Deposition, Diagenesis and Hydrocarbon Generation in the Ordovician Point Pleasant Limestone and the Devonian Marcellus Shale:

Comparing and Contrasting Two Appalachian Basin Unconventional Reservoirs*

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Editor's note: For the presentation at the Eastern Section Meeting, the author received the EMD Ralph L. Miller Best Paper Award and the Pittsburgh Geological Society award for Best Presentation on Appalachian Geology. Further, for a somewhat shorter version presented at the 2018 AAPG Annual Convention &Exhibition in Salt Lake City, Utah, the author received the Energy Minerals Division Frank Kottlowski Memorial Award as the best paper presented.

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Abstract

Appalachian Basin shale gas has now become a well known component of U.S. natural gas production. Indeed, as of 2015, Pennsylvania accounted for 18% of domestic dry natural gas production, driven largely by the Devonian Marcellus Shale, and to a lesser extent, the Ordovician Point Pleasant Limestone. While these two shale plays display similar production mechanisms, the conditions under which these deposits accumulated were markedly different. Vertical chemostratigraphic profiles and pyrite morphology trends were developed on core taken from both formations. The Marcellus exhibits enrichments in redox sensitive trace elements, a framboid population detailing abundant small, <5 µm framboids, with subordinate large framboids, and occasional bioturbation. These observations suggest that sediments accumulated under dominantly anoxic to euxinic bottom waters that were occasionally subjected to periods of (dys)oxia. The high total organic carbon content of the Marcellus is the result of increased preservation, due in part to favorable oxygen-depleted conditions, while concentration was controlled by dilution from clastic influx. Conversely, the Point Pleasant comprises mudstones and marls largely devoid of redox sensitive trace elements, with minimal pyrite, a paucity of iron, and a number of in situ shell bed horizons. These observations suggest the Point Pleasant accumulated under oxic to dysoxic bottom water conditions. Further, the lack of biolimiting iron, and lower preservation potential due to oxidation of organic matter, yielded a formation of lower organic carbon concentration, where preservation occurred via rapid burial. It is noteworthy that, despite the lower organic carbon content, the Point Pleasant hosts a pore pressure gradient far in excess of that observed in the Marcellus. While expulsion fractures, including Mode I vertical catagenic fractures, are common to the Marcellus, they are infrequent to absent in the Point Pleasant study area. One explanation is that the pressure needed to overcome the compressive stress carried by higher modulus, carbonate-rich sediments was never achieved, thus limiting fracturing and hydrocarbon expulsion and preserving its high pressure. Conversely,

stress build-up from pore pressure resulting from hydrocarbon generation in lower modulus, more clay-rich Marcellus sediments achieved the tensile strength of the rock causing it to fracture and release hydrocarbons, subsequently lowering its pressure.

Selected References

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46th Annual meeting of the Eastern Section AAPG

EASTERN SECTION AAPG MORGANTOWN 2017
BEASTS OF THE EAST
UNCONVENTIONAL SHALES

AAPG

Randy Blood
9/26/2017

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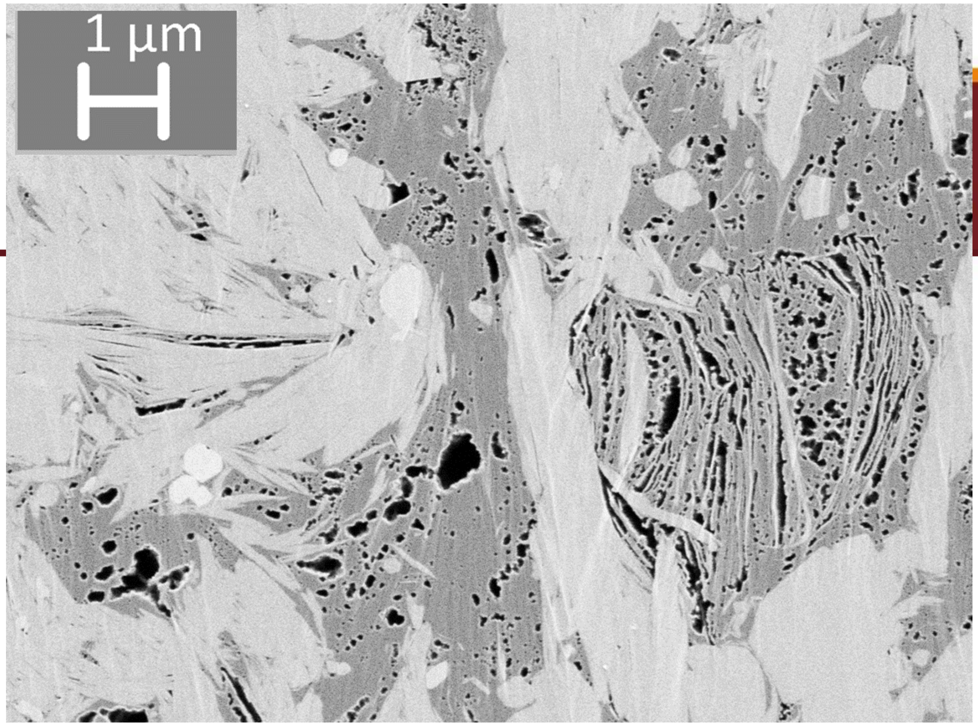
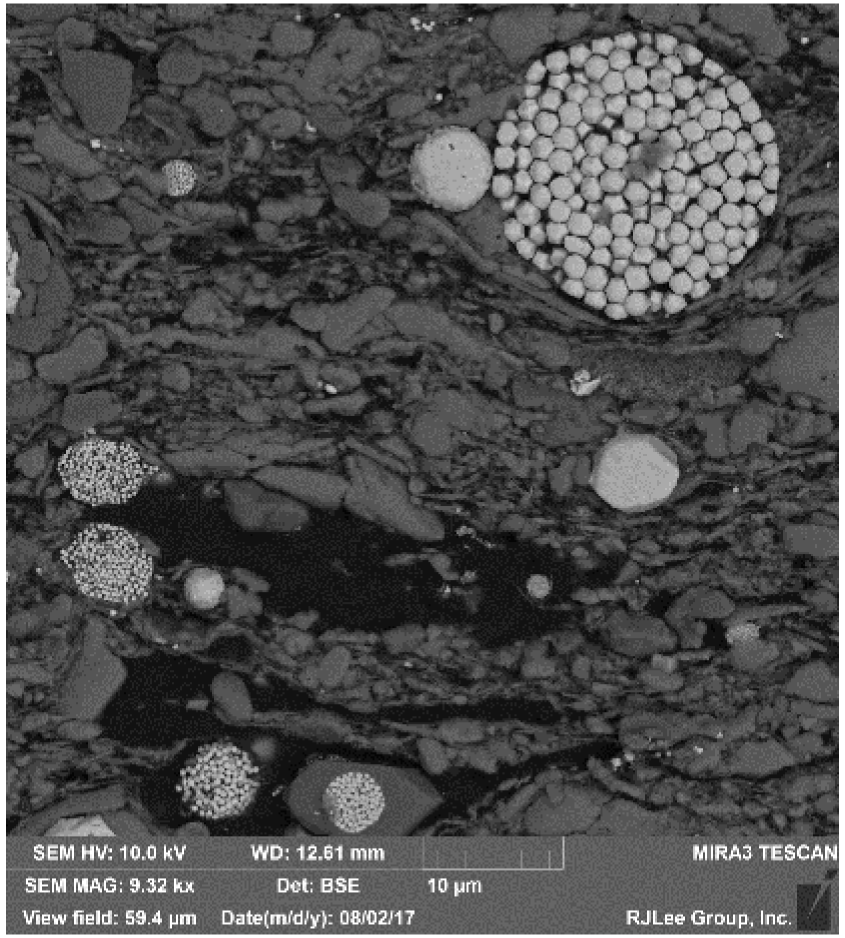
"Science is a collaborative effort. The combined results of several people working together is often much more effective than could be that of an individual scientist working alone."

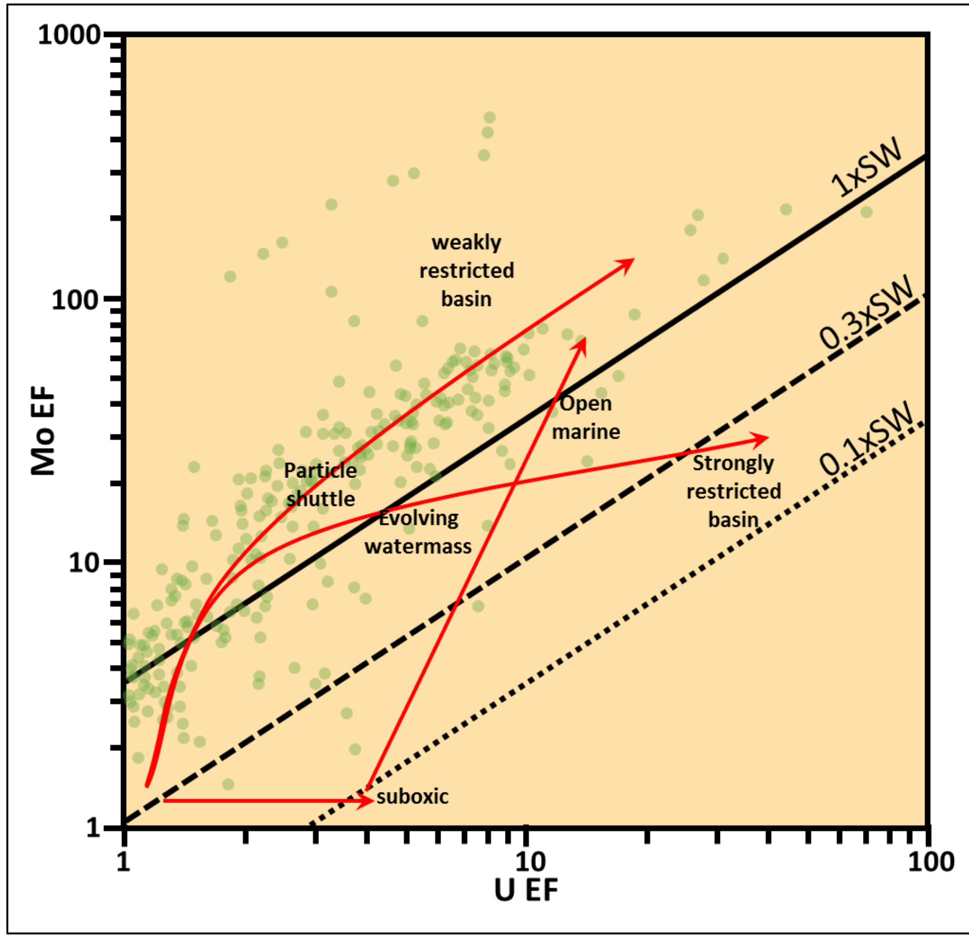
-John Bardeen
2nd Nobel Prize Speech, 1972

Outline

- Production Mechanisms
- Inorganic geochemistry considerations
- Pyrite morphology
- Discussion
- Conclusions







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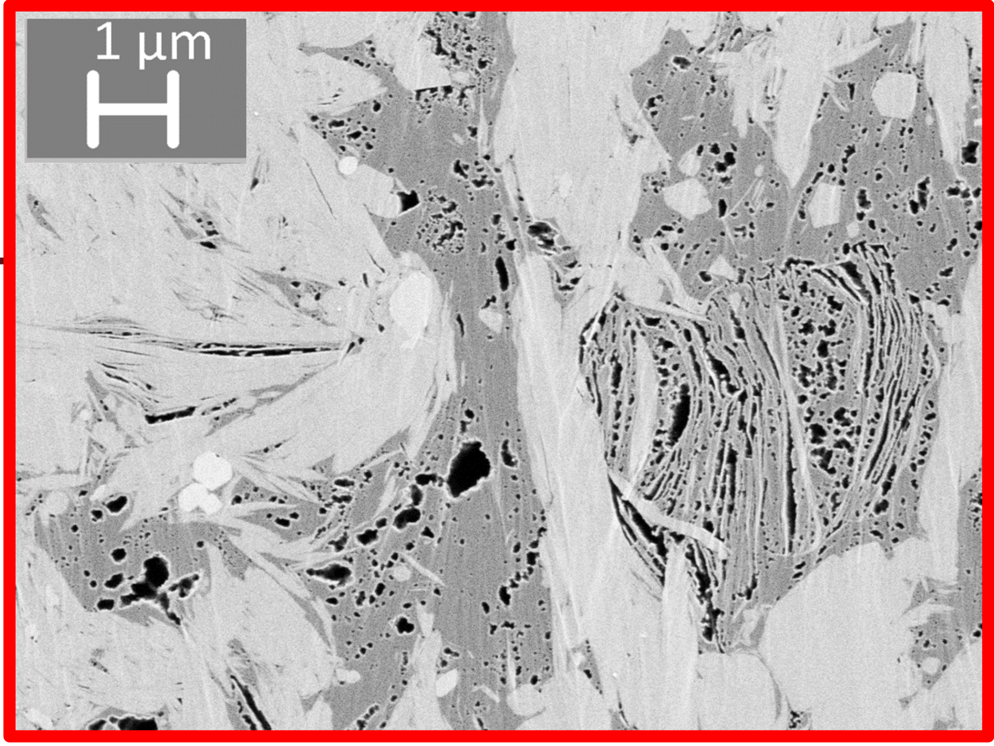
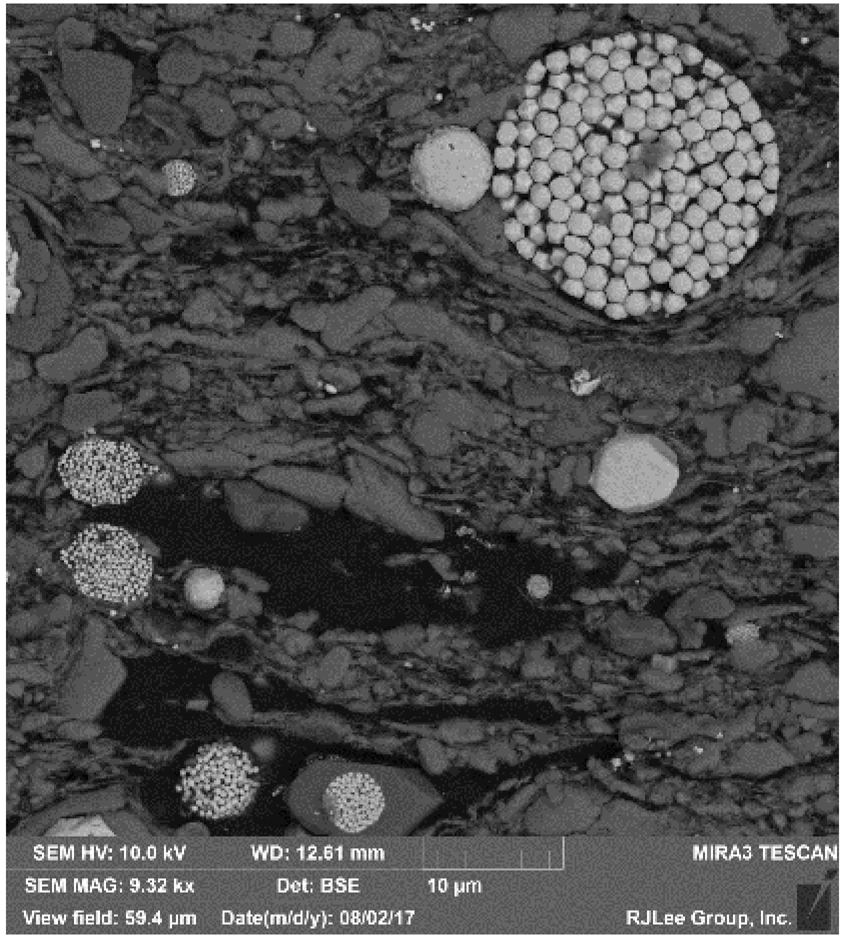
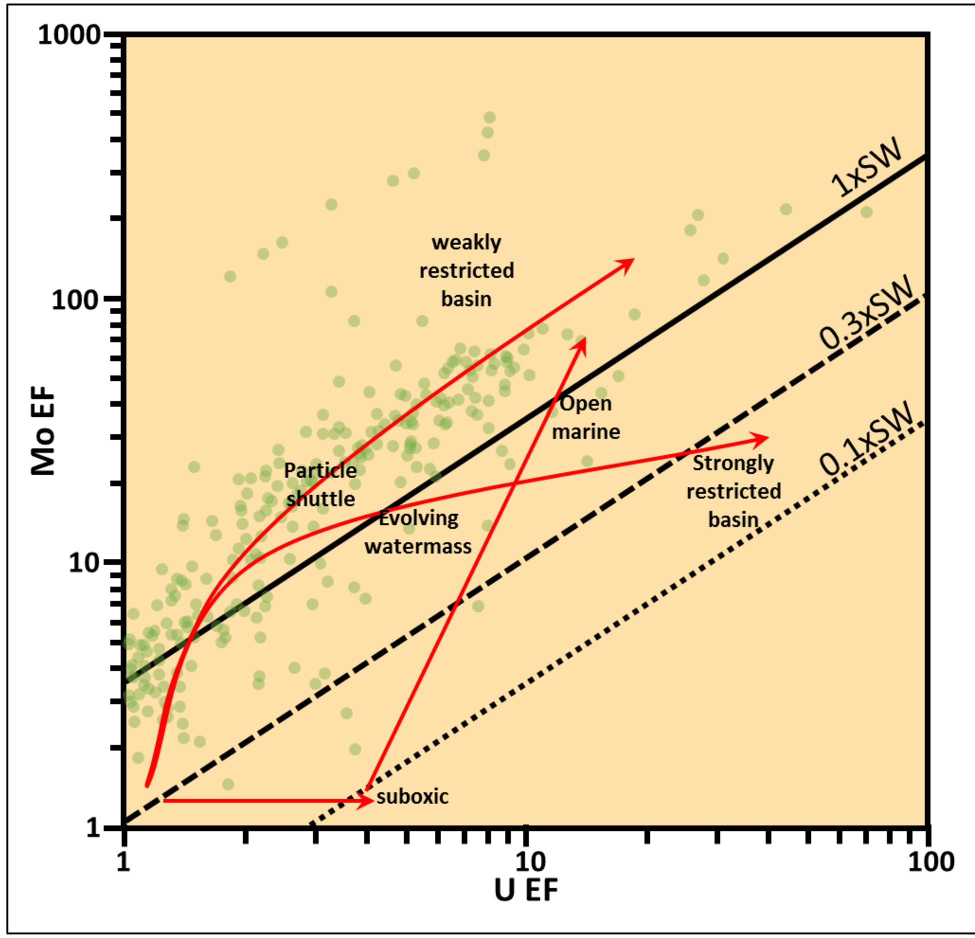


