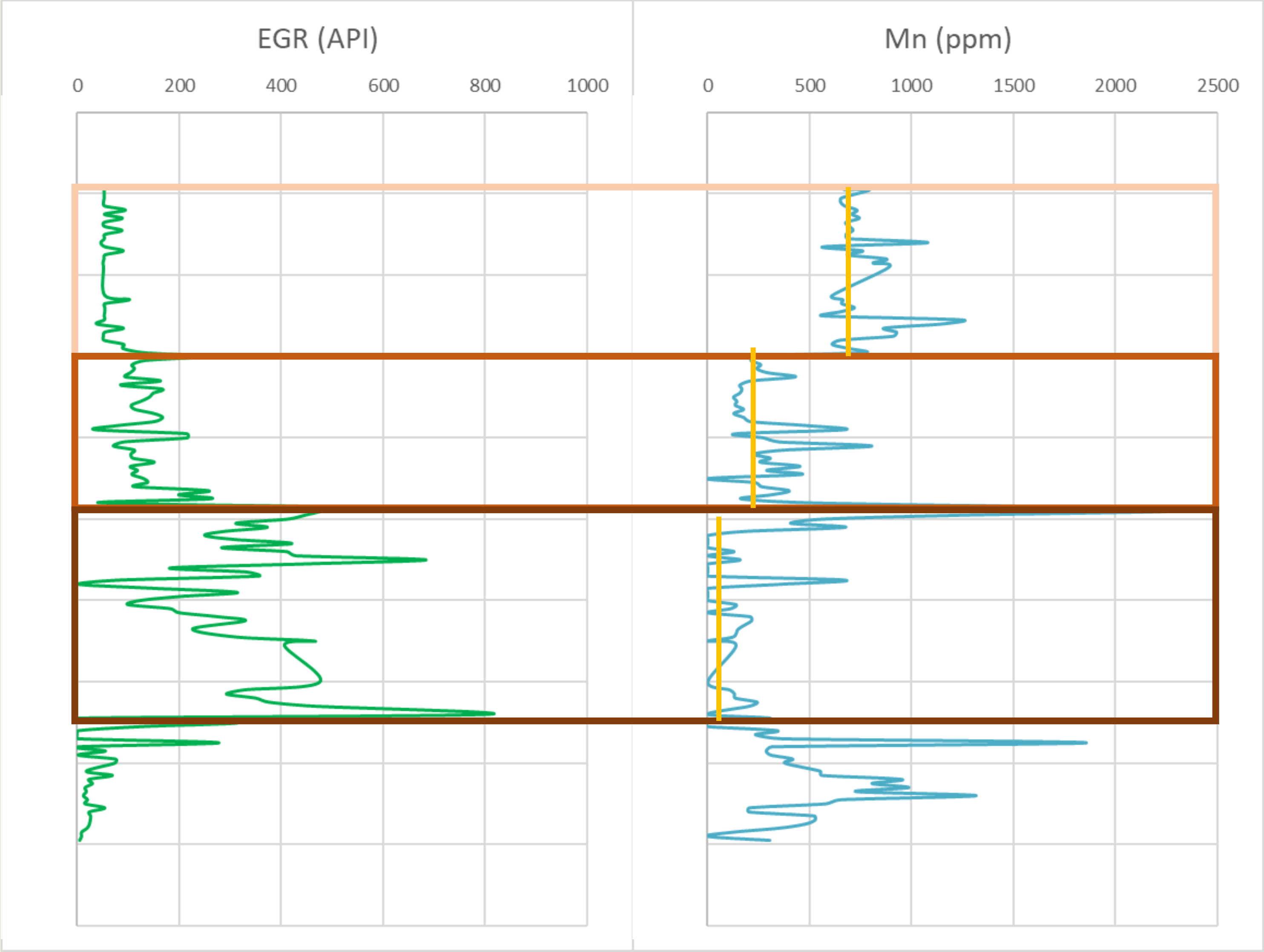
Geochemical proxies for redox conditions



Sageman et al., 2003

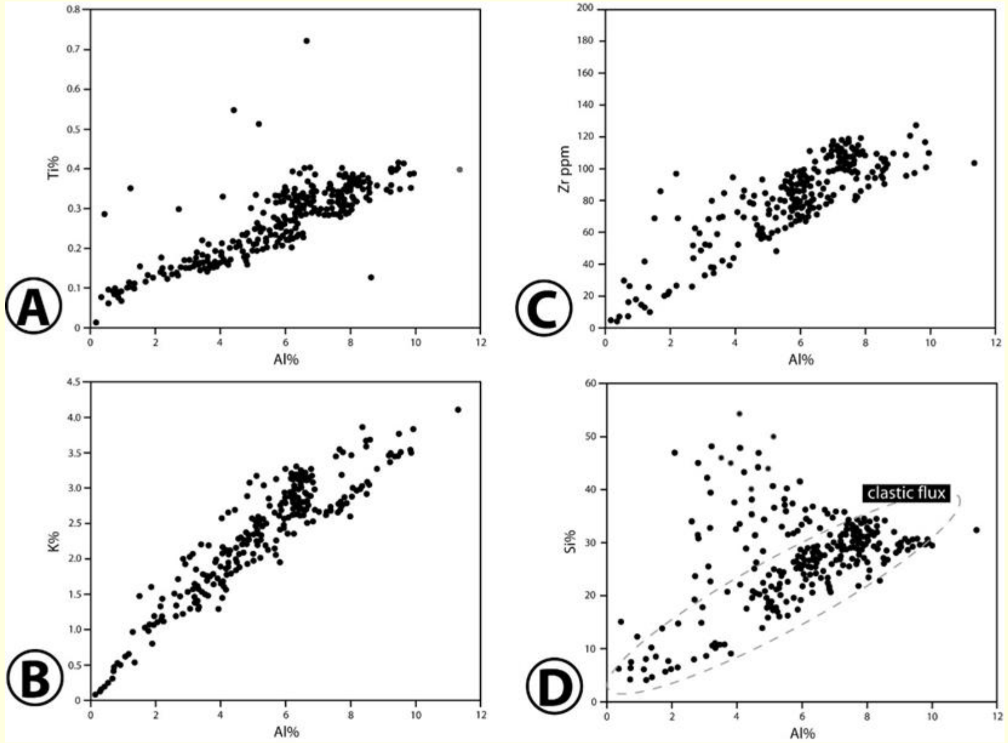
Geochemical proxies for redox conditions

Manganese (Mn) and oxygen



Ludlowville Shale	Dominantly oxic gray shale
Levanna Shale	Dysoxic-anoxic black shale
Marcellus Shale	Anoxic-Euxinic black shale
Onondaga Limestone	Oxic limestone

Al normalization and enrichment factors



- Al cross plotted against clastic-derived elements Ti, Zr, and K.
- Note that while much of Si defines a clastic trend, the relationship is more nuanced.
- While Al, Ti, Zr, and K demonstrate positive covariance, their relationships to Al (dominantly a signal for clay) provides insight into the grainsize and energy of sediment delivered to the basin.

$$\text{Enrichment Factor (EF)} = \frac{\text{Element}_{\text{sample}} / \text{Al}_{\text{sample}}}{\text{Element}_{\text{average shale}} / \text{Al}_{\text{average shale}}}$$

- Elemental data commonly cast as an enrichment factor.

- The element is normalized to the Al content of the sample
  - Accounts for an increase in abundance due to increased sediment supply
- The element/Al is then normalized to the average shale value (Wedephol 1971, 1991).
  - Unity implies elemental abundance is typical of shales
  - EF>3 implies significant enrichment of that element
  - EF<1 suggests depletion of that element

Uranium and Molybdenum profiles

- Mo and U
  - Redox sensitive metals especially useful for paleoenvironmental and hydrographic studies
- Present in low concentrations in the upper crust-
  - Mo ~3.7 ppm
  - U ~ 2.7 ppm (Taylor and McLennan, 1985)
- Both exhibit conservative behavior under oxic conditions;
- Both elements have long residence times in seawater
  - Mo ~0.78 MY
  - U ~0.45 MY
- Both exhibit roughly equal concentrations in seawater globally:
  - Mo/U = 7.53 molar ratio – Pacific Ocean
  - Mo/U = 7.90 molar ratio – Atlantic Ocean
- Both exhibit low concentrations in plankton – enrichment in sediment can be related to authigenic uptake from seawater;

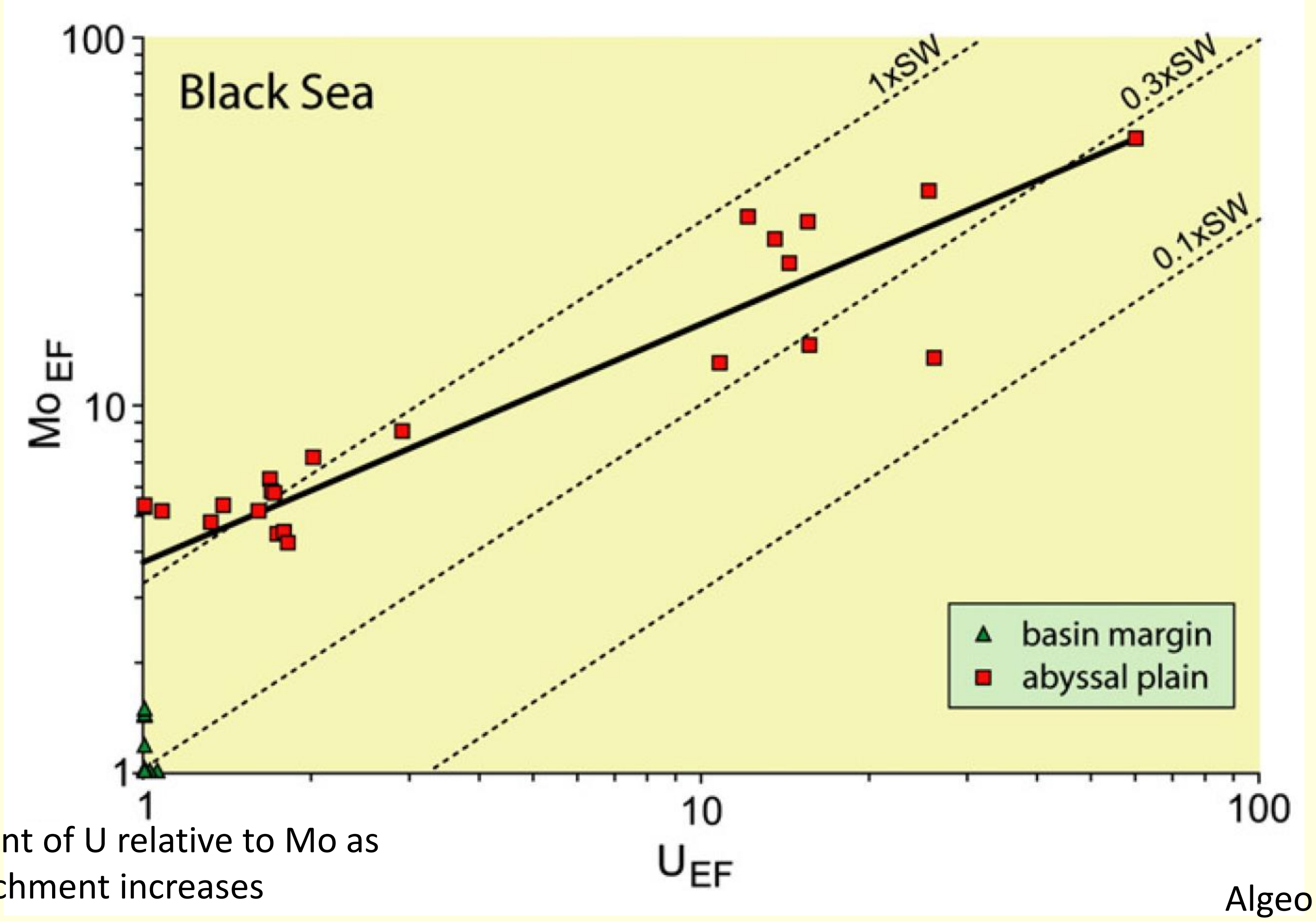
Uranium and Molybdenum profiles

- Significant differences

- U uptake is linked to organic carbon content (TOC) and occurs by diffusion across the sediment-water interface…organic matter serves as a sorbant…sedimentation rate is very important to this

