

# Chemostratigraphic Trends of the Middle Devonian Marcellus Shale, Appalachian Basin: Preliminary Observations\*

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## Abstract

Trace element and metals abundances have been used to elucidate the hydrography of silled basins as well as watermass chemistry and deep-water residence times. The database of our preliminary study of the Middle Devonian Marcellus Shale comprises chemostratigraphic (X-ray fluorescence) elemental concentrations determined from cores recovered from eastern New York, southwest Pennsylvania, and northern West Virginia. Regional covariance trends of authigenic molybdenum ( $\text{Mo}_{\text{auth}}$ ) and uranium ( $\text{U}_{\text{auth}}$ ) and their respective enrichment factors (EFs) define a uniform  $(\text{Mo}/\text{U})_{\text{auth}}$  ratio of  $\approx 2 - 3$  times the  $\text{Mo}/\text{U}$  molar ratio of seawater.  $\text{Mo}_{\text{auth}}$  is enriched relative to  $\text{U}_{\text{auth}}$  by a factor of 5:1 to 10:1, suggesting accelerated transport of Mo to the seafloor by a particulate (Mn) transport mechanism that would have required frequent fluctuations between suboxic and moderately sulfidic water column conditions. Indeed, the relationship of total organic carbon and Mo(ppm) in eastern New York suggests water renewal times on the order of several hundred years. A data subset defined by diminishing  $\text{Mo}_{\text{auth}}$  and  $\text{U}_{\text{auth}}$  EFs at reduced aqueous  $\text{Mo}/\text{U}$  ratios may reflect the preferential uptake of U under largely suboxic conditions. Moreover, data from a well in northern West Virginia defines  $\text{Mo}_{\text{auth}}$  and  $\text{U}_{\text{auth}}$  values typical of bottom water depleted in Mo ( $\text{Mo}/\text{U} = 0.1 - 0.3 \times$  seawater) and  $(\text{Mo}/\text{U})_{\text{auth}}$  ratios of  $\approx 1:1$ . Thus, whereas the Marcellus basin may have experienced frequent episodes of suboxic to sulfidic conditions that accelerated Mo enrichment, local hydrographic conditions (i.e., stronger degree of water column stratification) appear to have favored Mo drawdown in bottom water. Equally intriguing is the regional concentration of barium in the upper part of the Marcellus, which may reflect an episode of enhanced paleoproductivity at this time. Further, chloride and strontium are especially concentrated in transgressive systems-tract deposits, perhaps reflecting salinity excursions that could have enhanced the preservation of organic matter in these intervals.

## References

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Blauch, M., N. Houston, M. Seyman, and R. Reese, 2009, Technique reuses frac water in shale: American Oil and Gas Reporter, v. 52/9, p. 103-107.

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 24 October 2011,  
[http://www.searchanddiscovery.com/abstracts/pdf/2010/intl/abstracts/ndx\\_smith.pdf](http://www.searchanddiscovery.com/abstracts/pdf/2010/intl/abstracts/ndx_smith.pdf)

Taylor, S.R., and S.M. McLennan, 1985, The Continental Crust: Its Composition and Evolution: Blackwell, Oxford, England, 312 p.

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Wedepohl, K.H., 1991, The composition of the upper earth's crust and the natural cycles of selected metals: metals in natural raw materials; natural resources, *in* E. Merian, (Ed.), Metals and their Compounds in the Natural Environment: Weinheim (VCH-Verlagsges), Germany, p. 3-17.

### **Website**

Blakey, R., 2011, North American Paleogeography: Web accessed October 14, 2011, <http://www2.nau.edu/rcb7/namD385.jpg>

# **Chemostratigraphic trends of the Middle Devonian Marcellus Shale, Appalachian Basin: preliminary observations**

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# Introduction

**chemostratigraphy** - especially suited to the study of fine-grained, seemingly homogenous (biostratigraphically barren) deposits...

...variations in elemental abundances reflect changes in such parameters as paleoclimate, hydrographic aspects of the paleocean, paleoredox conditions (including oceanic anoxic events), and mineralogy...

...high resolution correlation of cm-scale units...

# analytical approach

## handheld XRF (HHXRF) analyzer ...

Thermo Scientific Niton XL3t 950 GOLDD+...  
equipped with a silicon drift detector...

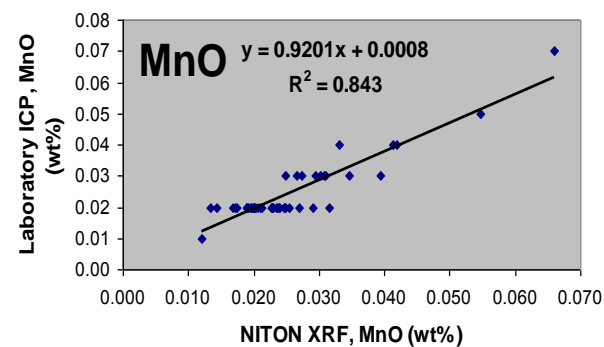
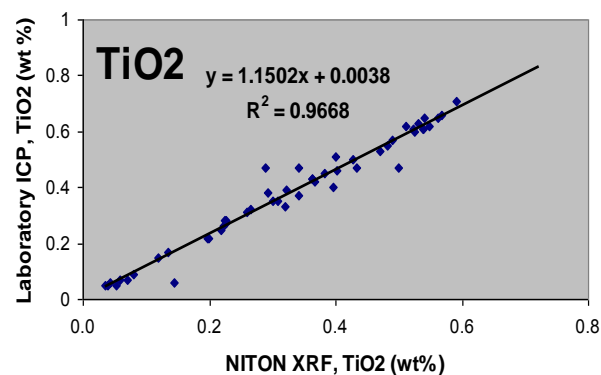
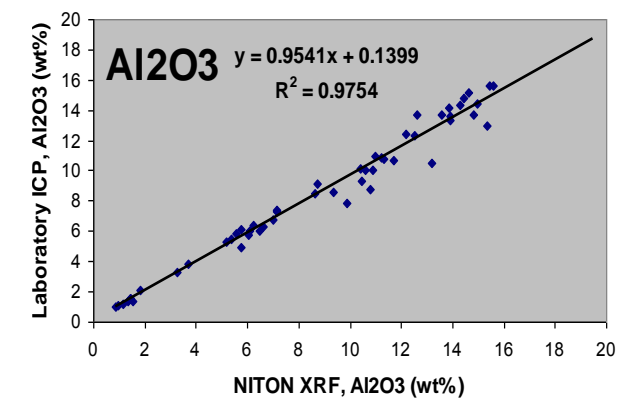
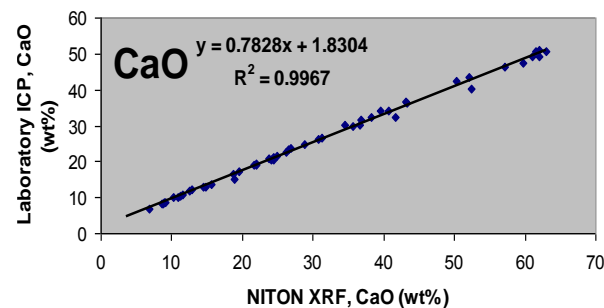
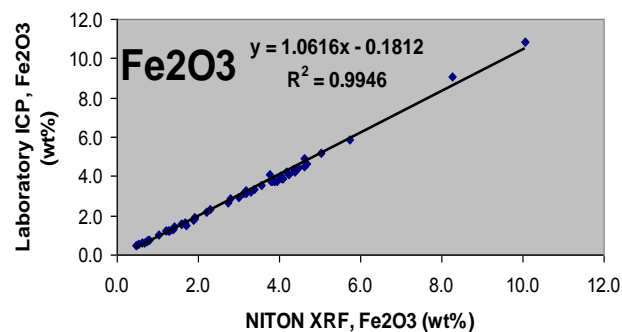
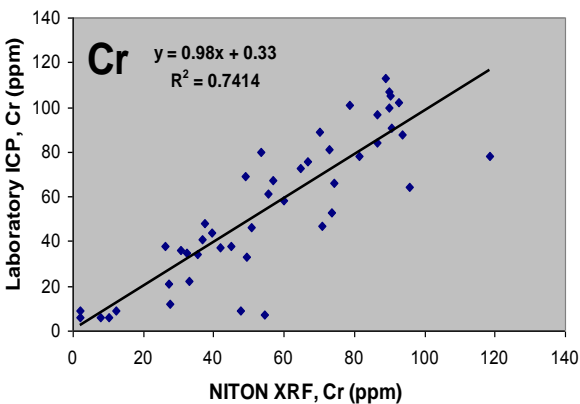
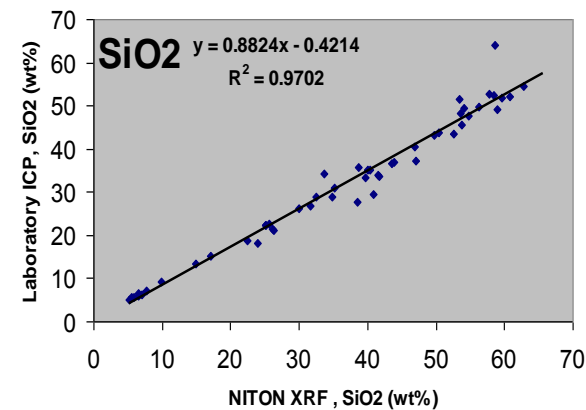
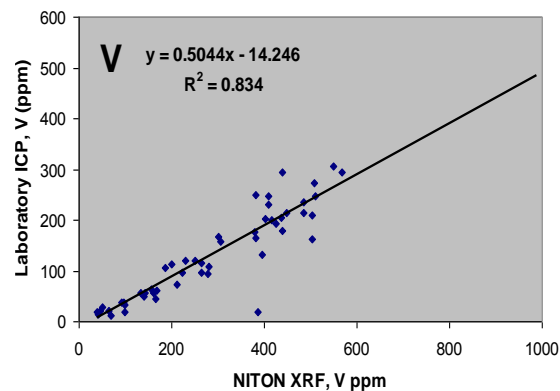
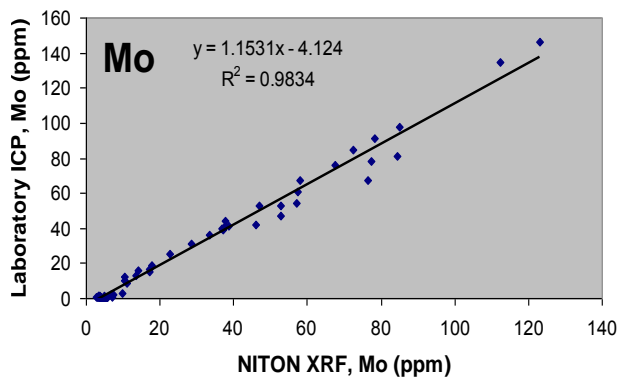
...hand (outcrop) samples, core, cuttings...

Smith and Malicse (2010)

comparison of HHXRF technology with  
results obtained via independent  
laboratory ICP-MS methodology...

160 sedimentary rock samples of mixed  
lithology...





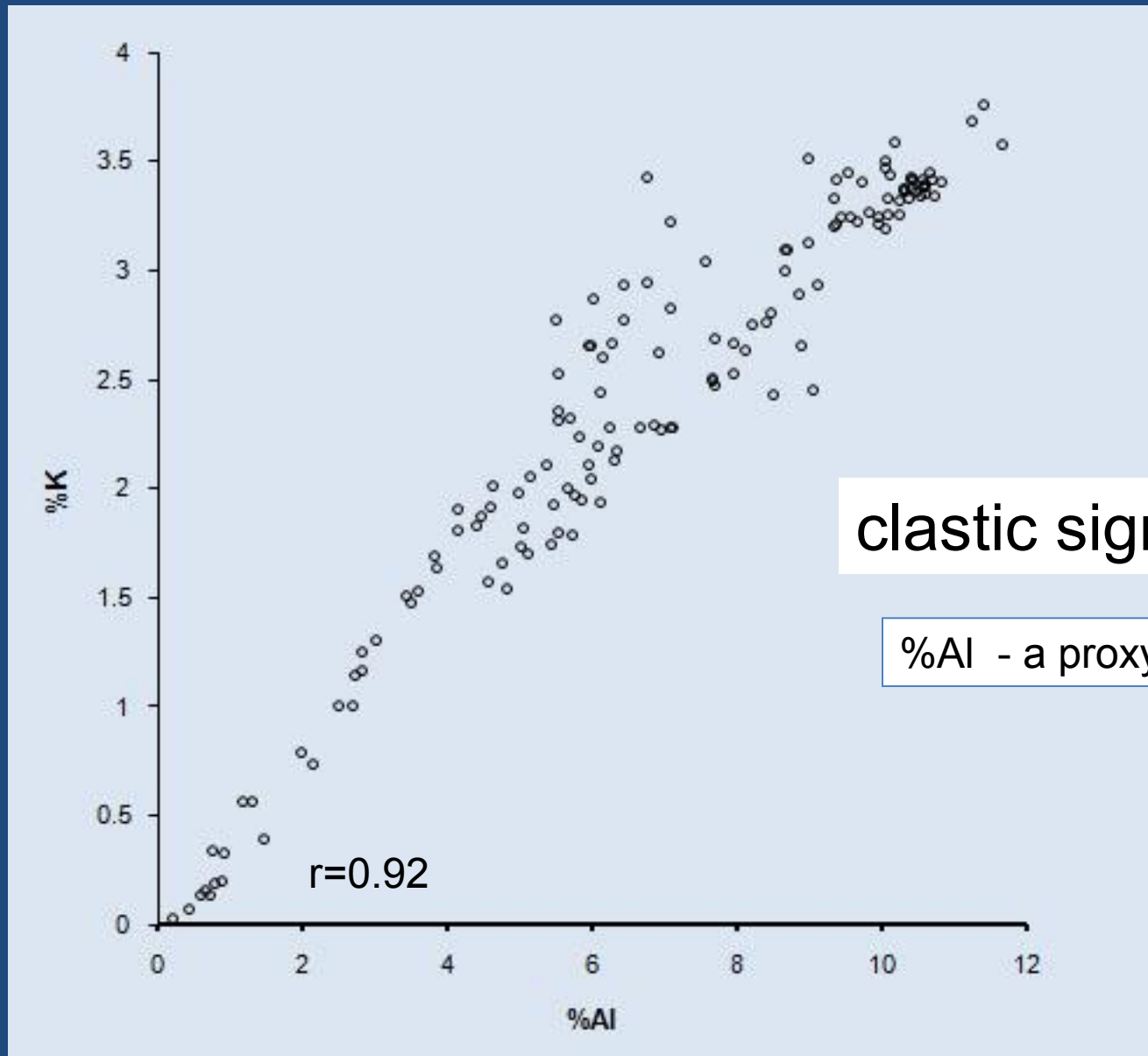
...very strong correlations ( $r^2 > 0.90$ ) with laboratory ICP-MS data for most major, minor and trace elements from Mg to U...

...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....