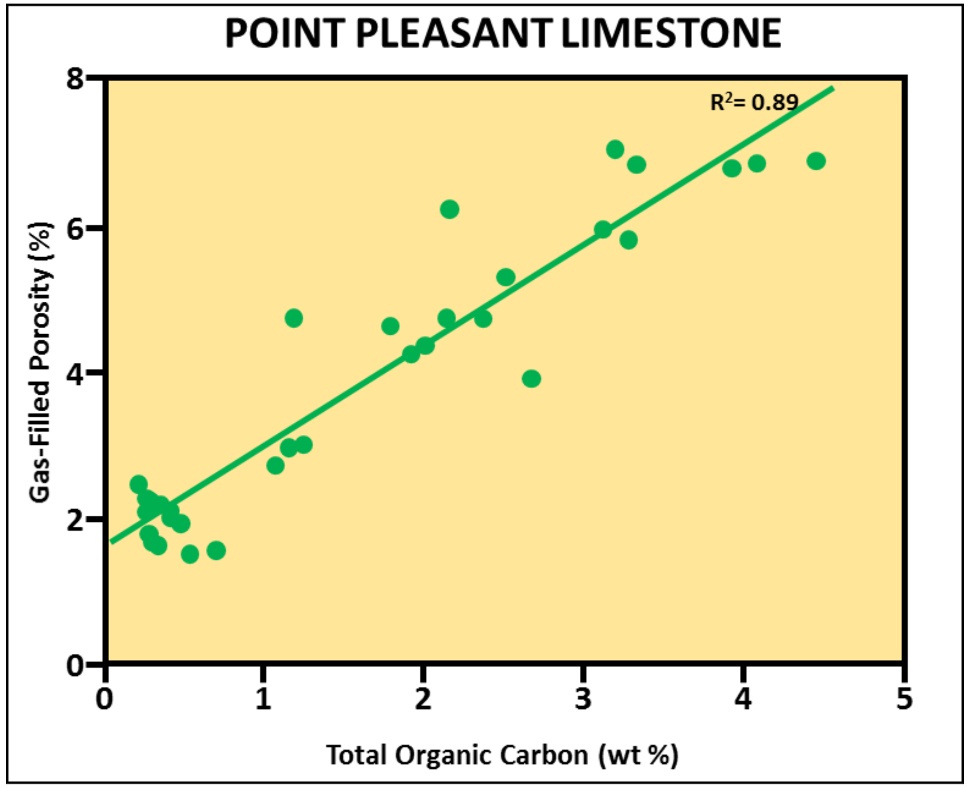


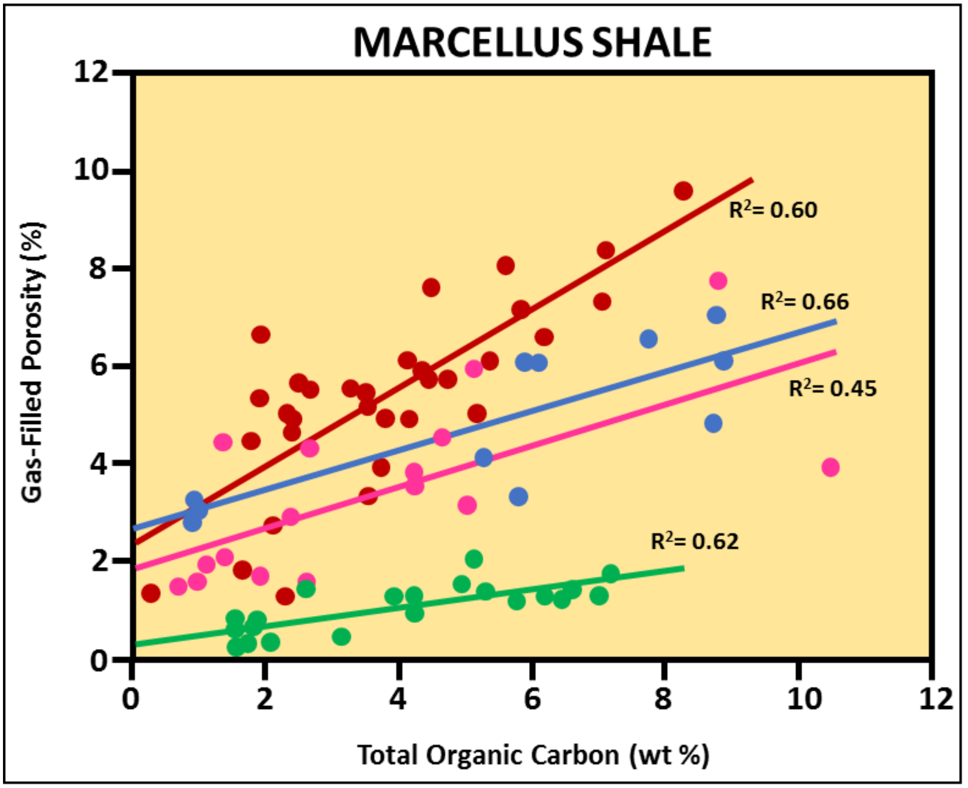


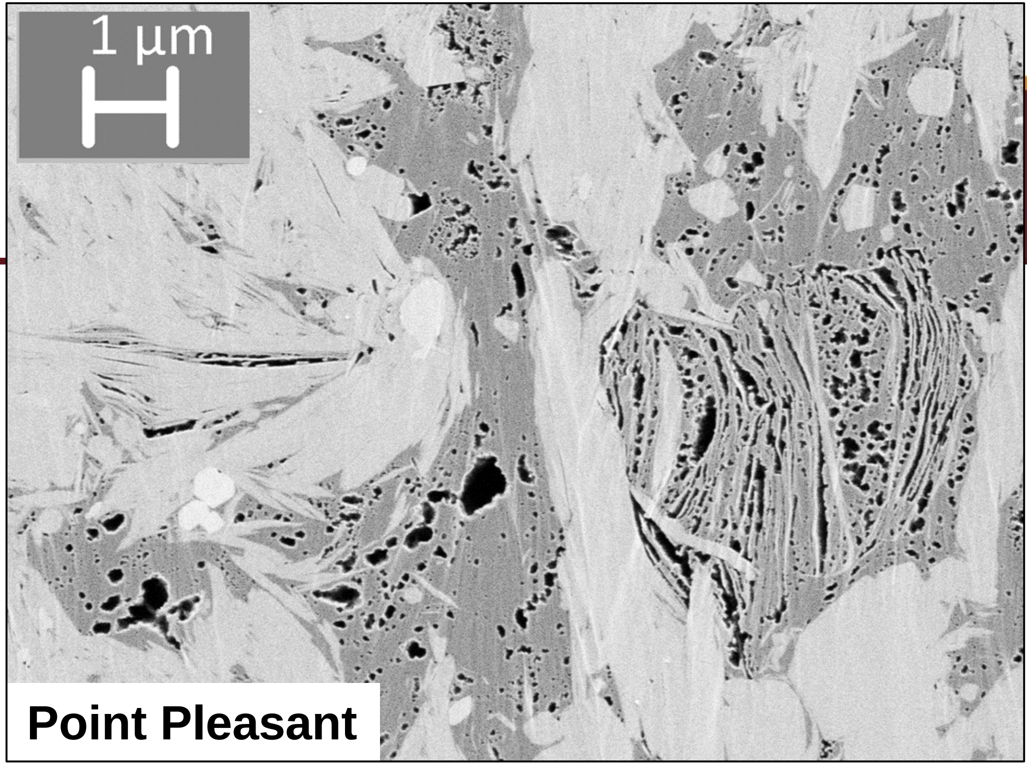
Production Mechanism

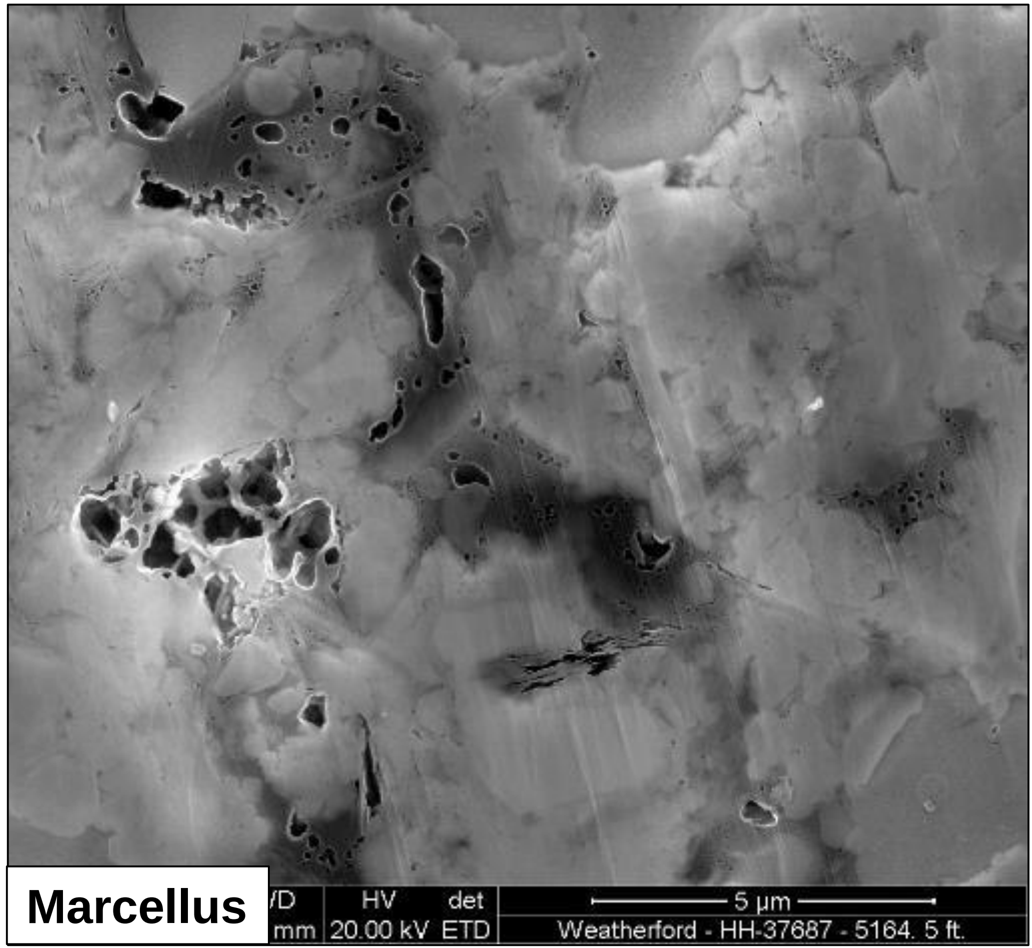
Organic porosity and why TOC preservation matters

- **In both the Point Pleasant and Marcellus organic matter hosts the majority of porosity.**
- **Indeed, a strong correlation exists between gas-filled porosity and TOC.**
- **Reservoirs are self-sourcing, the original TOC represents the starting material for hydrocarbon generation.**









