Molybdenum, Uranium, and Chloride Abundances in the Marcellus Shale — Significance to Basin Hydrography and Organic Matter Preservation*

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Abstract

Trace element and metals abundances have proven useful to elucidating the hydrography and water mass chemistry of shale basins. Our analysis of several Marcellus Shale cores by use of handheld XRF technology has yielded a robust dataset that sheds light on the nature and evolution of the water column of the Marcellus basin. Regional covariance trends of molybdenum and uranium and their respective enrichment factors define a uniform Mo/U molar ratio of ≈ 2-3 times that of seawater. Moreover, Mo is enriched relative to U by as much as 10:1 suggesting accelerated transport of Mo to the seafloor by a particulate transport mechanism that would have been enhanced by an intermittently sulfidic water column and a fluctuating chemocline. However, a data subset defined by Mo and U values typical of bottom water depleted in Mo (Mo/U = 0.1 - 0.3 x seawater) is suggestive of local water column stratification and consequent drawdown of Mo. Intermediate FeT/Al values, seemingly inconsistent with anoxic to sulfidic conditions, reflect, instead, the relatively high clastic flux of the Marcellus system. An especially intriguing aspect of the Marcellus inorganic geochemistry is local enrichment of chloride, generally within early transgressive systems tract deposits. Chloride well in excess of background levels as well as the documented presence of evaporite minerals appears to record the episodic introduction of dense saline water, likely sourced on the flooded subtropical shelf, into the Marcellus basin to the east. Injection of such saline water would have favored the establishment and maintenance of anoxic or even euxinic conditions thereby contributing to the preservation of organic matter in the Marcellus Shale, especially its lower organic-rich interval, the Union Springs Member.

References

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.

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Website

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Molybdenum, uranium, and chloride abundances in the Marcellus Shale – significance to basin hydrography and organic matter preservation

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Introduction

…variations in elemental abundances (Mo, U, V, Ni, Co, Mn) reflect changes in such parameters as paleoclimate, hydrographic aspects of the paleocean, and paleoredox conditions (including oceanic anoxic events)…

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 data for most major, minor and trace elements from Mg to U (Smith and Malicse, 2010)…

…analysis of Marcellus cores at ~ 1

Phaser

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 but enhanced uptake where water masses are anoxic;

--both elements have long residence times in seawater-

-Mo ~ 0.78 MY

-U ~ 0.45 MY

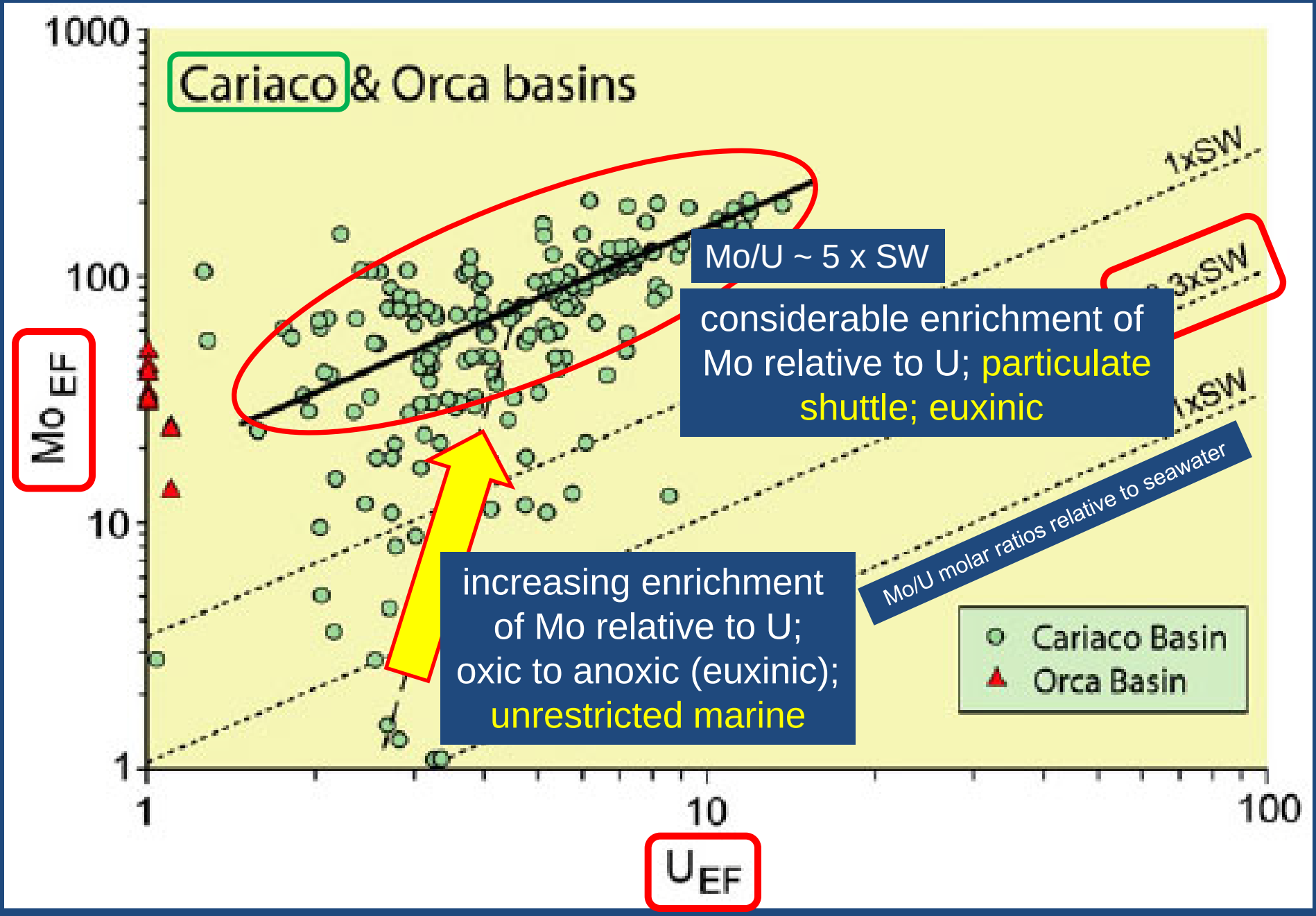
--both exhibit low concentrations in plankton – enrichment in sediment can be related to authigenic uptake from seawater;

--enrichment of Mo and U in sedimentary rocks may be interpreted in terms of authigenic uptake from seawater (Algeo and Tribovillard , 2009; Tribovillard et al., 2012)

EF = enrichment factor…

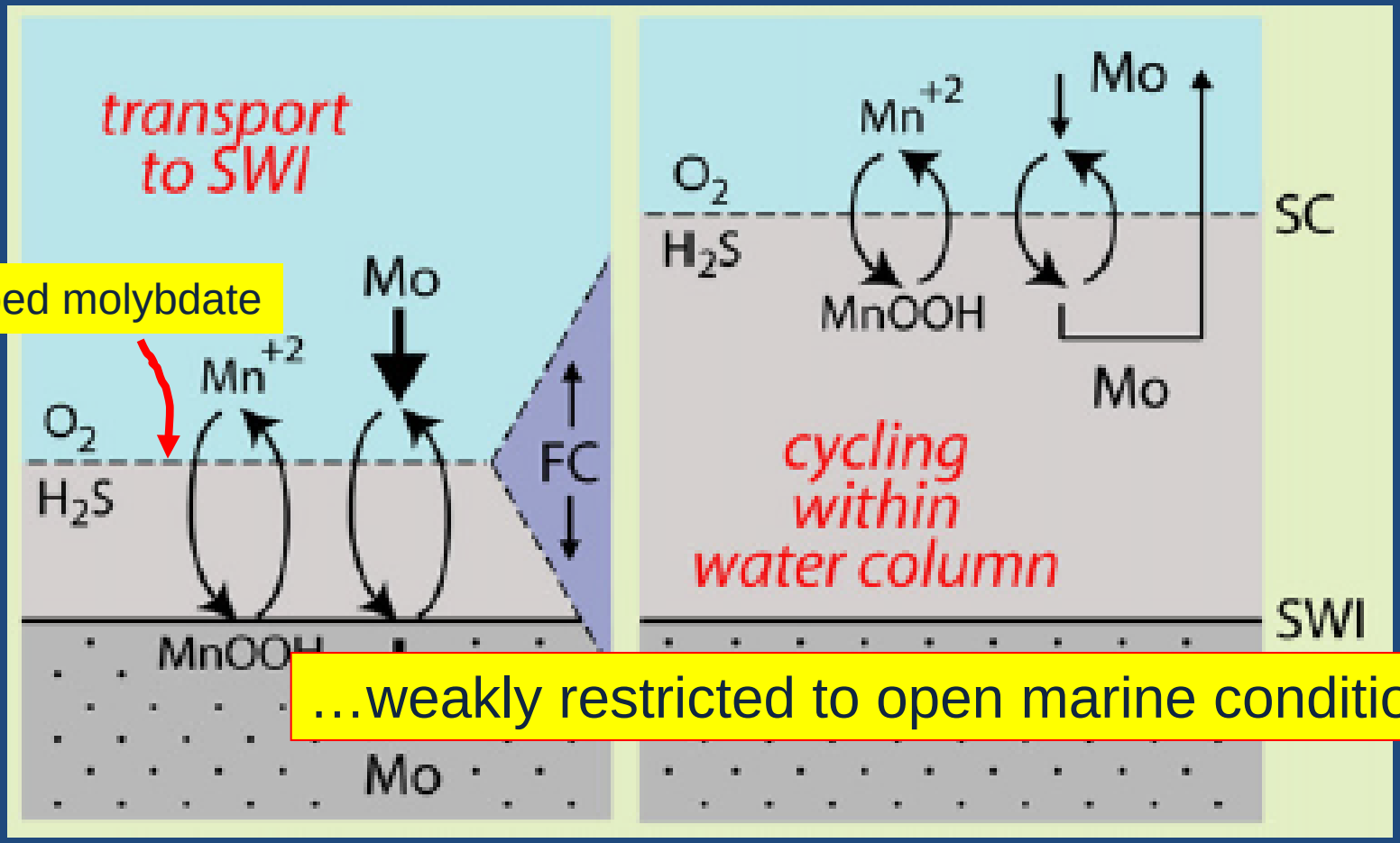
$$= \frac{element_{sample} / Al_{sample}}{element_{"average"} / Al_{"average"}}$$