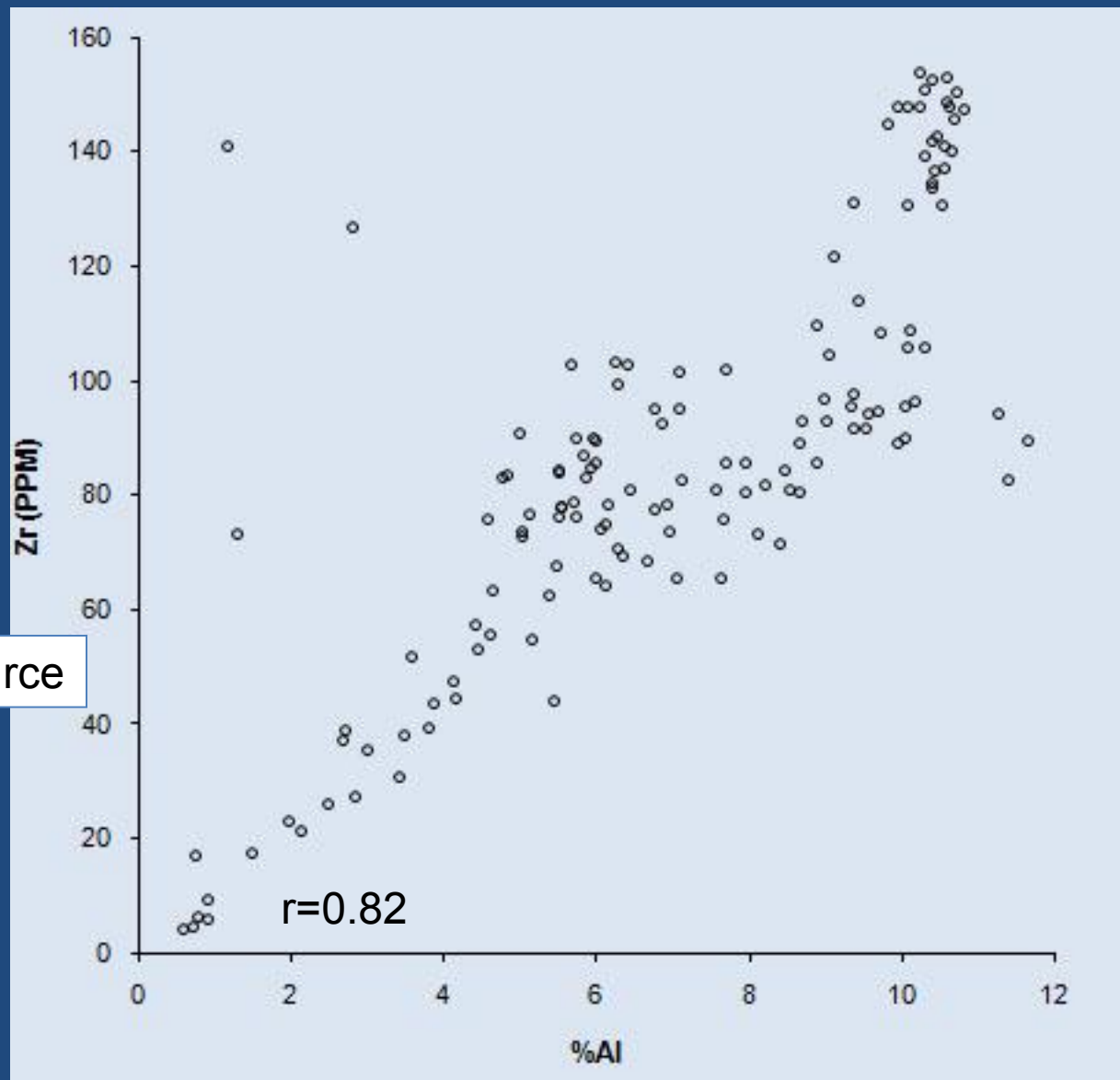
...analysis of Marcellus cores at ~2.5 – 3 cm intervals...

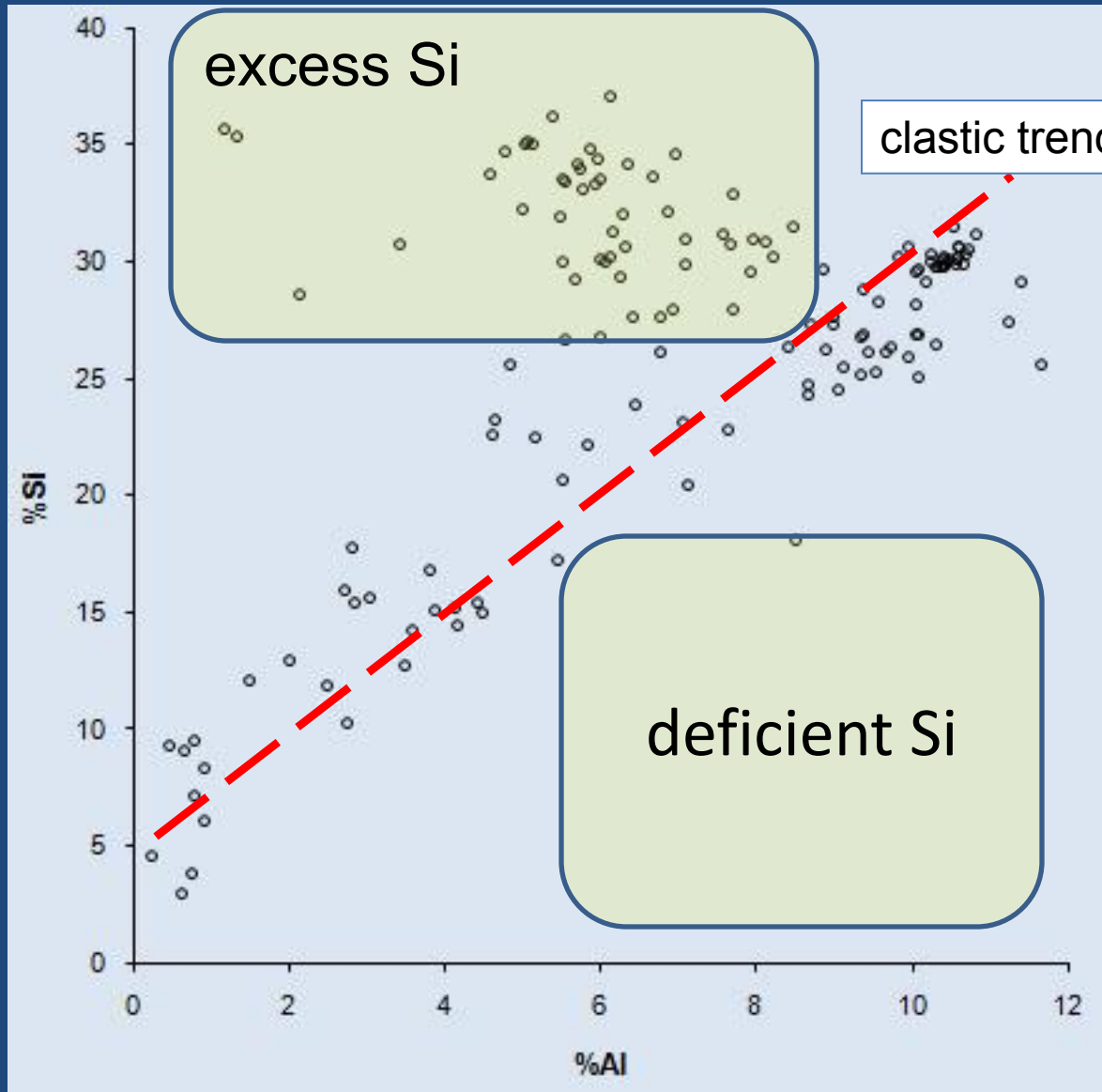
## ...general observations...



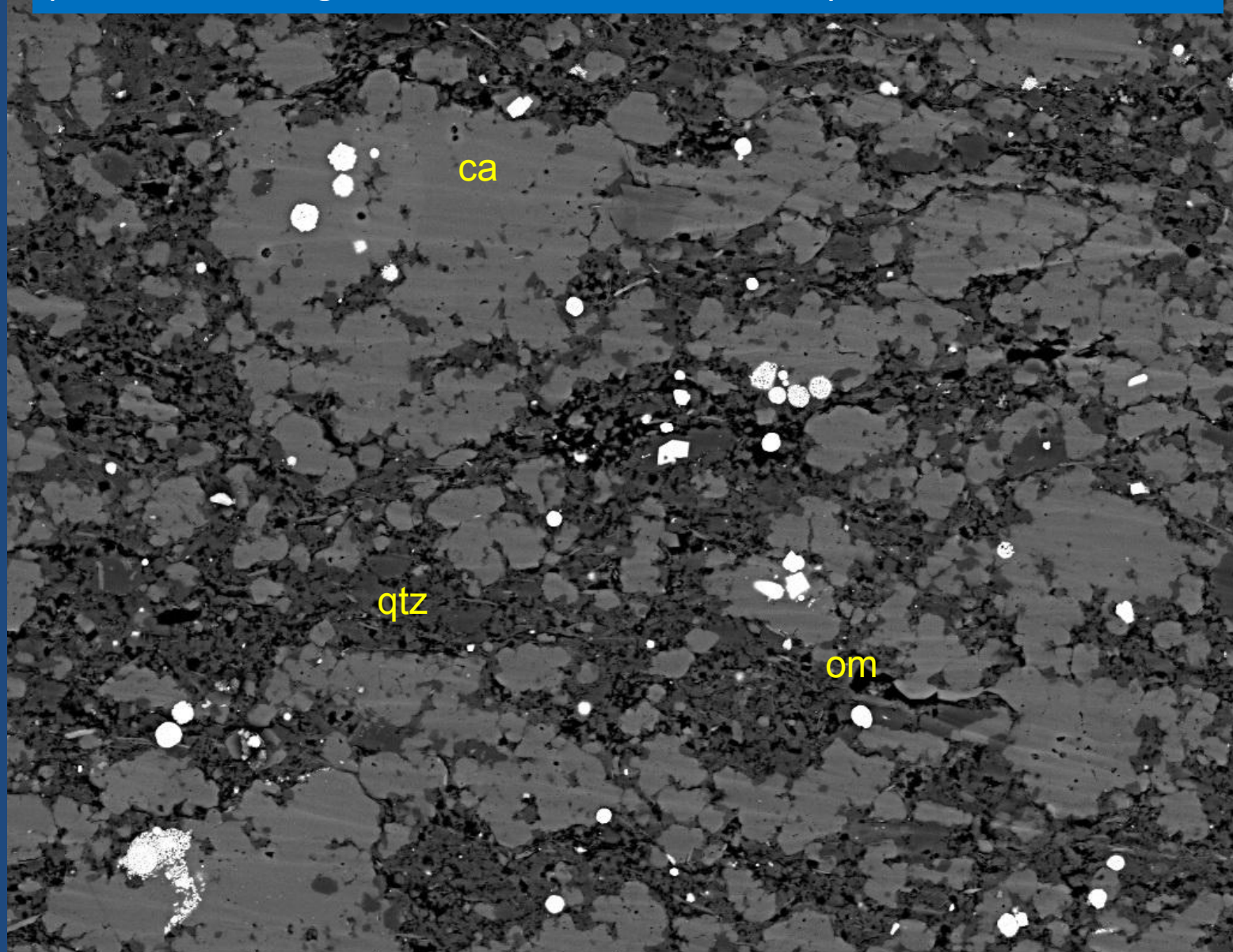


Zr – clastic source



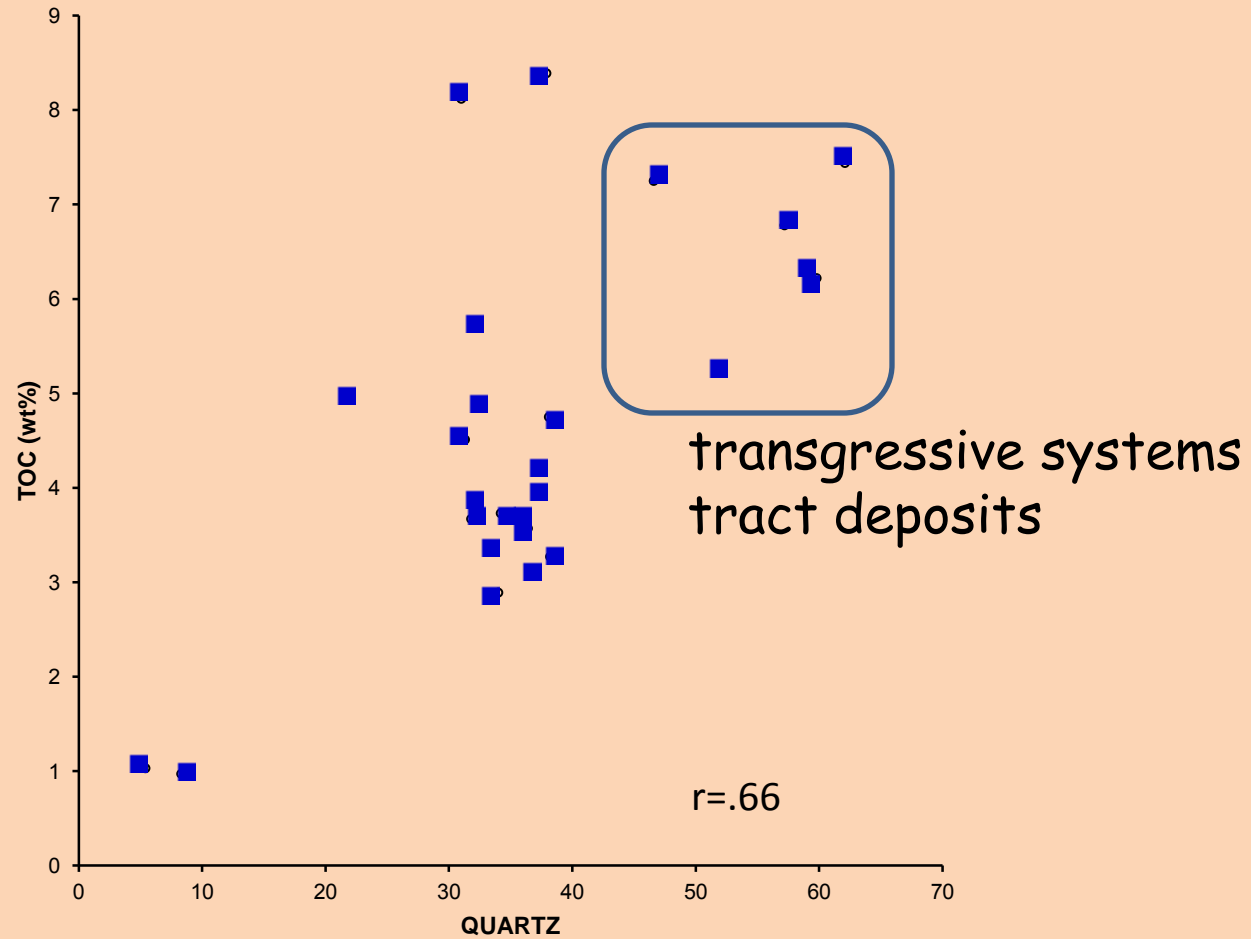


...quartz (authigenic; closely associated with organic matter) ...  
pervasive throughout a matrix deficient in clay...