- Mo uptake by sediment requires the presence of H_2S (euxinic conditions) and can be accelerated by particulate Mn-Fe-oxyhydroxide shuttle (U is unaffected by this); less covariance with TOC

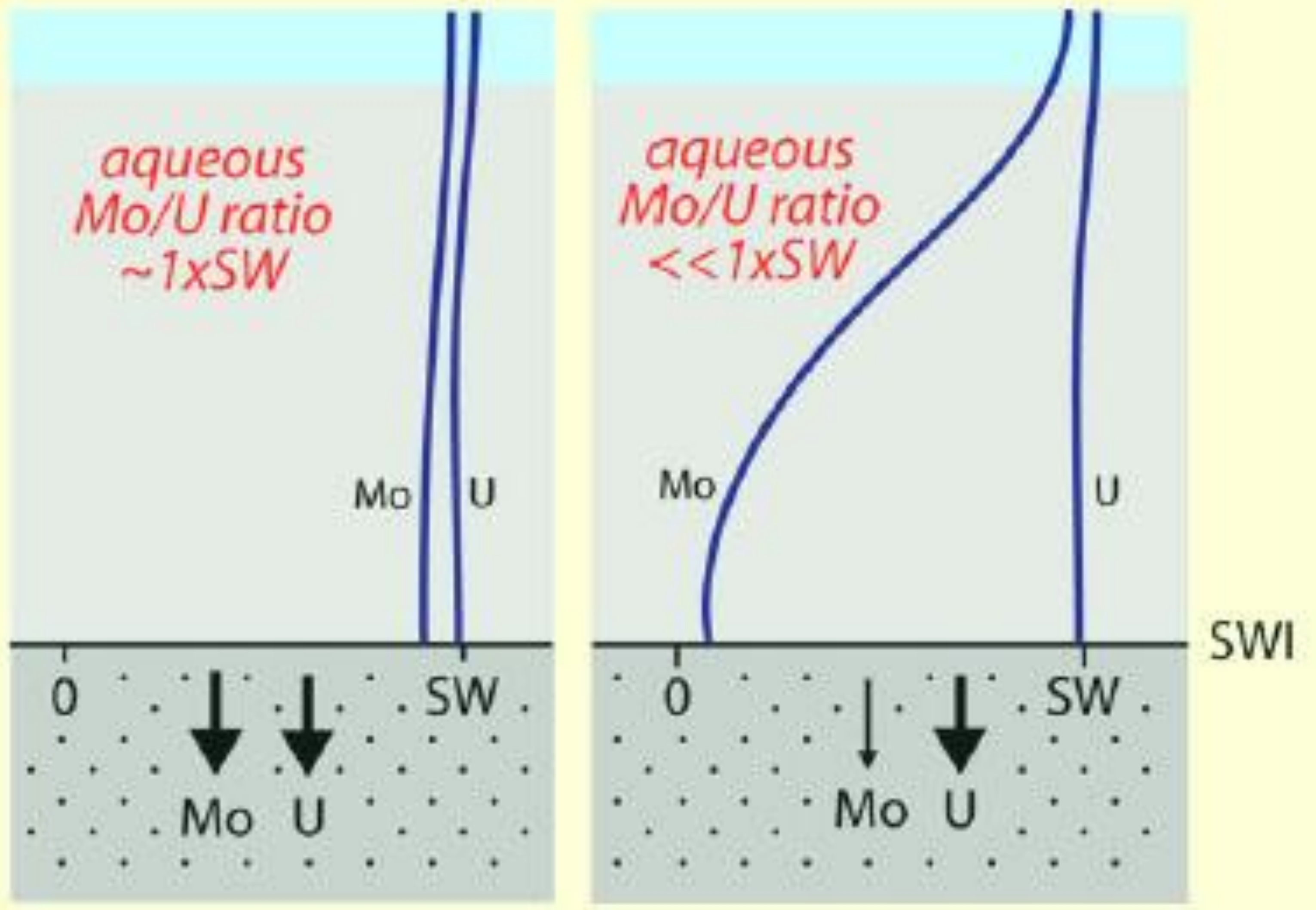
Uranium and Molybdenum profiles



Progressive enrichment of U relative to Mo as total authegenic enrichment increases