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



Algeo and Tribovillard, 2009

…Mn (Fe)-oxyhydroxide particulate shuttle (continuous scavenging)…

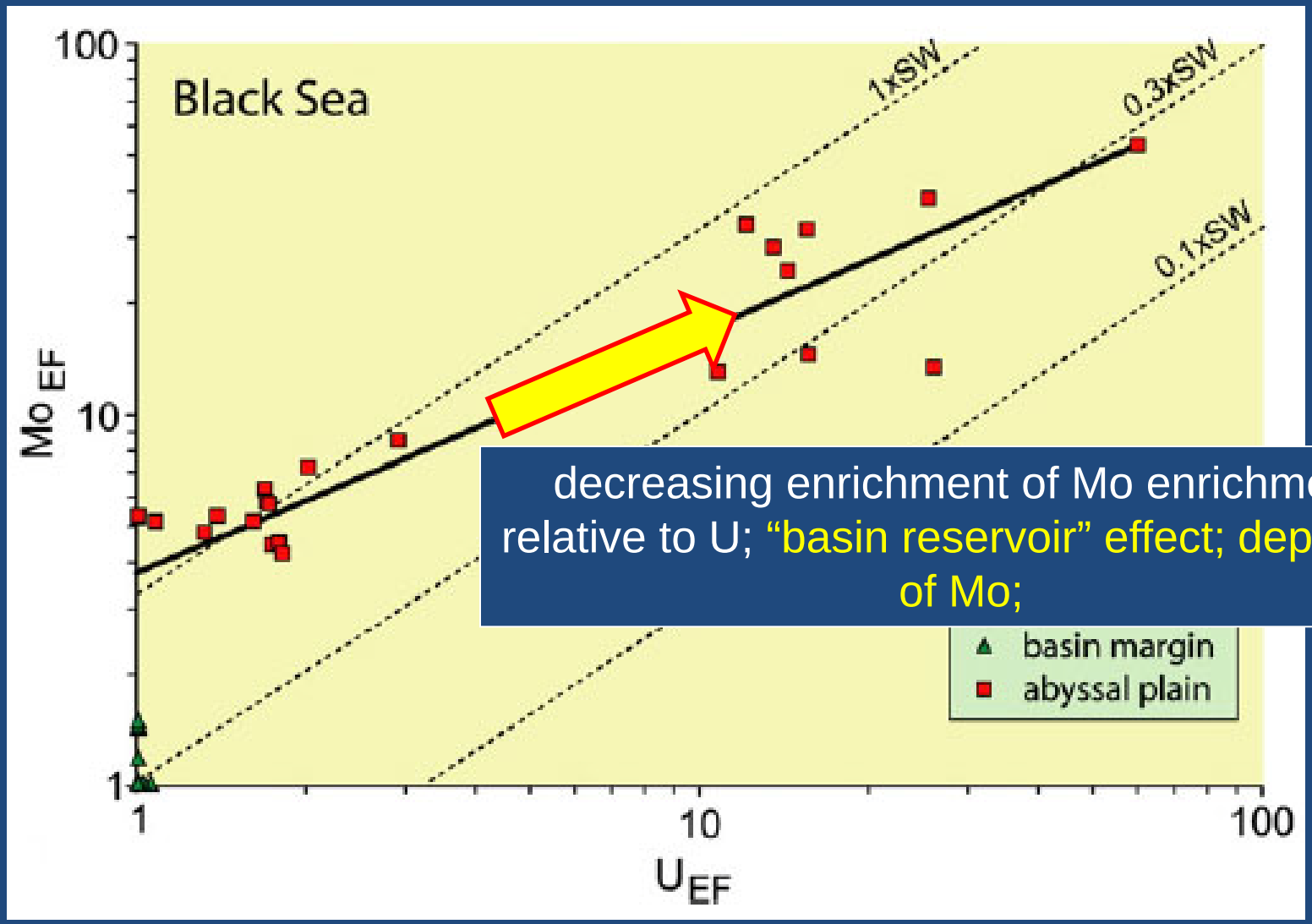


…weakly restricted to open marine conditions…

requirement – intermittently sulfidic (dissolved H_2S) bottom waters

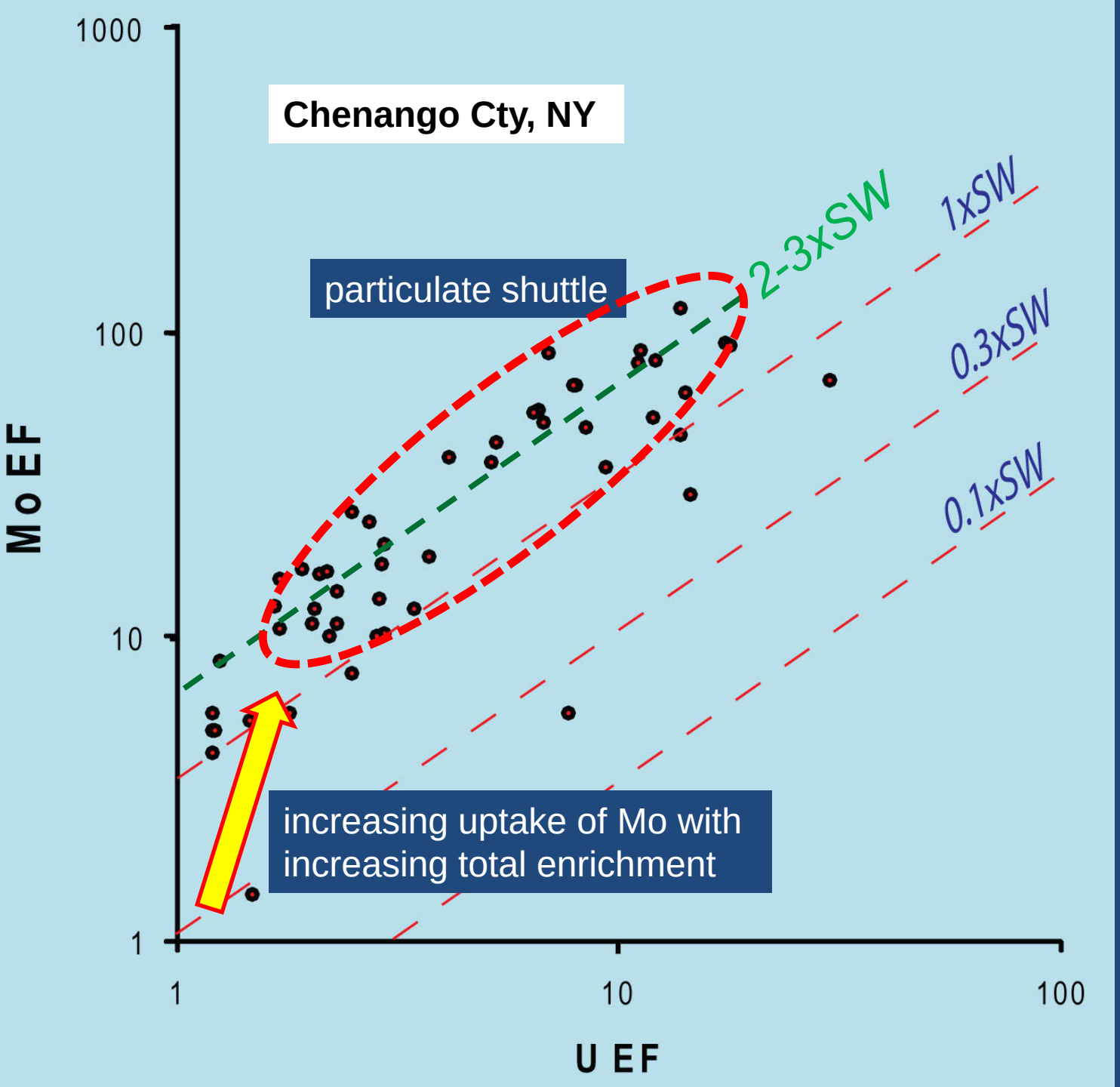
Algeo and Tribovillard, 2009

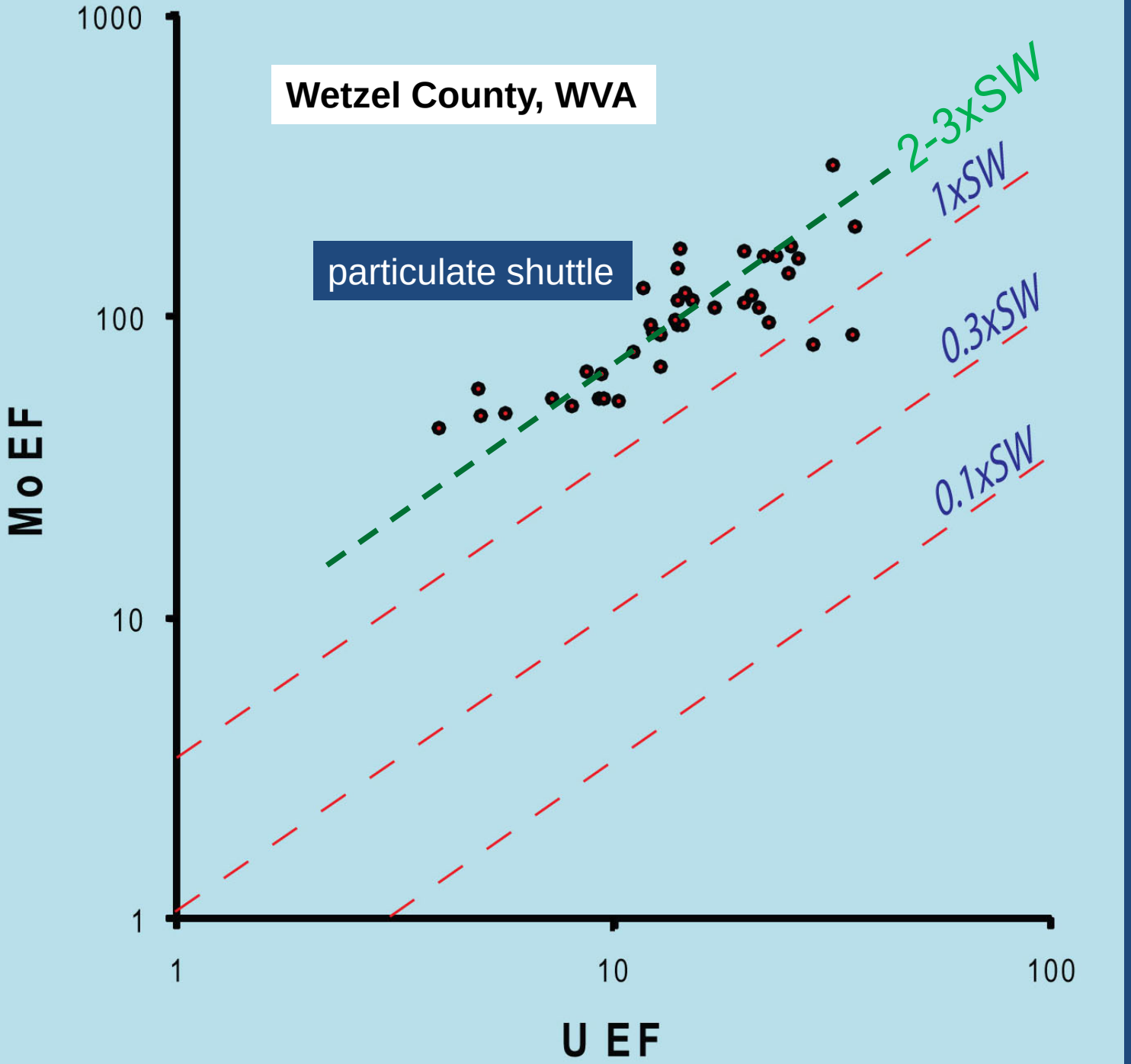
…extended deepwater isolation…



decreasing enrichment of Mo enrichment relative to U; "basin reservoir" effect; depletion of Mo;