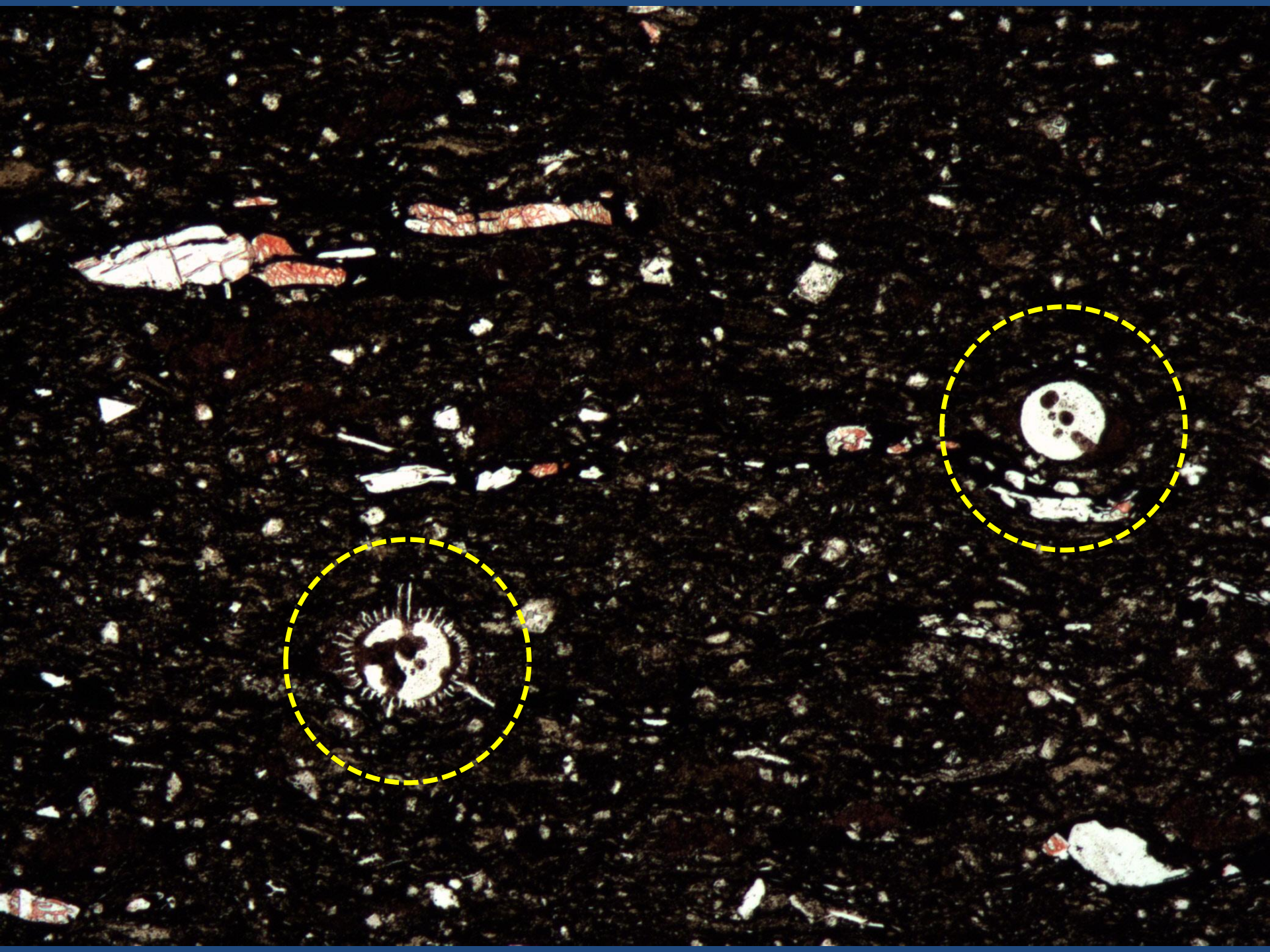


mag	500 x	HFW	298 μm	WD	9.9 mm	HV	20.00 kV	det	BSED	100 μm	
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# TOC vs. quartz







Shale

Marcellus

Onondaga  
Ls.