Algeo and Tribovillard, 2009

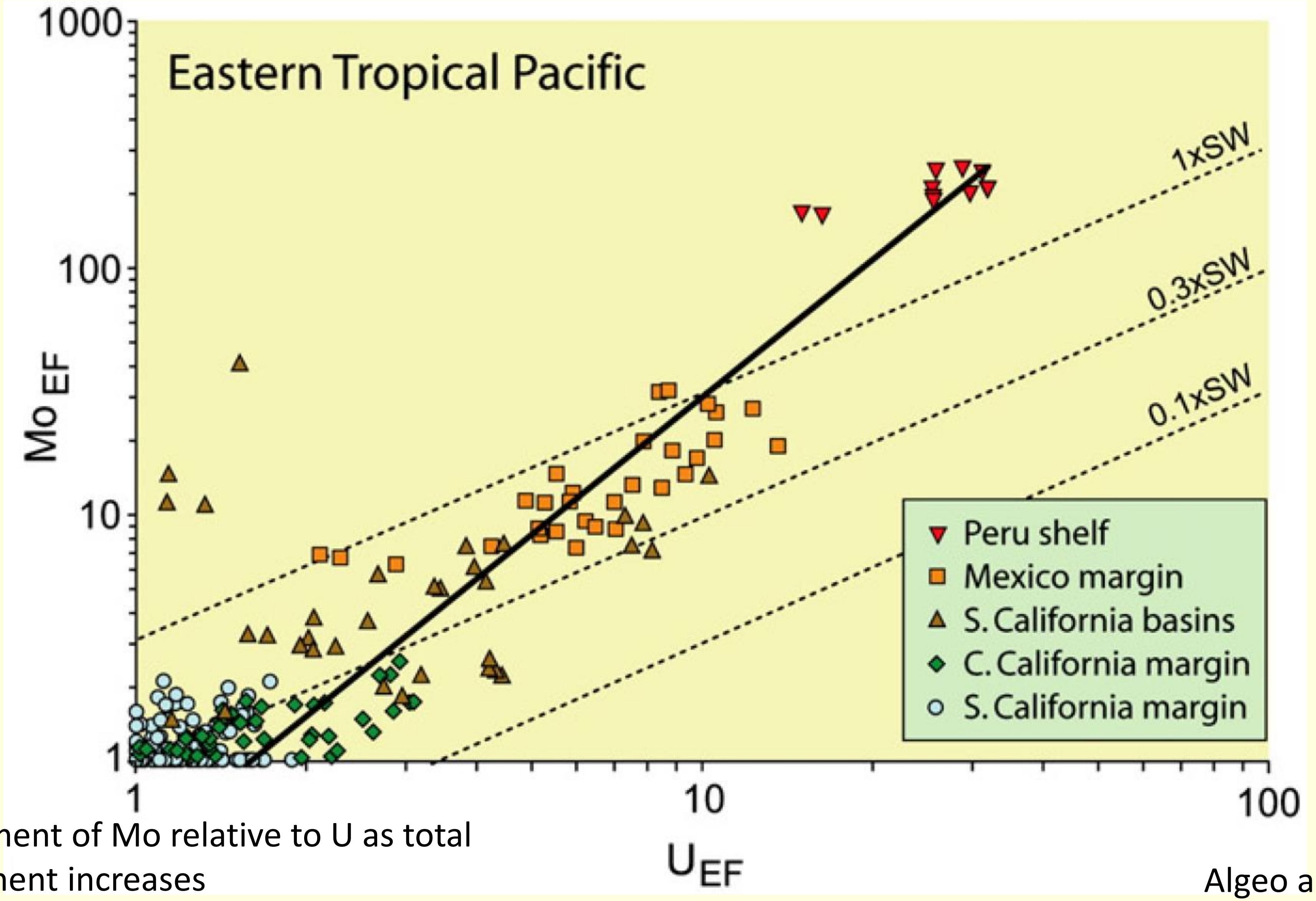
Uranium and Molybdenum profiles



Mo depleted water mass (basin reservoir effect) → restricted basin

Algeo and Tribovillard, 2009

Uranium and Molybdenum profiles



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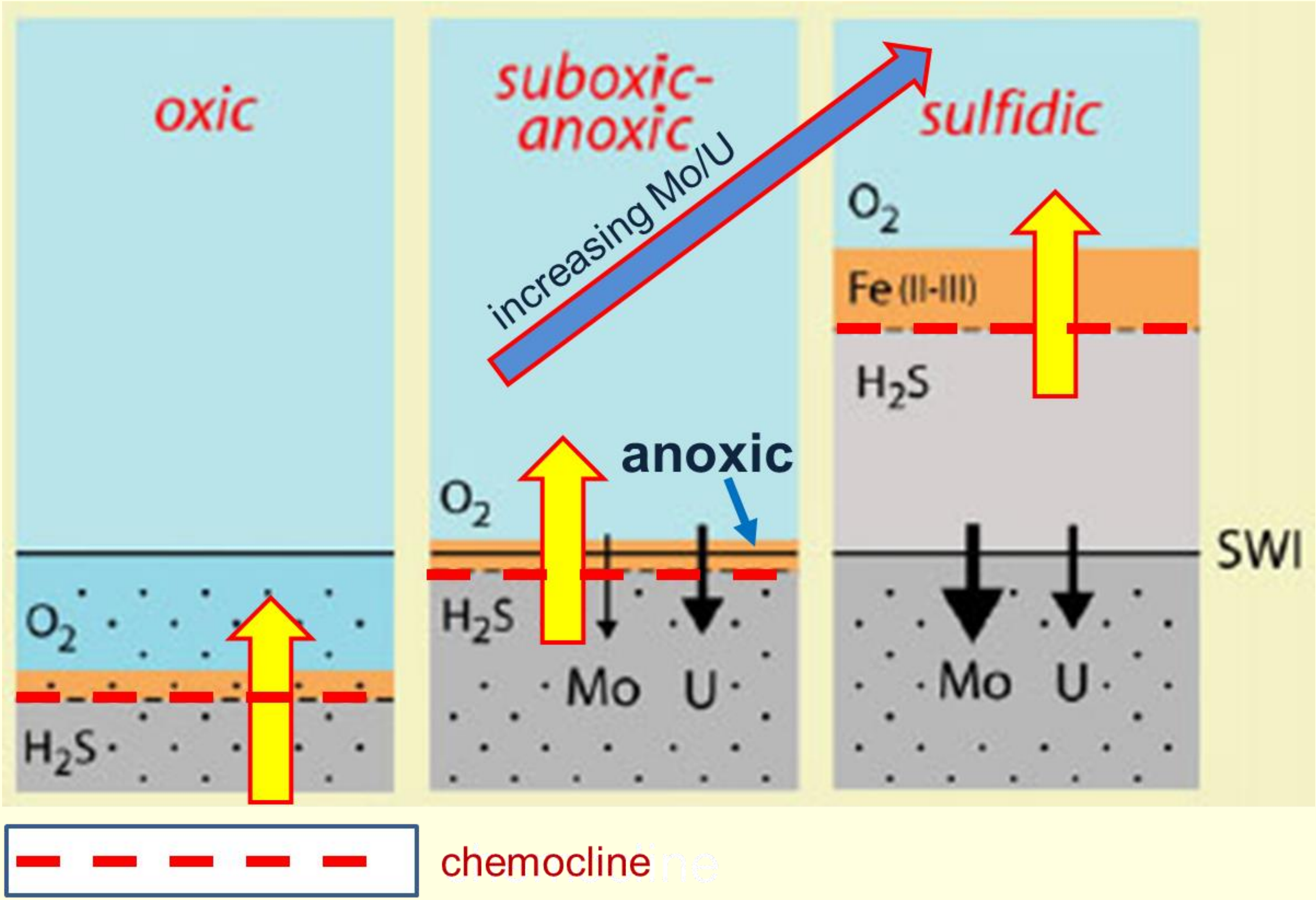
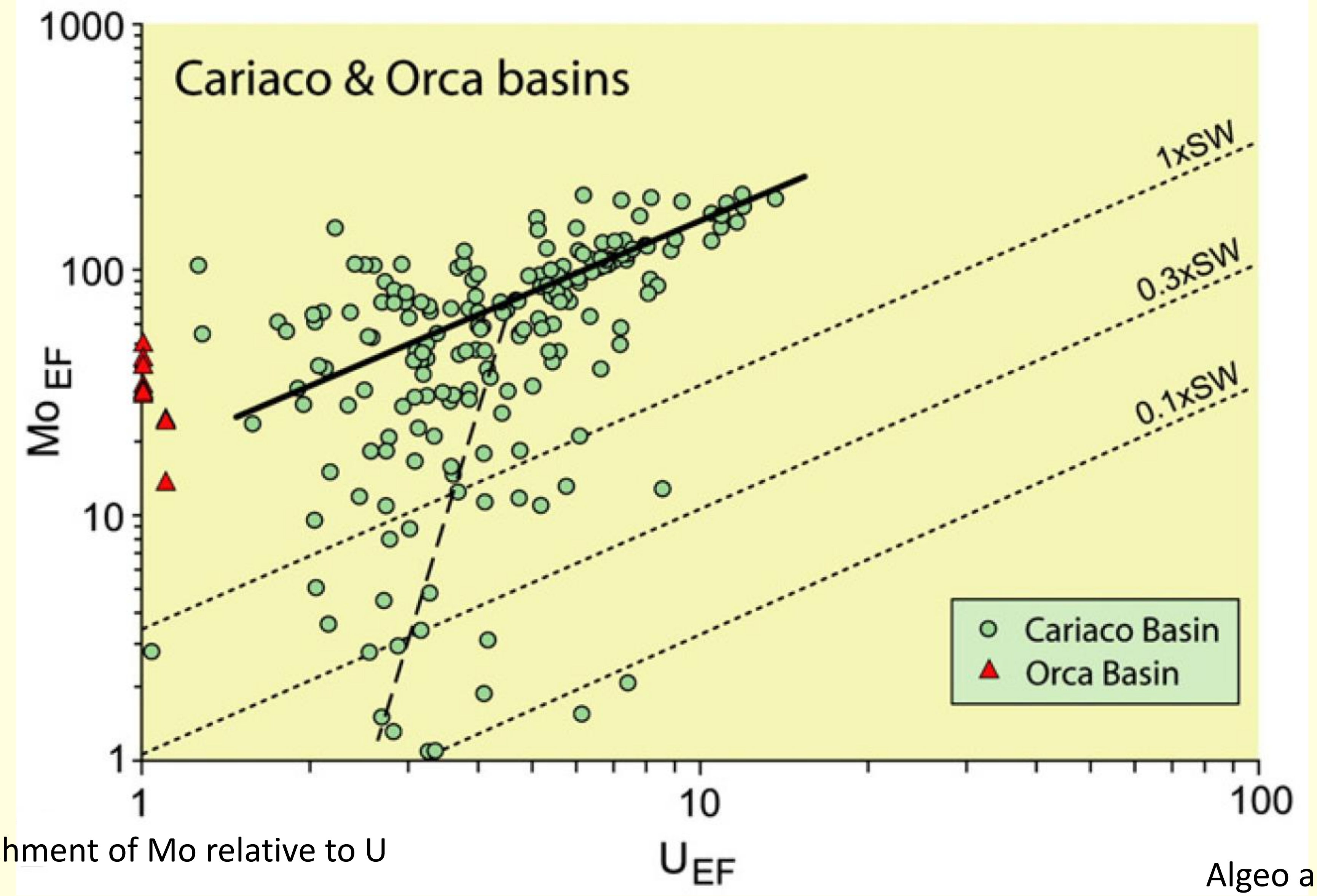


Weakly restricted to open marine setting

Algeo and Tribovillard, 2009

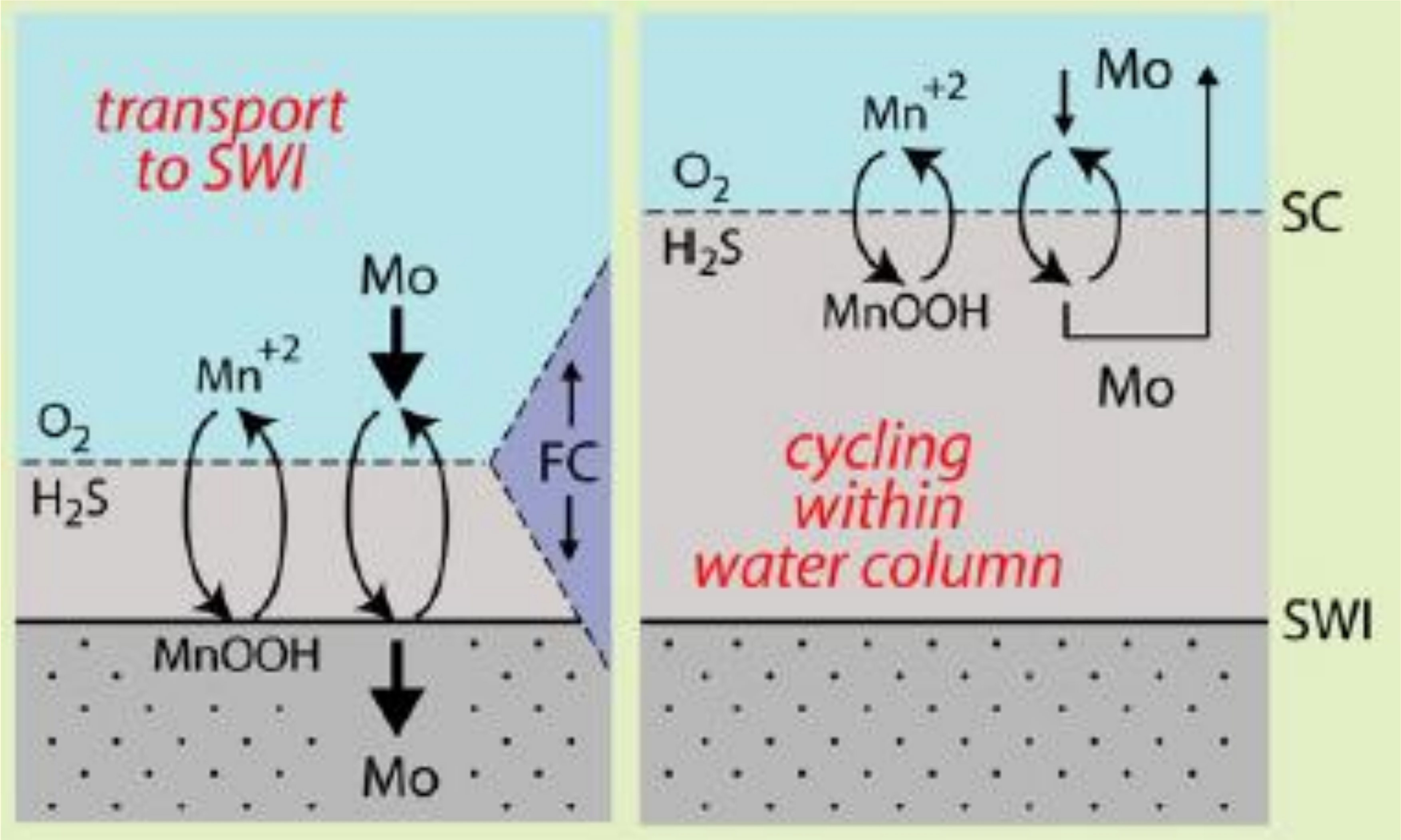
Uranium and Molybdenum profiles



Considerable enrichment of Mo relative to U

Algeo and Tribovillard, 2009

Uranium and Molybdenum profiles

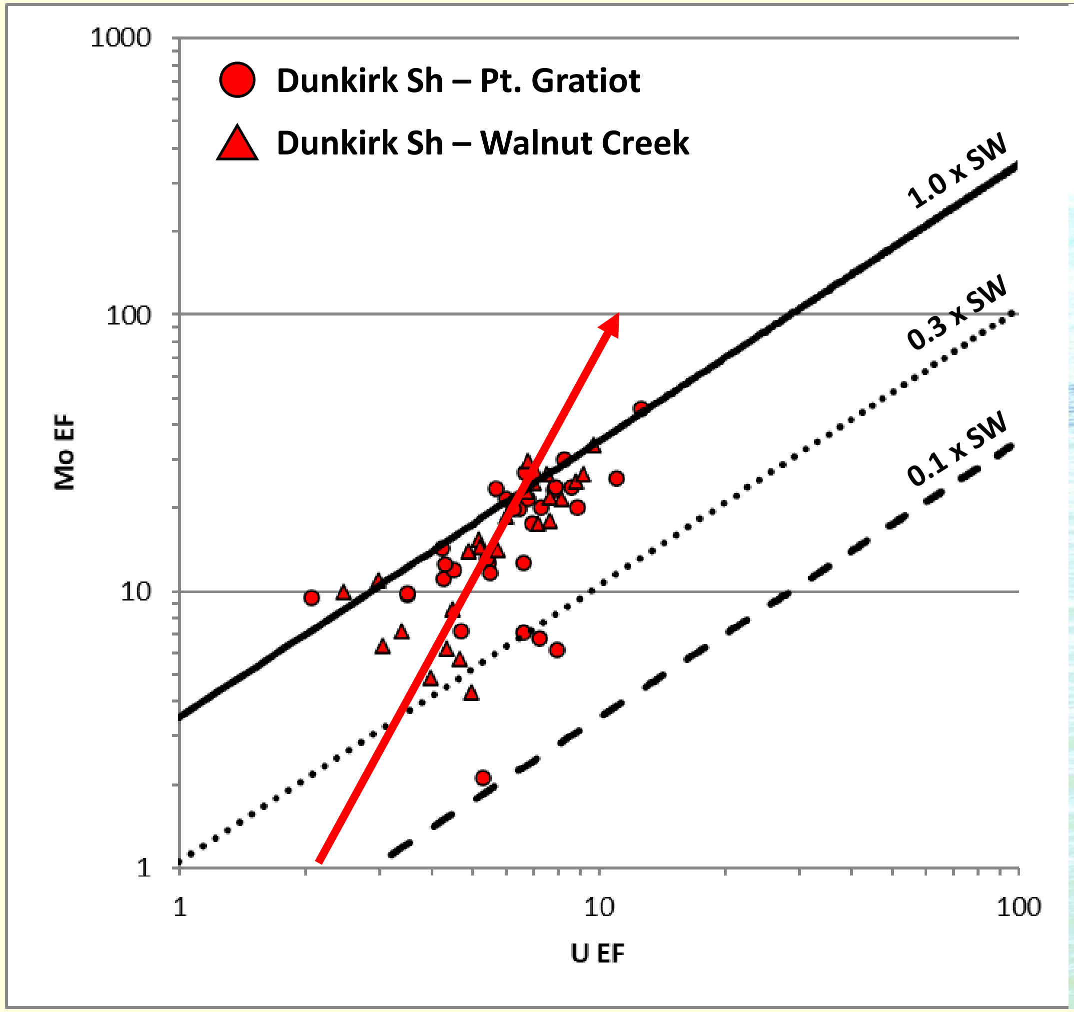


Weakly restricted basin – requires intermittently sulfidic (dissolved H_2S) bottom water