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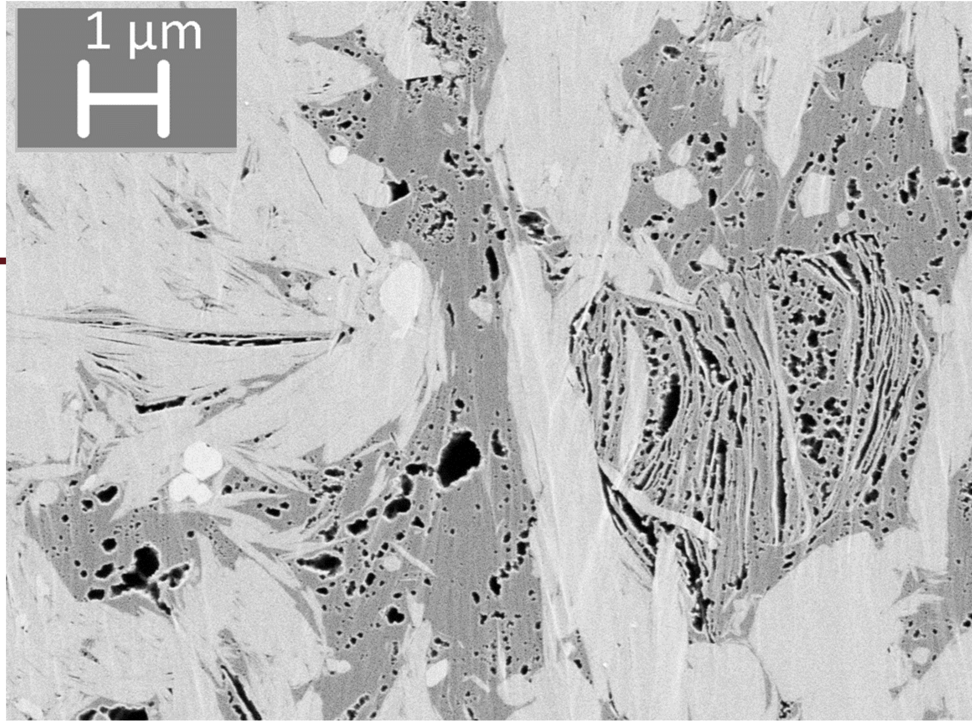
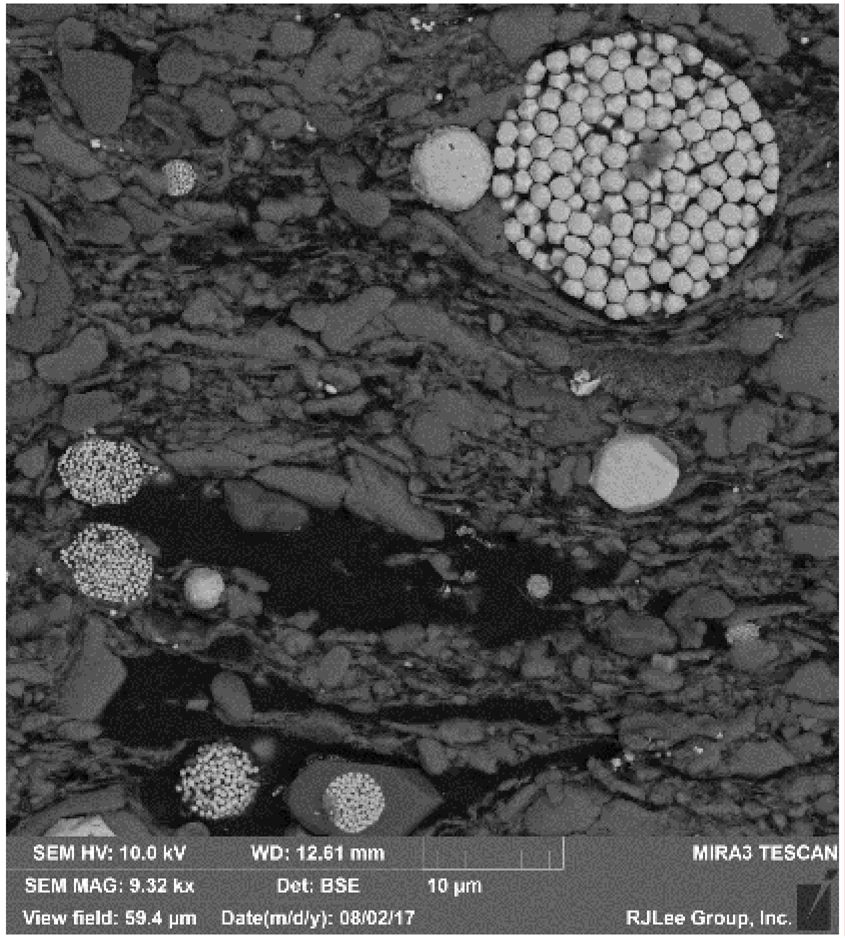
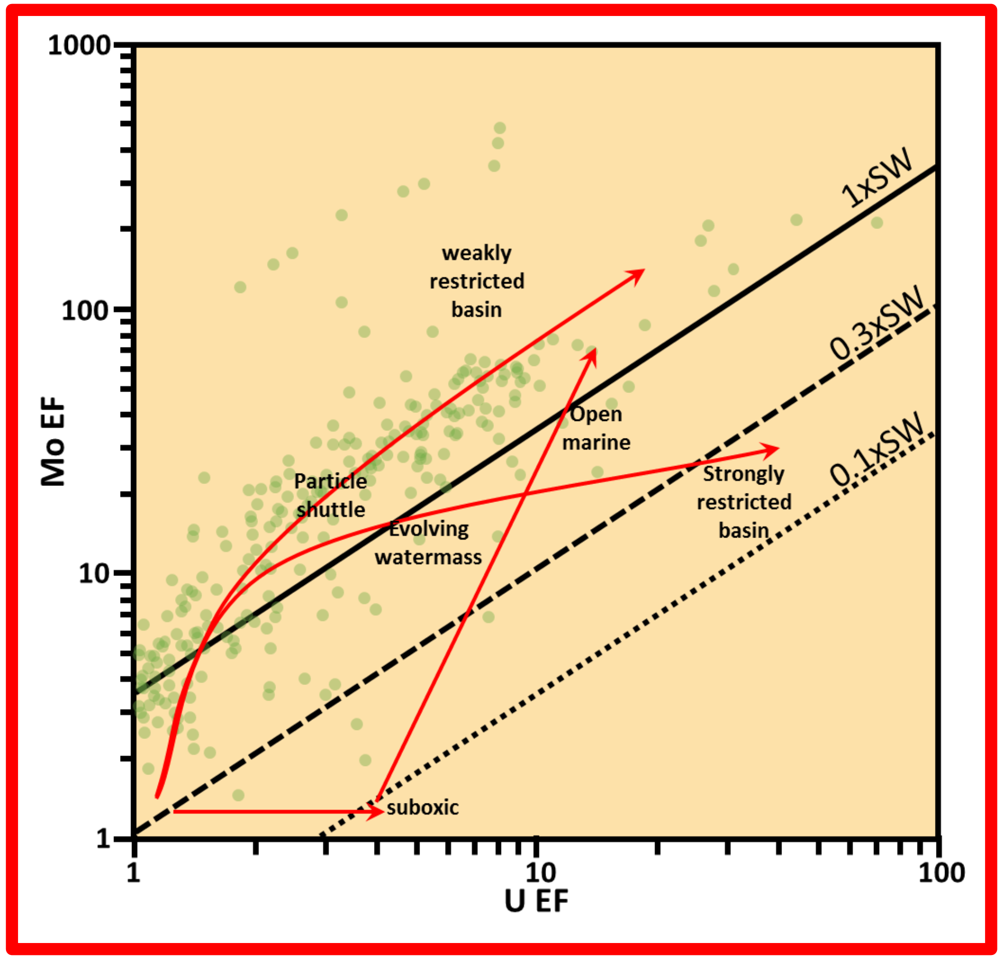
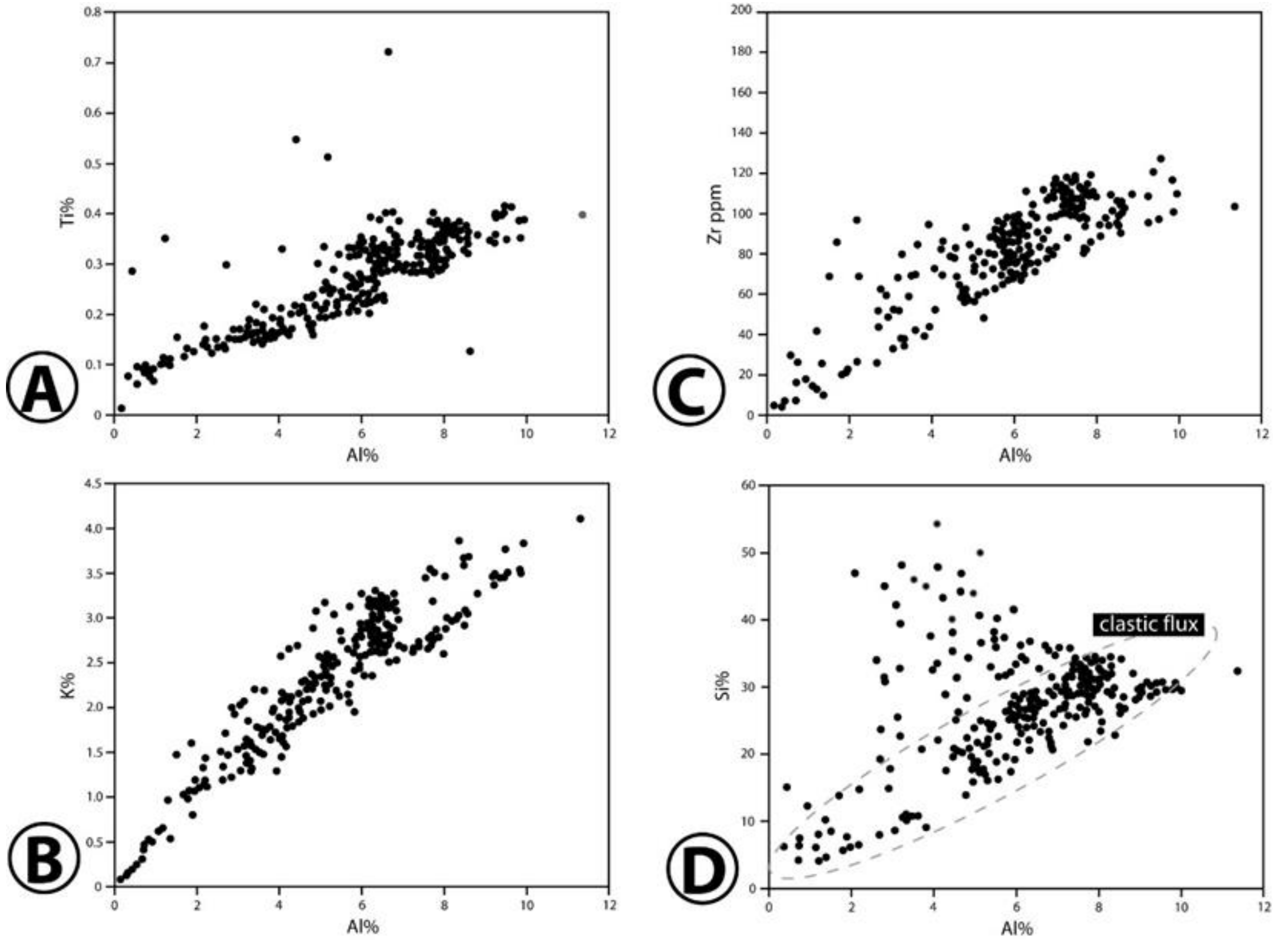






Al normalization and Enrichment factors

Applications of elemental data



- 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 grain size and energy of sediment delivered to the basin.

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

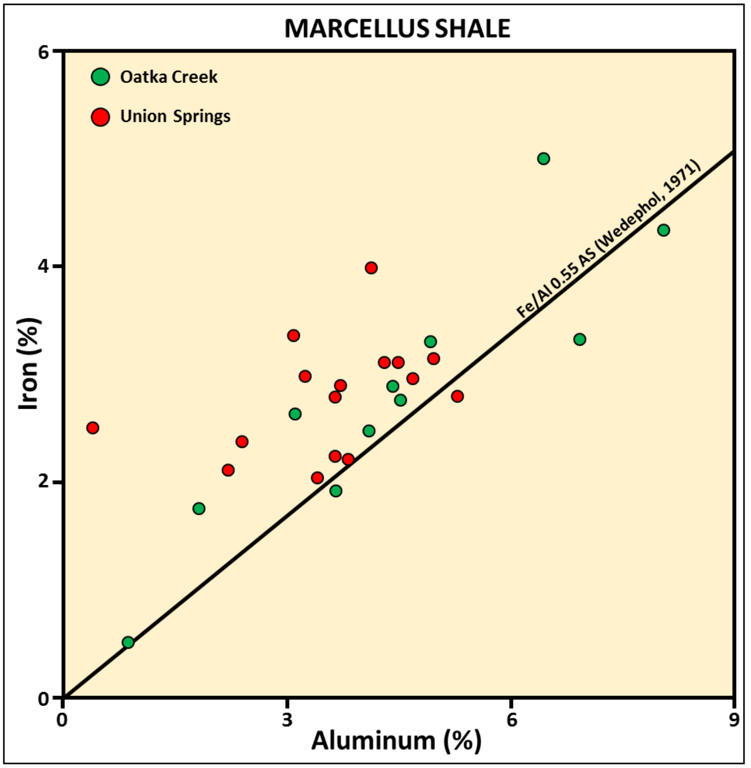
- Elemental data commonly cast as an enrichment factor.

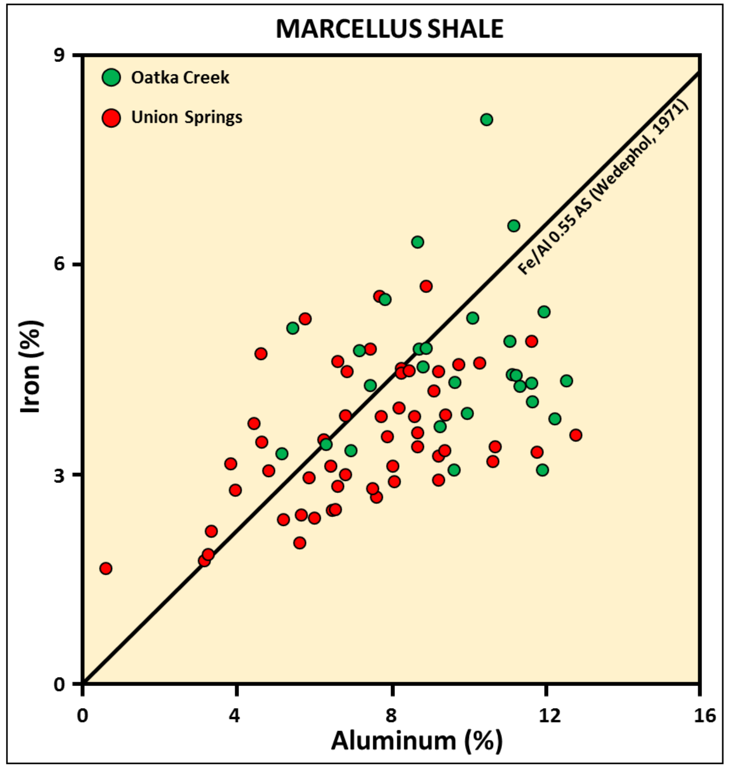
- The element is normalized to the Al content of the sample
  - Accounts for an increase in abundance due to increased sediment supply
- The element/Al is then normalized to the average shale value (Wedephol 1971, 1991).
  - Unity implies elemental abundance is typical of shales
  - EF>3 implies significant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