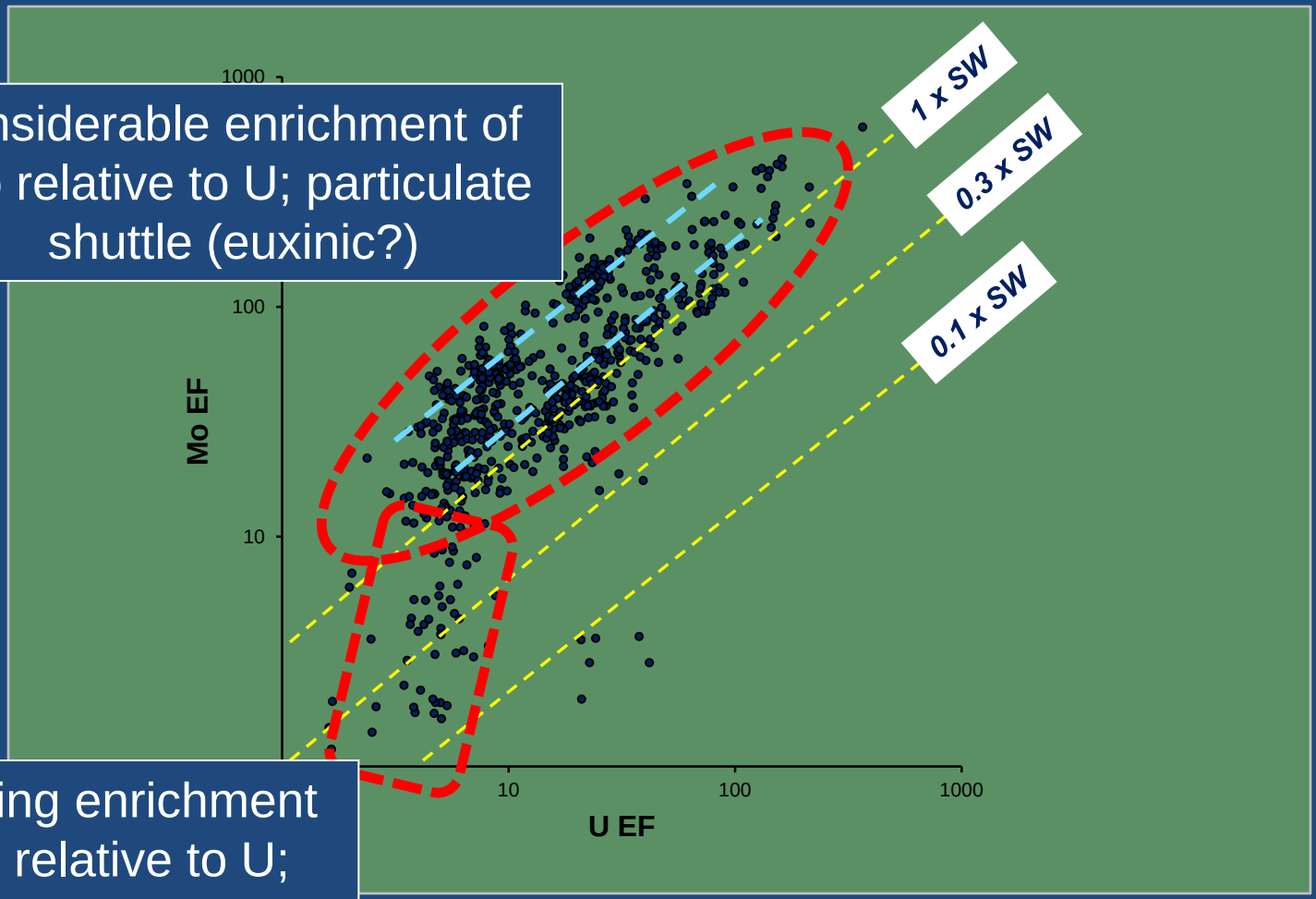
Algeo and Tribovillard, 2009


Chenango Cty, NY
particulate shuttle
2-3xSW
1xSW
0.3xSW
0.1xSW
increasing uptake of Mo with
increasing total enrichment
Mo EF
U EF
1000
100
10
1
1
10
100

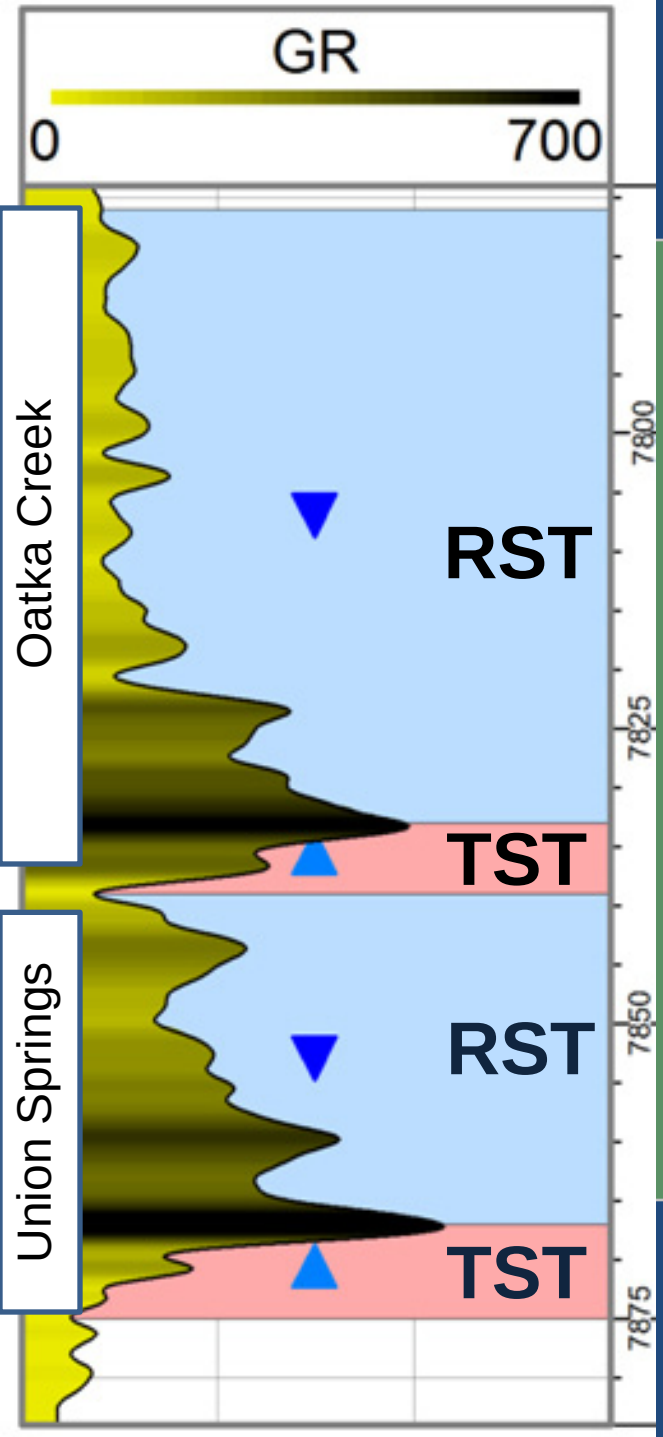

Wetzel County, WVA
particulate shuttle
2-3xSW
1xSW
0.3xSW
0.1xSW
1000
100
10
1
Mo EF
1
10
100
U EF

Greene County, PA

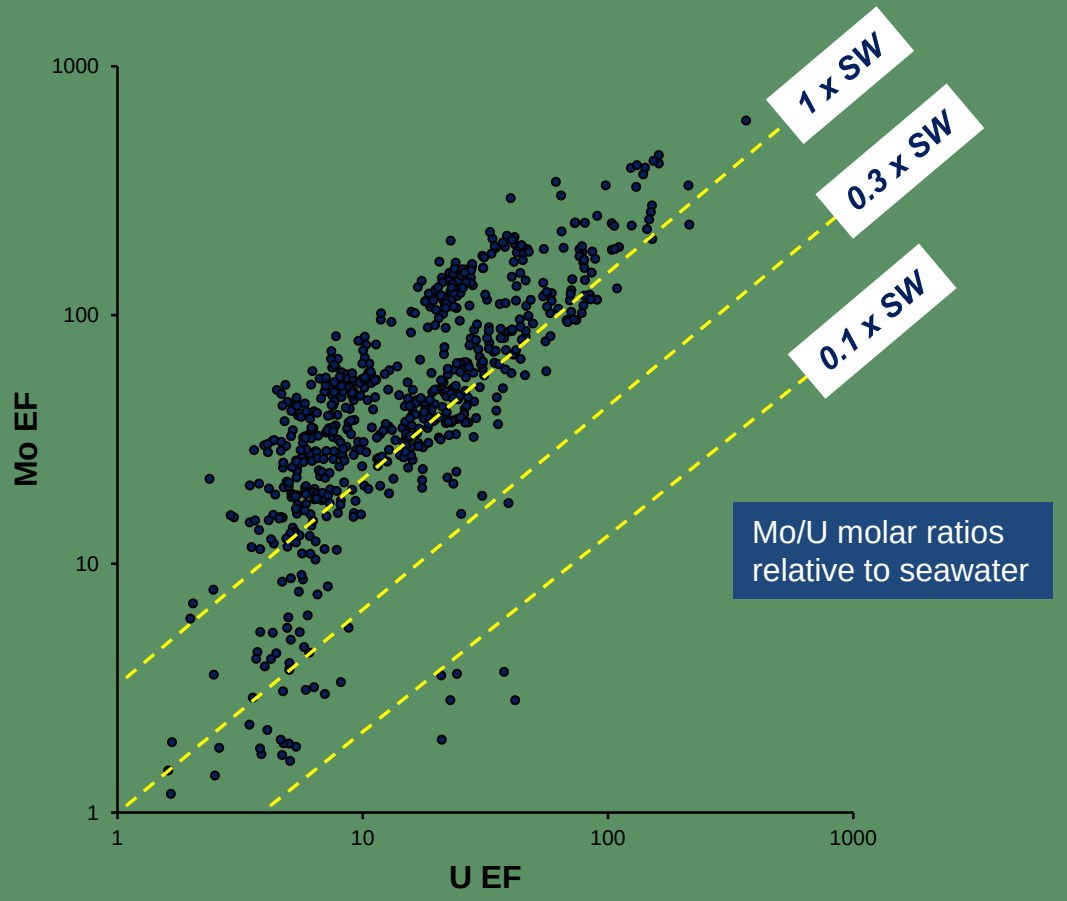
considerable enrichment of Mo relative to U; particulate shuttle (euxinic?)