Algeo and Tribovillard, 2009

Uranium and Molybdenum profiles

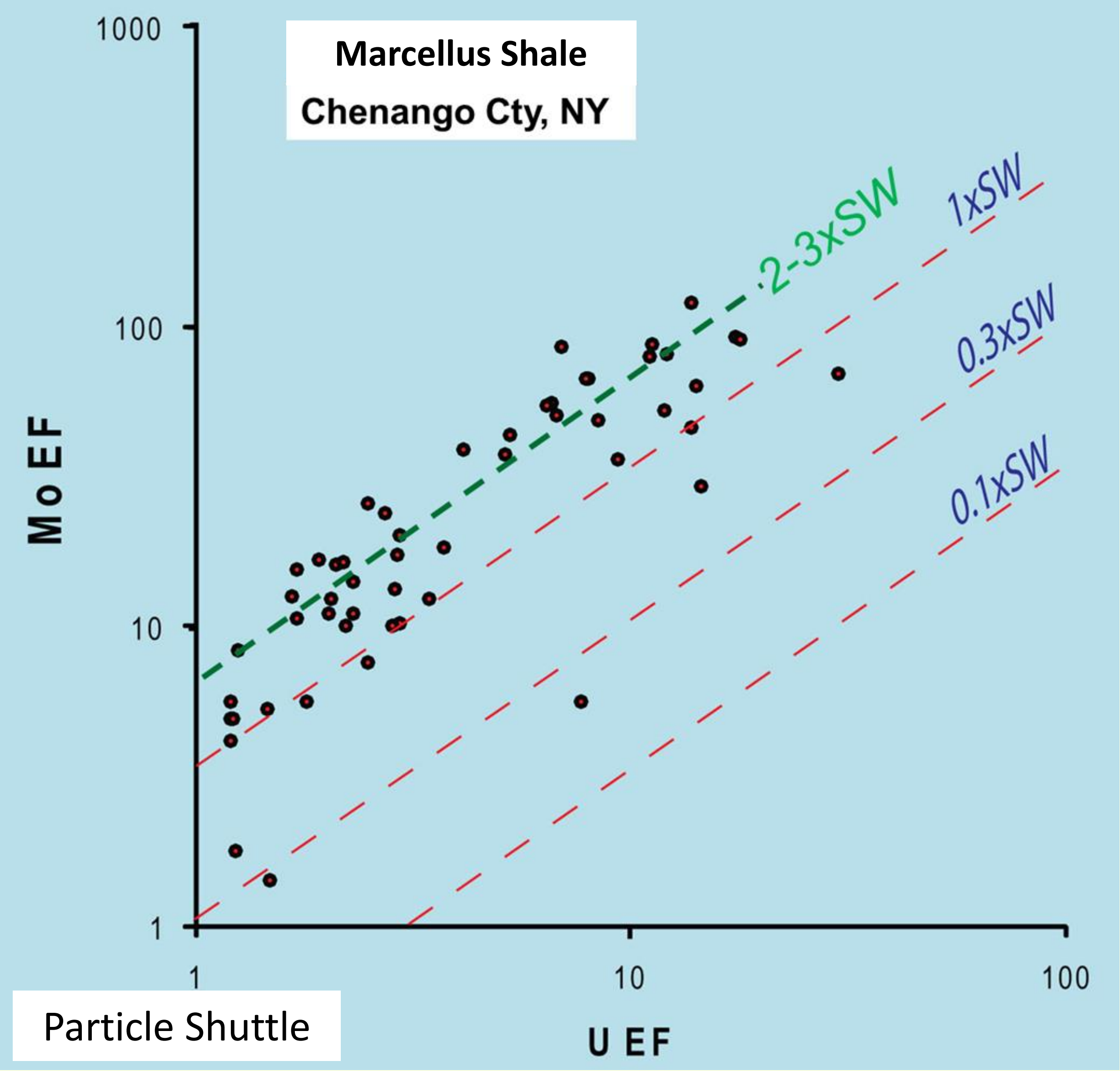
Dunkirk Shale



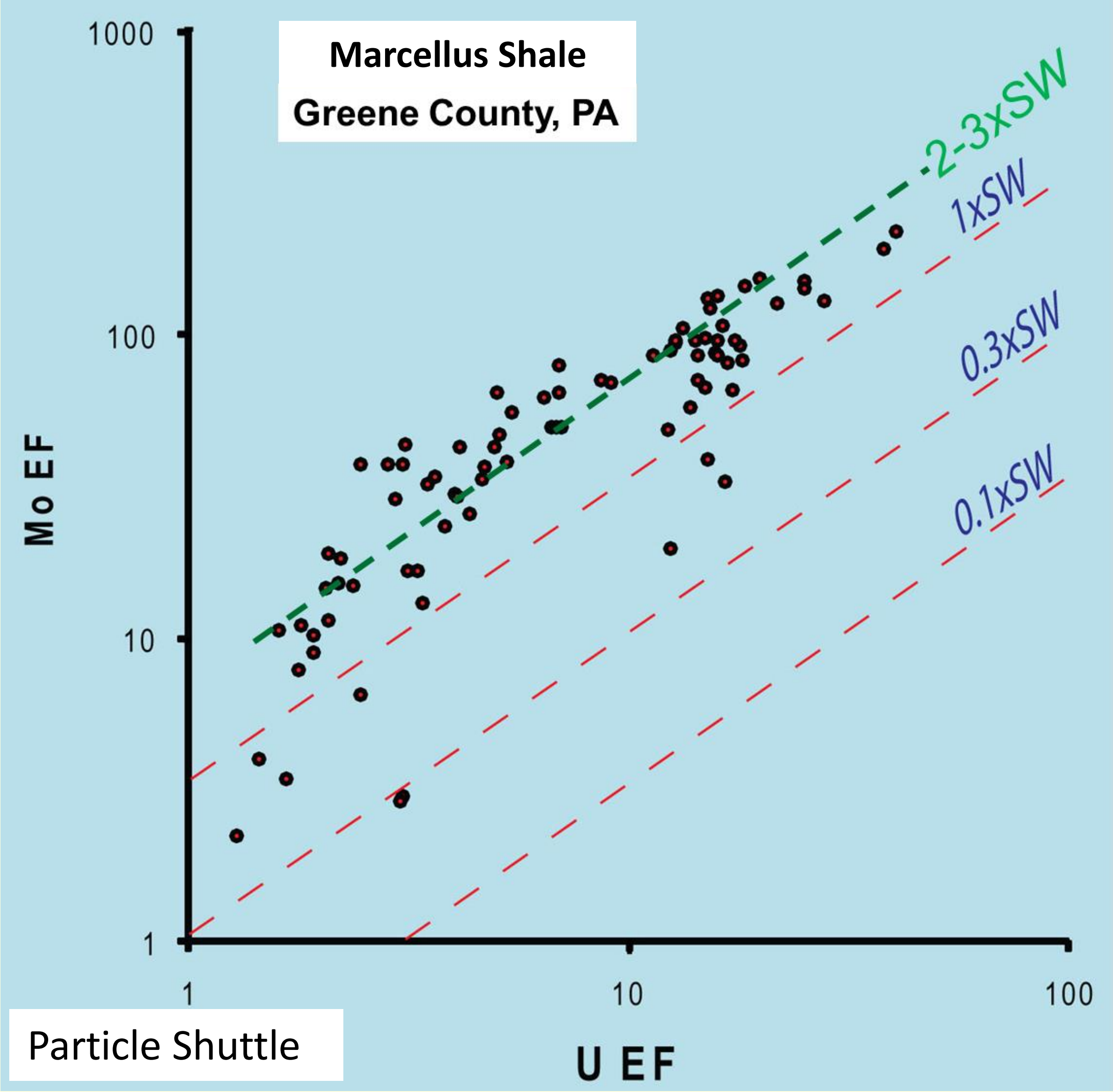
Weakly restricted basin

Uranium and Molybdenum profiles

Marcellus Shale



Particle Shuttle

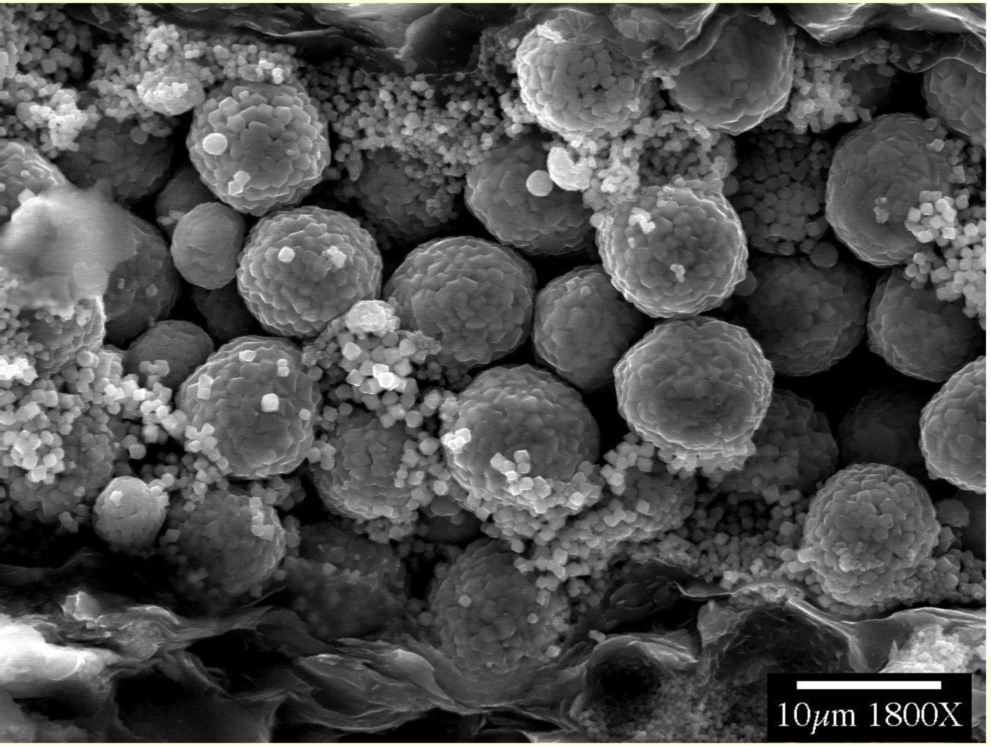


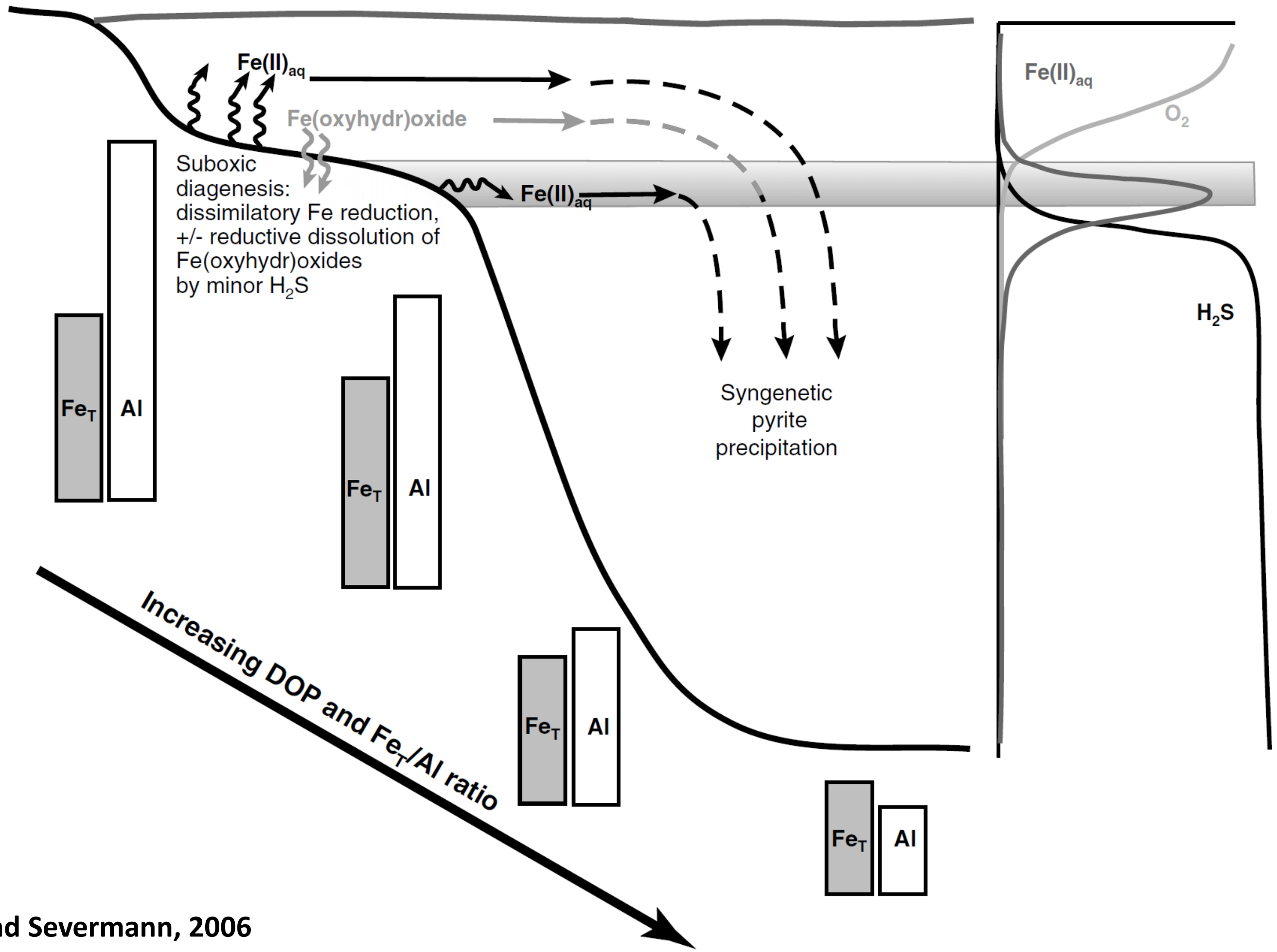
Particle Shuttle

Interpretations that are not straight forward

Iron sequestration

- The average shale value for Fe/Al is 0.55
- Diagenesis in shelf environments produce dissolved Fe II, some portion of which is exported to the bottom water
- In the euxinic bottom water, this Fe is sequestered into the sediment in the form of syngenetic/diagenetic pyrite





Lyons and Severmann, 2006

*DOP can be calculated from elemental data, but requires assumption that all S is in pyrite

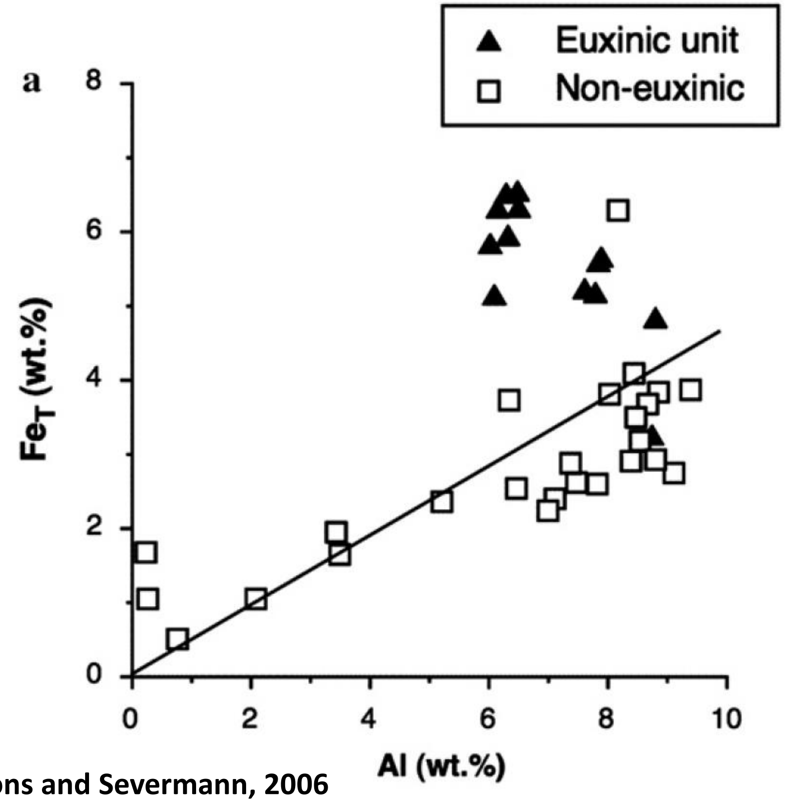
Interpretations that are not straight forward

Iron sequestration

- Two observations can be made about Fe/Al in euxinic settings:
  - Bacterial sulfate production is ubiquitous, therefore sedimentary pyrite concentrations and organic carbon are not linked to one another (although both are often elevated)

    - Under oxic water conditions sulfide production is limited to anoxic pore waters and therefore entirely dependent on the local availability of organic carbon.

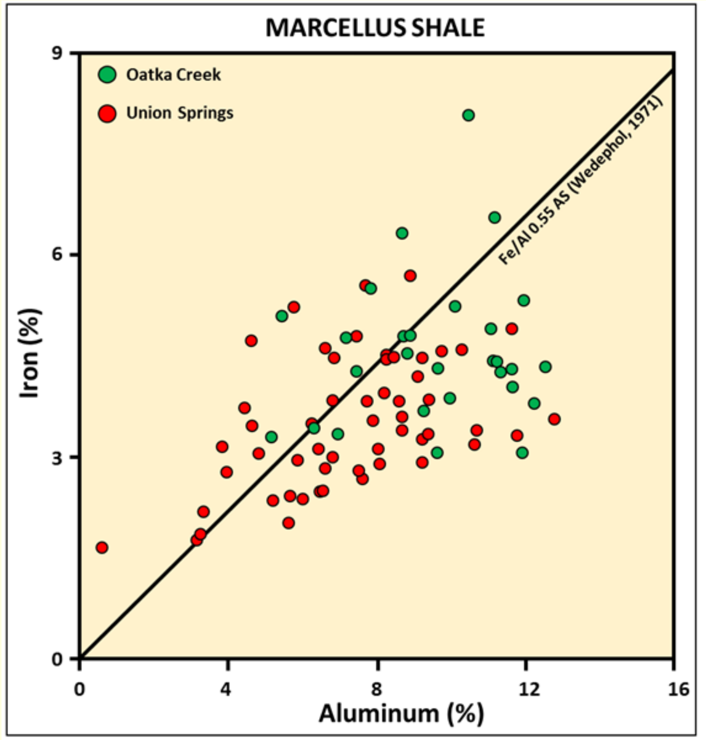
  - Fe/Al increase and Fe is no longer only a function of Fe delivery to the basin.
    - Fe/Al exceeds 0.55 and the trend is decoupled from Al.



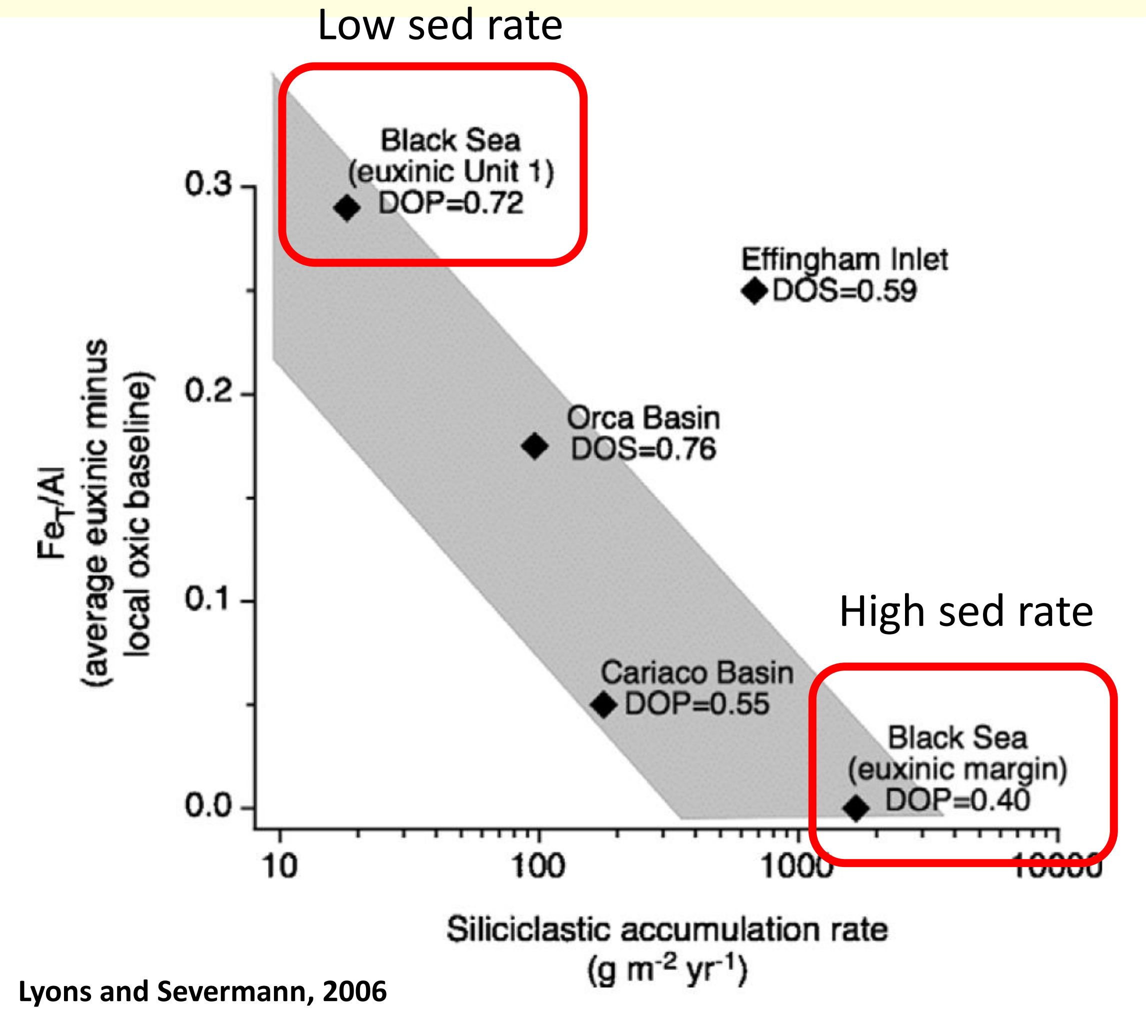
Lyons and Severmann, 2006

Interpretations that are not straight forward

Iron sequestration



- Lack of correlation with Al argues against an oxic environment



Lyons and Severmann, 2006

- Must also consider sedimentation rate
- At high sedimentation rates, delivery of non-reactive Fe to the basin can exceed pyrite production leading to lower Fe/Al ratio