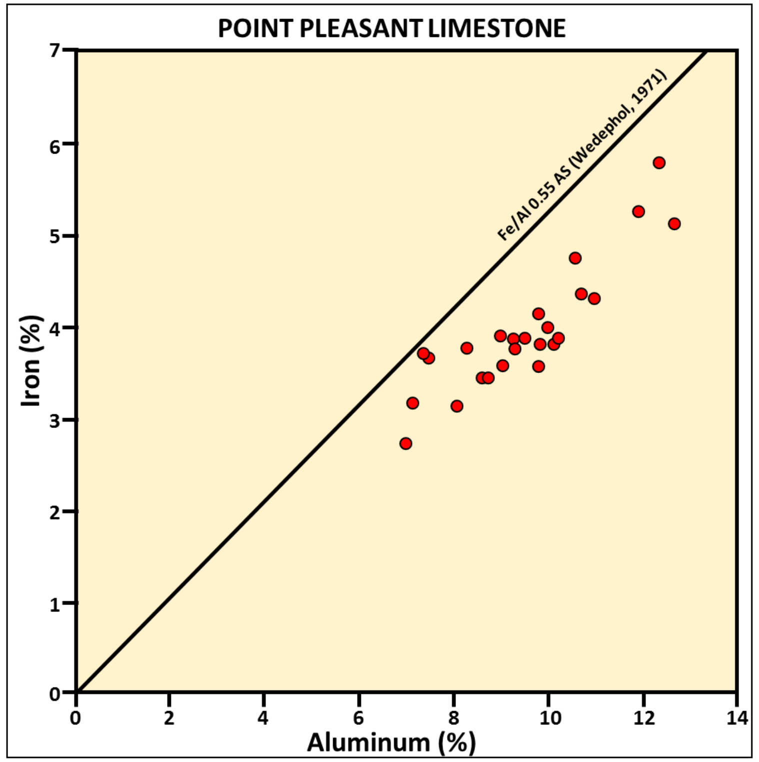
Fe/Al ratio

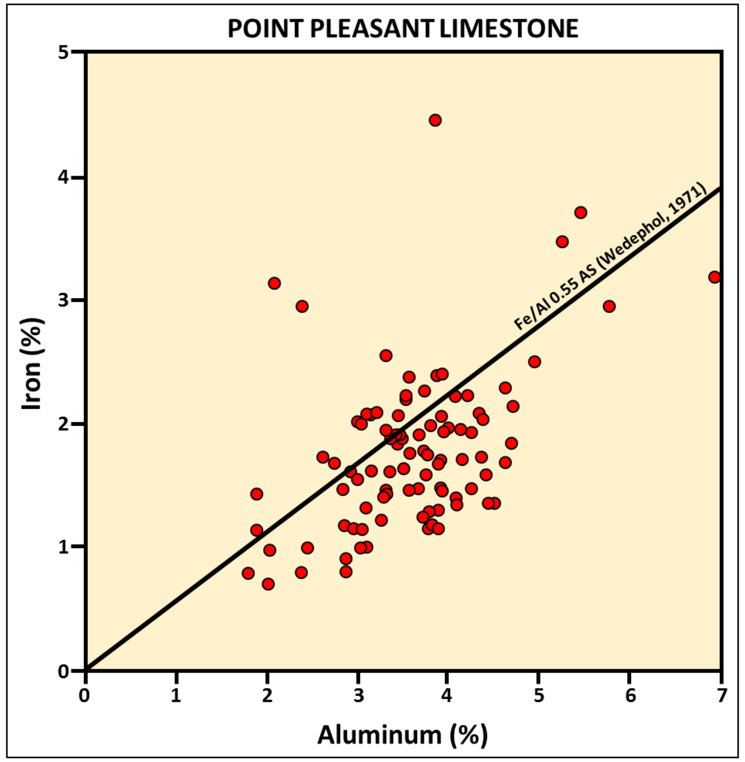
Fe sequestration in pyrite

- **Enrichment of Fe/Al (> average shale value 0.55) → sequestering of reactive iron as pyrite → anoxic/euxinic conditions**
  - **Fe often decoupled from Al.**
  - **Where clastic influx swamps the reactive Fe with less reactive detrital Fe, Fe/Al is often lower under euxinic conditions**
- **The Point Pleasant Fe/Al ranges from 0.42 - 0.45**
  - **suggestive of oxic/dysoxic conditions.**
- **Marcellus Fe/Al ranges from 0.55 - 0.76**
  - **suggesting anoxic/euxinic conditions.**
  - **Lower Fe/Al likely depict swamping of reactive Fe signal.**





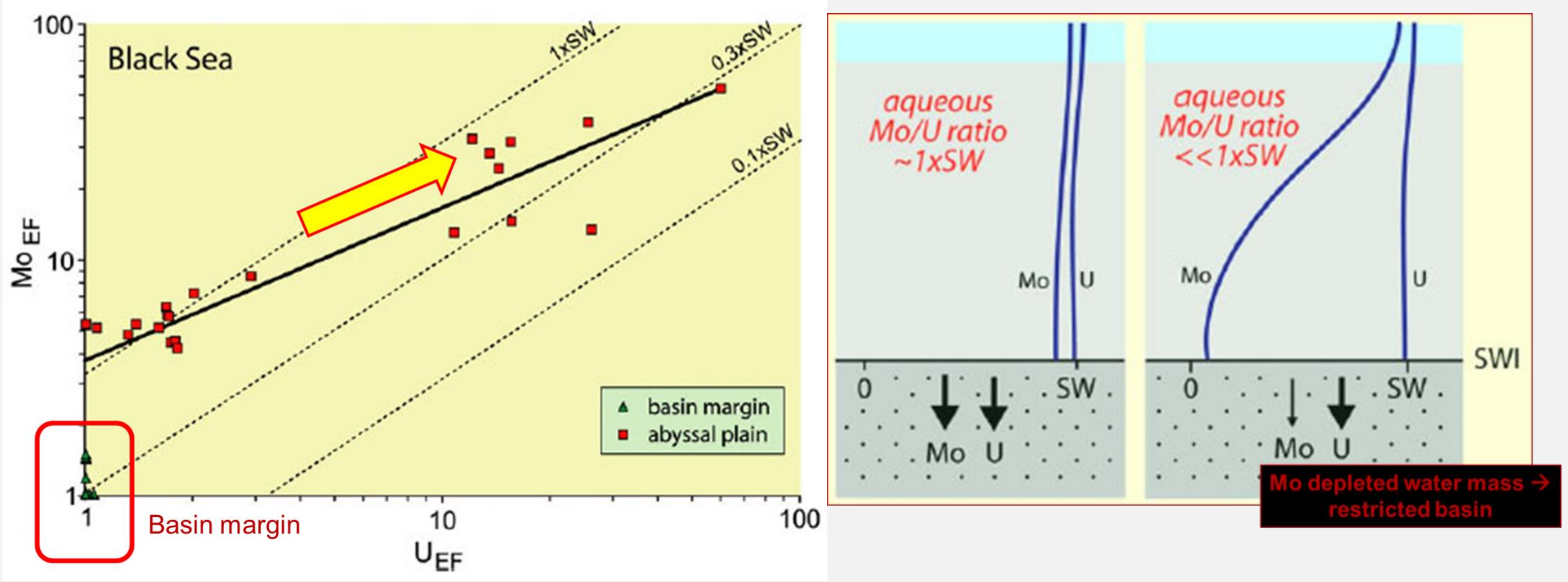




U EF Mo EF

Redox history as recorded by Molybdenum and Uranium

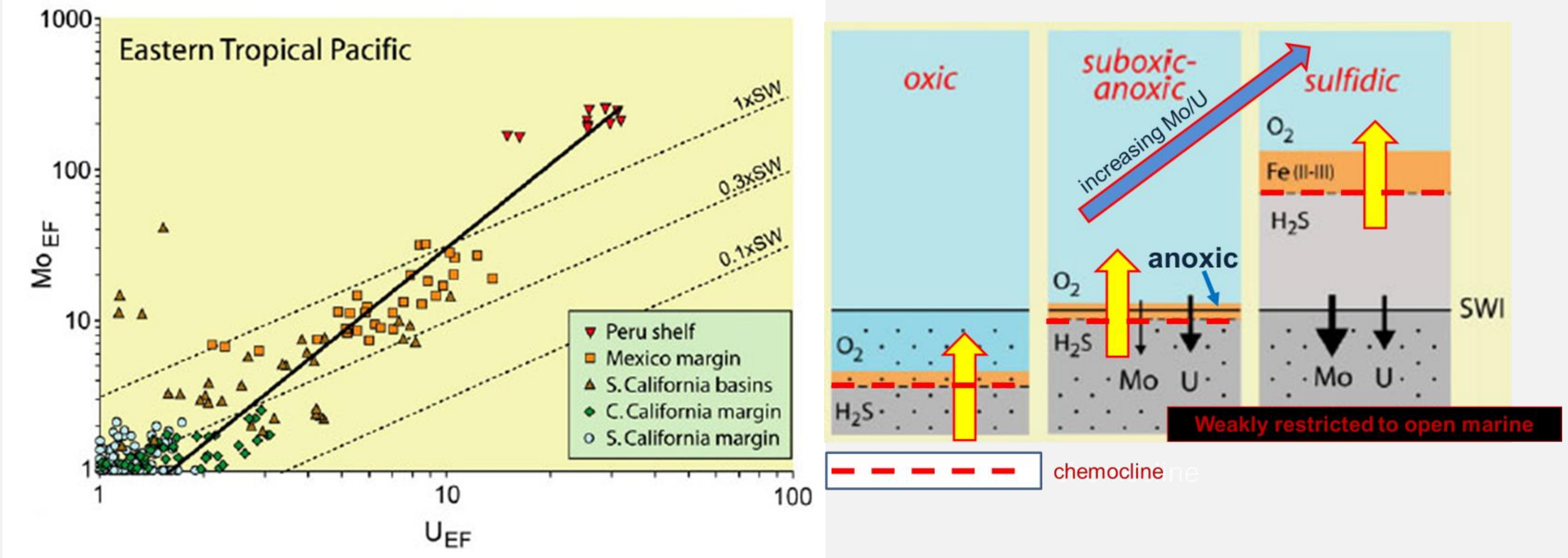
Algeo and Tribovillard, 2009



Basin margin

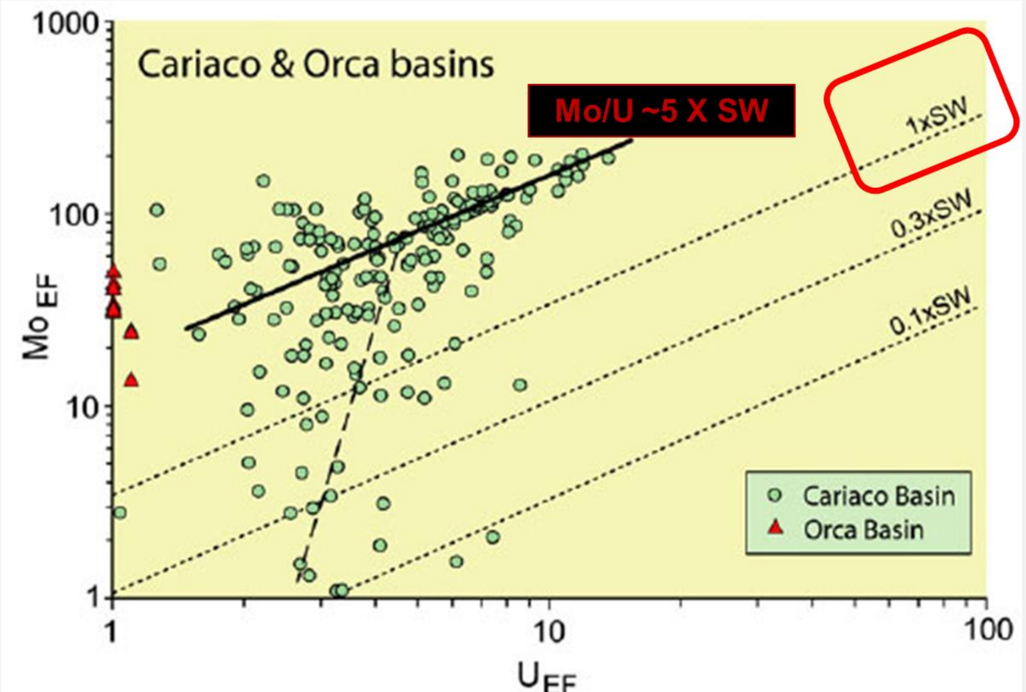
Mo depleted water mass → restricted basin

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



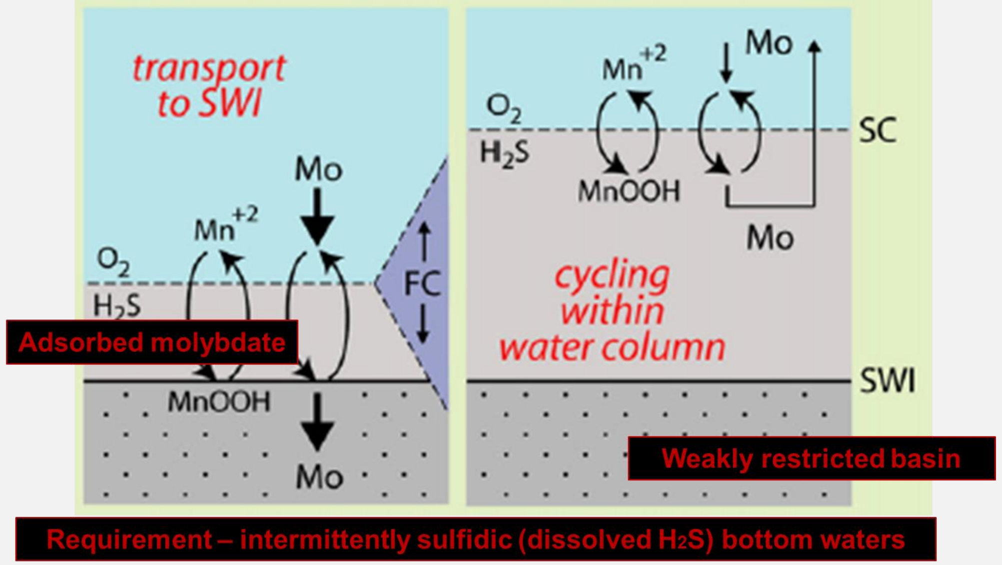
Weakly restricted to open marine

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



Mo/U ~5 X SW

Considerable enrichment of Mo relative to U



Adsorbed molybdate

Weakly restricted basin

Requirement – intermittently sulfidic (dissolved H2S) bottom waters

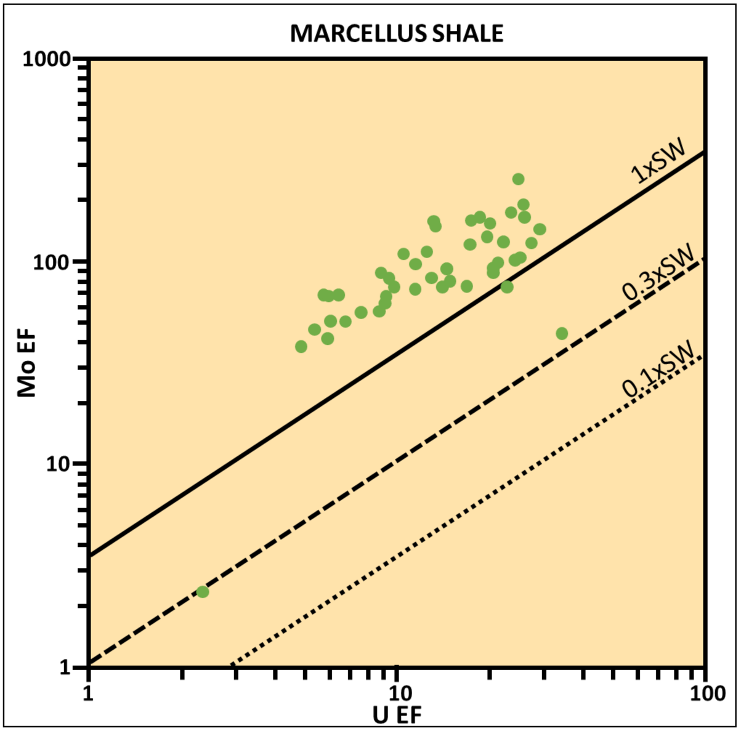
U EF Mo EF

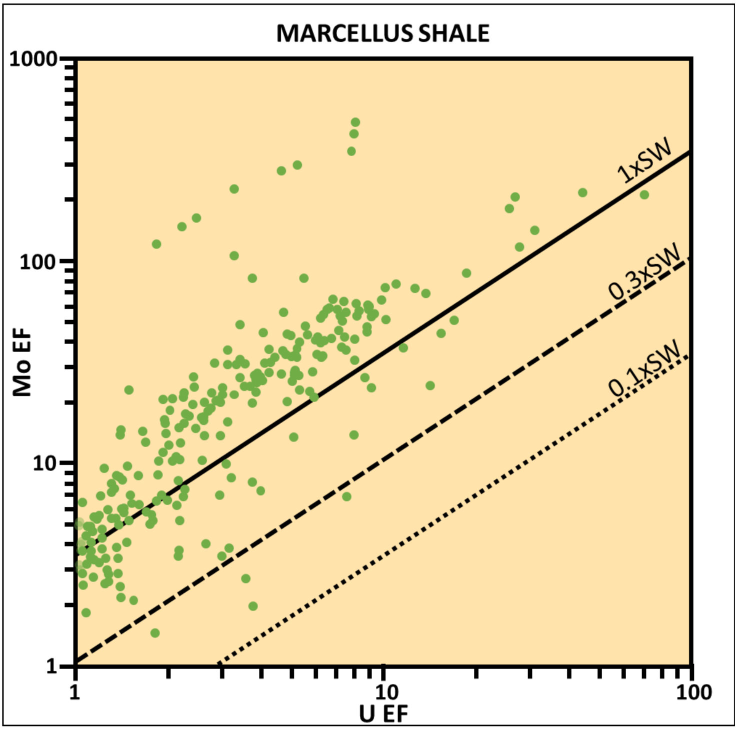
Redox history as recorded by Molybdenum and Uranium