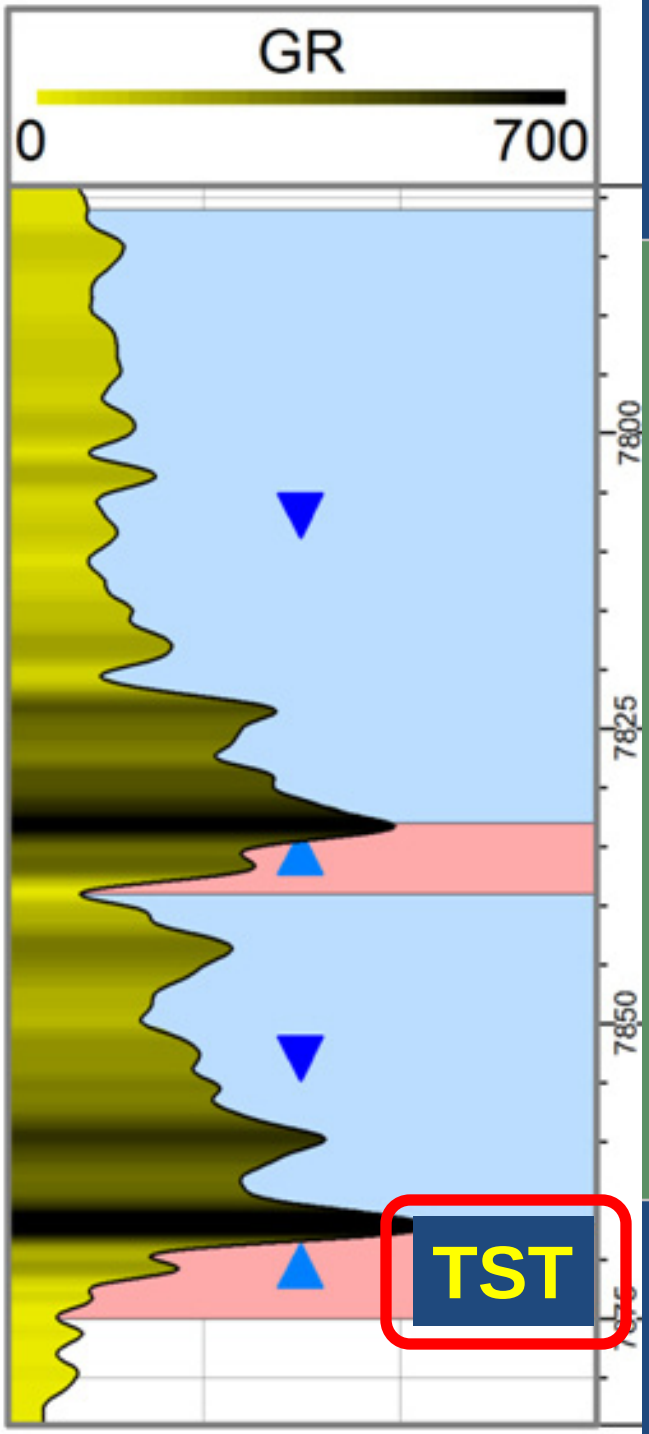


increasing enrichment of Mo relative to U; oxic to anoxic;