Oatka Creek

CV

Union  
Springs

GR

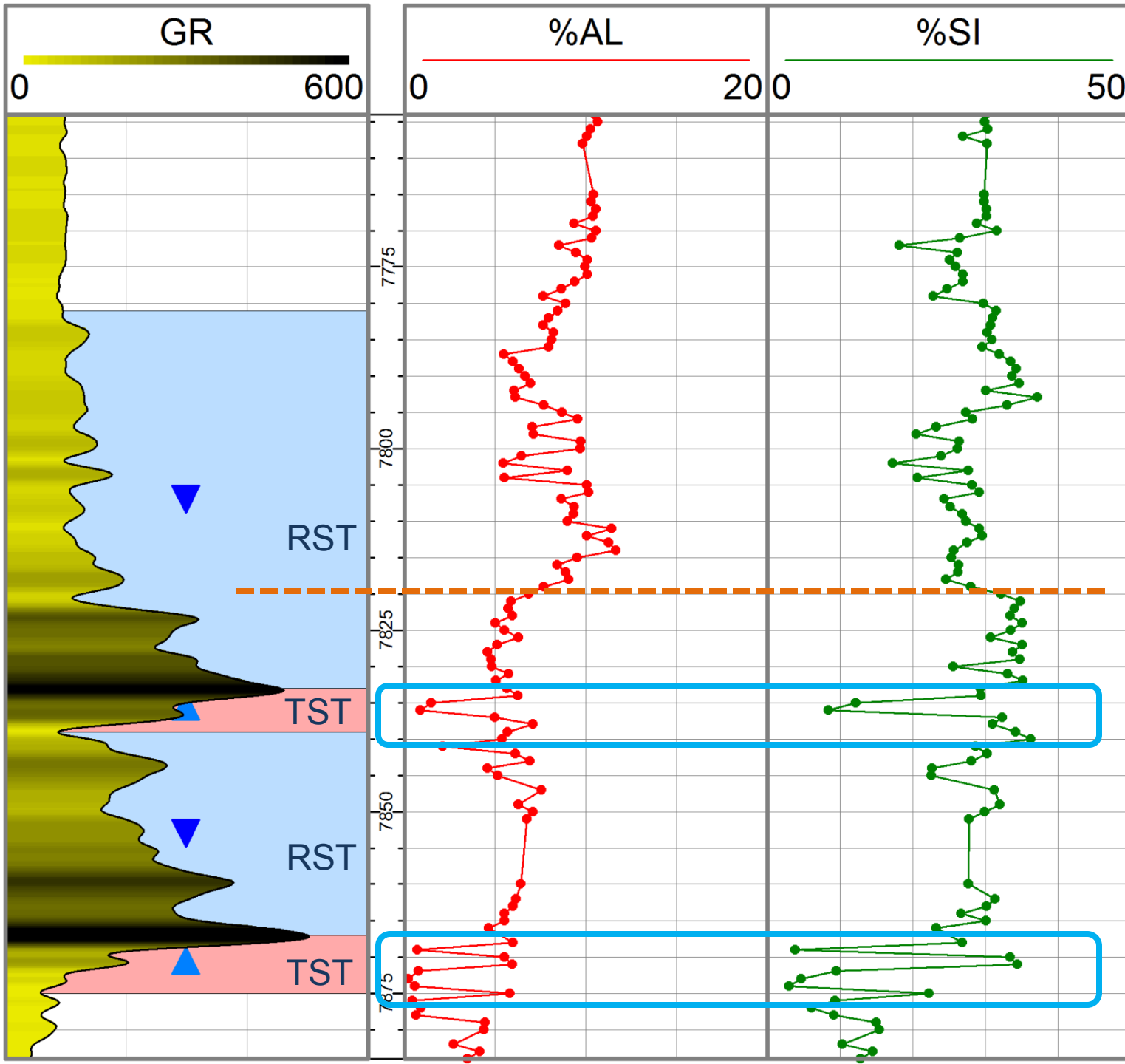
0 600

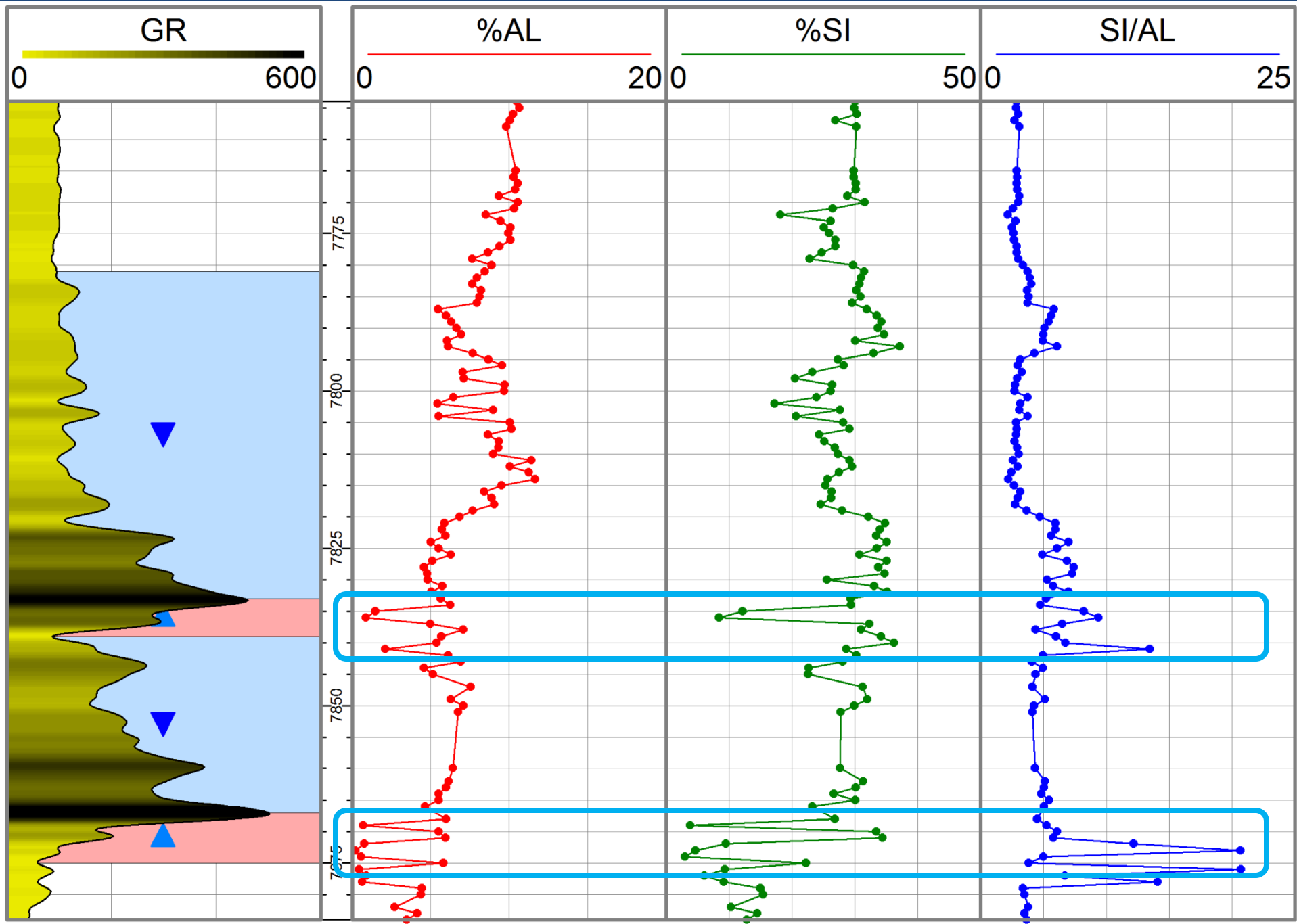
%AL

0 20

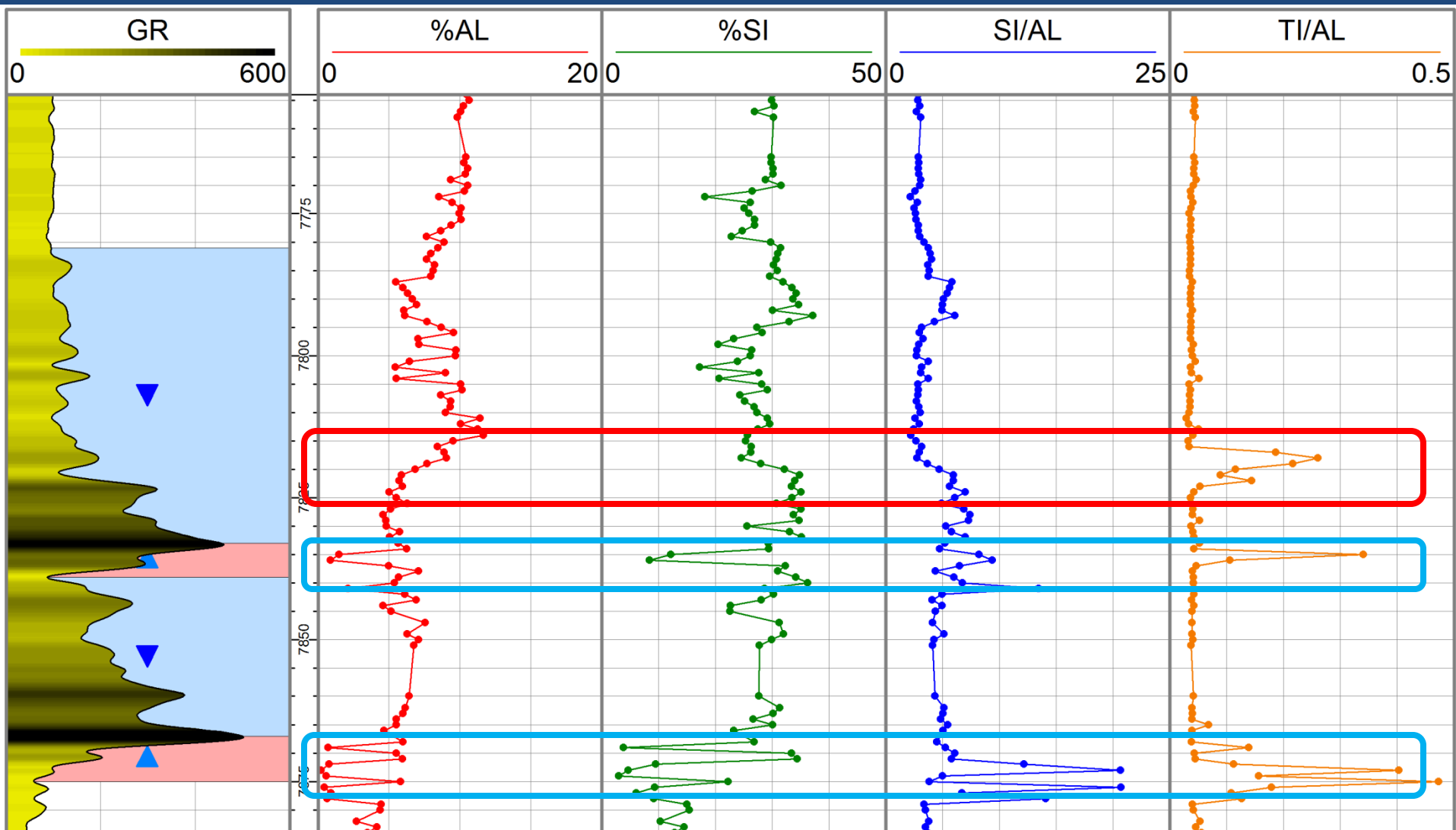
%SI

0 50

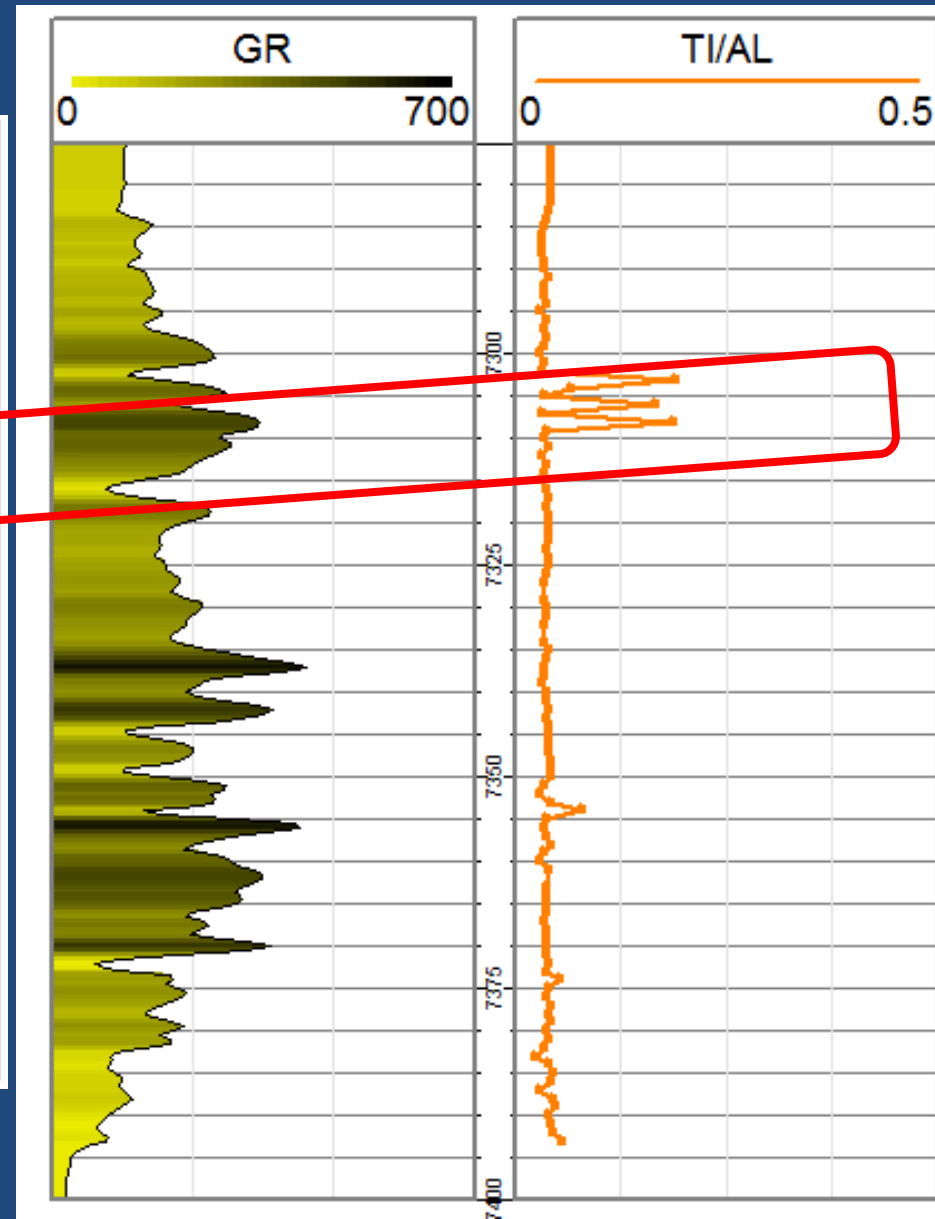
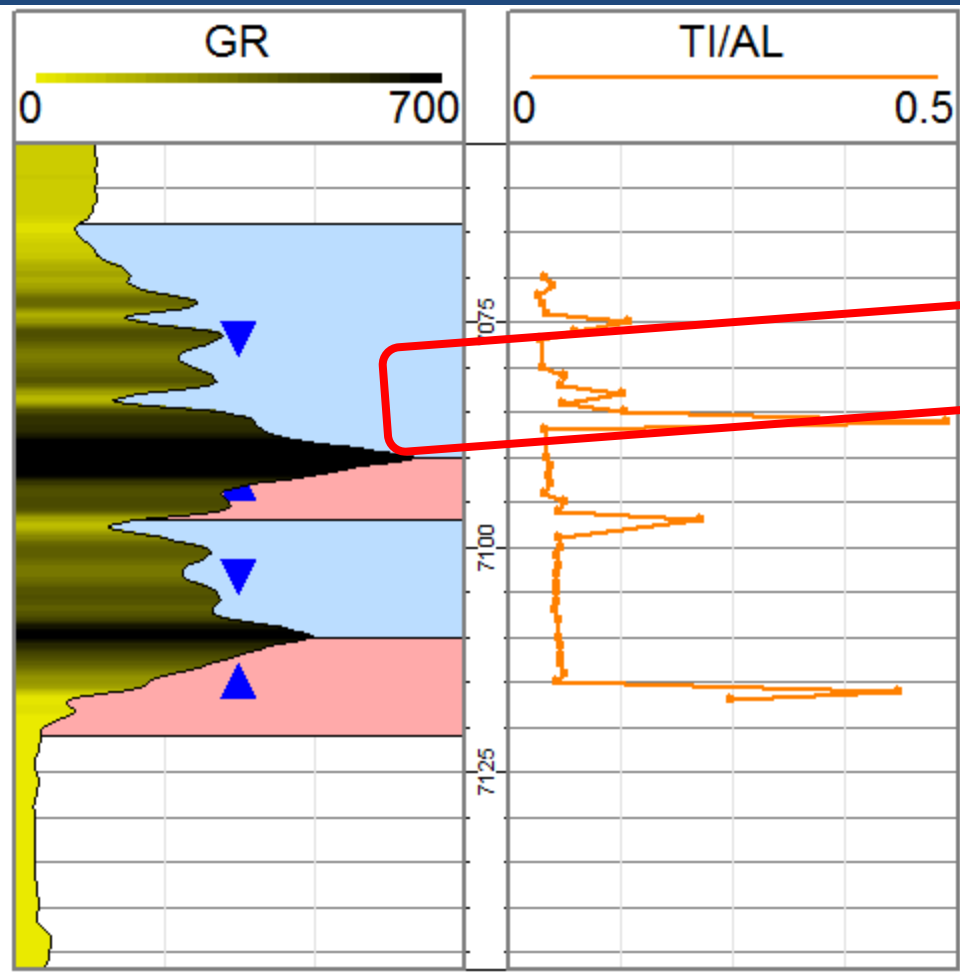












# Mo and U

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;

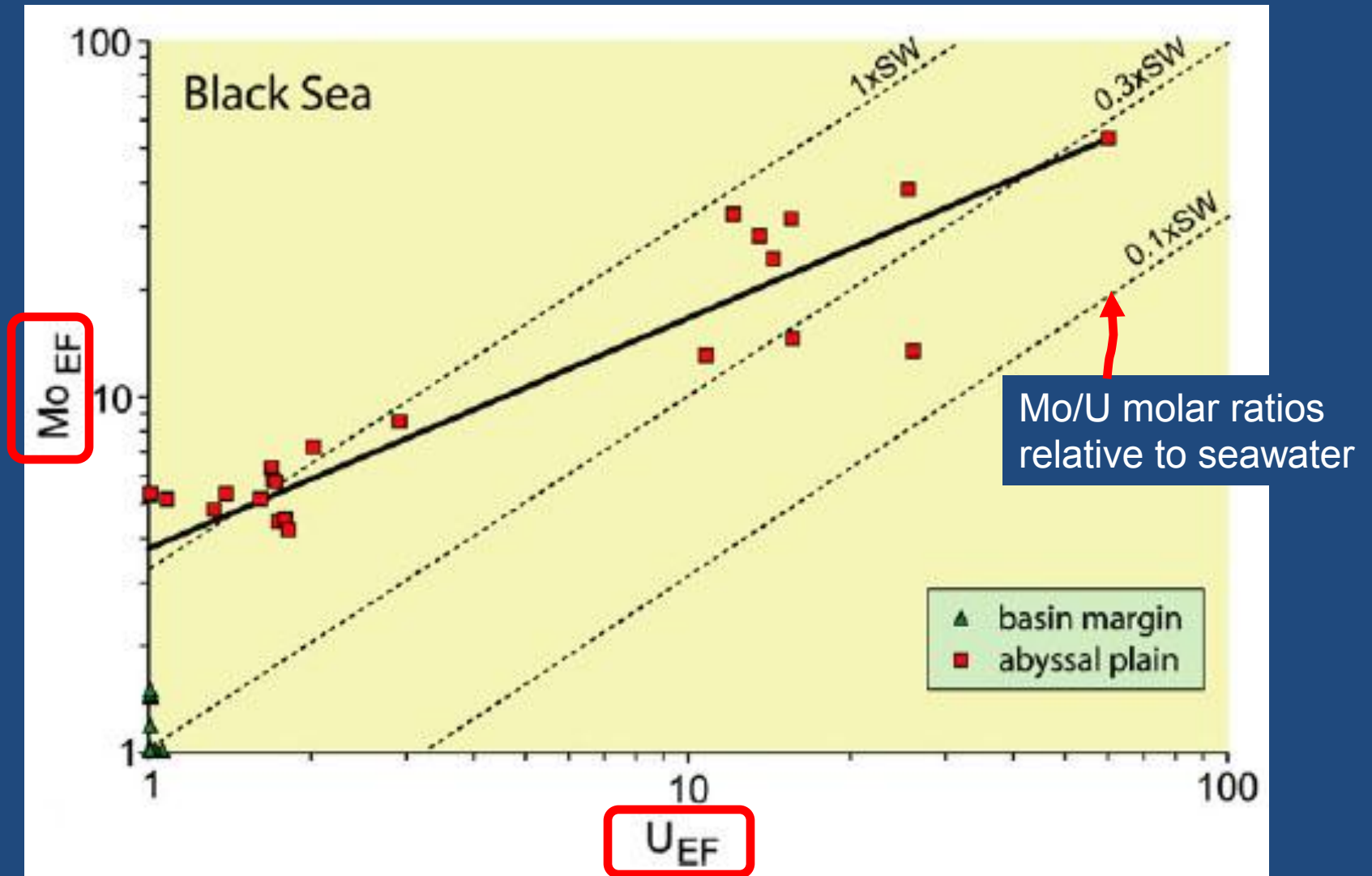
...significant differences...

...U uptake is linked to organic carbon content (TOC) and occurs by diffusion across the sediment-water interface (i.e., within the sediment)

...organic matter serves as a sorbent...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...unlike U...

EF = enrichment factor...elemental abundance

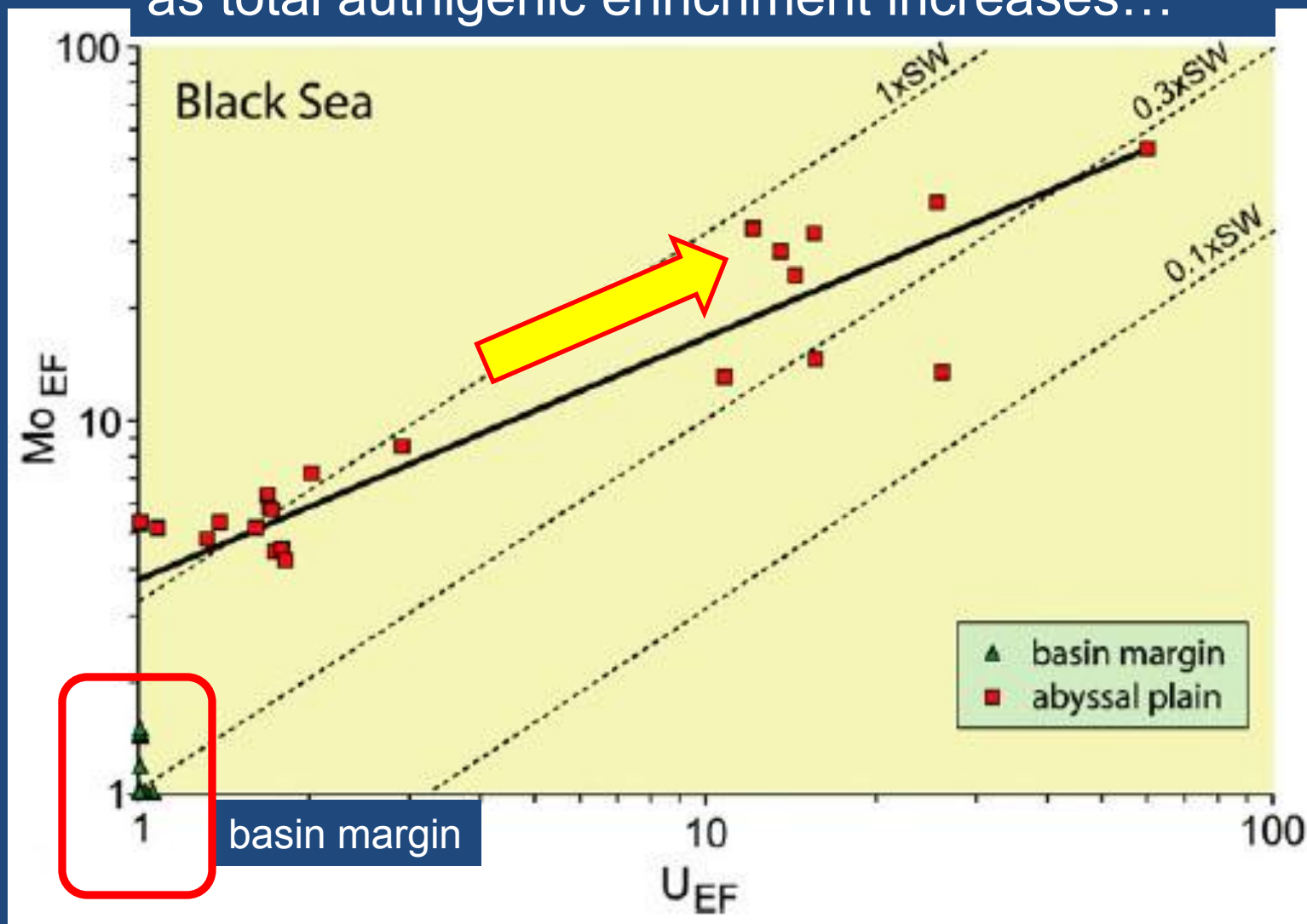


EF = enrichment factor...