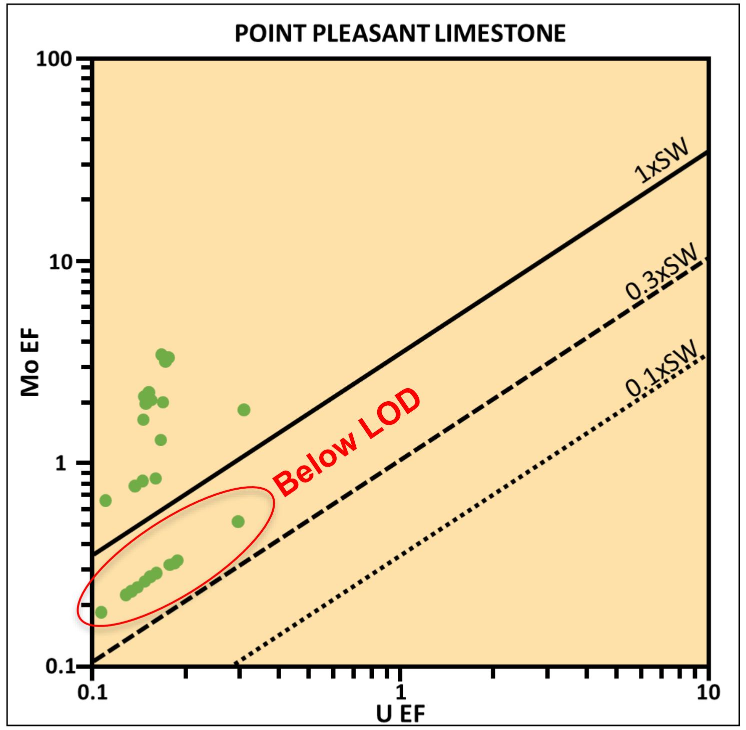
- **Point Pleasant depleted values**
  - **Indicative of oxic-dysoxic bottom water**

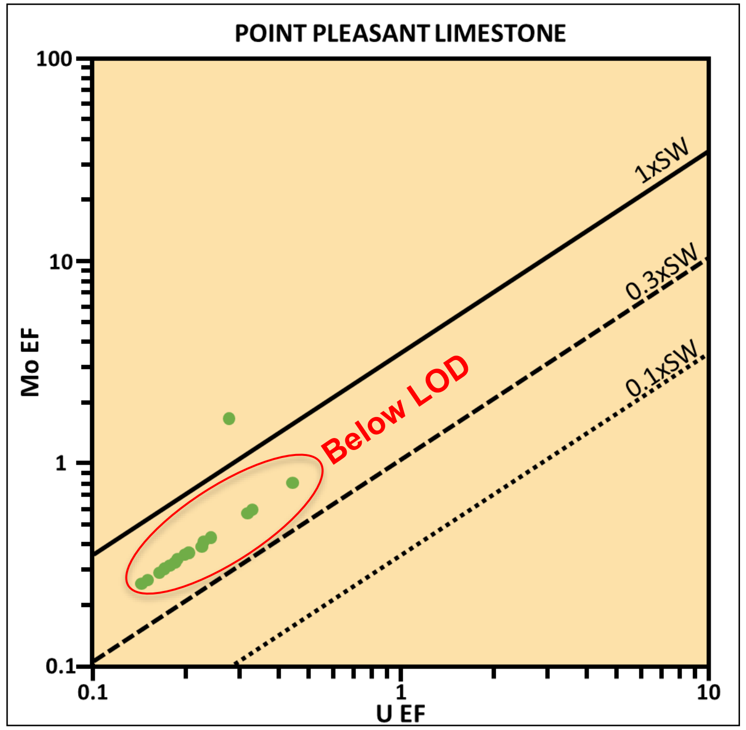
- **Marcellus parallel to molar sea –water ratio, but enriched 3-5x**
  - **Indicative of particulate shuttle mechanism**
  - **Requires fluctuating redox conditions (euxinic-dysoxic) and intermittent connection to global ocean**

Note the scale change from the Marcellus plots.





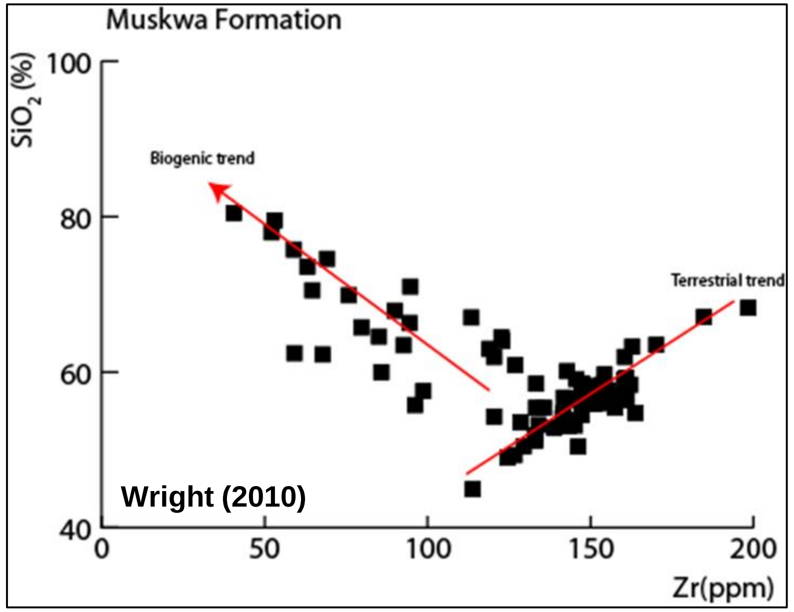


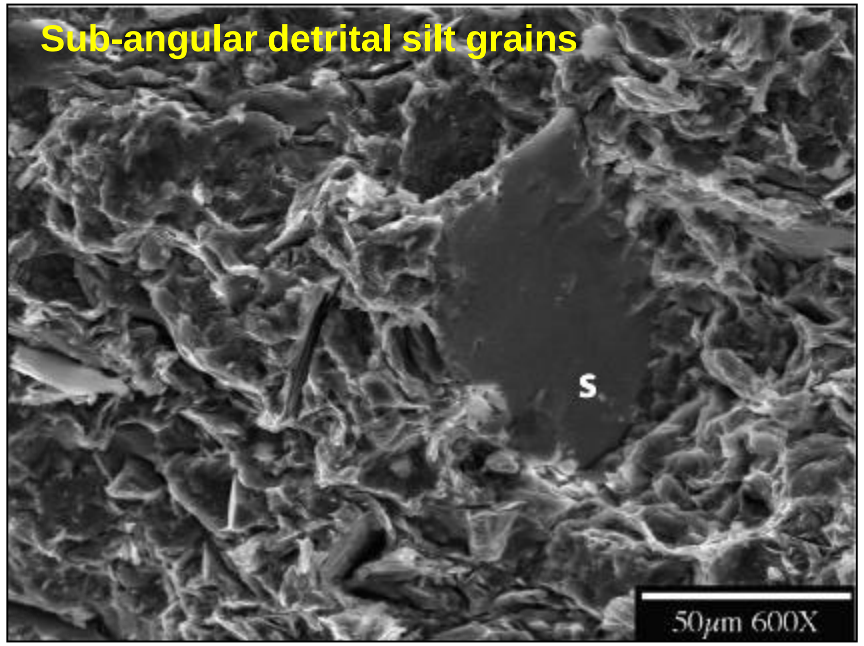


Quartz in the Point Pleasant and Marcellus

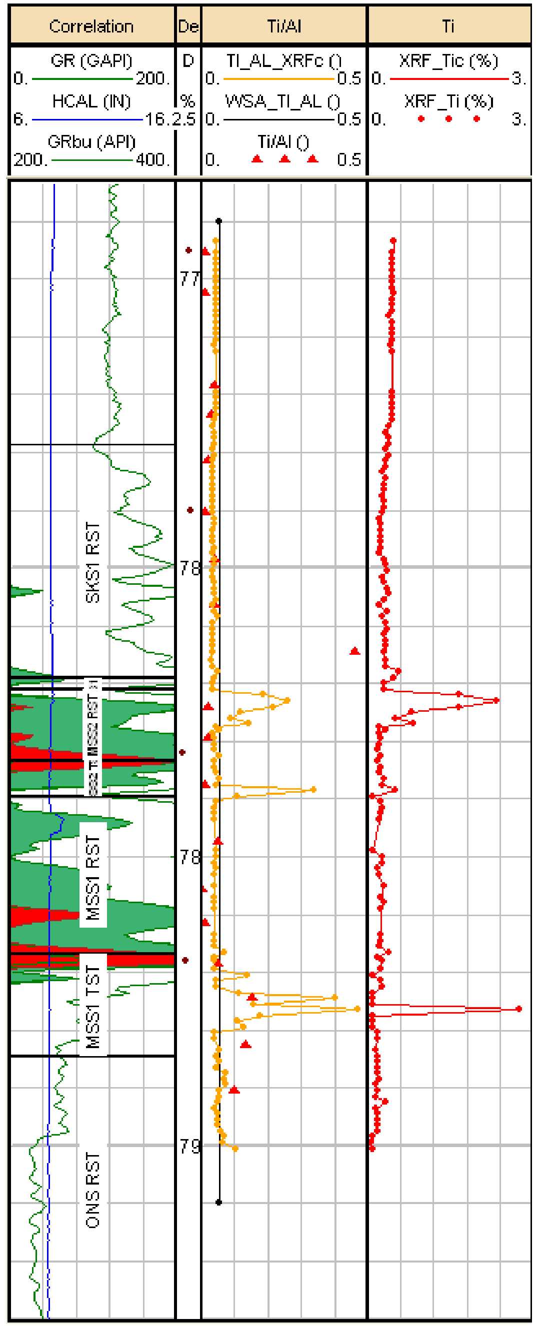
Extra-basinal vs Intra-basinal quartz

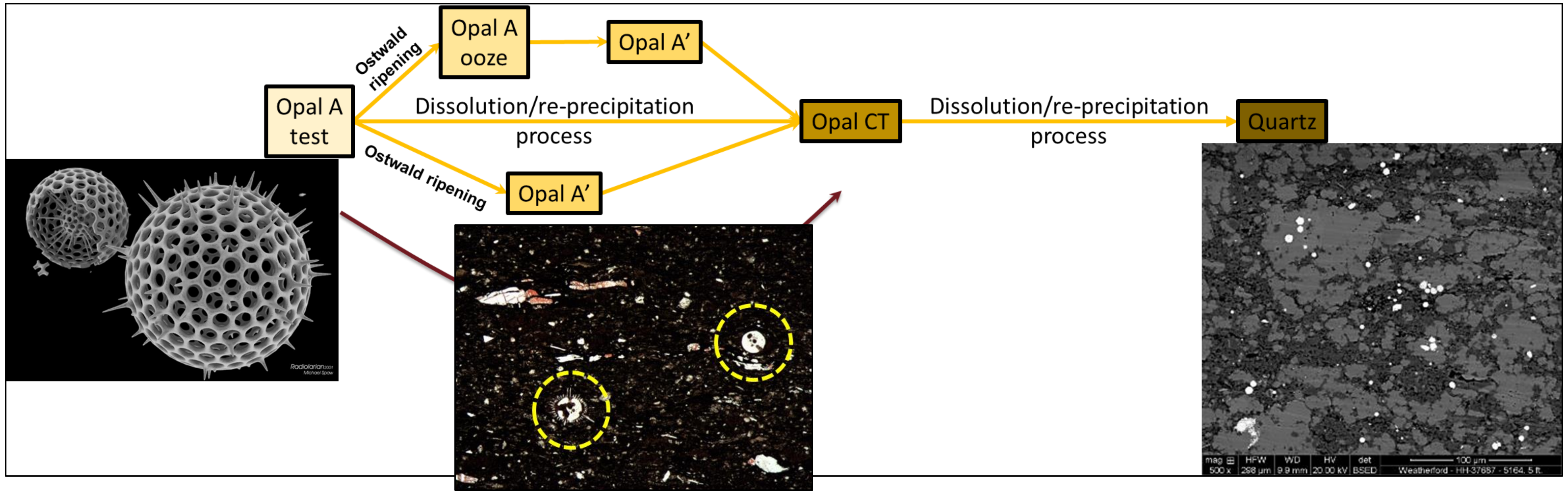
- Wright (2010) demonstrated that Zr can be used to differentiate detrital (extra-basinal) vs biogenic (inter-basinal) quartz.





- Ti/Al values of less than 0.05 suggest minimal eolian input.
- Few zones of elevated of Ti/Al, while possibly the result of eolian transport, more likely the result of winnowing of clays and/or concentration of heavier Ti-bearing minerals (these values are an order of magnitude higher than typical eolian Ti/Al values).