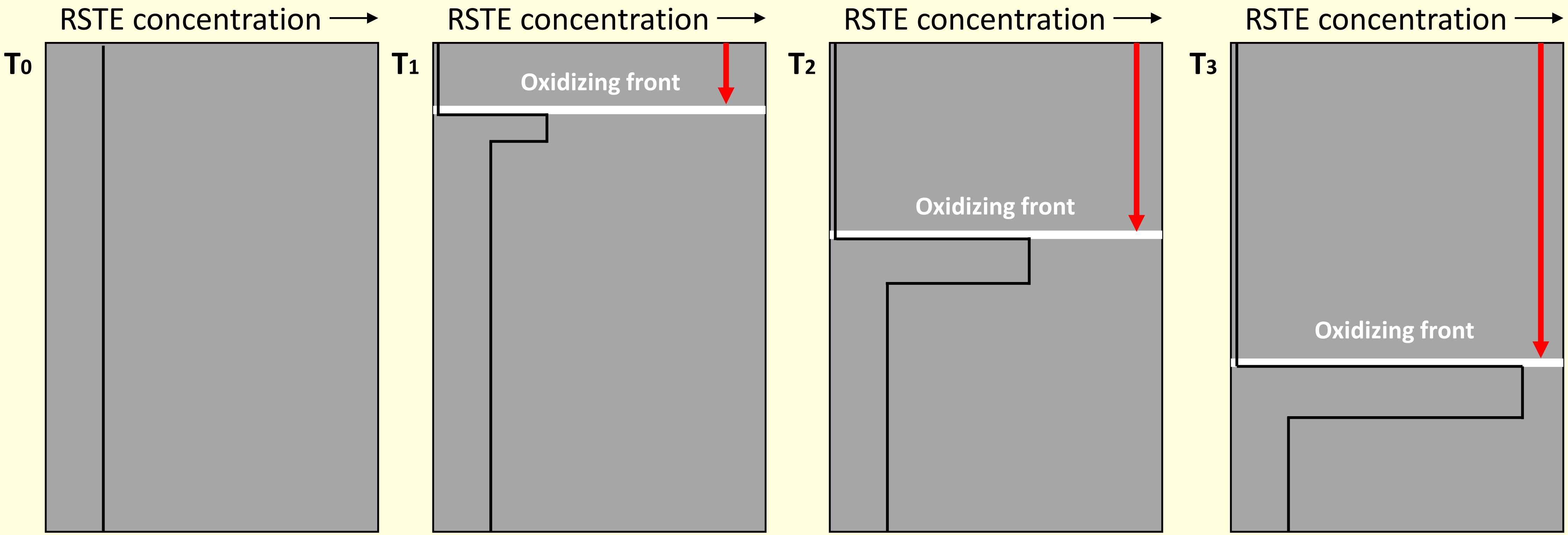
- The Marcellus accumulated over 1.0-1.5 my
  - Compare to the Barnett Shale → similar thickness yet accumulated over ~22 my…much lower sedimentation rate

Remobilization of elements

Burn Down

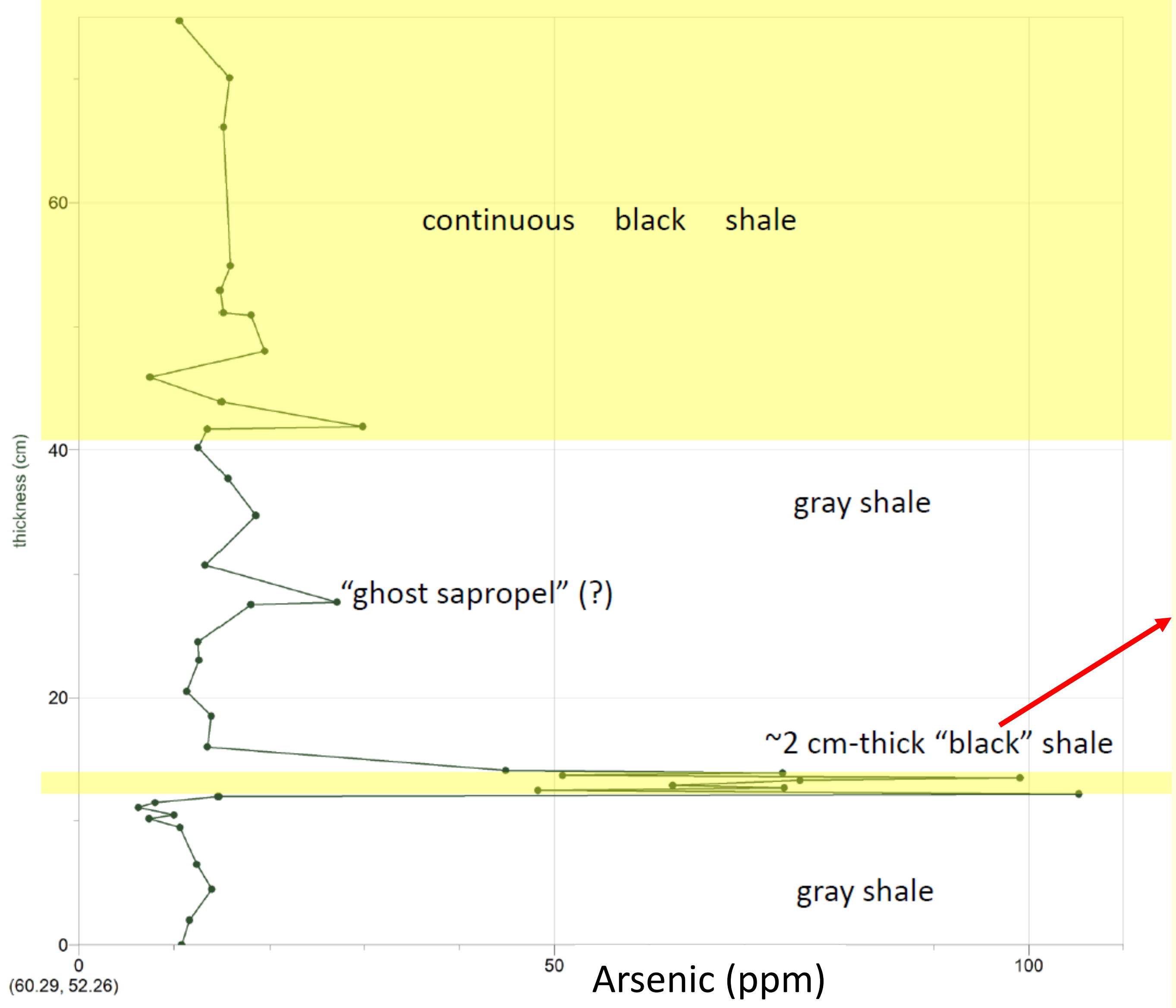
- Burn down has been offered as a way of explaining high concentrations of RSTE in black shales assumed to have been deposited under oxic conditions

- Burn down is a process by which an oxidizing front moves down through the sediment pile
  - This acts to dissolve and mobilize elements that are conservative under oxic conditions.
  - When the front stops moving these elements precipitate out in anoxic pores of sediment at higher concentrations



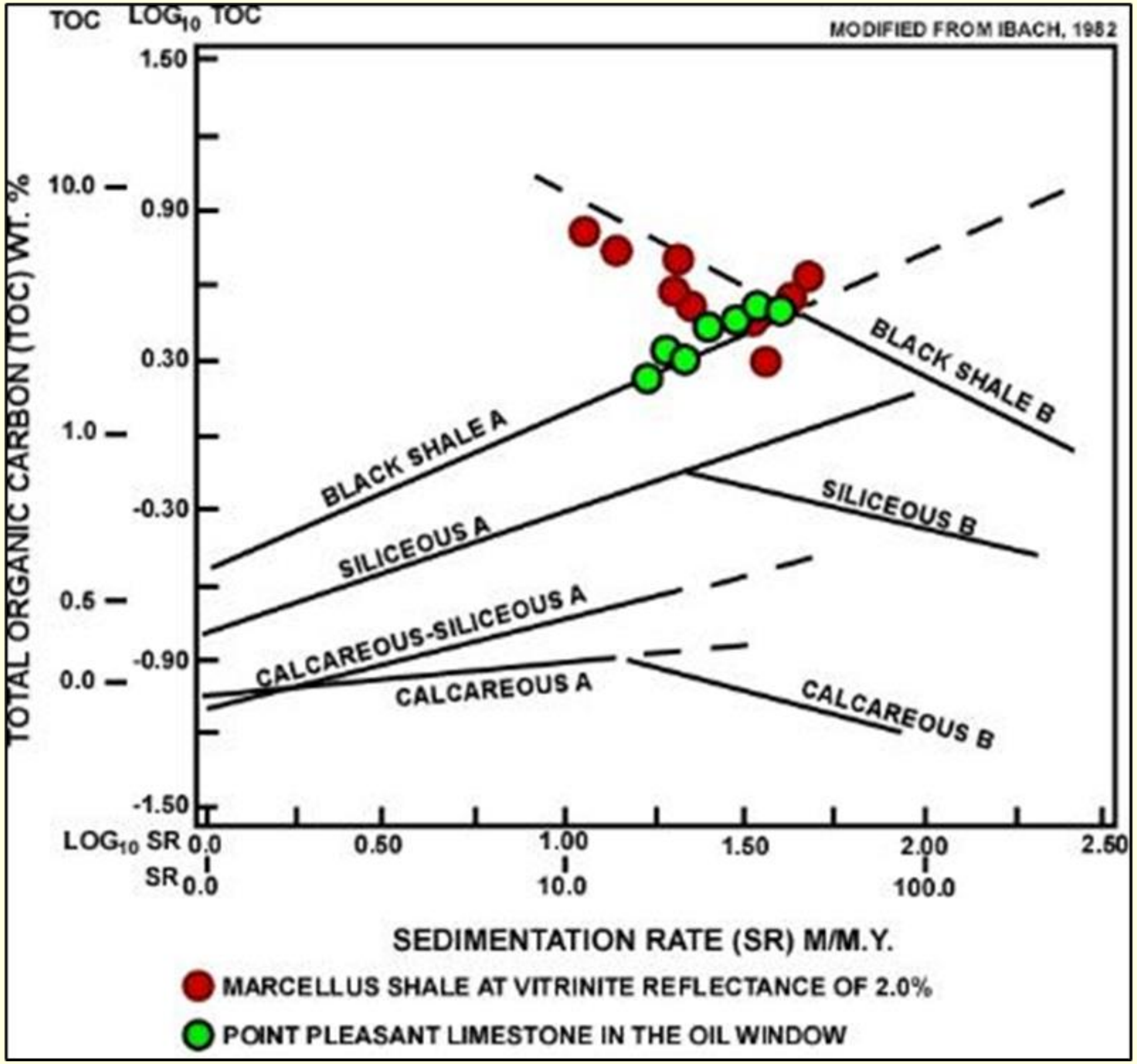
Remobilization of elements

Burn Down



Purpose of the Work

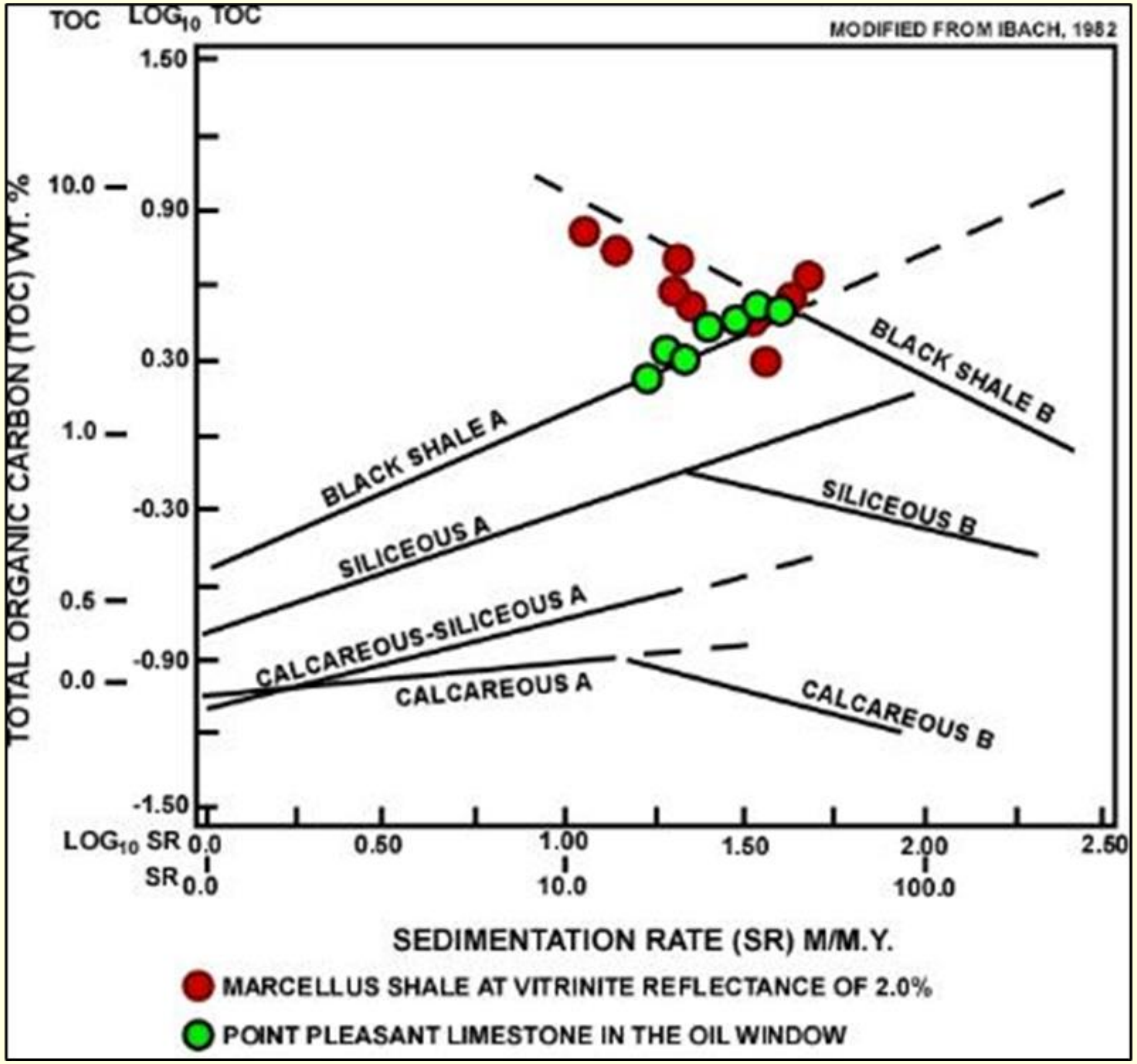
Where is the reservoir?