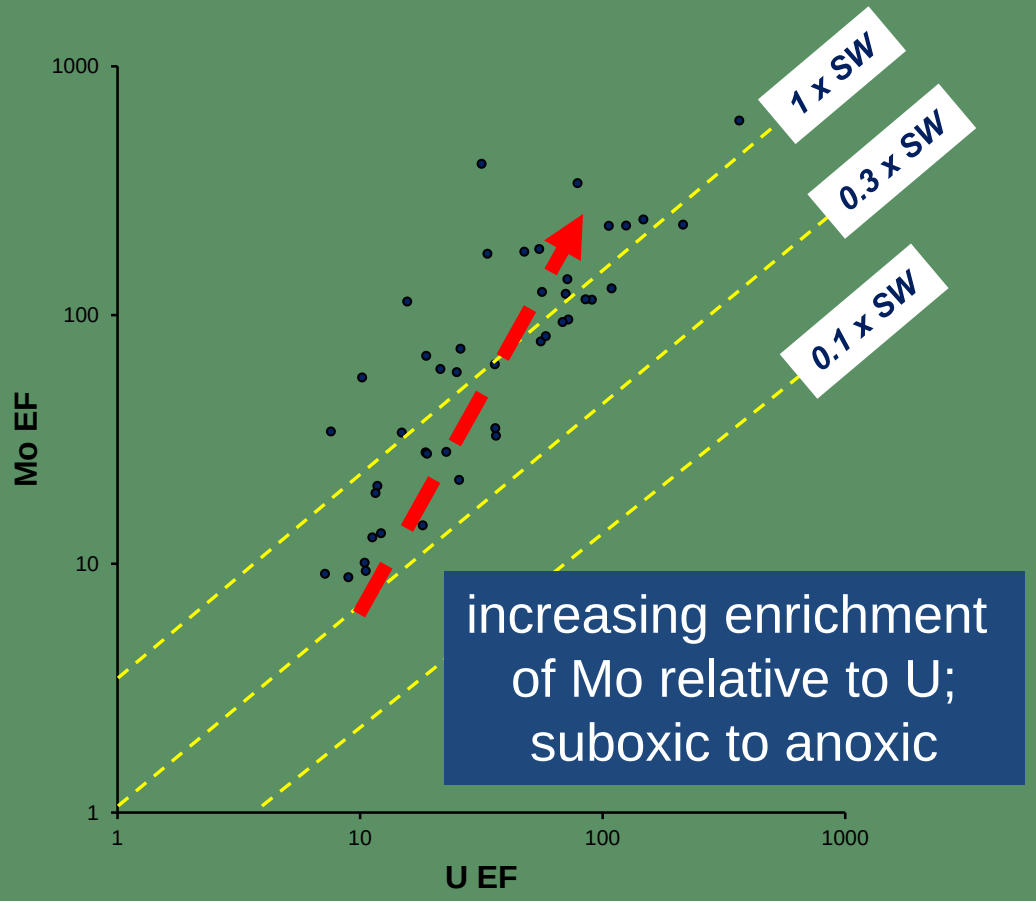
Greene County, PA



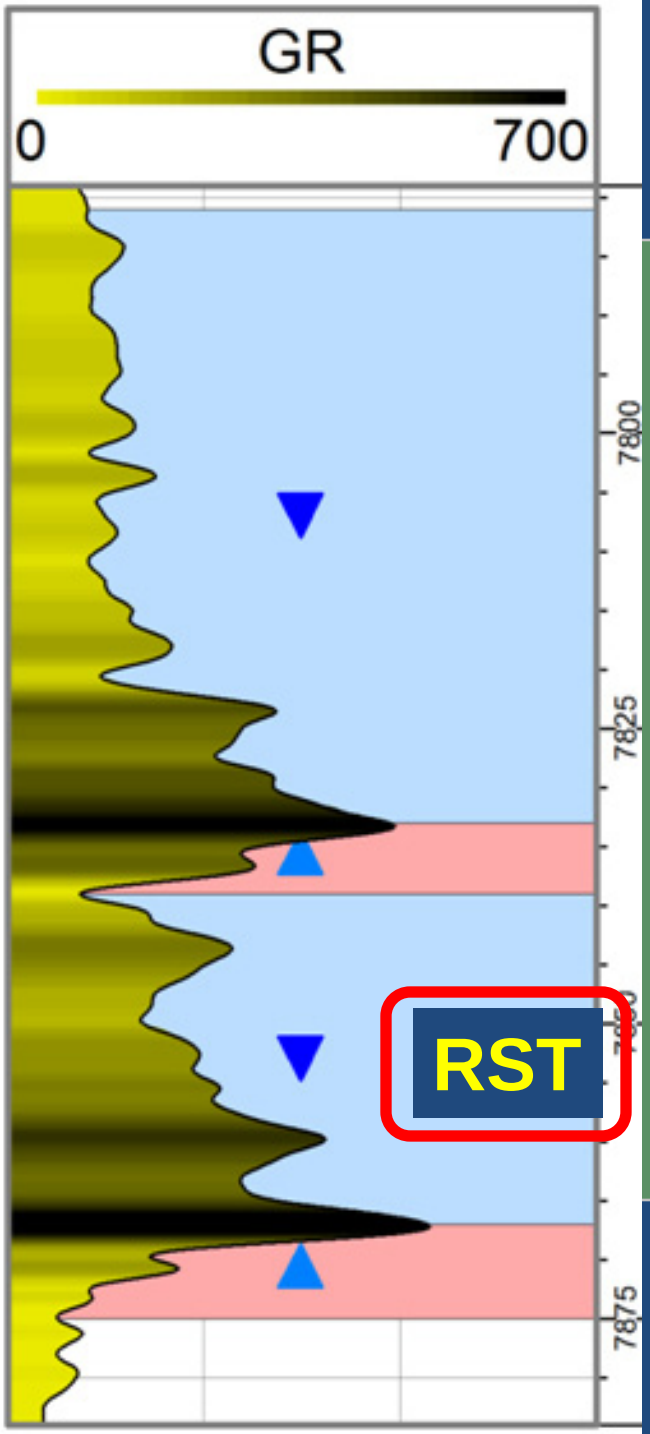


transgressive systems tract

Union Springs

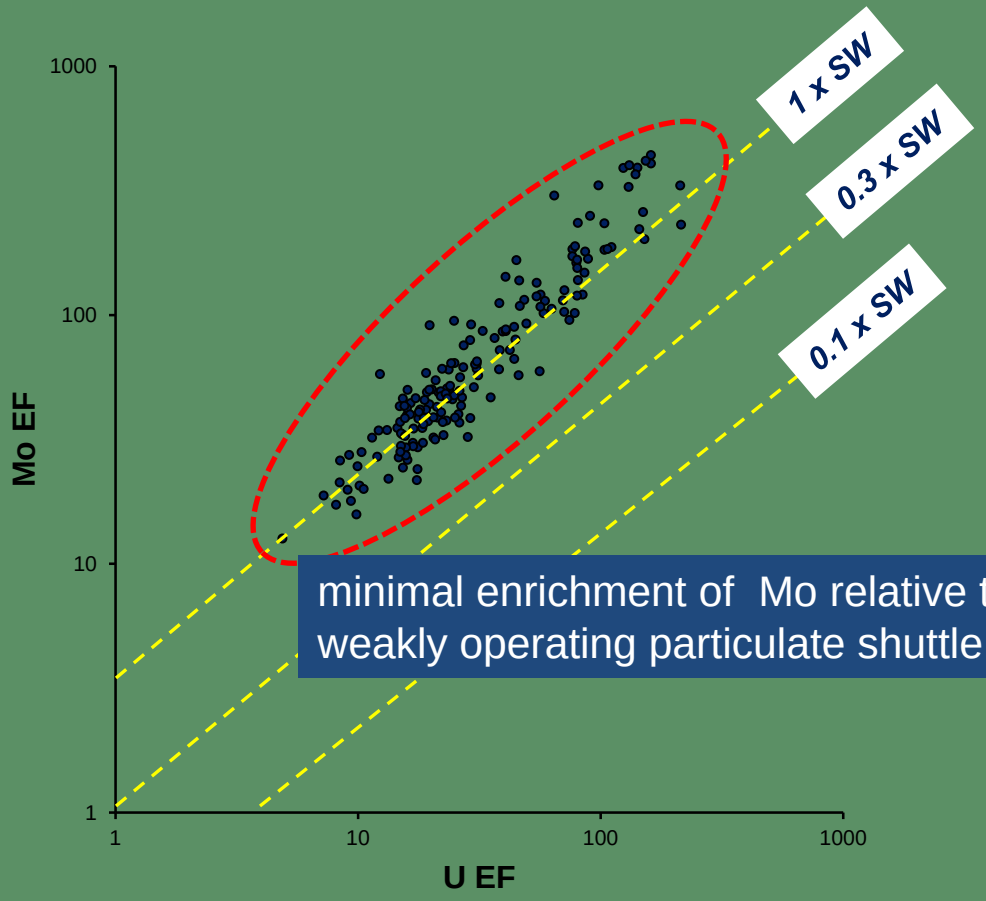


increasing enrichment of Mo relative to U; suboxic to anoxic



regressive systems tract

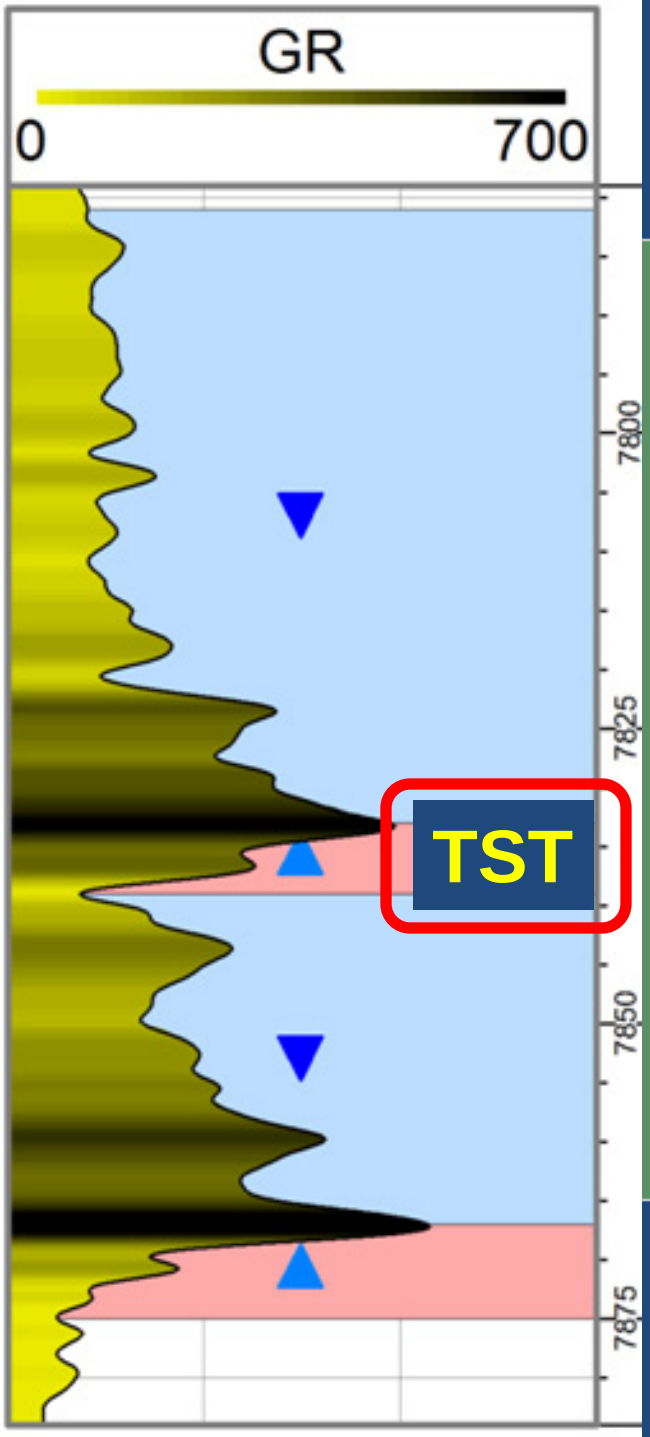
Union Springs

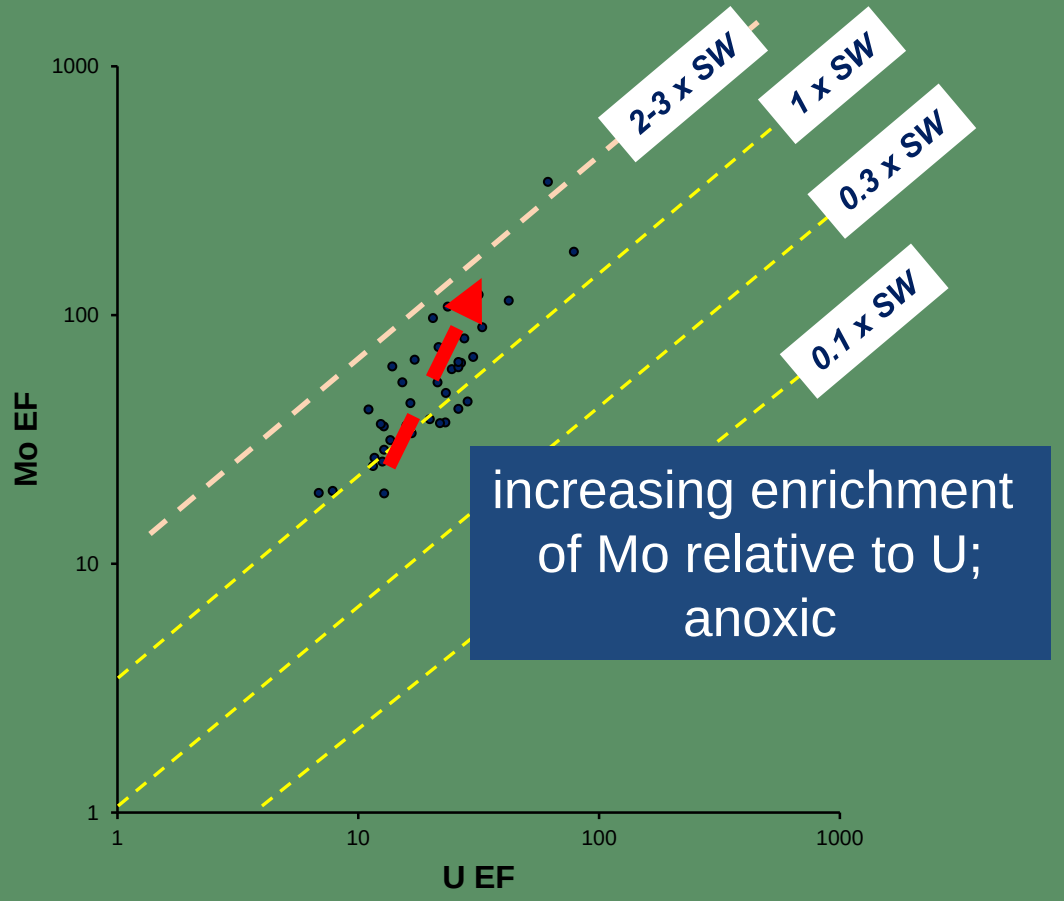


minimal enrichment of Mo relative to U;
weakly operating particulate shuttle

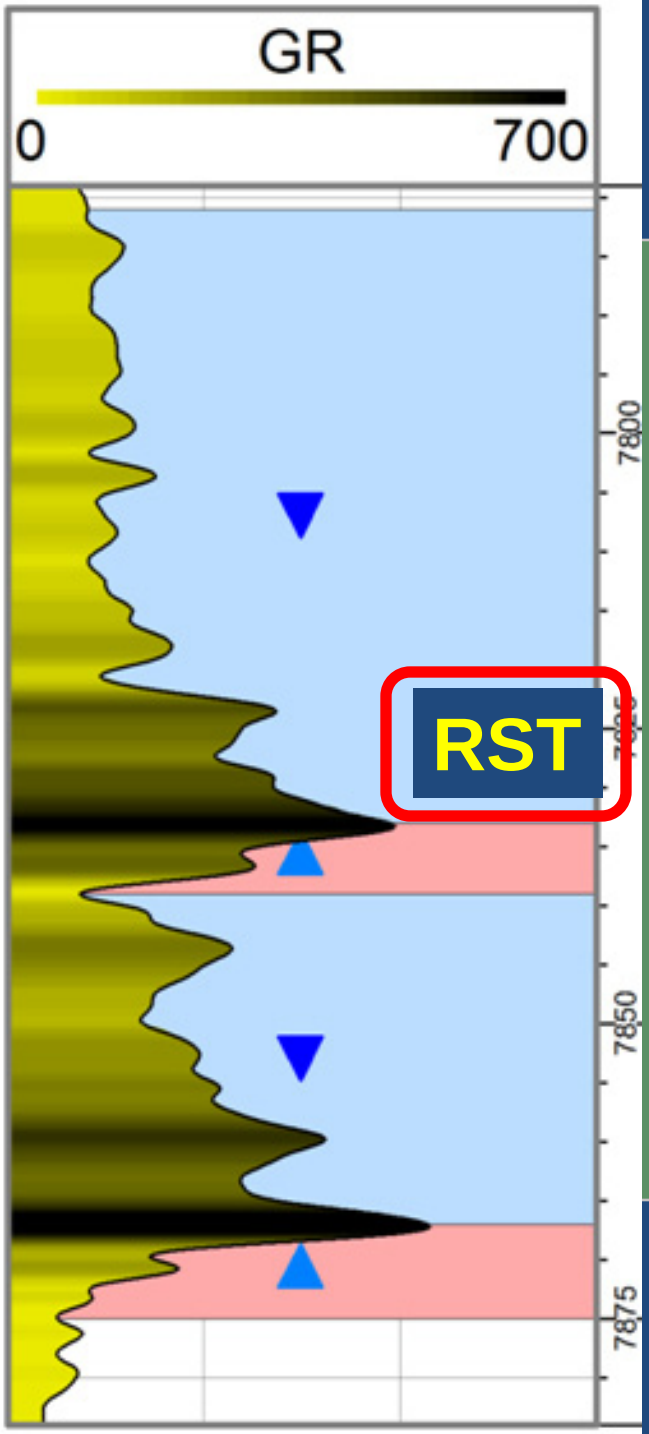