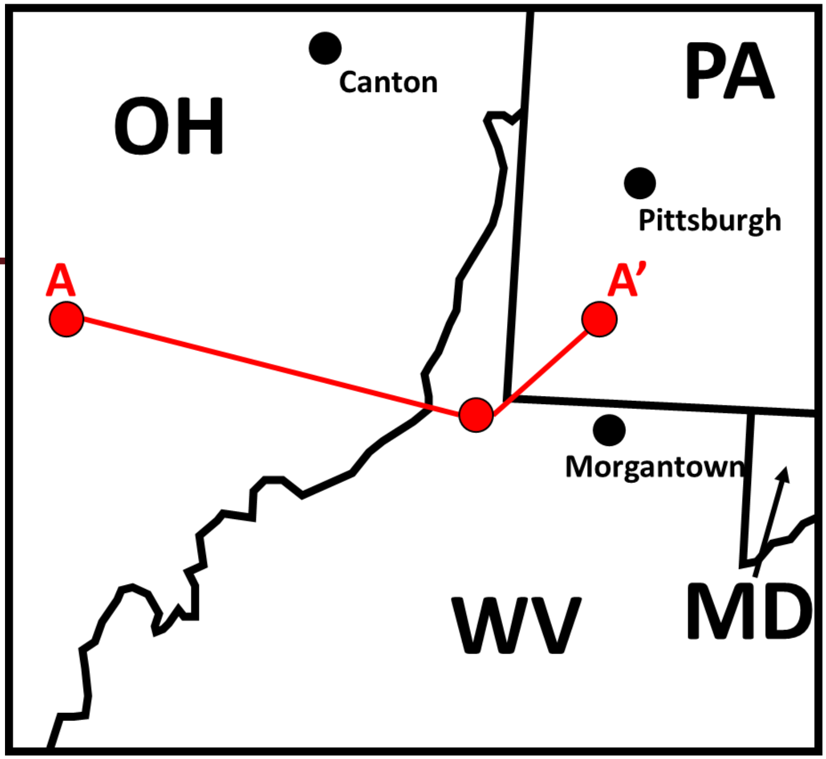


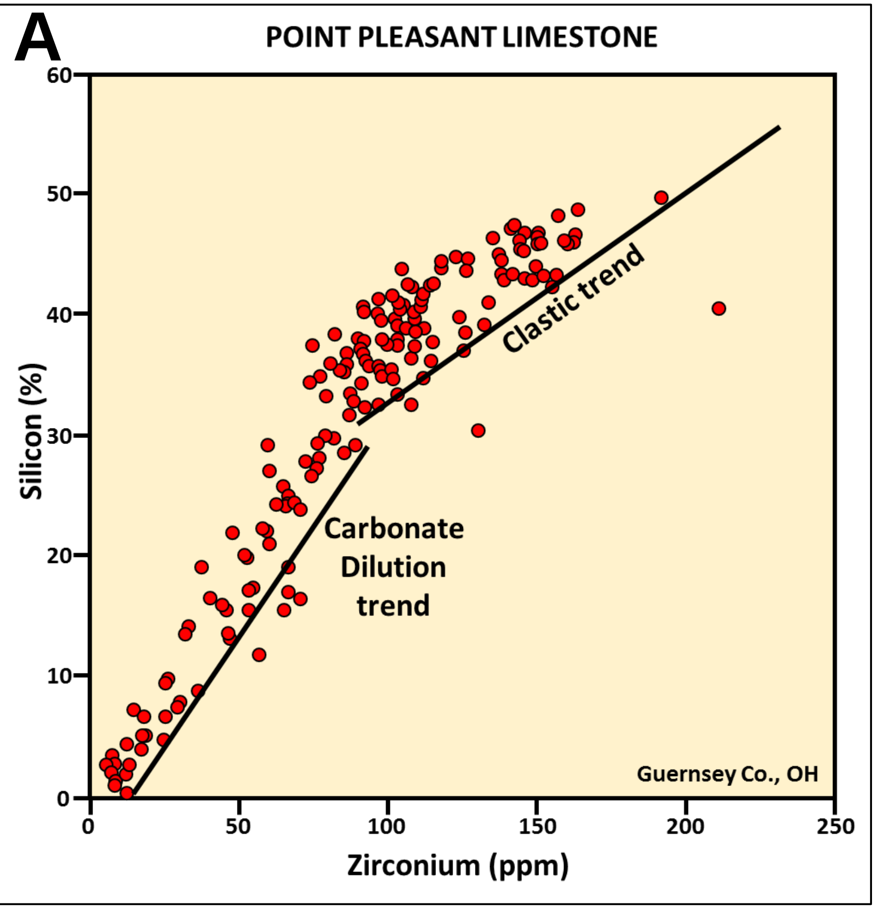
Biogenic Quartz in the Point Pleasant

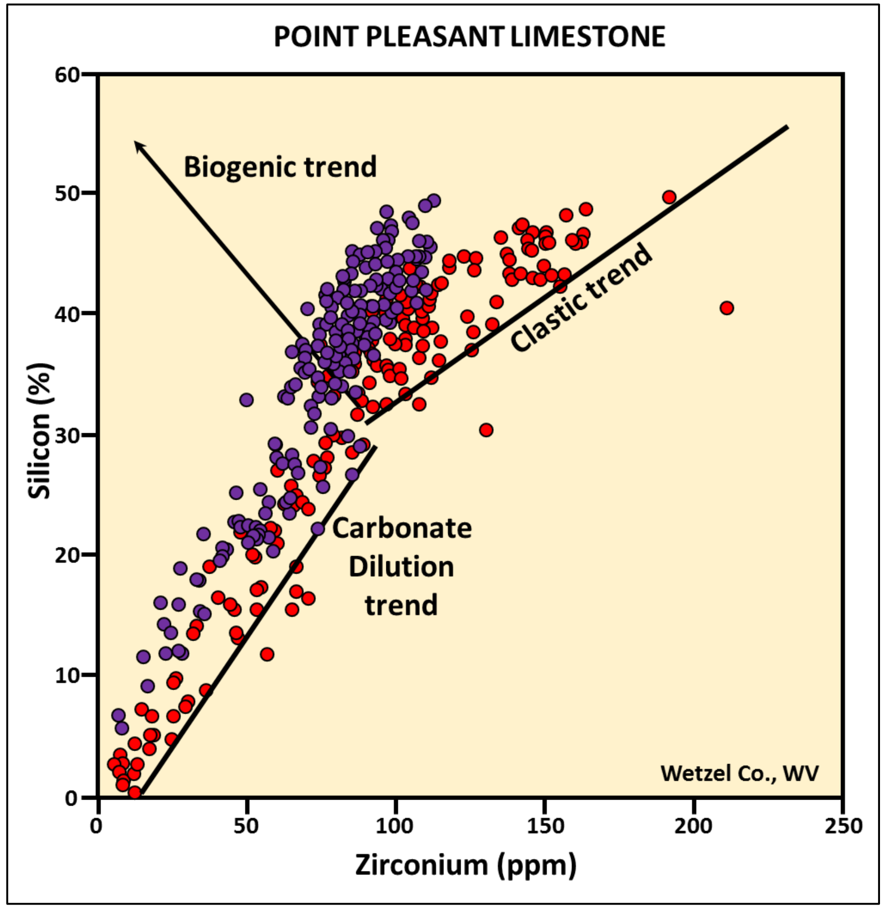
Extra-basinal vs Intra-basinal quartz

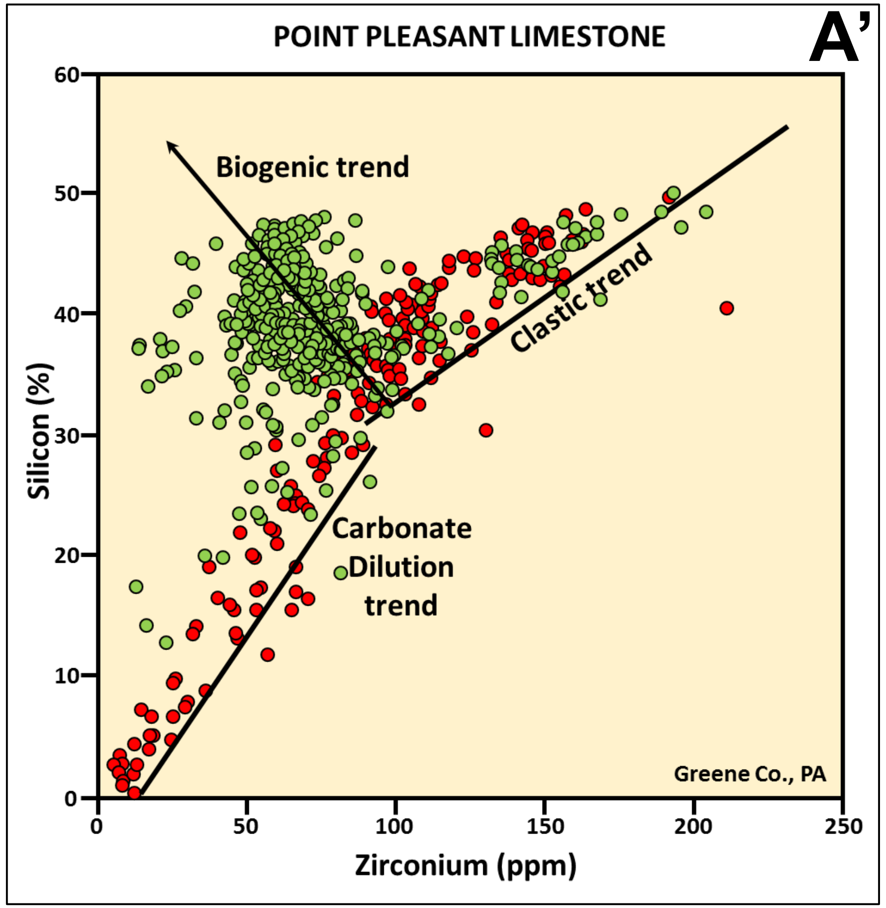
- **Point Pleasant demonstrates a variety of Si/Zr relationships**

  - **Dominantly clastic quartz to the west**
  - **Change in ratio of Si/Zr in WV, biogenic quartz?**
  - **Strong occurrence of biogenic quartz in Greene Co.**