- **Redox conditions can influence exploration, drilling, and completion techniques.**
- **Under oxic conditions, organic matter is preserved by rapid burial.**
  - **This removes organic material from zones of oxidation and scavenging by benthos**
  - **Under such conditions organic material is usually greatest in the thickest parts of the sedimentary pile, which may also include the greatest clay content.**

Purpose of the Work

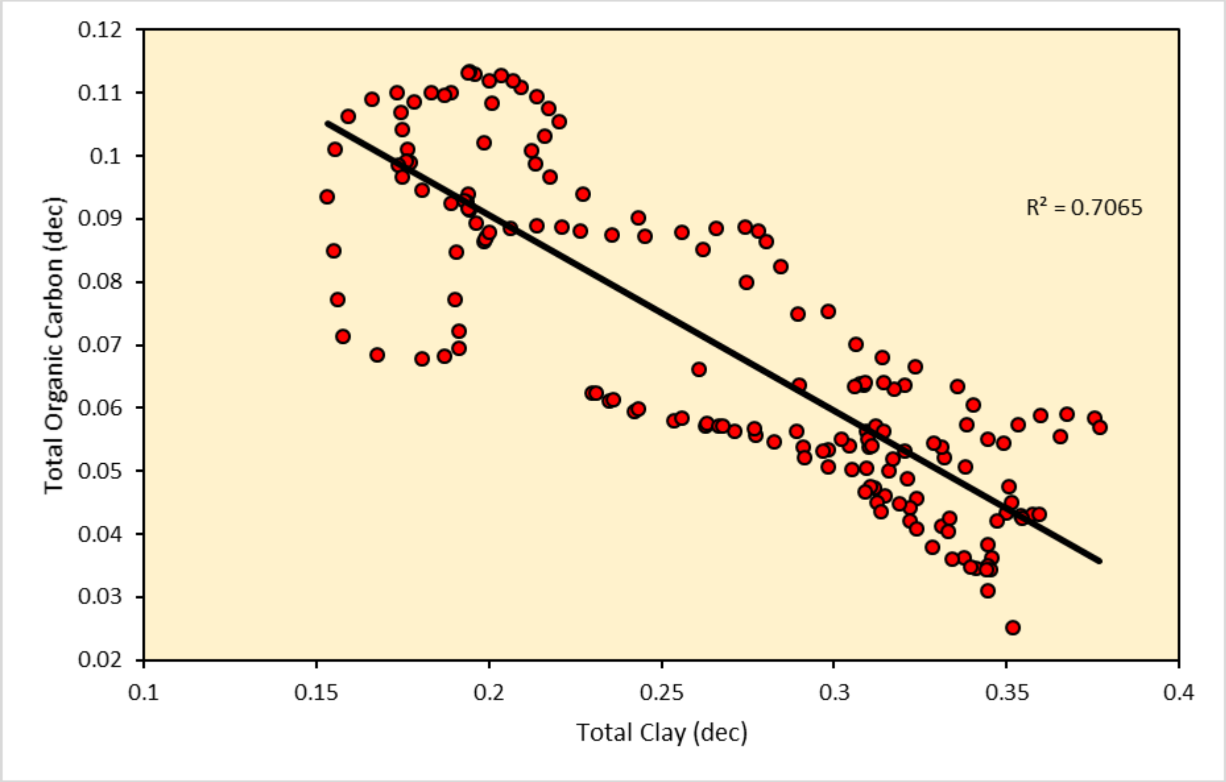
Where is the reservoir?

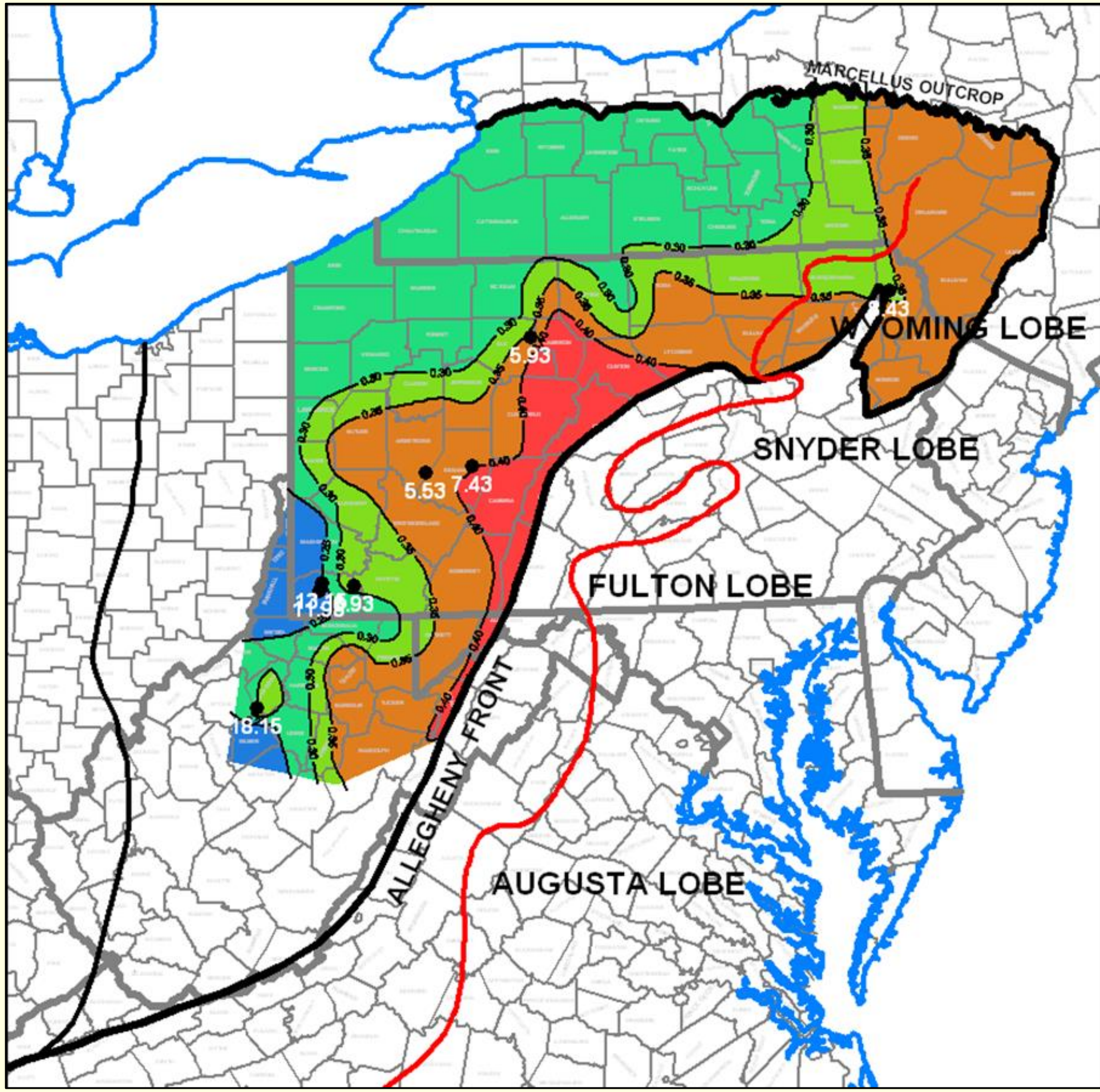


- **Redox conditions can influence exploration, drilling, and completion techniques.**
- **Under anoxic conditions, dilution controls organic matter concentration.**
  - **A lack of oxygen and benthos increases the preservation potential of organic matter**
  - **If productivity is viewed as a constant, then organic matter concentration decreases with increasing sedimentation rate.**

Depositional environment

Marcellus Shale



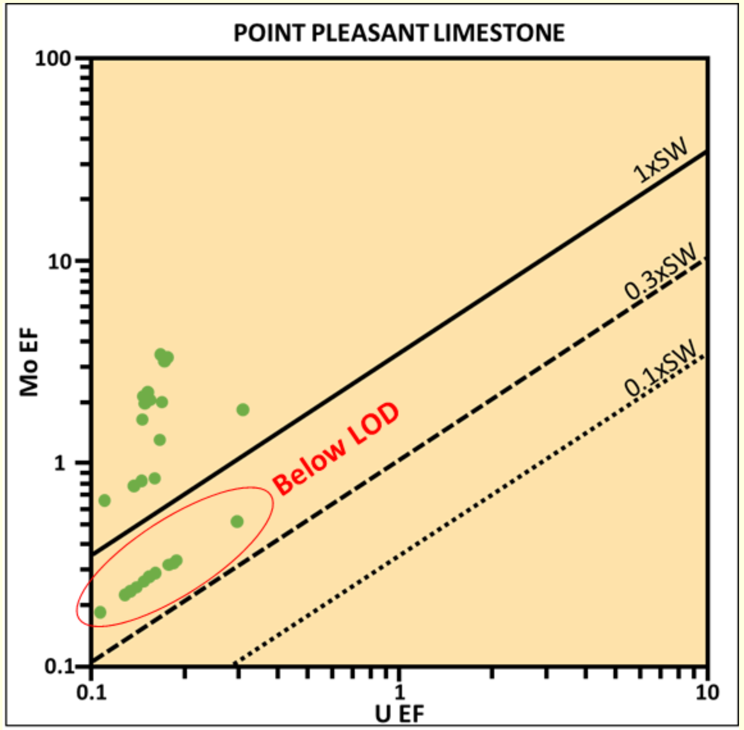


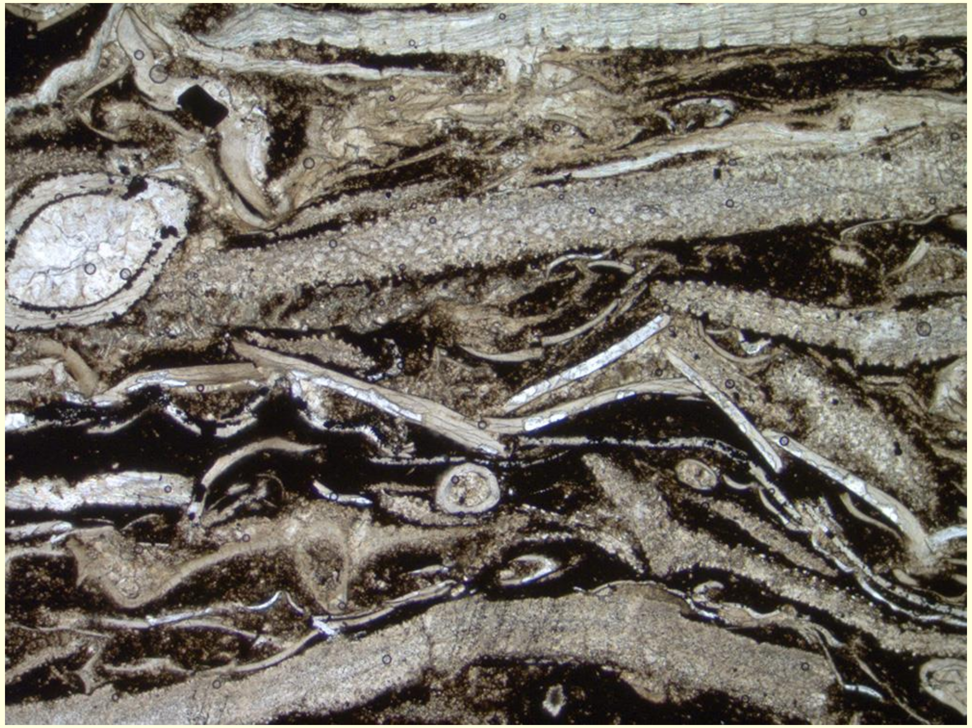
- TOC is inversely related to clastic influx