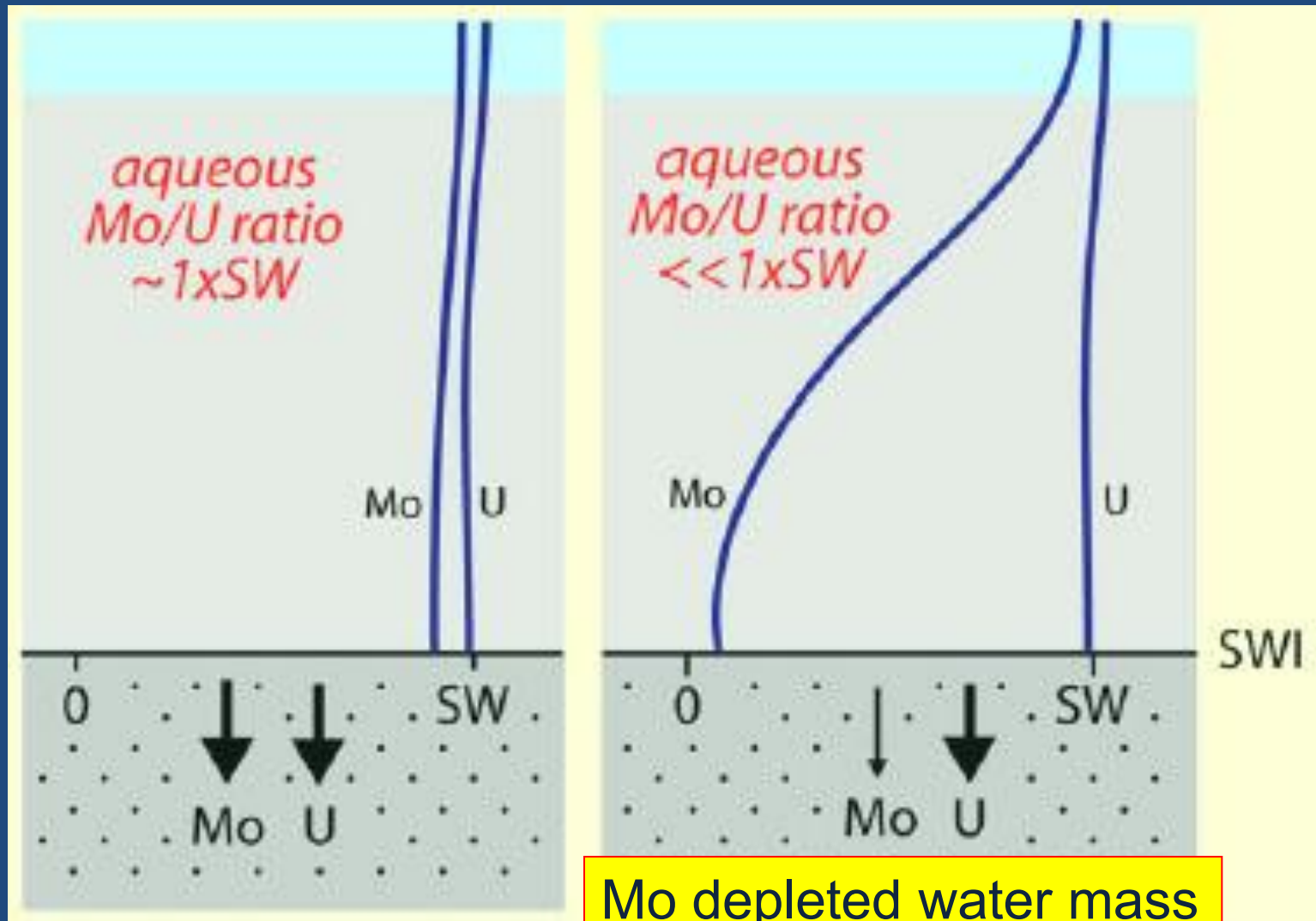
$$= \frac{\textit{element}_{sample} / Al_{sample}}{\textit{element}_{\textit{"average"}} / Al_{\textit{"average"}}}$$

“average” shale values from Wedepohl (1971, 1991)

...progressive enrichment of U relative to Mo  
as total authigenic enrichment increases...

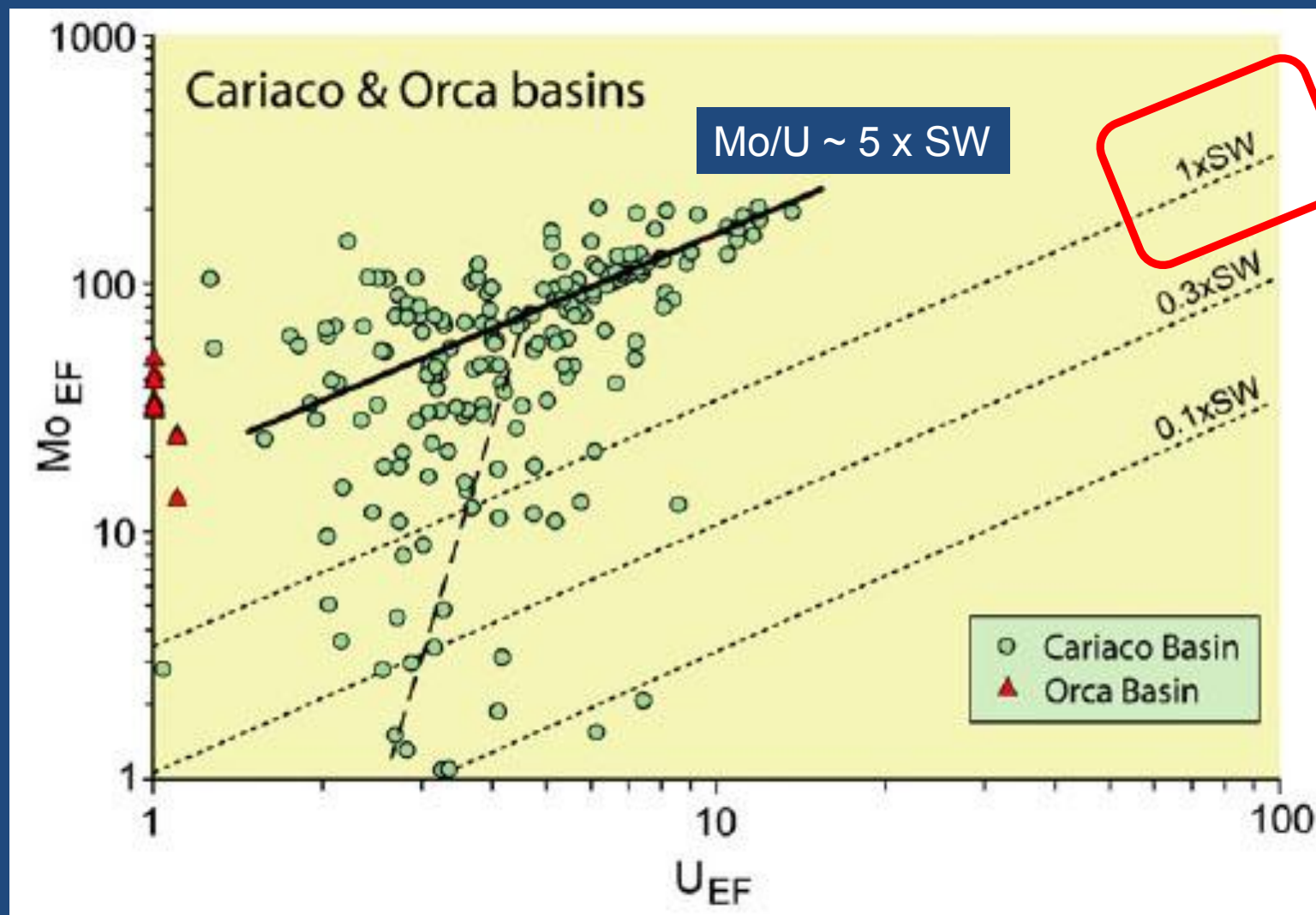


# ...evolving water mass chemistry...



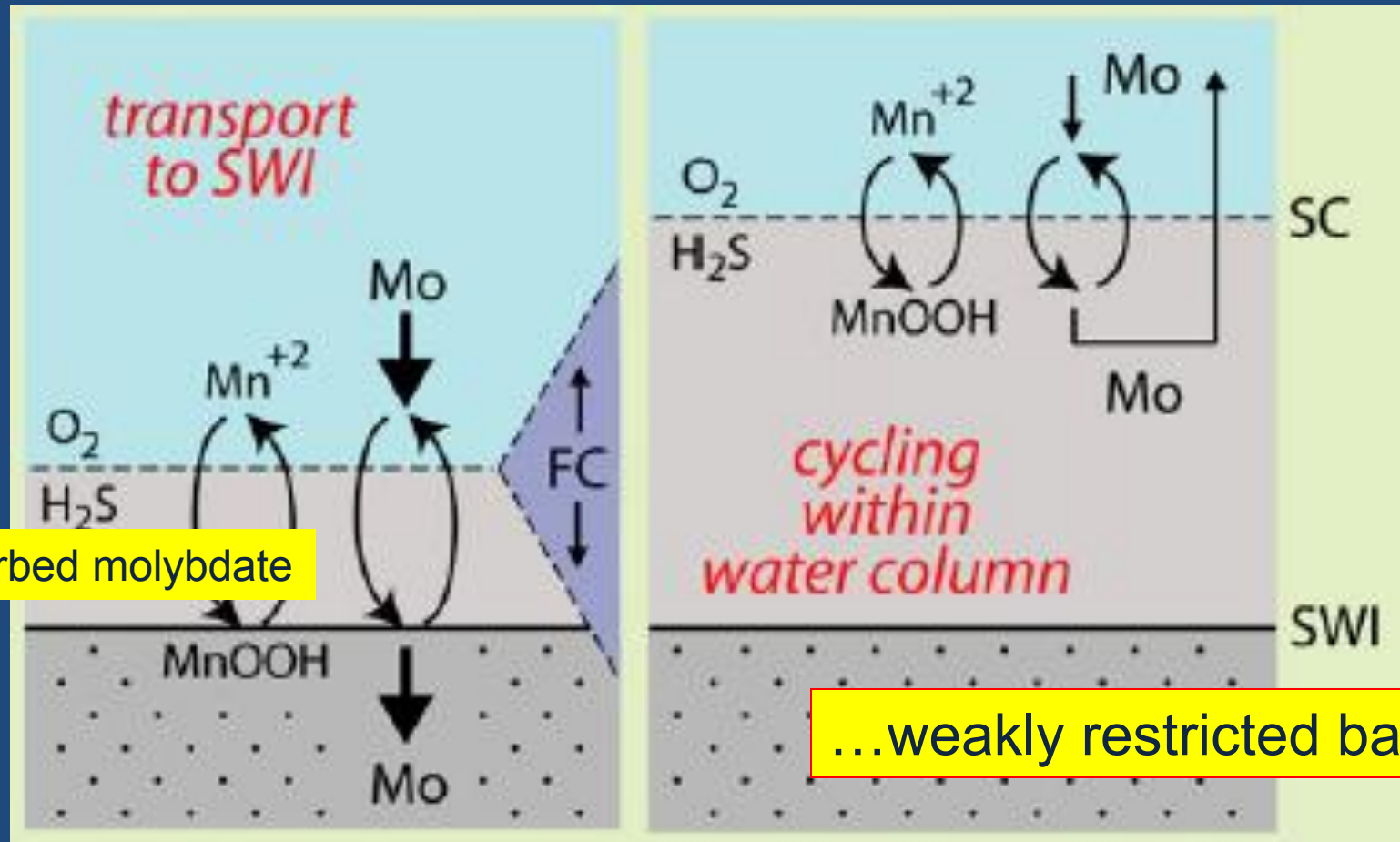
Mo depleted water mass  
... restricted basin...

considerable enrichment of Mo relative to U...





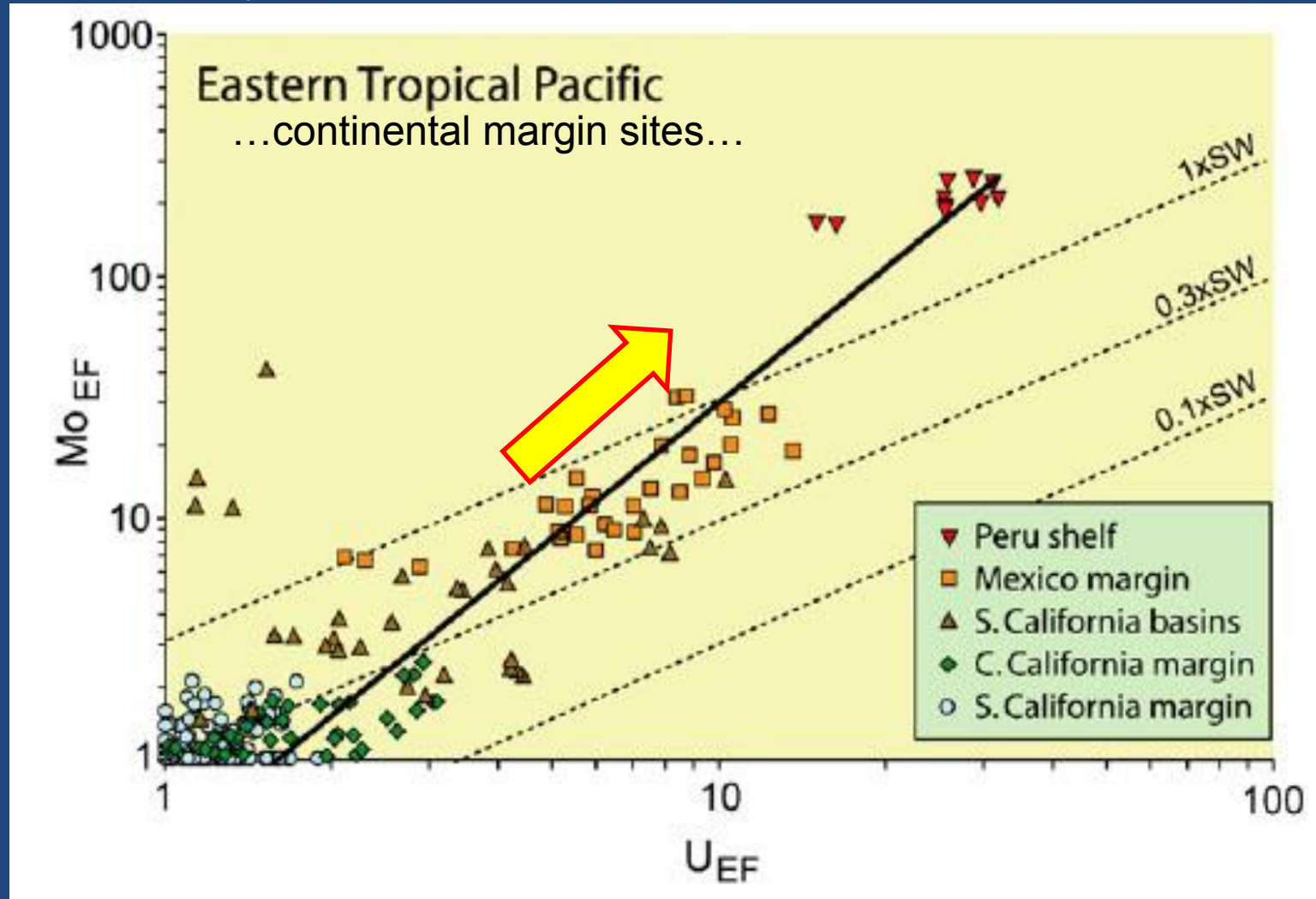
# ...Mn (Fe)-oxyhydroxide particulate shuttle (continuous scavenging)...