transgressive systems tract

Oatka Creek



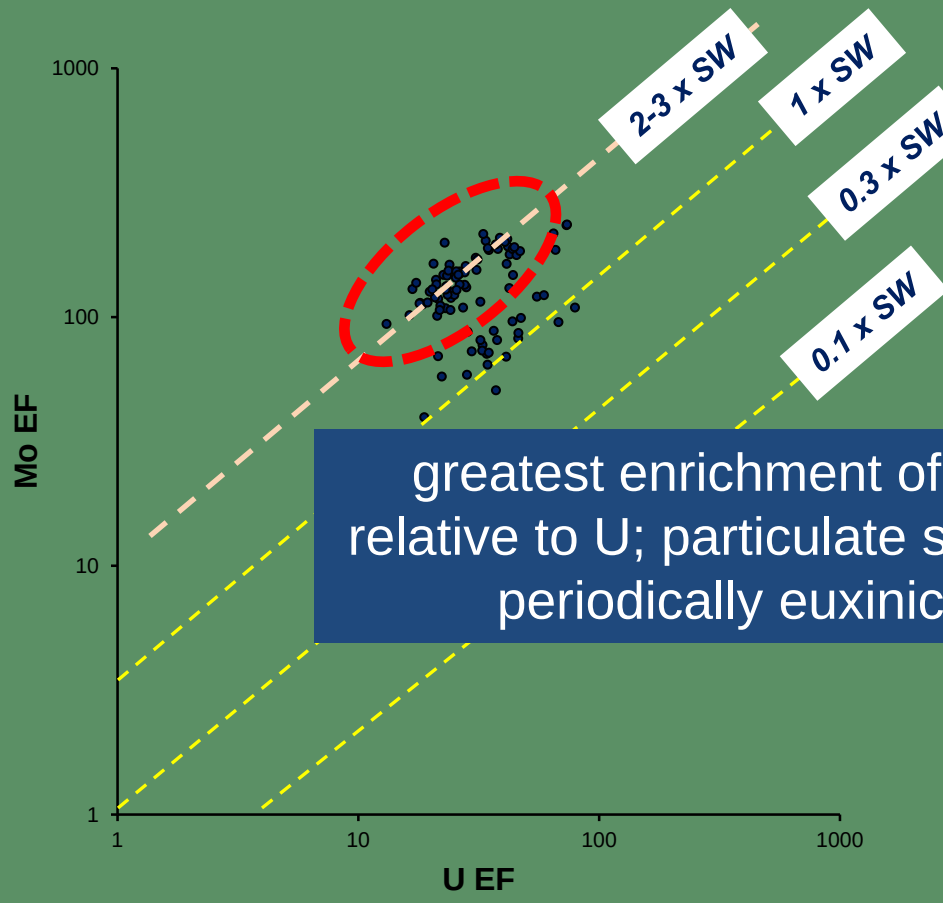


increasing enrichment of Mo relative to U; anoxic



lower regressive systems tract

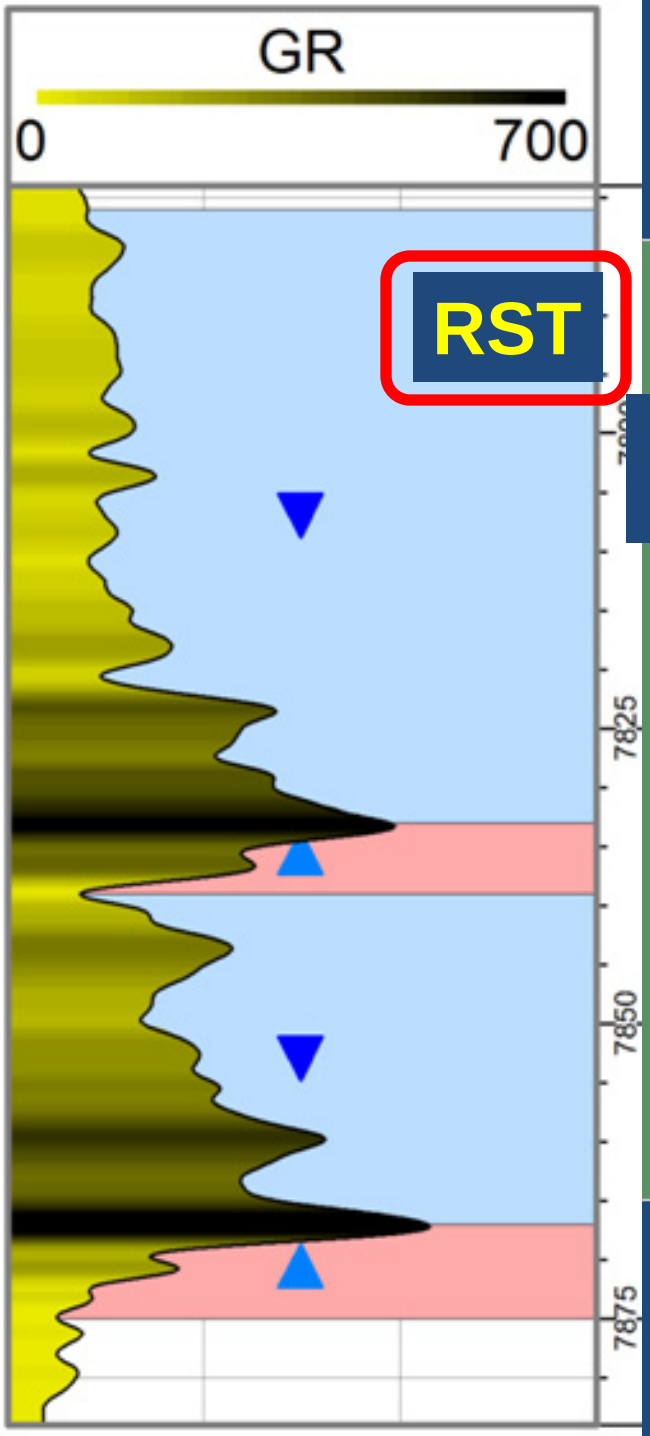
Oatka Creek



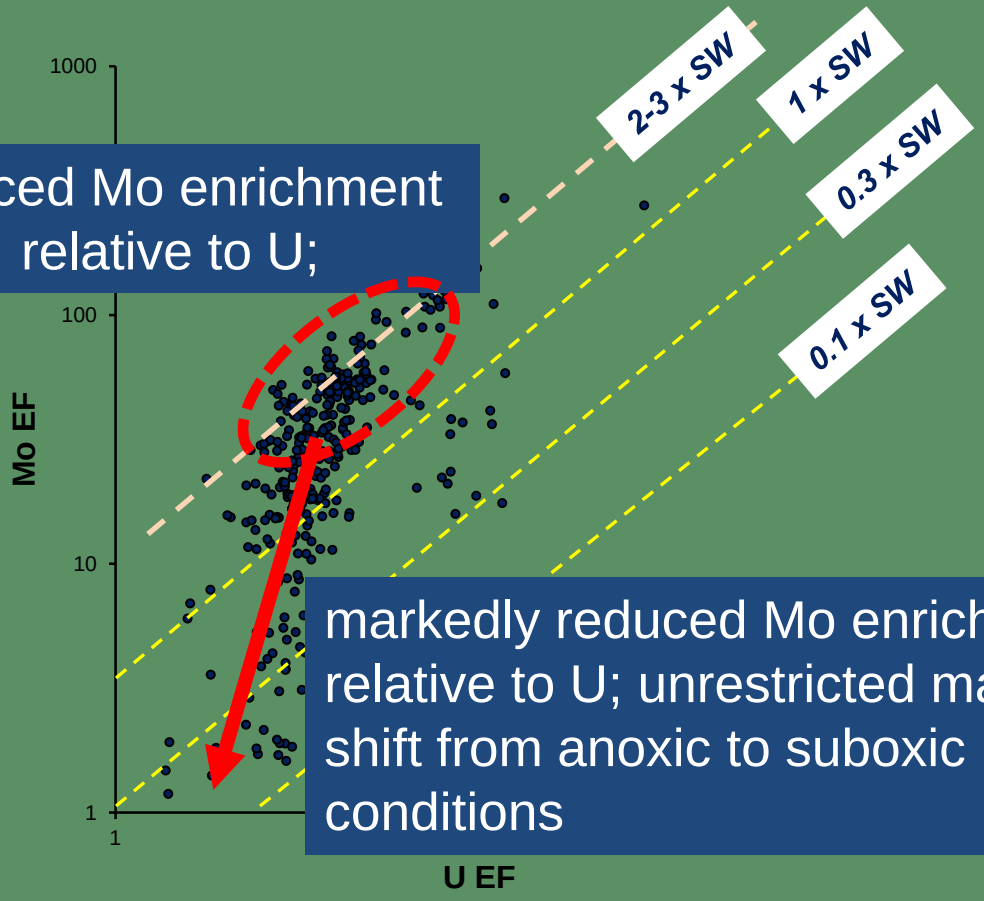
greatest enrichment of Mo relative to U; particulate shuttle; periodically euxinic

upper regressive systems tract

Oatka Creek



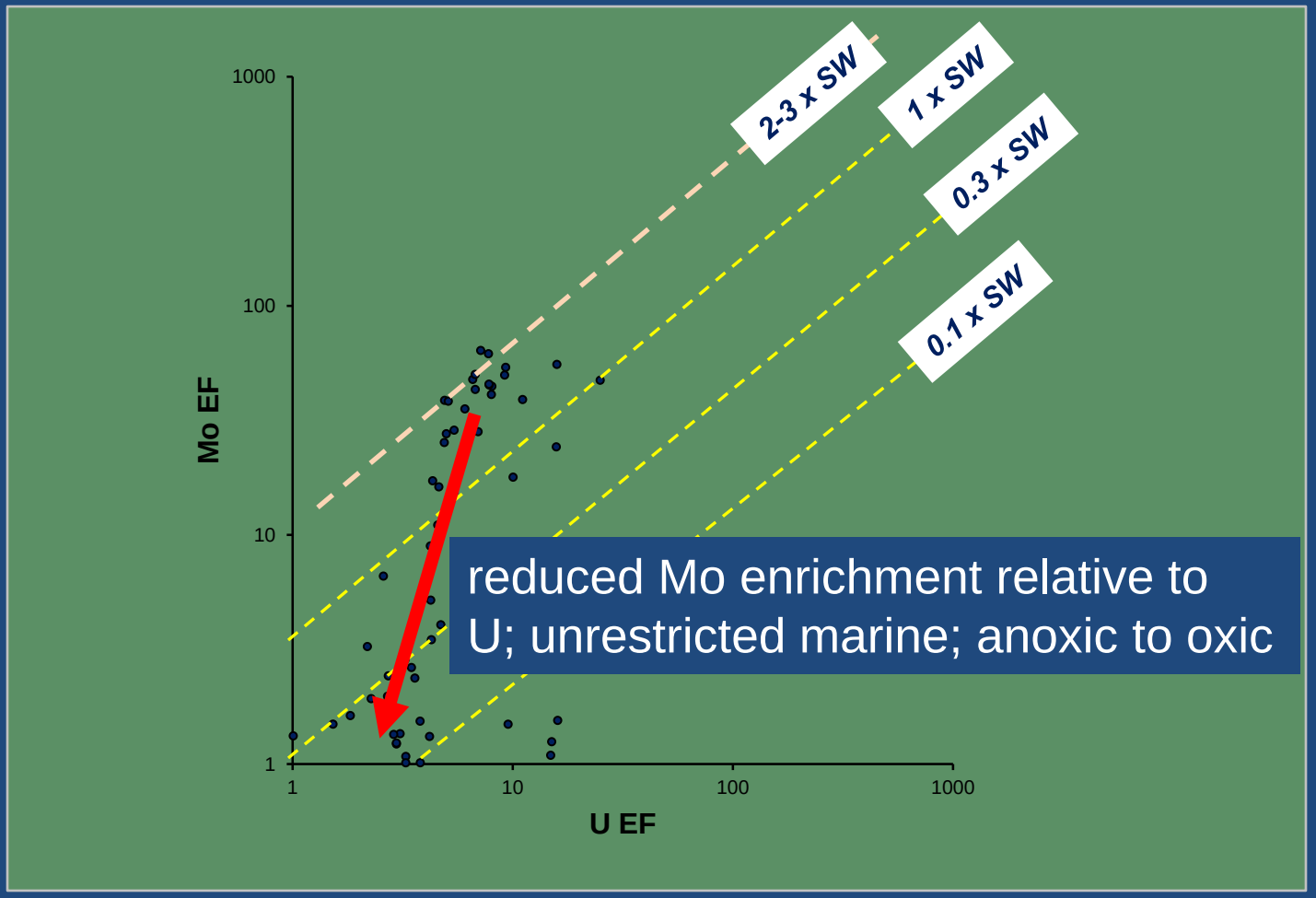
reduced Mo enrichment relative to U;