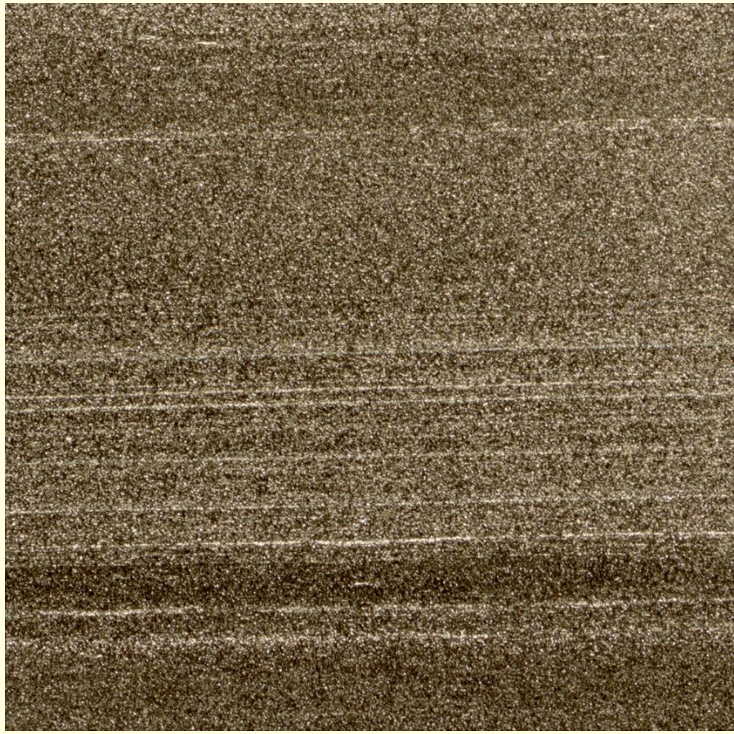
Organic matter concentration is controlled by dilution

(Dys)oxic organic-rich deposits

Point Pleasant Limestone







- Most RSTE below levels of detection
- Note scale change from previous plots (down one order of magnitude)

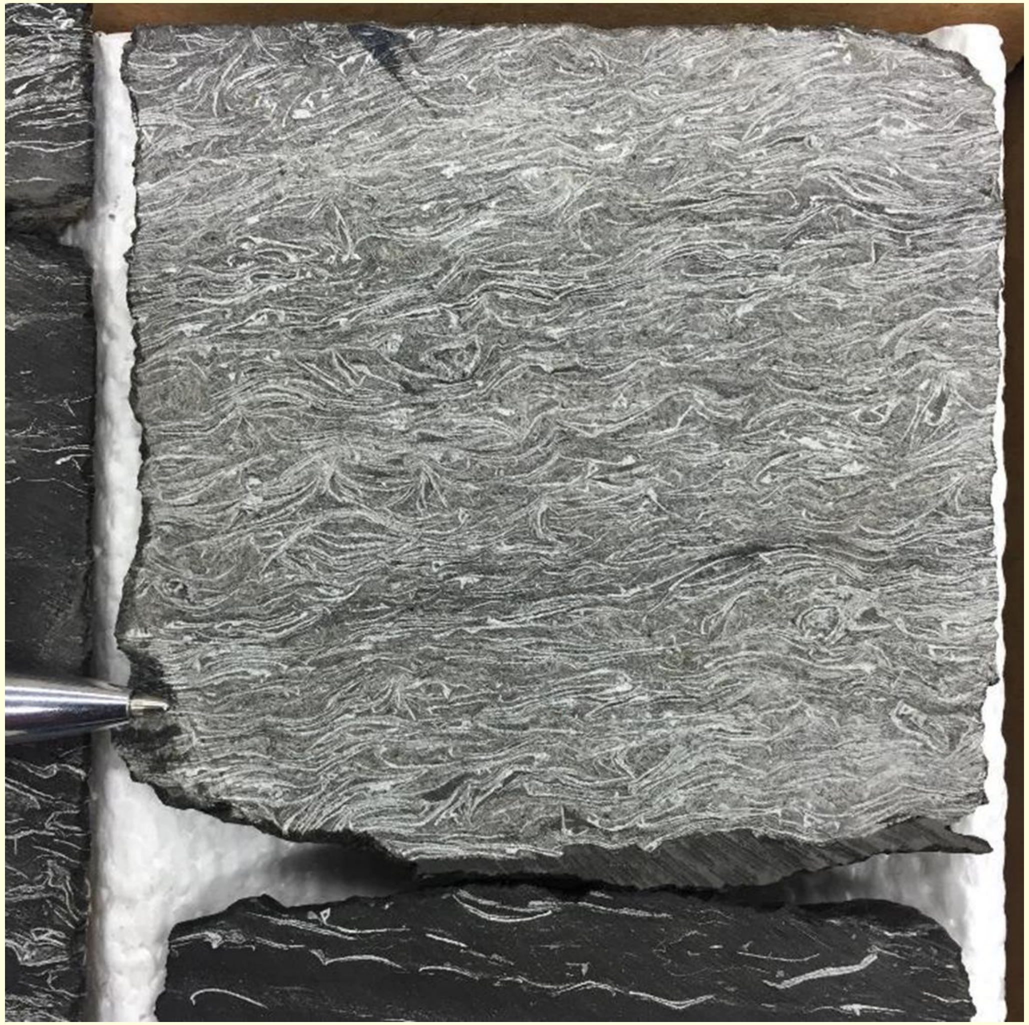
- Shell beds not transported
- Poorly sorted
- Articulated fossils present
- Grew *in situ*
- **Time-rich intervals**

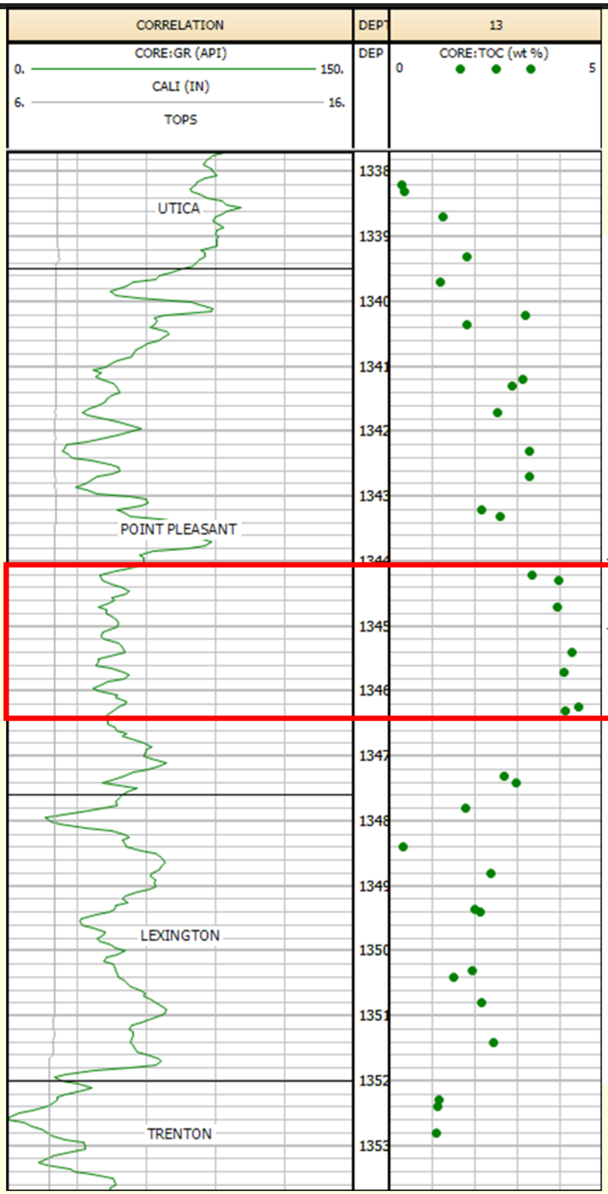
- Muds are well sorted
- Often show fining-up sequences
- Represent event beds
- Obrution (suffocation) layers
- **Time-poor intervals**

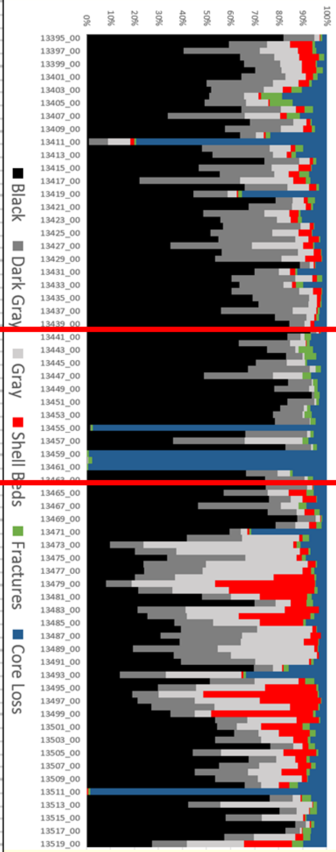
Rapid deposition in an (dys)oxic environment led to the preservation of TOC

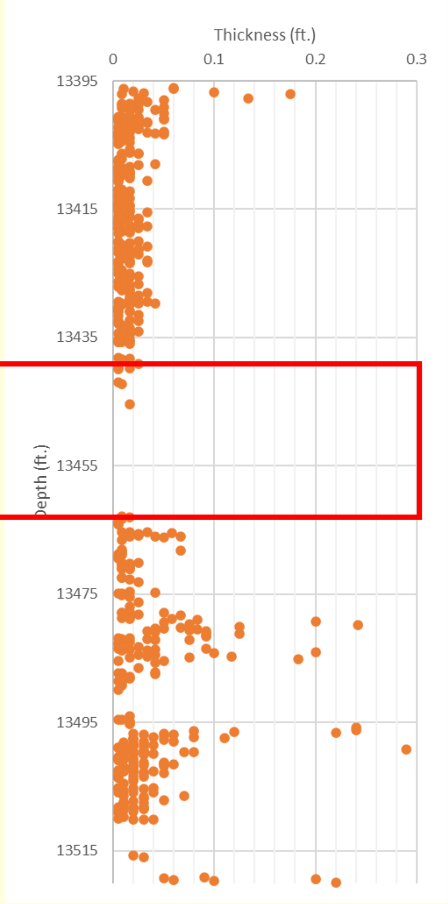
(Dys)oxic organic-rich deposits

Point Pleasant Limestone









Conclusions

- Not all interpretations are straight forward – integrate both elemental and sedimentological data sets

- Remember sample size – sidewall cores and core plugs can represent 100s to 1000s to 10,000s to even 100,000s of years
    - This results in a time-averaged interpretation of the rock record

- Elemental relationships are not universal. For example, a correlation between uranium and TOC in one shale may not be applicable or exist in another shale.

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