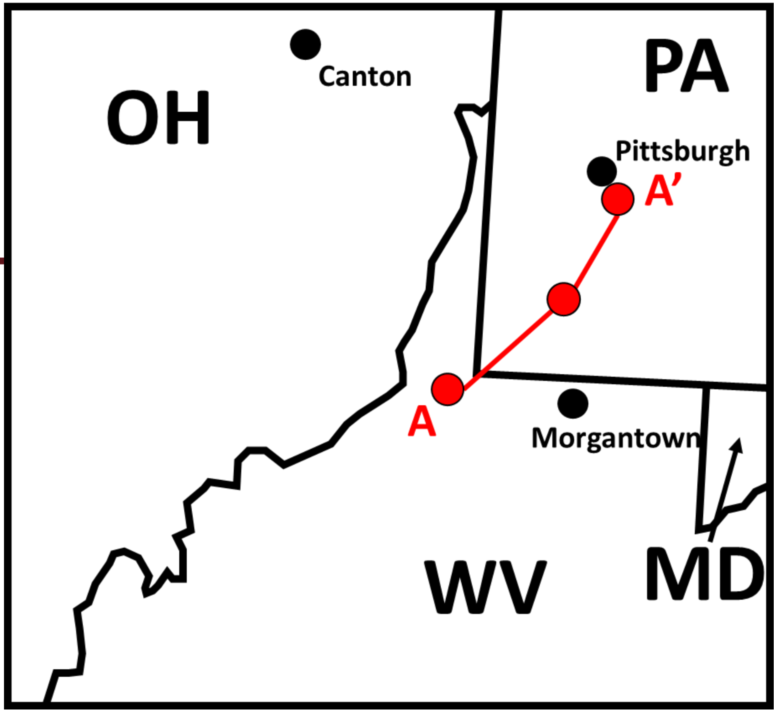




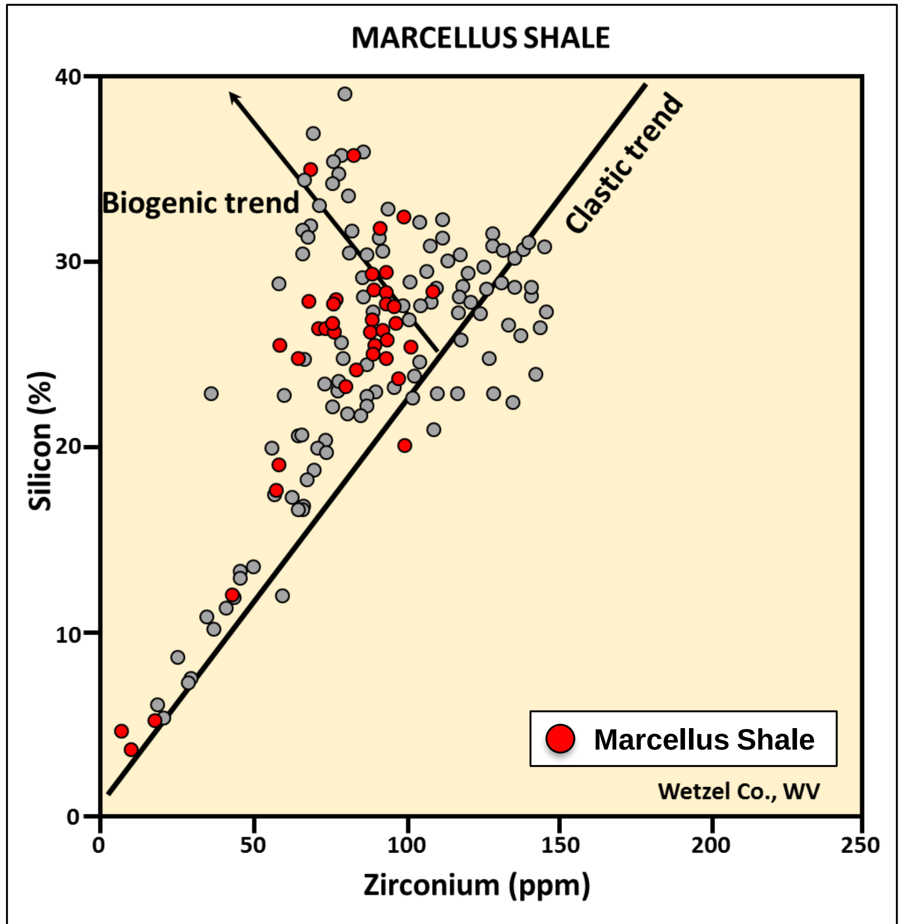


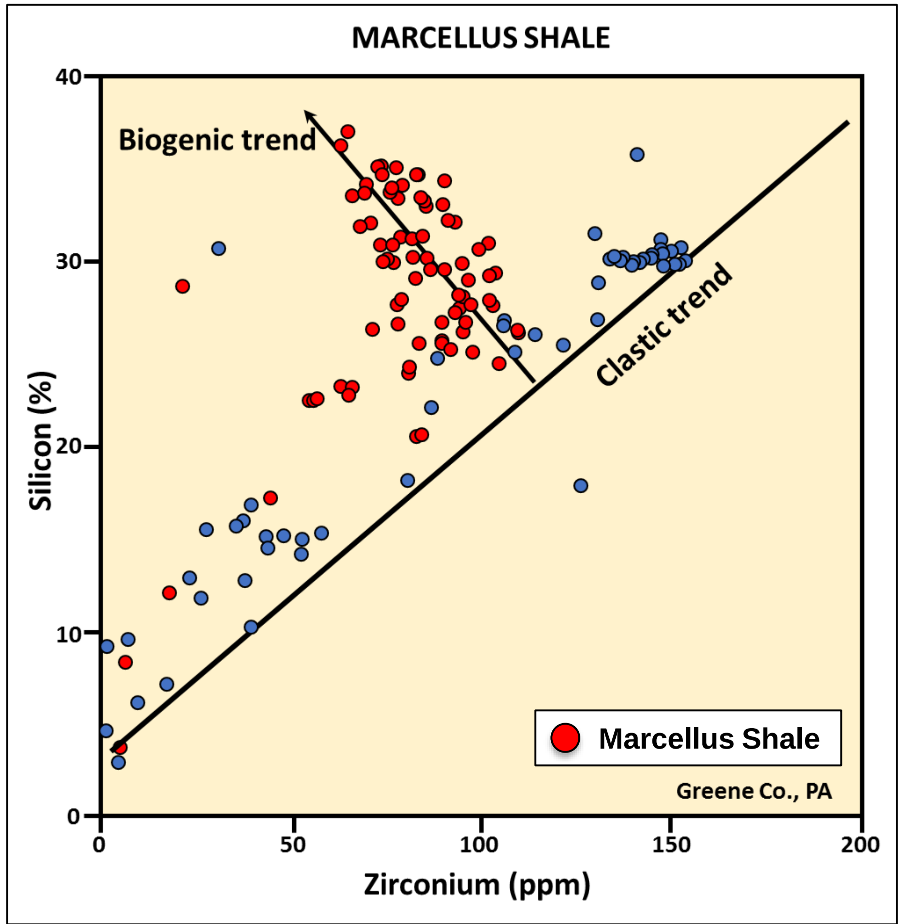
Biogenic Quartz in the Marcellus Shale

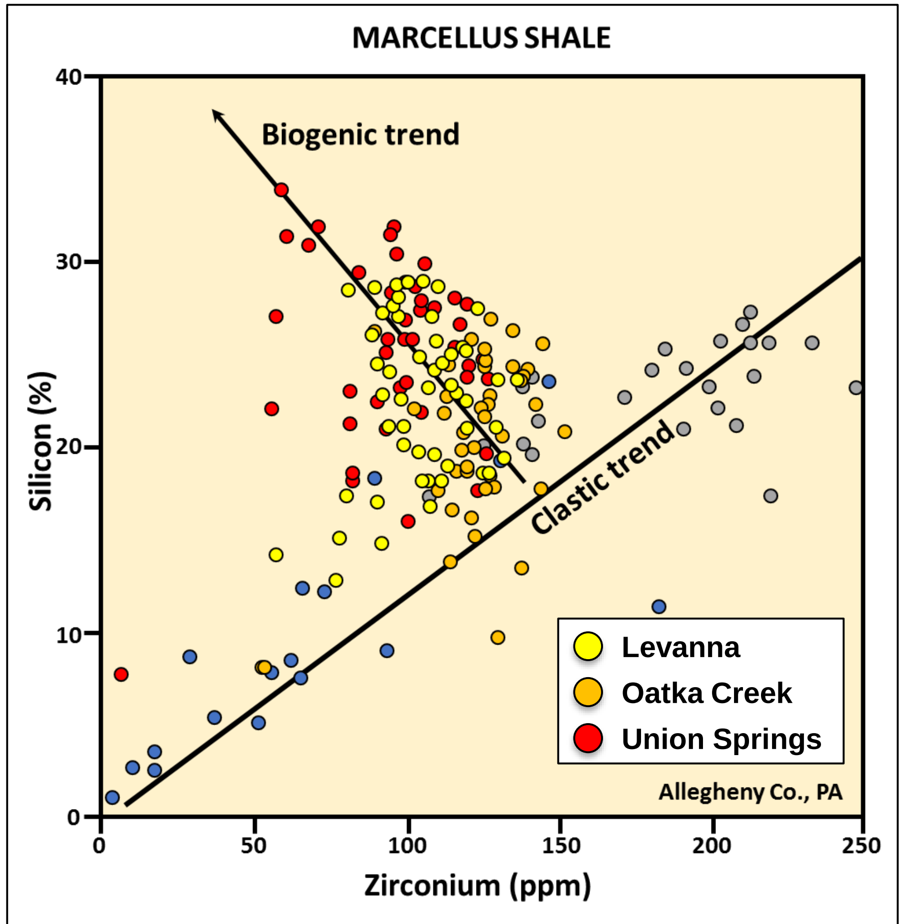
Extra-basinal vs Intra-basinal quartz



- **Across most the basin biogenic quartz is present in the Marcellus**
- **More prevalent in distal parts of the basin.**







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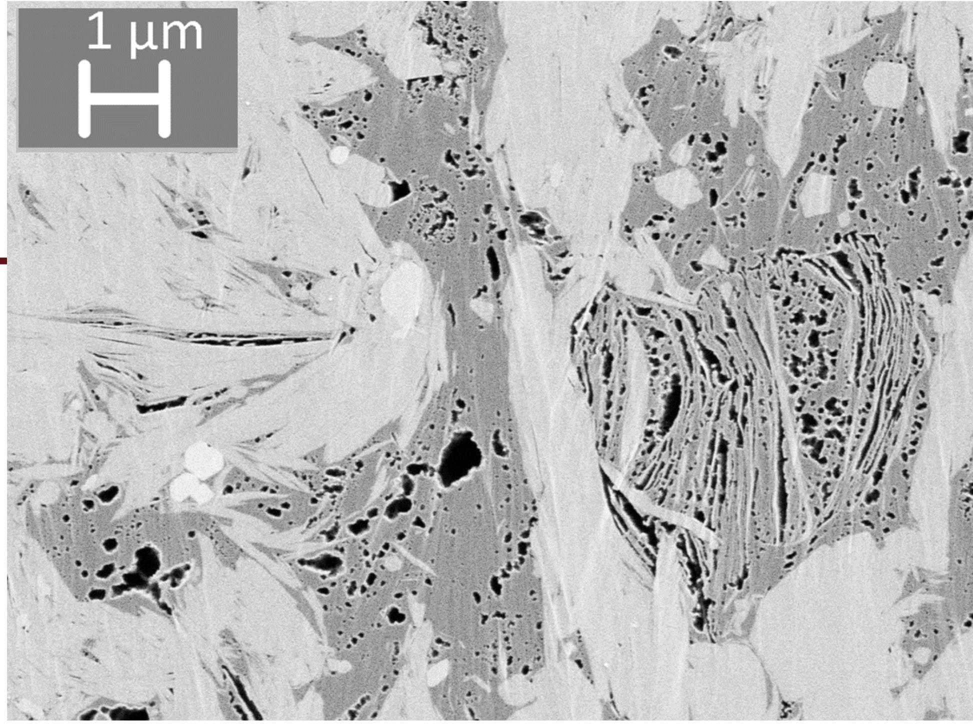
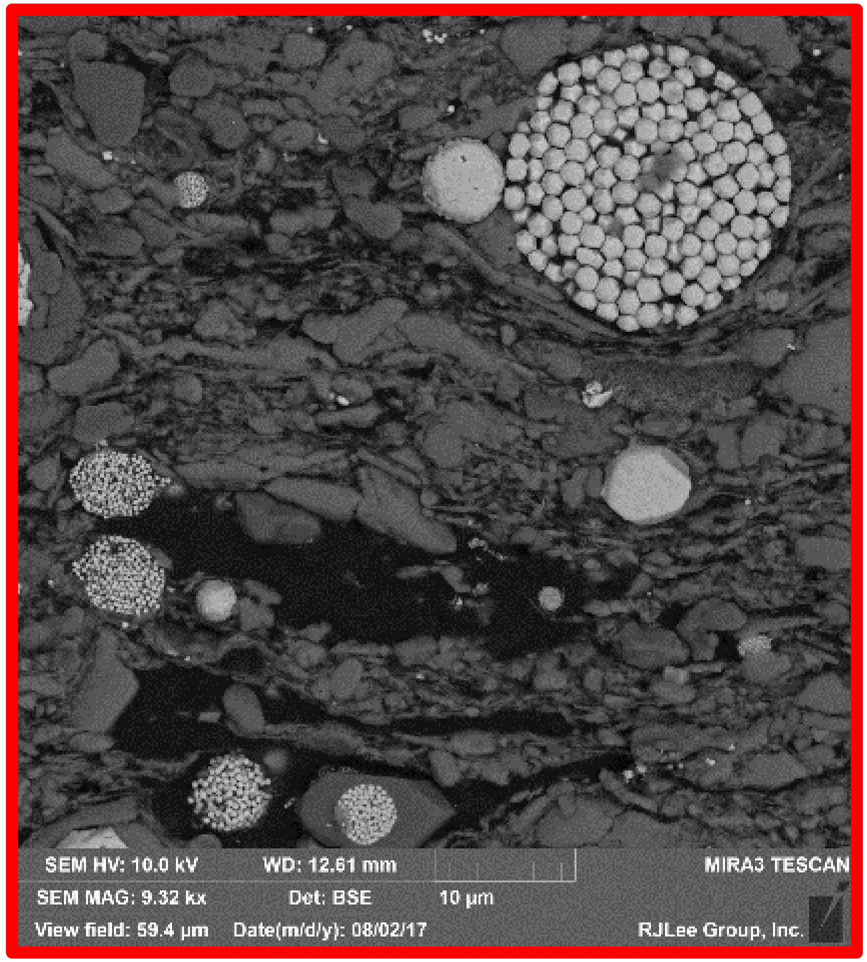
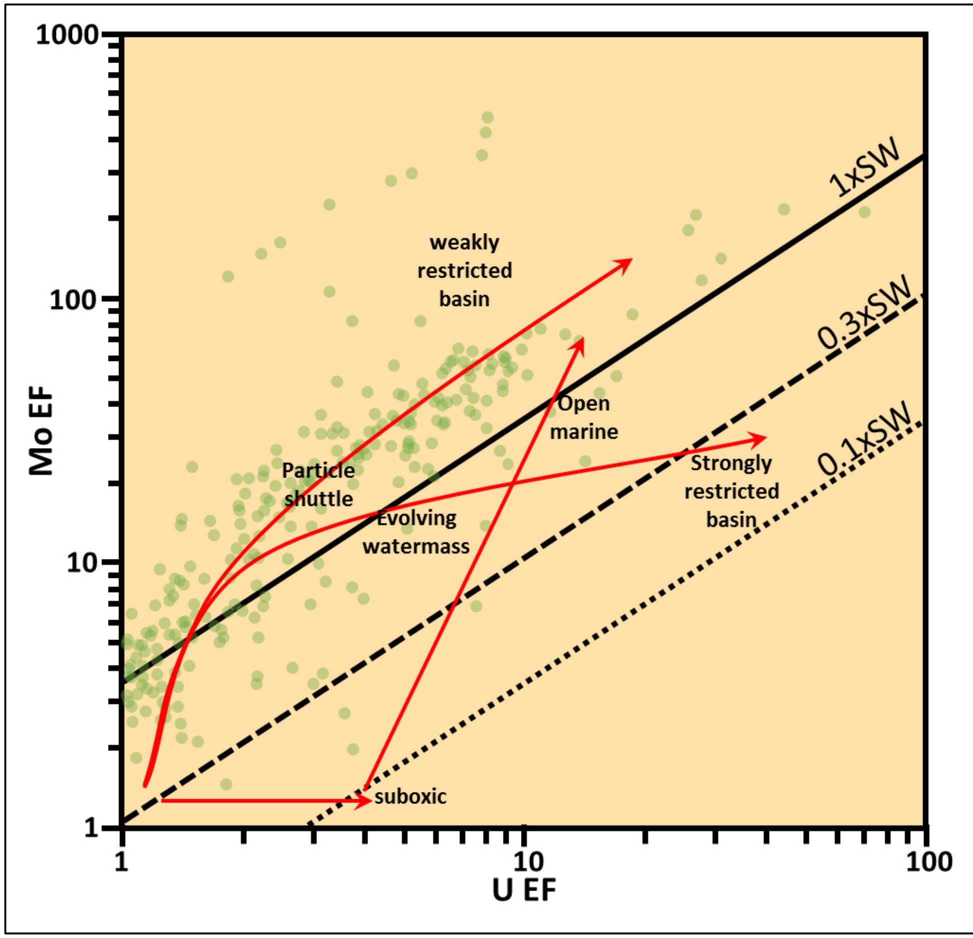
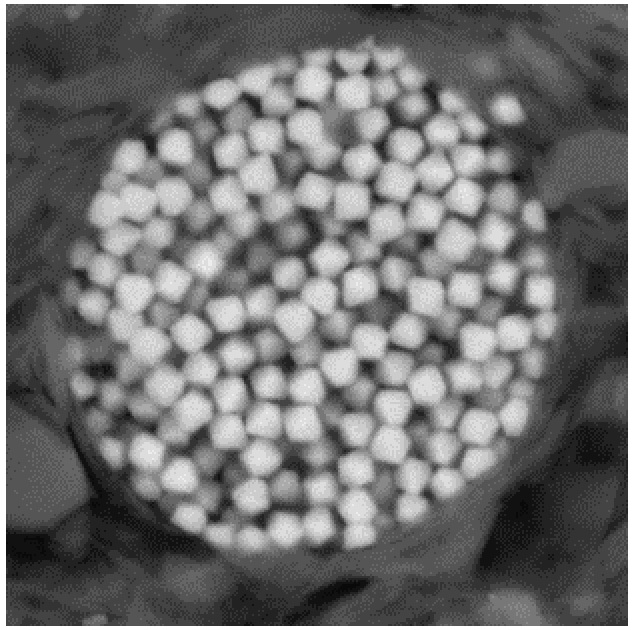






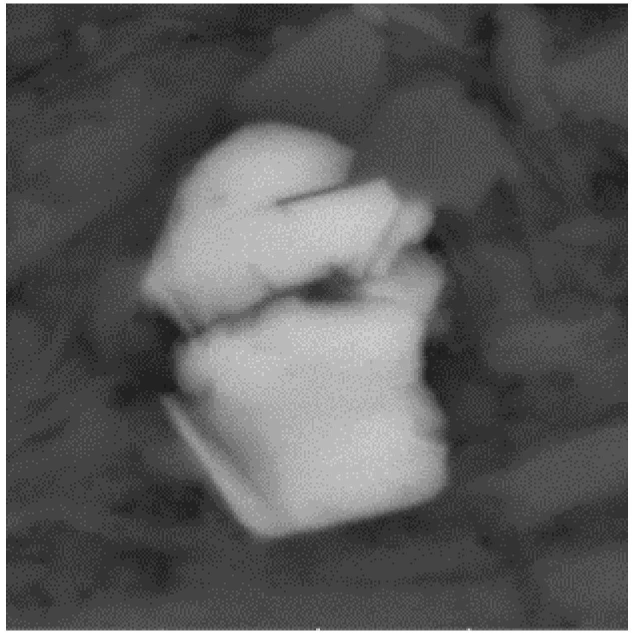
Pyrite in Mudstones

Framboids and euhedral grains



- The mode and occurrence of pyrite dispersed throughout the sediment provides insight into the redox conditions of bottom waters at the time sediments were deposited in both recent and ancient deposits.

- types of pyrite of interest
  - **Framboids**: spherical aggregates of pyrite microcrystallites that **form at the chemocline** (the transition from sulfide-bearing anoxic water and oxygen-bearing water). They can form suspended in the water column and sink to accumulate in the mud and can also form in anoxic muds.