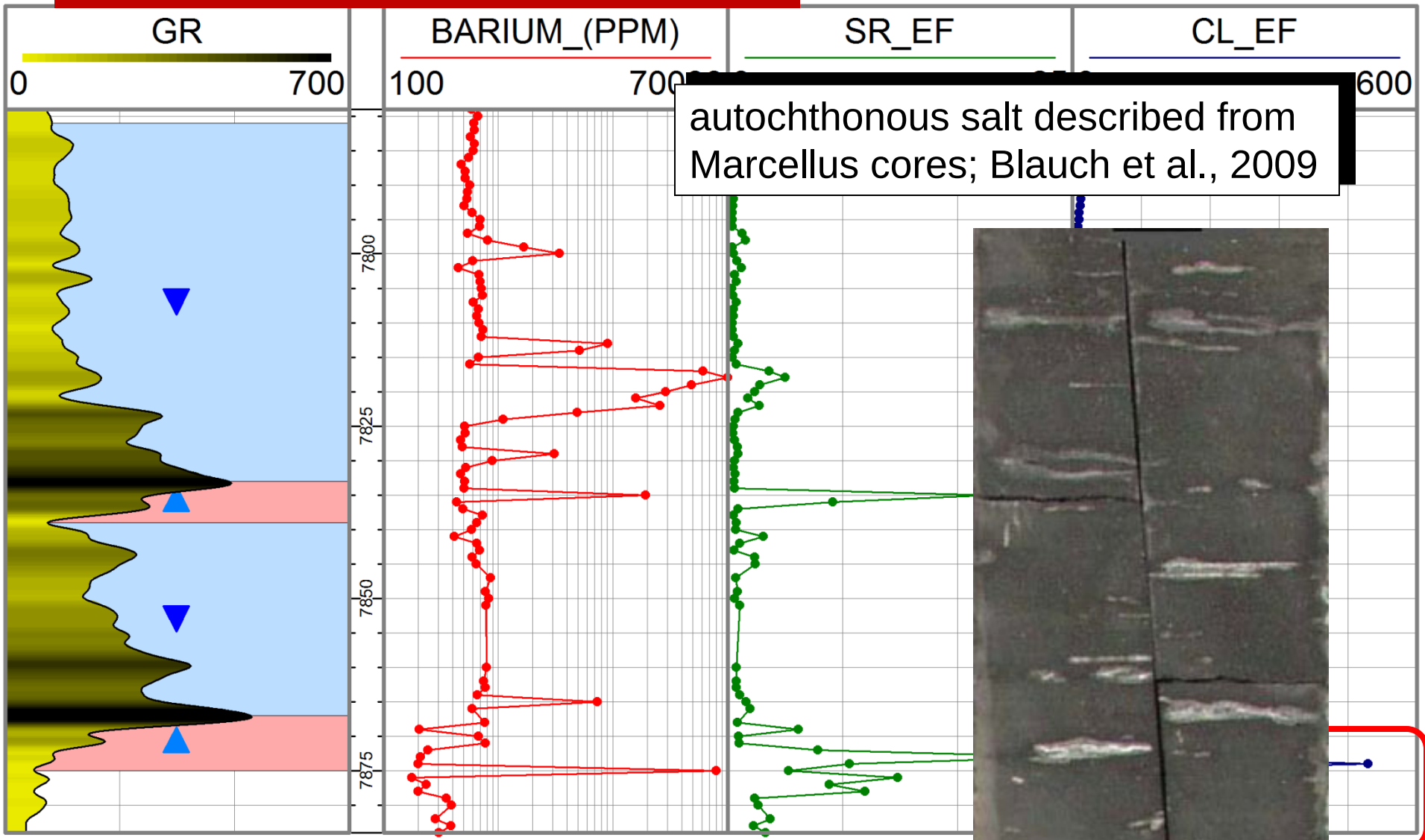
markedly reduced Mo enrichment relative to U; unrestricted marine; shift from anoxic to suboxic (oxic) conditions

…not recognized in earlier RST deposits…

Skaneateles Formation (Hamilton Group)

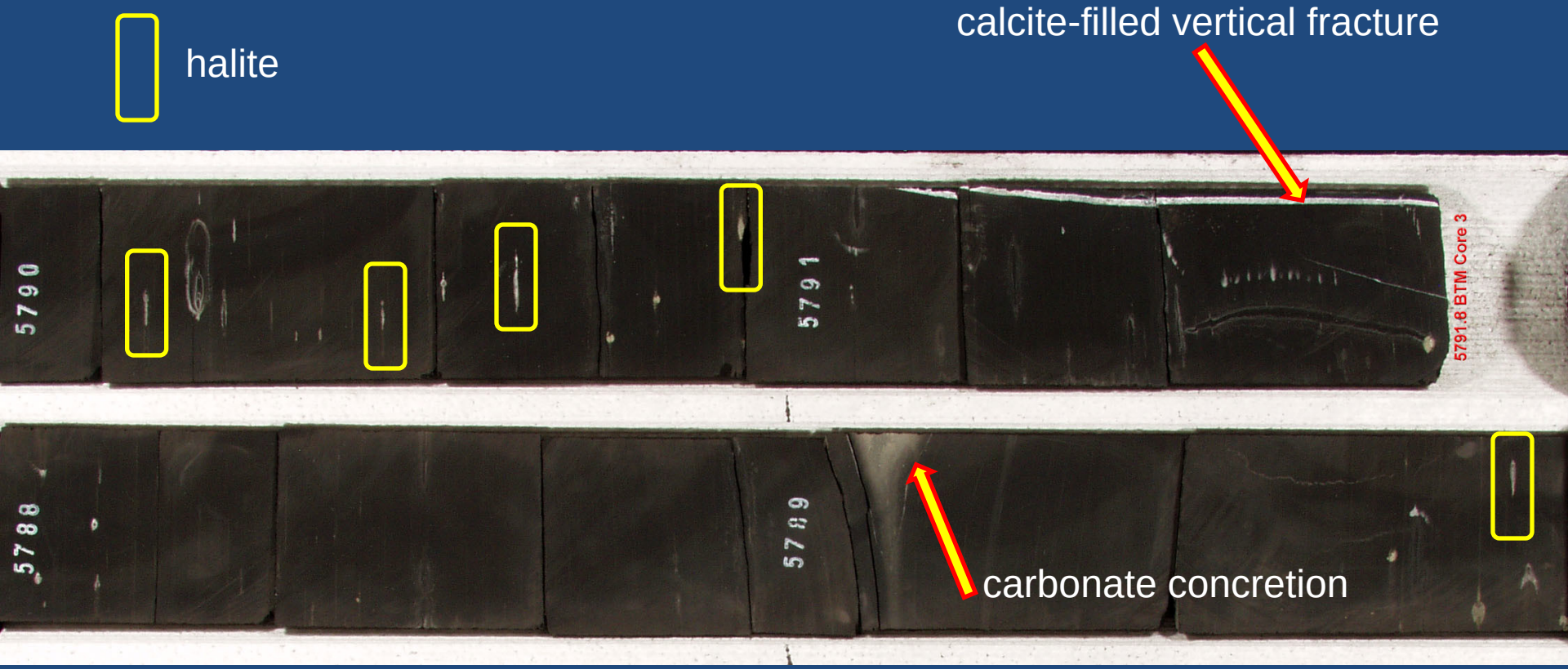


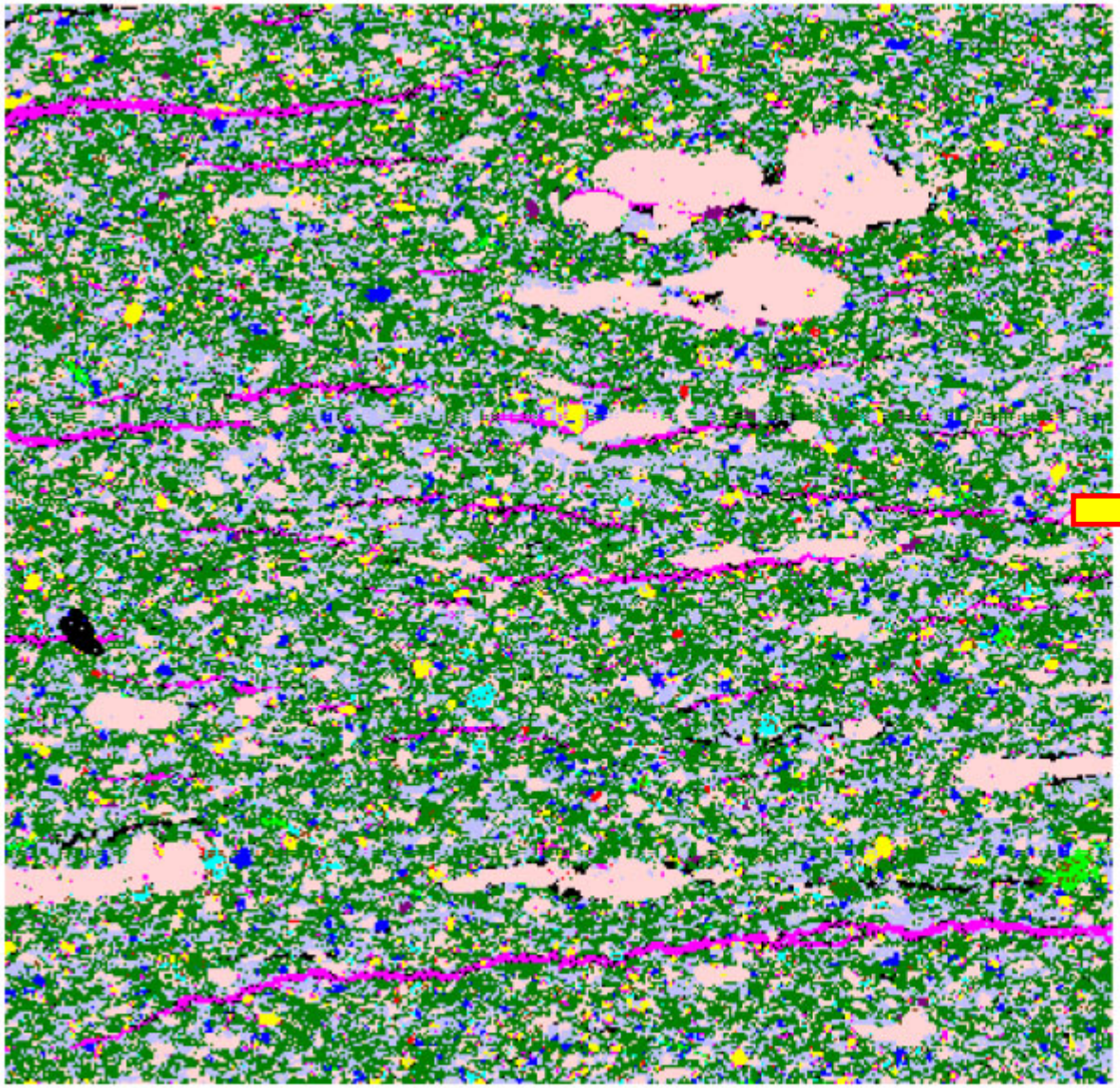
Marcellus Shale, southwestern Pennsylvania