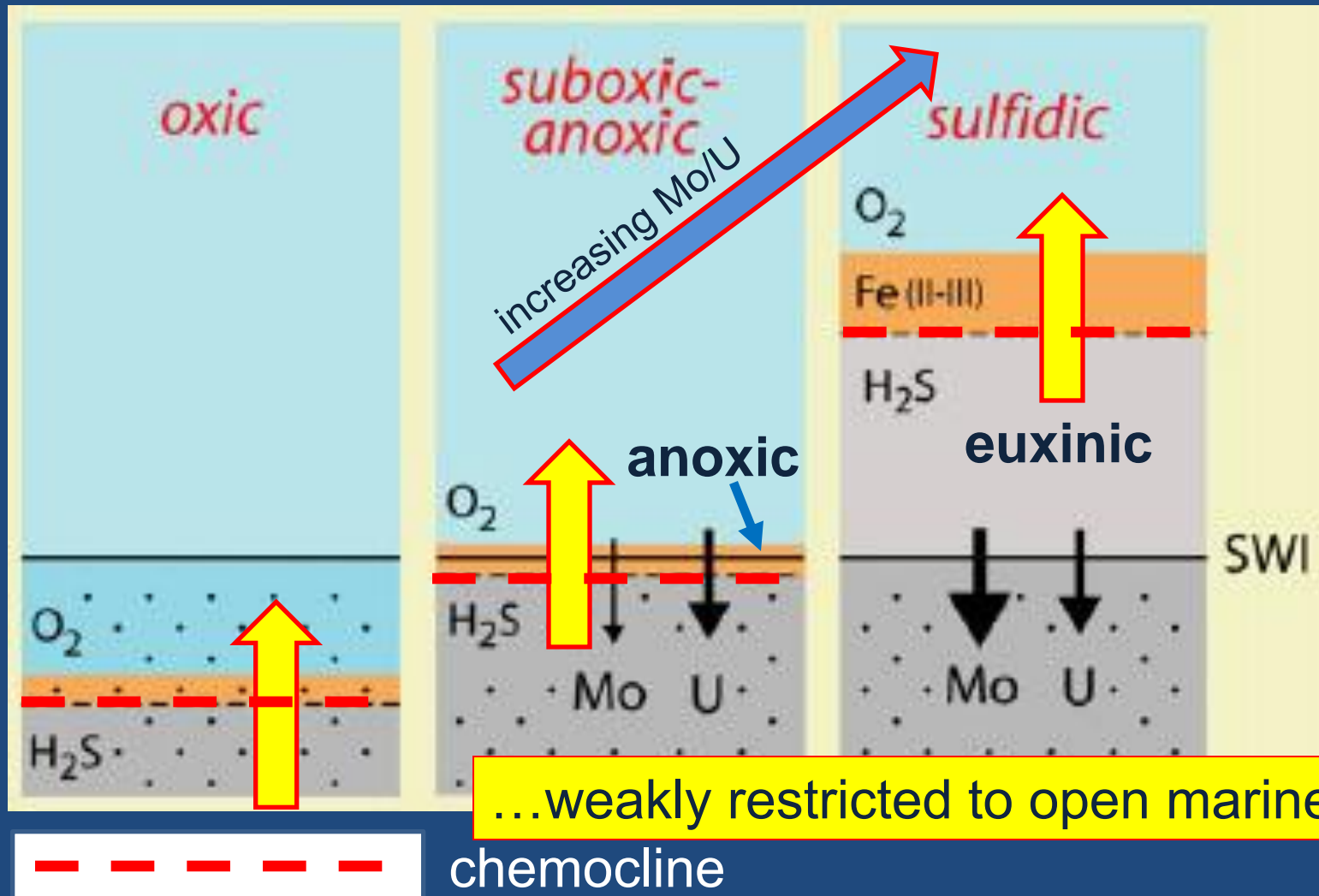
...weakly restricted basin...

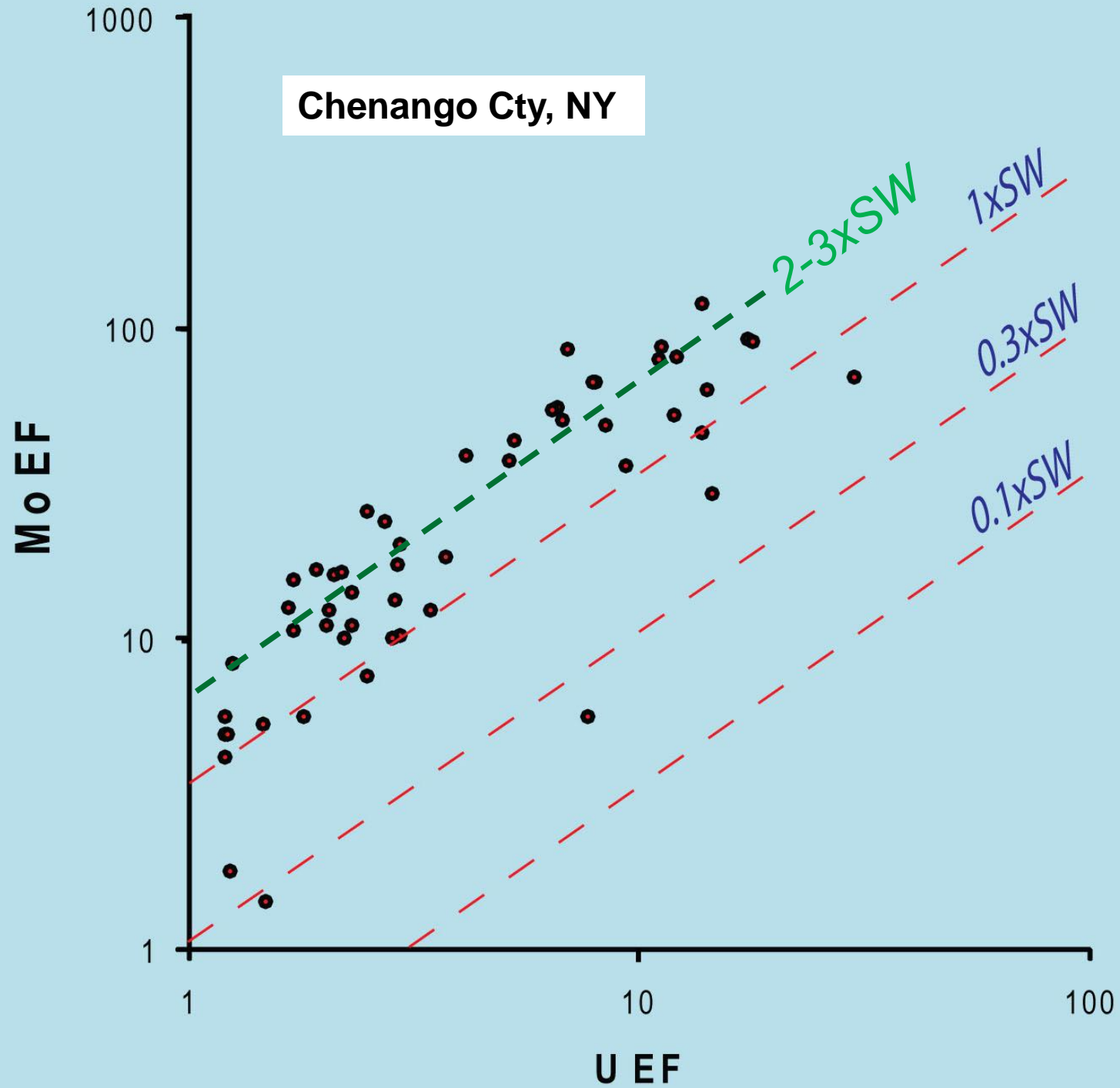
requirement – intermittently sulfidic (dissolved  $\text{H}_2\text{S}$ ) bottom waters

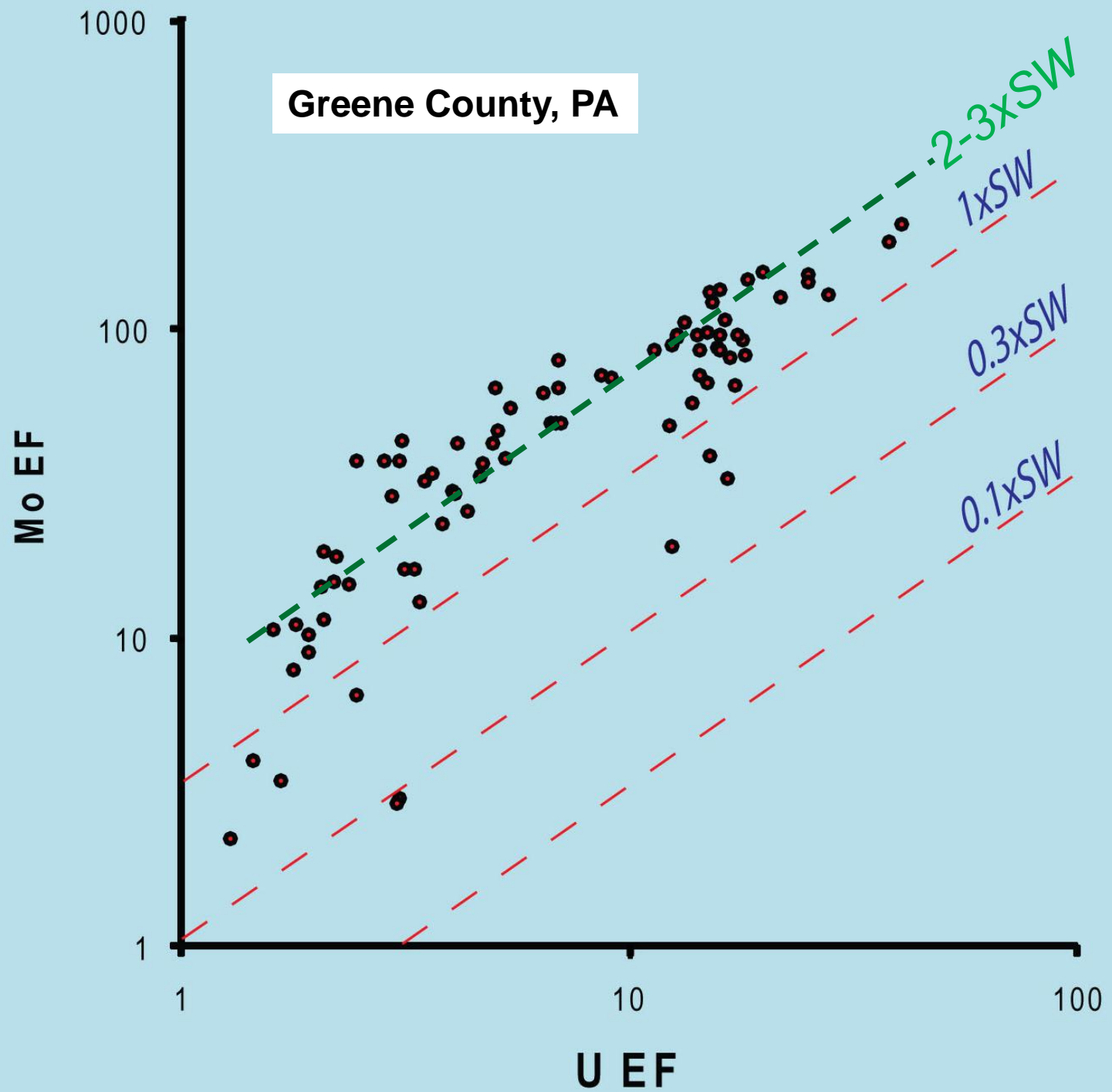
progressively higher abundances of U (in excess of Mo)  
and eventually enrichment of Mo relative to U...

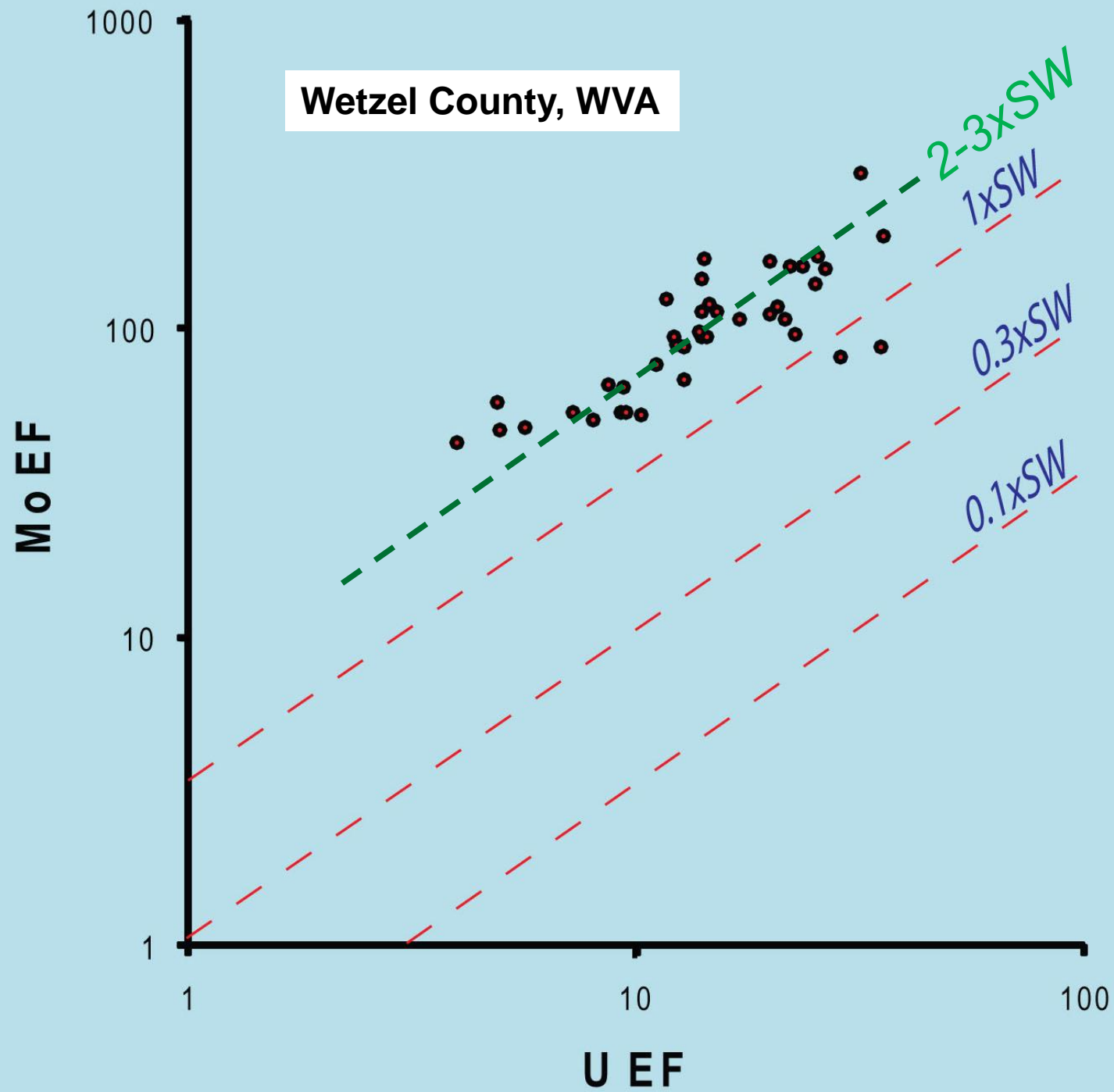


...increasingly reducing conditions...