autochthonous salt described from Marcellus cores; Blauch et al., 2009

elevated chloride

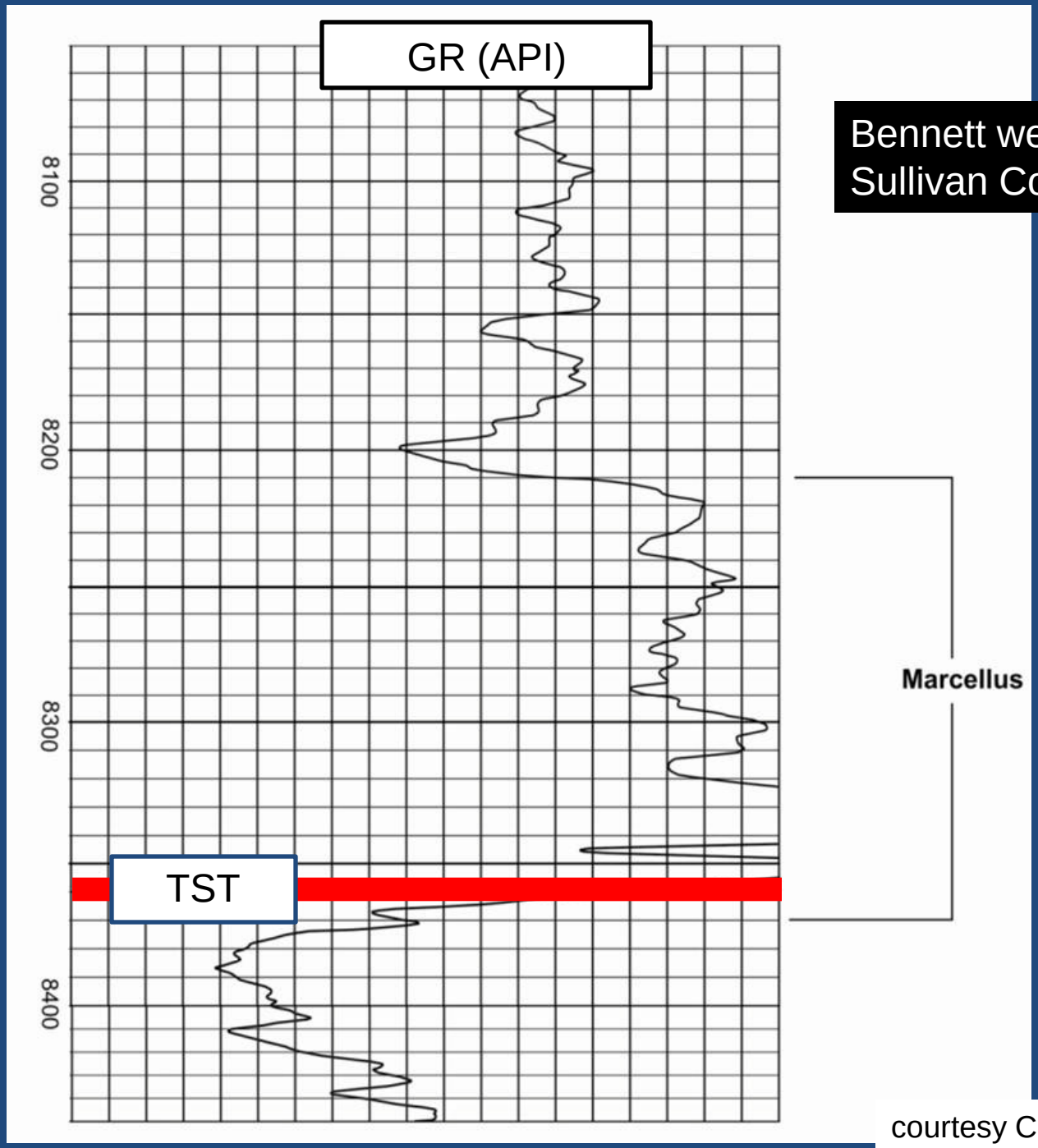

halite
calcite-filled vertical fracture
5790
5791
5791.8 BTM Core 3
5788
5789
carbonate concretion



1mm, EDX every 2.5micron

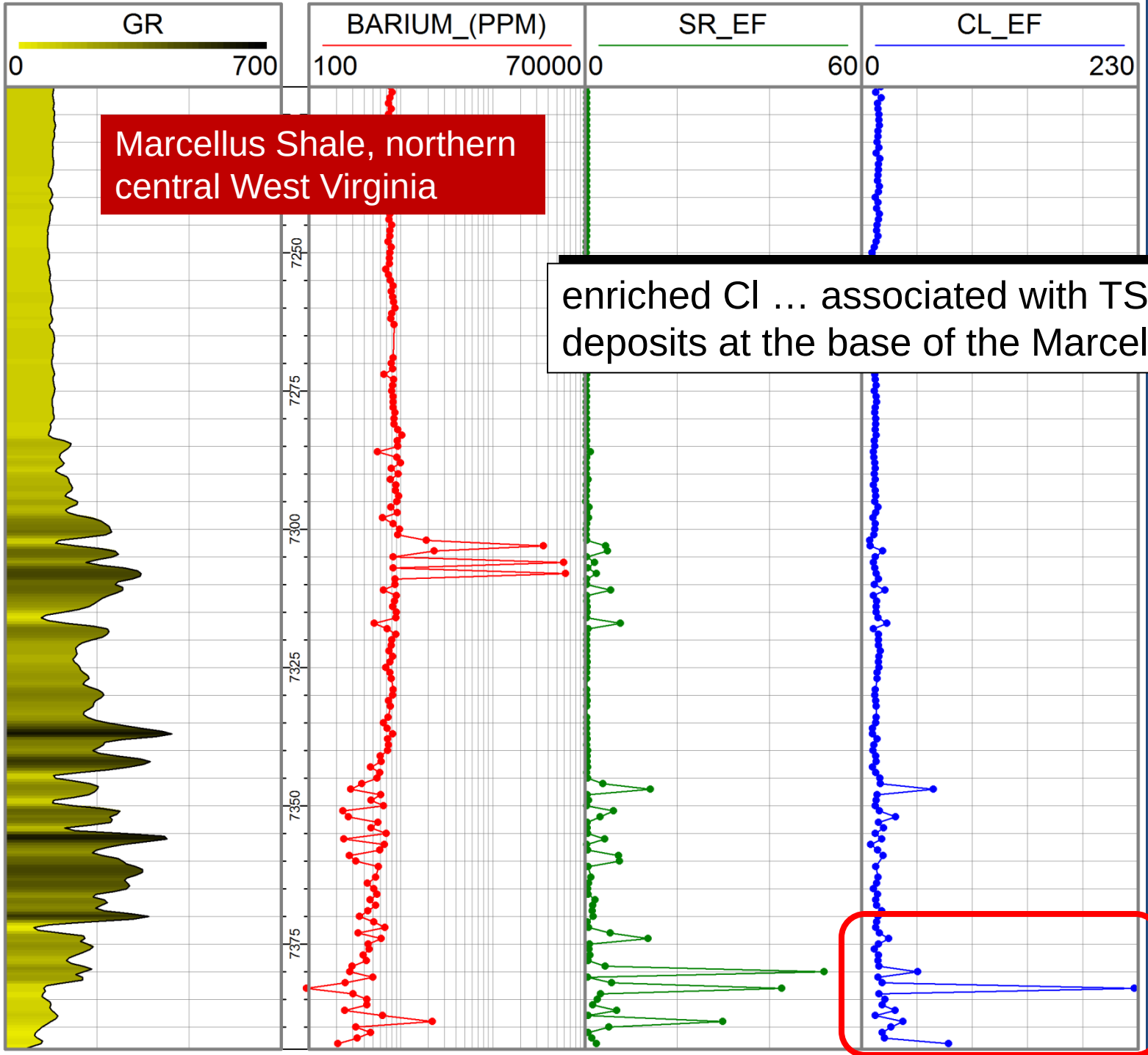
- Background
- Illite
- Quartz
- Calcite
- Alkali Feldspar
- Plagioclase Feldspar
- Chlorite
- Dolomite
- Ankerite/Siderite
- Apatite
- Anhydrite/Gypsum
- Rutile/Anatase
- Pyrite/Marcasite
- Kaolinite
- Organics
- Others

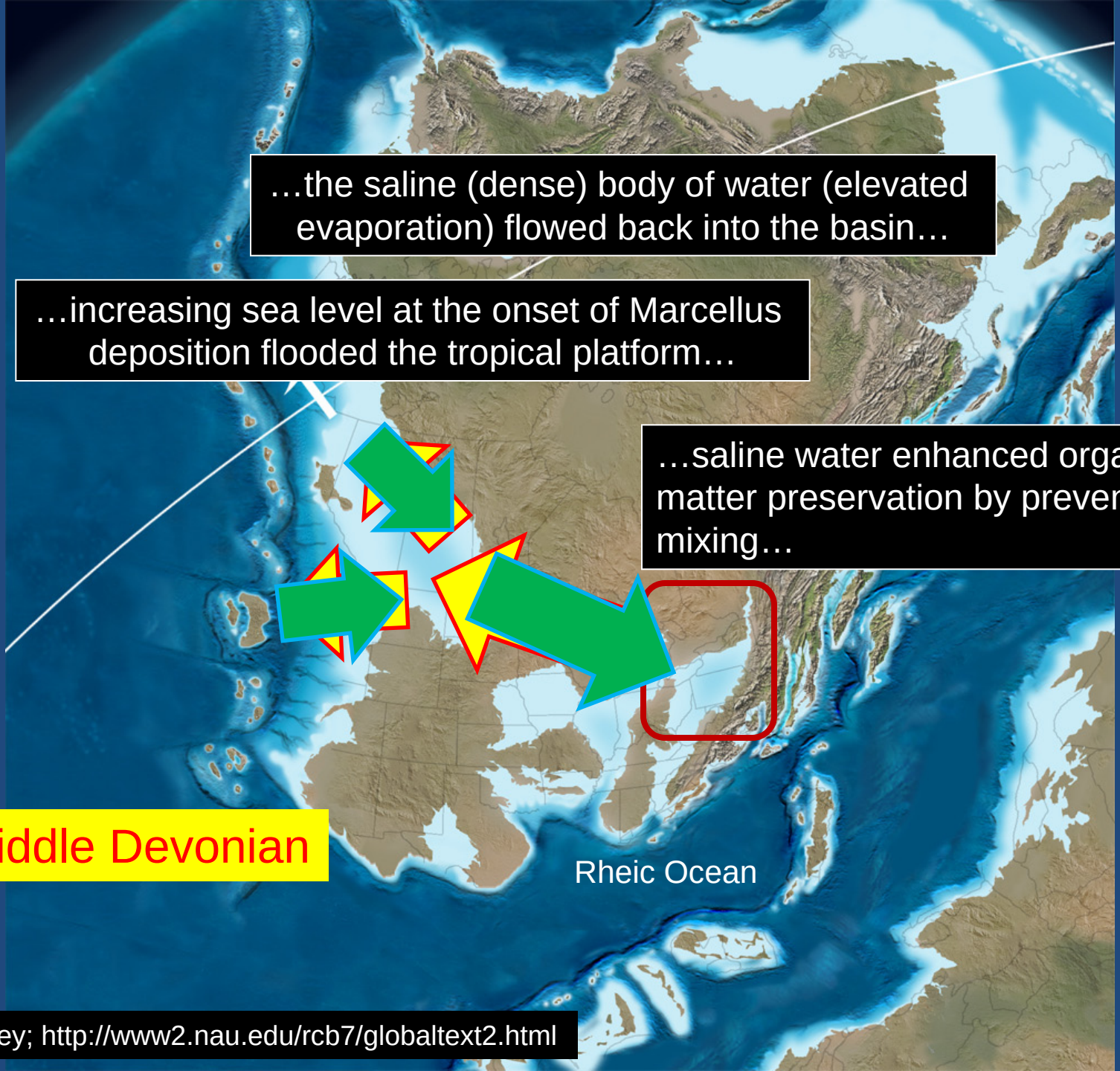
courtesy Chris Laughrey



Bennett well
Sullivan County, PA

courtesy Chris Laughrey


GR
0
700
BARIUM_(PPM)
100
70000
SR_EF
0
60
CL_EF
0
230
7250
7275
7300
7325
7350
7375
Marcellus Shale, northern central West Virginia
enriched Cl … associated with TST deposits at the base of the Marcellus



Ron Blakey; http://www2.nau.edu/rcb7/globaltext2.html

Conclusions

-Mo – U covariance of the Marcellus Shale provides no evidence of a Black Sea depositional model (i.e., isolation of the deep water mass);

-the basin was likely at least semi-connected with the global ocean enabling Mo enrichment to actually increase over the duration Marcellus deposition;

-covariance of Mo and U enrichment in the Marcellus is most consistent with a particulate shuttle mechanism as a means of accelerating Mo transport to the sea floor;

-the particulate shuttle requires a threshold" level of H_2S in the water column (periodically euxinic conditions) to "activate" the Mo;

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;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