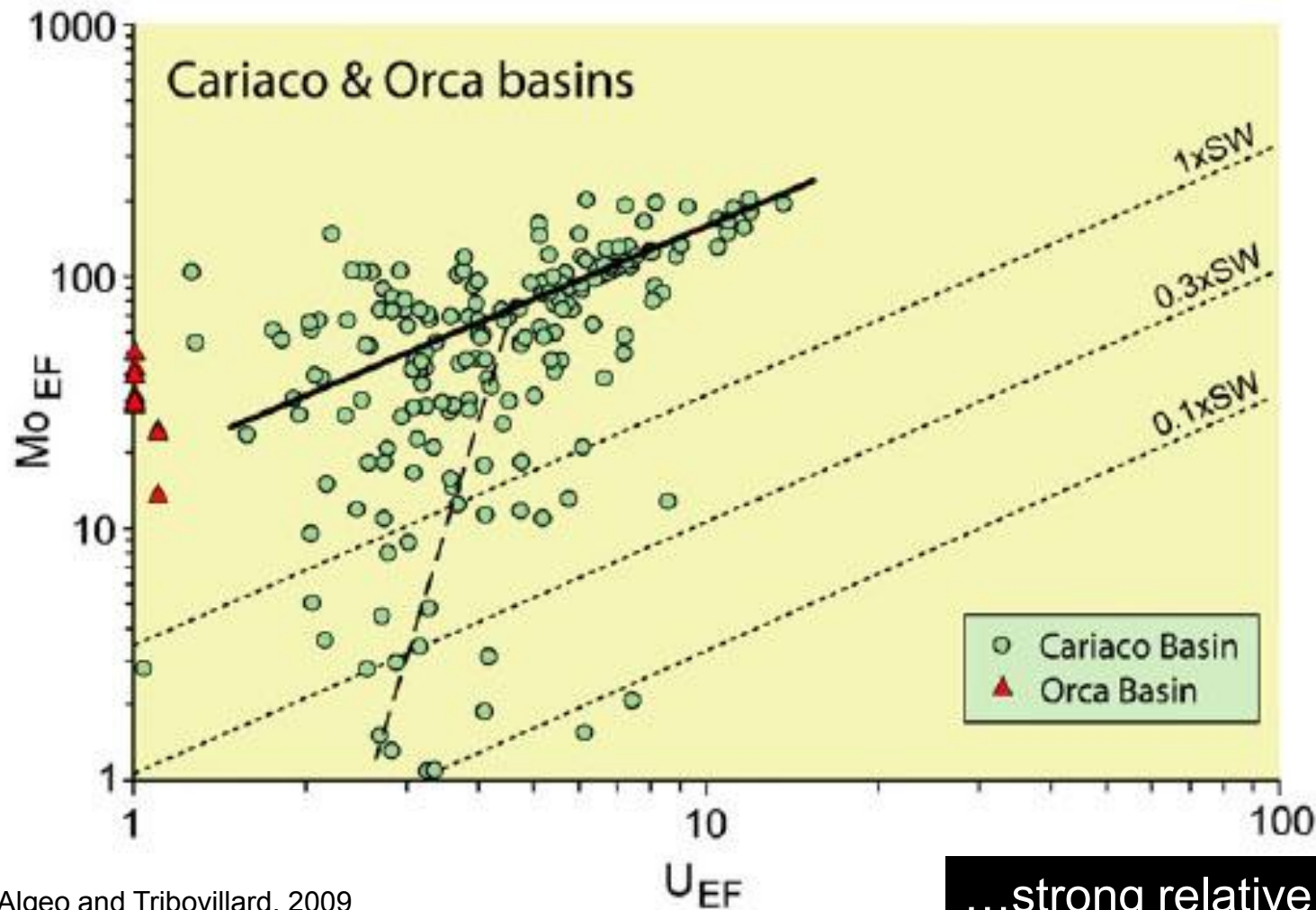












Algeo and Tribovillard, 2009

...strong relative enrichment  
of Mo relative to U...

...operation of a particulate shuttle mechanism that  
enhanced transfer of Mo to the seafloor...

bioturbated dark-gray shale

fossil debris



shoaling redox boundary

diminished bioturbation;  
increased uranium

...frequent redox fluctuations ...



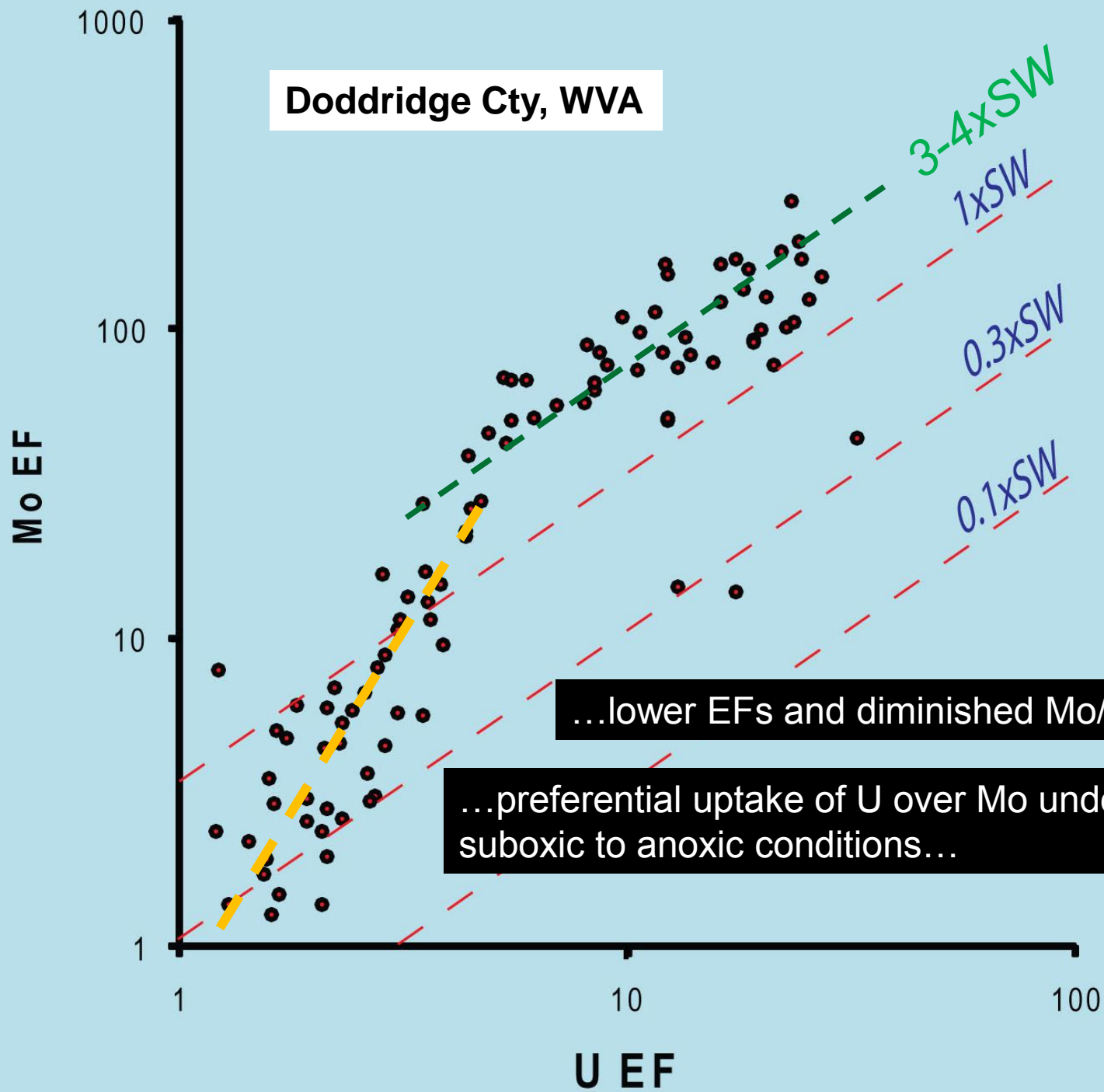


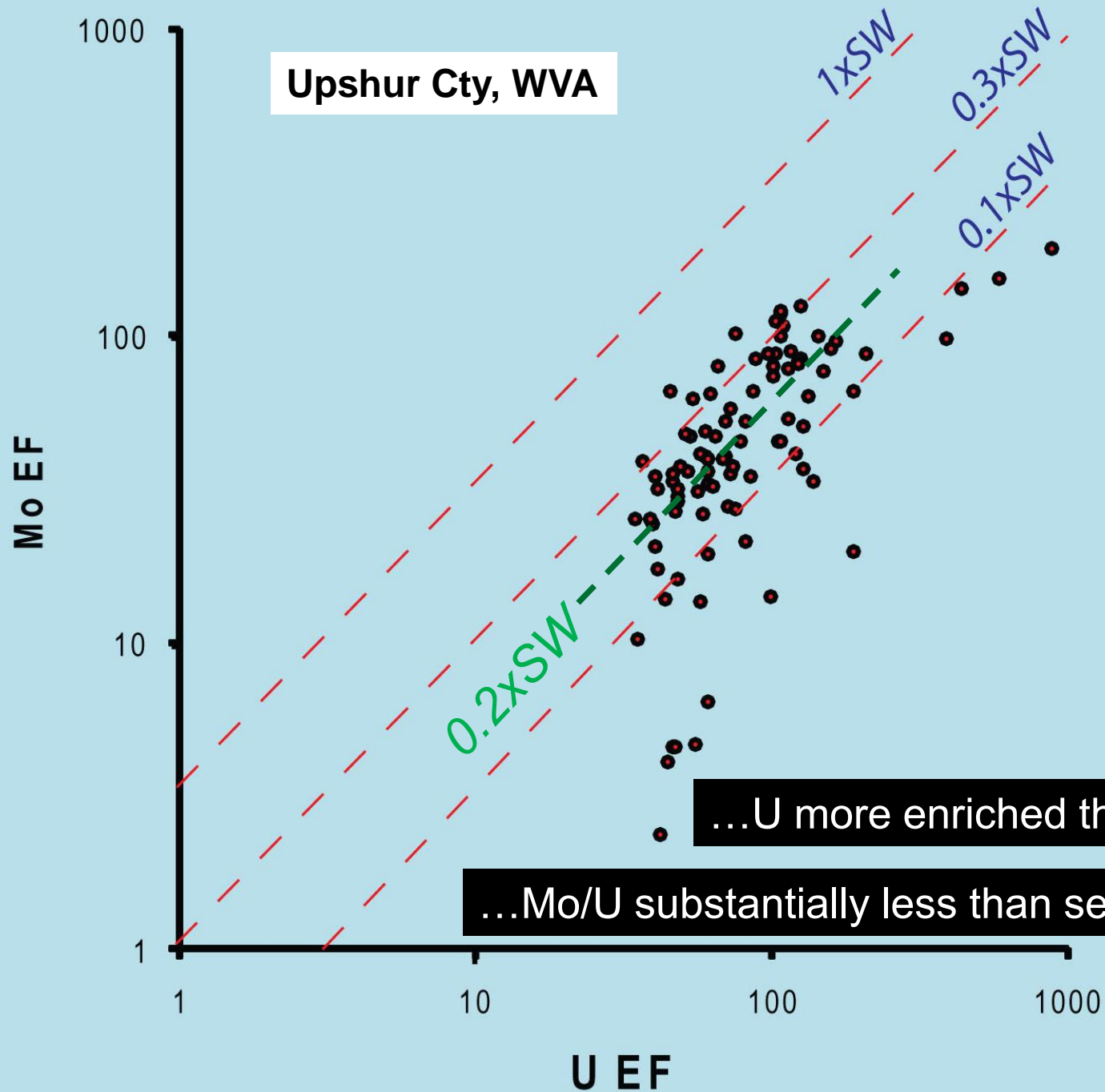
...water mass exchange with the global Rheic Ocean...



Middle Devonian

Rheic Ocean





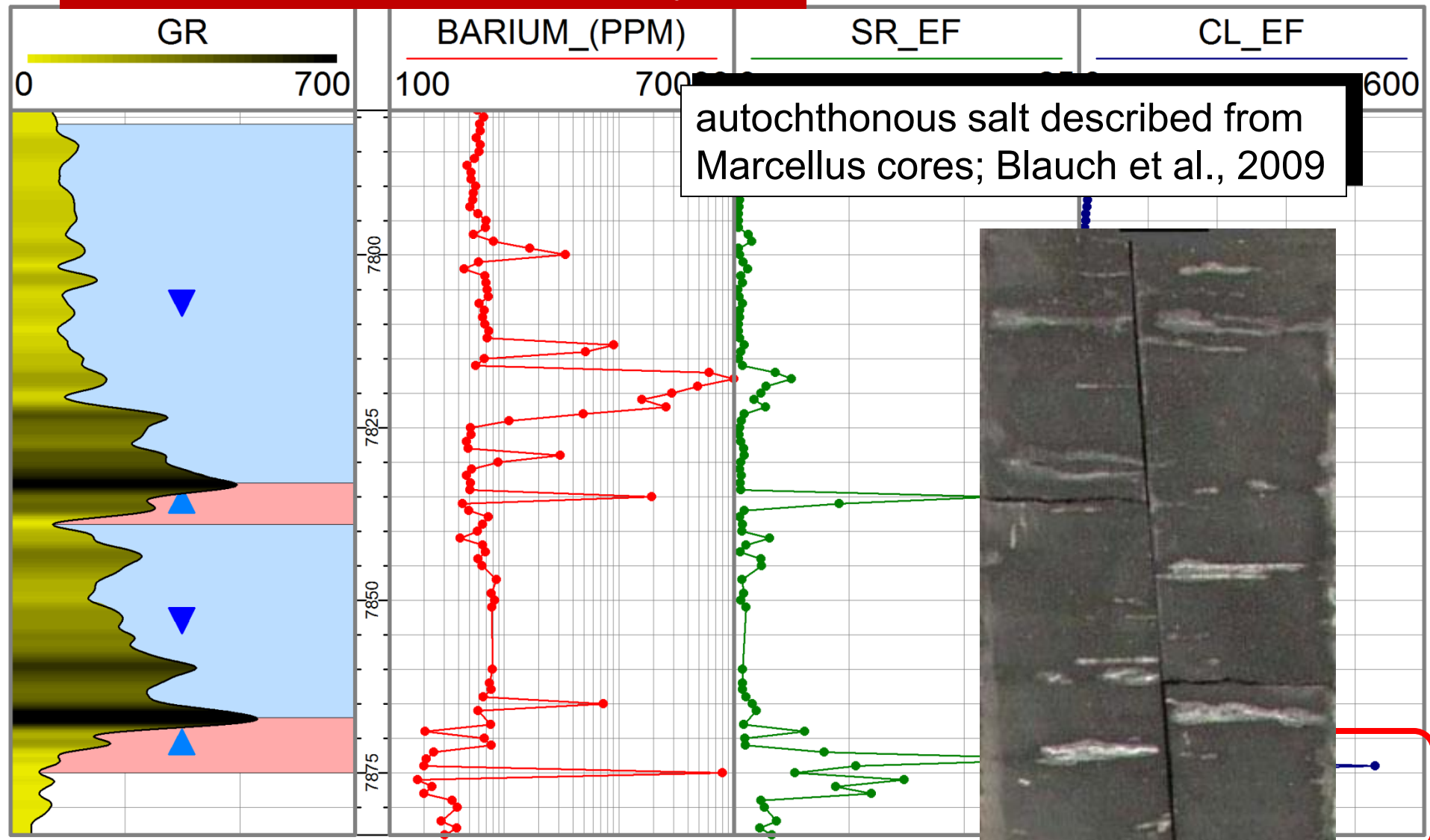




...isolation from the Rheic Ocean and consequent depletion of Mo relative to U...

Rheic Ocean

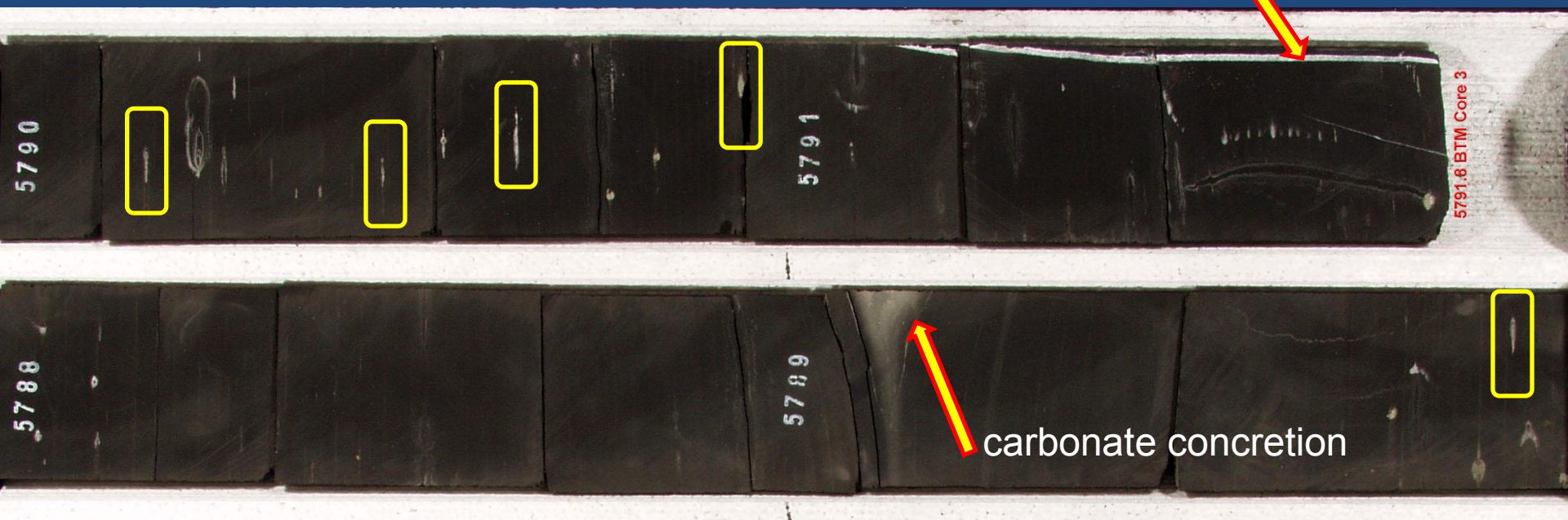
# Marcellus Shale, southwestern Pennsylvania



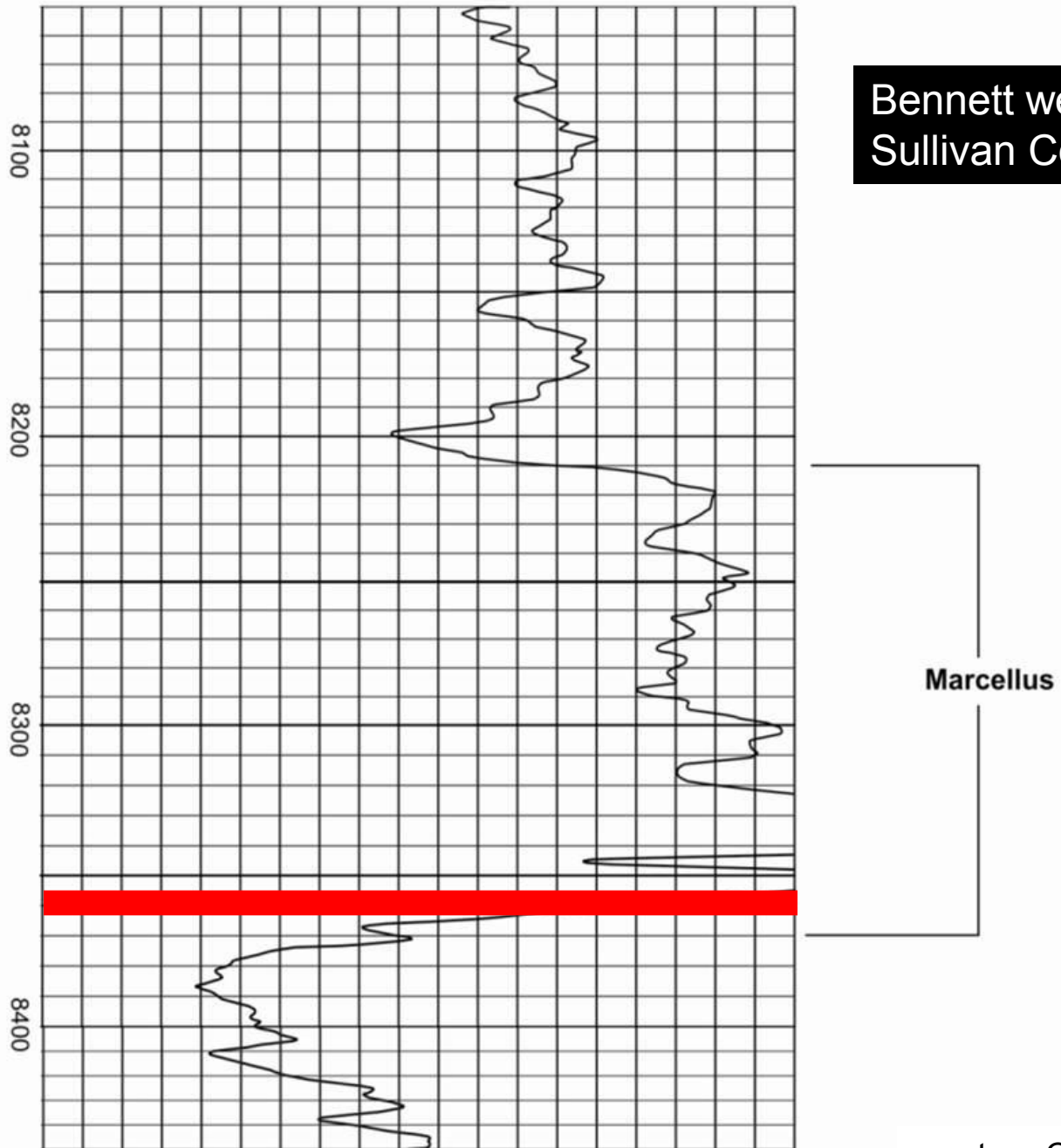


halite

calcite-filled vertical fracture



Bennett well  
Sullivan County, PA



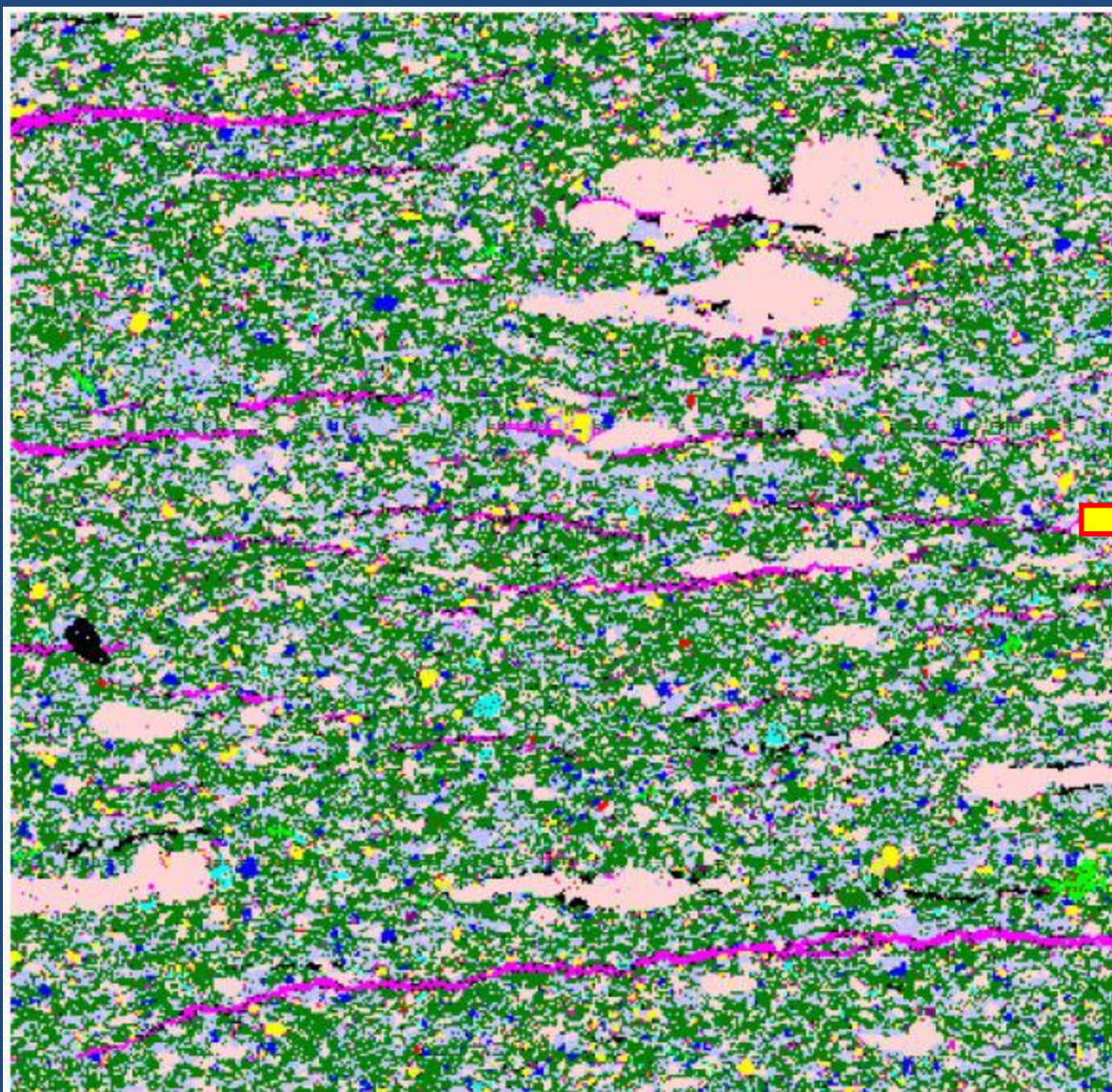
courtesy Chris Laughrey





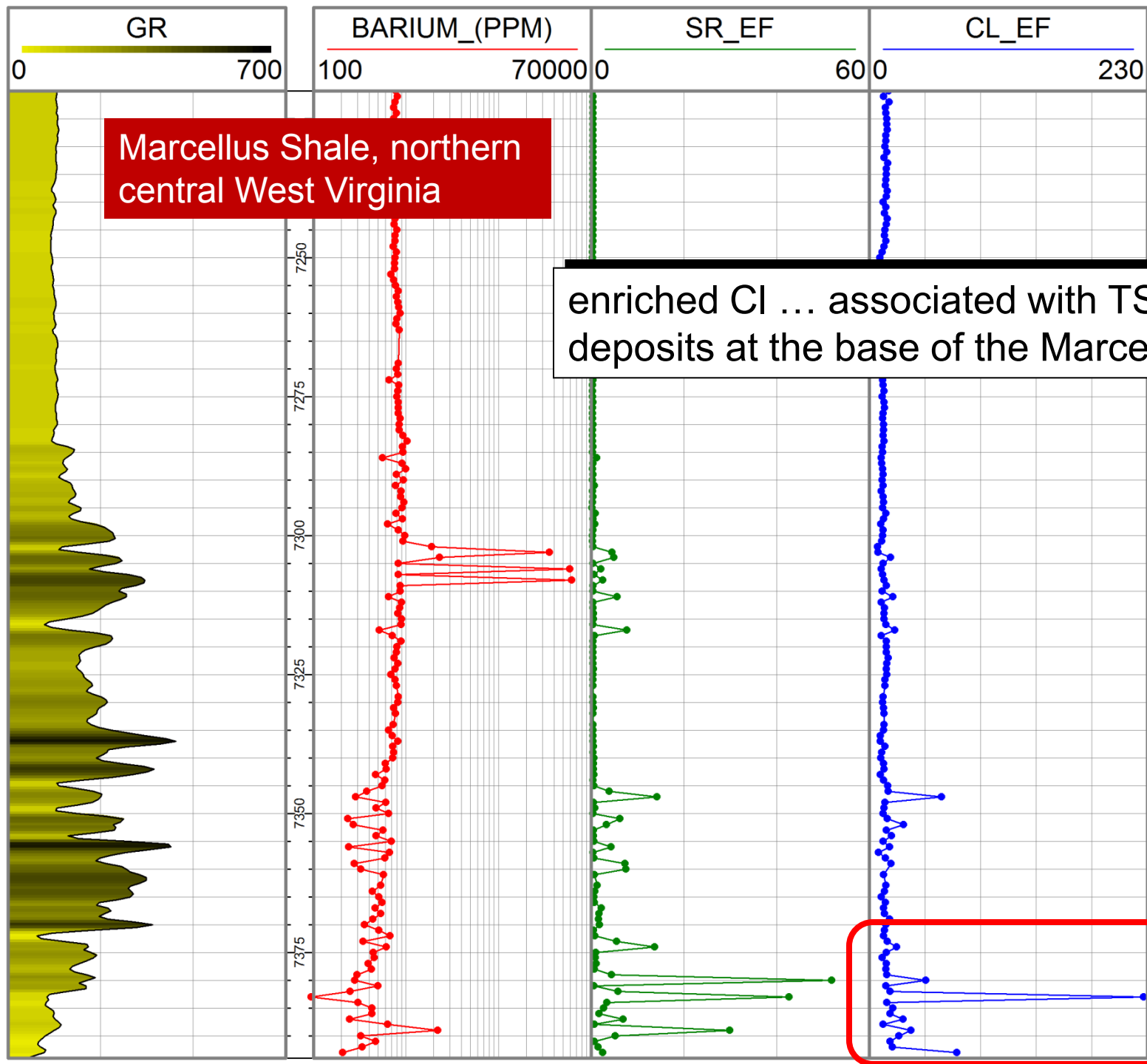
31mm, EDX every 10micron





- Background
- Illite
- Quartz
- Calcite
- Alkali Feldspar
- Plagioclase Feldspar
- Chlorite
- Dolomite
- Ankerite/Siderite
- Apatite
- Anhydrite/Gypsum
- Rutile/Anatase
- Pyrite/Marcasite
- Kaolinite
- Organics
- Others

1mm, EDS every 2.5micron



## Conclusions

- covariance of Mo and U in the Marcellus is consistent with a particulate shuttle as a means of accelerating Mo transport to the sea floor;
- the particulate shuttle requires a “threshold” level of  $\text{H}_2\text{S}$  in the water column (euxinic conditions) to “activate” the Mo;
- the locally silled nature of the Marcellus basin is suggested by the presence of diminished Mo enrichment relative to U;
- fluctuation of the chemocline (necessary for particulate shuttle) may have been aided by episodic introduction of seawater from the global (tropical or Rheic) ocean as a means of replenishing Mo and U;

## Conclusions

- sulfidic conditions and enhanced organic matter enrichment of the lower Marcellus Shale (Union Springs) may have been aided by the early influx of saline shelf waters produced as a consequence of the initial Marcellus transgression (perhaps one causal mechanism for the Middle Devonian (late Eifelian - Union Springs) Kačák Event or earlier Bakoven bioevent