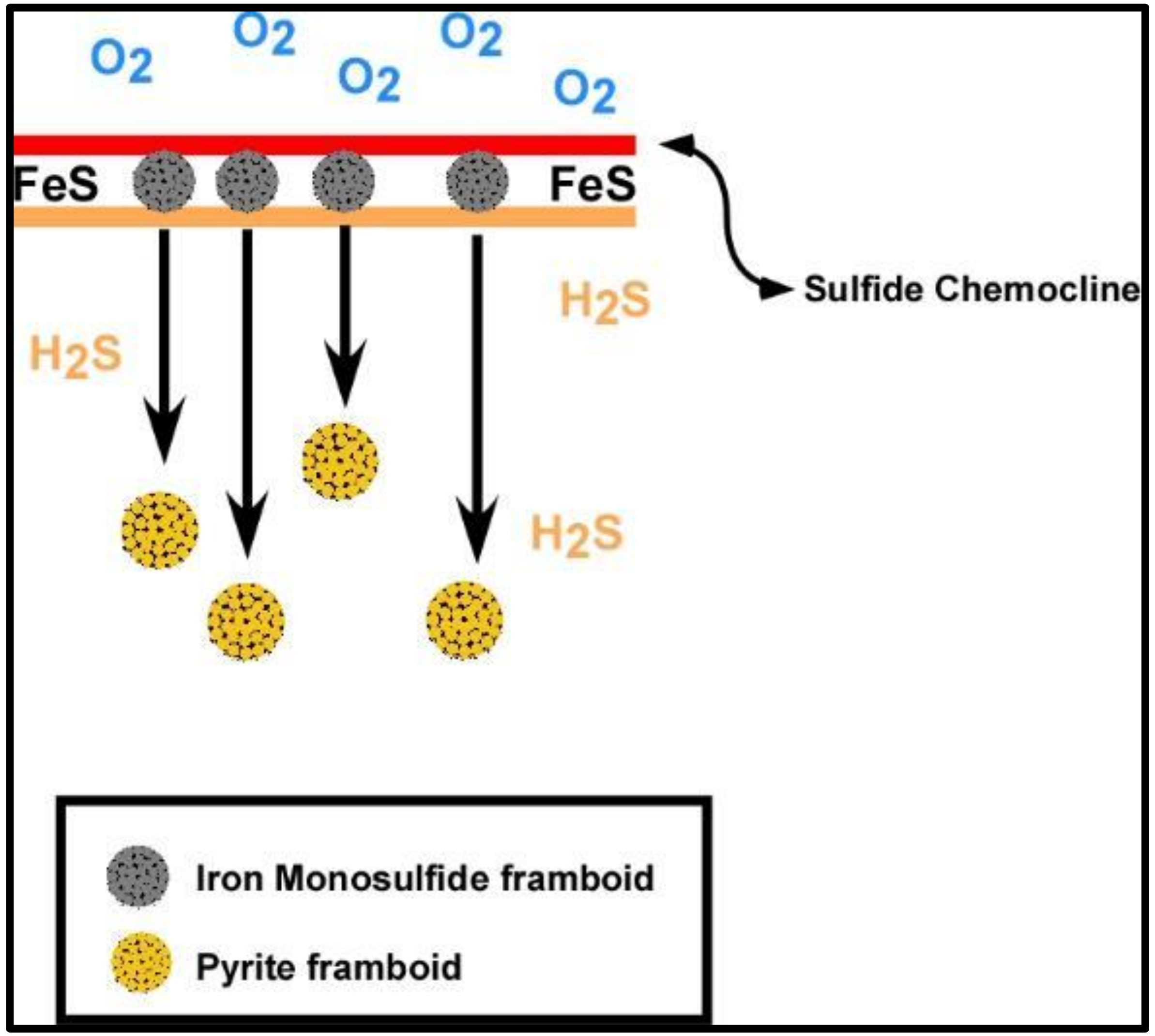


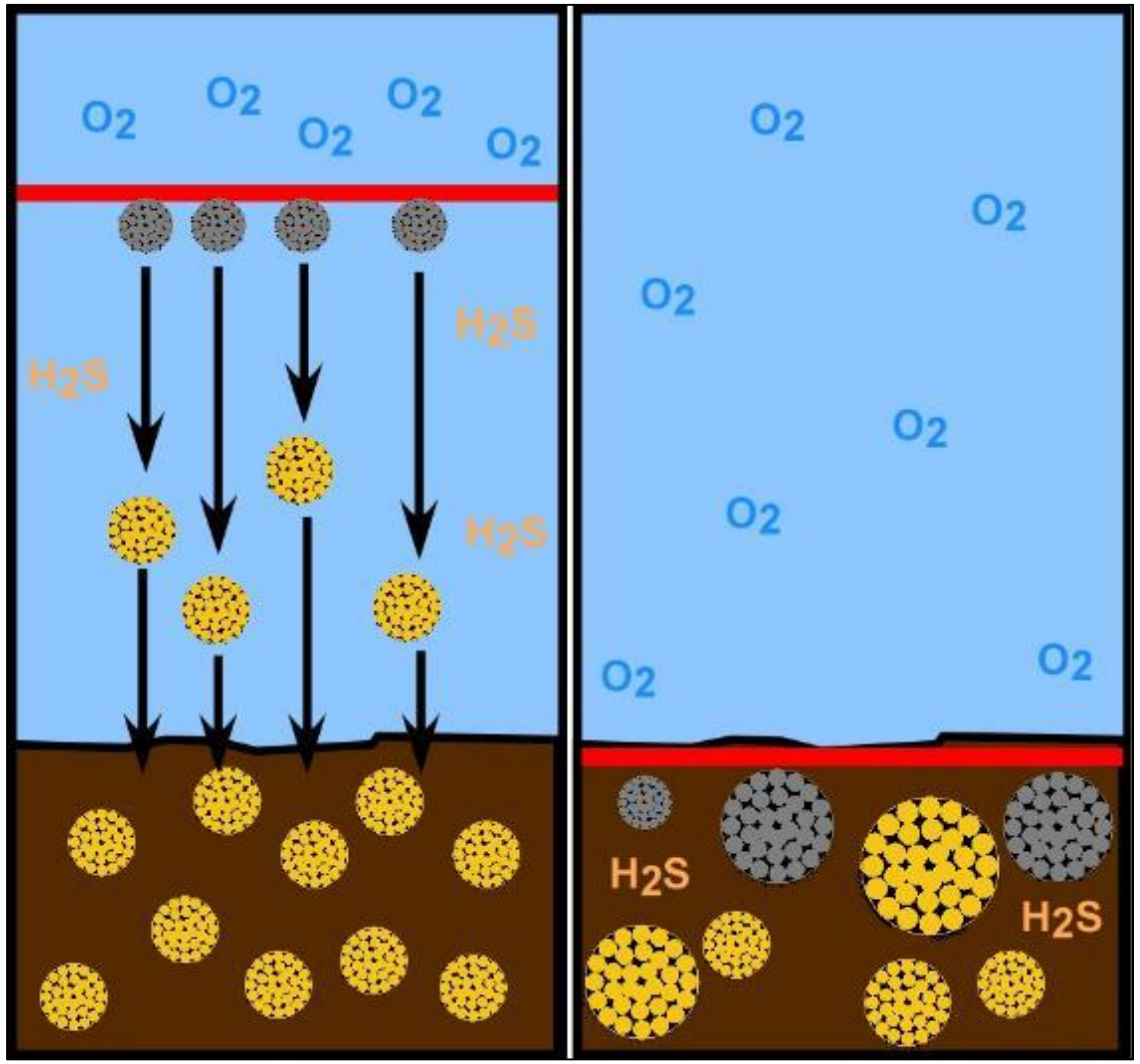
  - **Euhedral:** large individual grains of pyrite that form in the sediment at a much slower rate and can precipitate directly from the interaction of hydrogen sulfide with reactive iron.

Pyrite in Mudstones

Framboid formation

- Framboids composed of iron monosulfides (mackinawite, griegite) form in the zone of Fe reduction immediately below the sulfide chemocline where magnetic properties of the elements attract microcrystallites to each other to form spherical aggregates.
- Framboids that form in the water column can grow to ~5µm before the water cannot support their weight and they sink out of this zone arresting their growth and quickly reacting with H_2S to form pyrite.
    - Statistical analysis of the framboid diameters show that under these conditions mean diameter is ~5 µm, with a narrow range (St. Dev 1.7 µm).
- Framboids forming in euxinic sediment are limited only by availability of reactants and can grow to much larger and diverse sizes, albeit at slower rates.

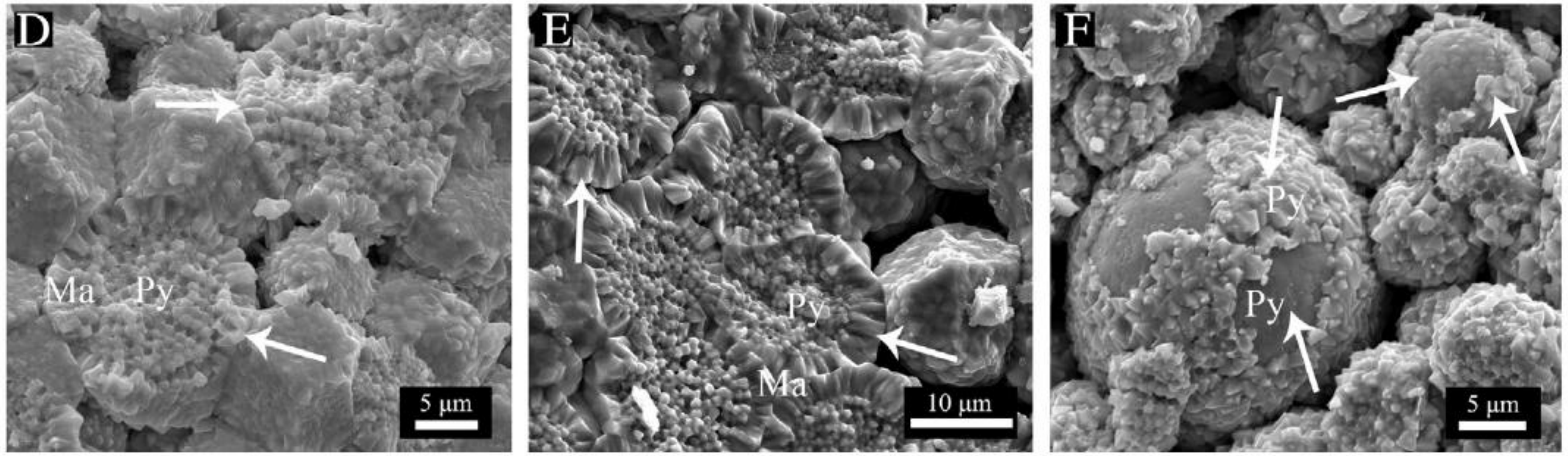




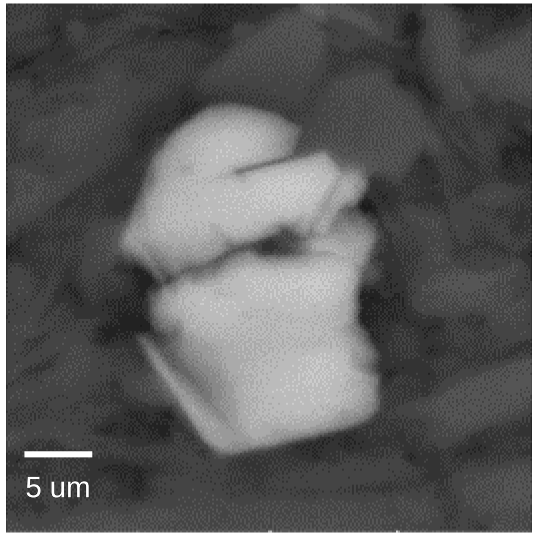
Pyrite in Mudstones

Euhedral pyrite occurrence

- Euhedral pyrite forms under more protracted rates from the direct interaction of highly to more poorly reactive Fe with hydrogen sulfide.
  - Euhedral pyrite forms as individual grains but can in some instances form as secondary overgrowths of preexisting framboids.



(Qi et. al., 2016)



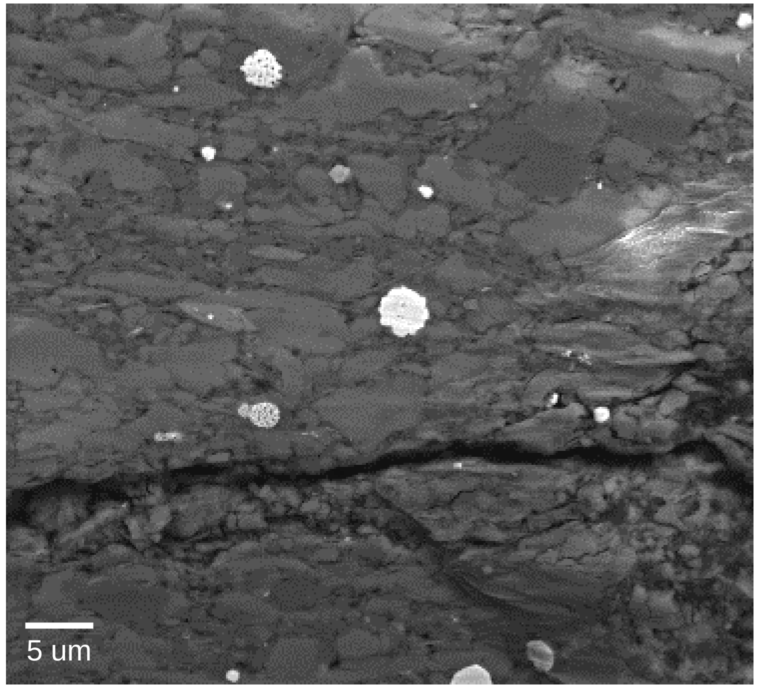
conditions	framboid diameters and associated data
euxinic (persistently sulfidic bottom water)	abundant small (mean diameter = 3-5 µm) framboids; narrow size range; few if any euhedral pyrite crystals;
anoxic (no oxygen in bottom water for extended periods of time)	abundant small (mean diameter = 4-6 µm) framboids, including a small number of larger framboids; few euhedral pyrite crystals;
lower dysoxic (weakly oxygenated bottom water)	framboids 6-10 µm in diameter are moderately common; subordinate larger framboids and euhedral pyrite crystals;
upper dysoxic (partial oxygen restriction in bottom water)	large framboids are common; rare small (< 5 µm diameter) framboids; most pyrite is euhedral crystalline;
oxic (on oxygen restriction)	no framboids; rare pyrite crystals;

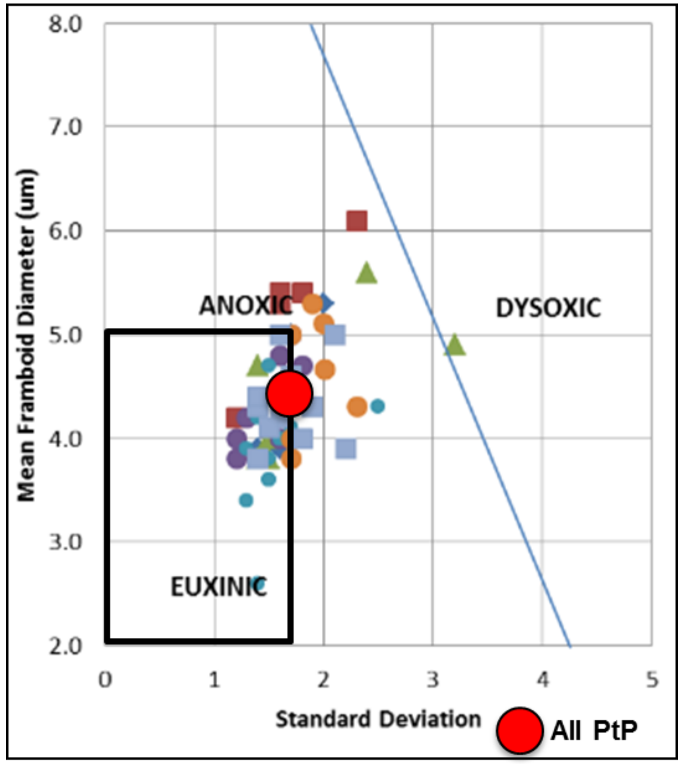
Pyrite in the Point Pleasant

Bulk pyrite and framboid observations

Well	Formation	% BR Pyrite	% framboidal Pyrite
Scott's Run	Point Pleasant	0.56%	35.46%
Scott's Run	Point Pleasant	0.56%	33.89%
Scott's Run	Point Pleasant	0.53%	30.11%
Scott's Run	Point Pleasant	1.37%	8.56%
Pettit	Point Pleasant	0.09%	4.79%
Pettit	Point Pleasant	0.02%	66.28%
Pettit	Point Pleasant	0.19%	6.96%
Pettit	Point Pleasant	0.18%	16.13%
Pettit	Point Pleasant	0.09%	16.60%
Pettit	Point Pleasant	0.27%	7.22%
BIG190	Point Pleasant	0.64%	19.25%
BIG190	Point Pleasant	0.44%	9.34%
BIG190	Point Pleasant	0.33%	3.98%
BIG190	Point Pleasant	0.44%	17.63%
BIG190	Point Pleasant	1.73%	23.09%
BIG190	Point Pleasant	0.86%	33.05%
	Average	**0.52%**	**20.77%**

Well	Formation	n	Mean Diameter (μm)	25th Percentile (μm)	75th Percentile (μm)	Standard deviation (μm)	Maximum Framboid Diameter (μm)	Population ≤ 5 μm (%)	Population ≥ 10 μm (%)	Framboid density (framboids/mm2)
Well A	Point Pleasant	109	3.9	3.0	4.7	1.6	9	86%	0%	23
	Point Pleasant	114	3.9	3.1	4.6	1.4	9	91%	0%	18
	Point Pleasant	116	5.3	4.0	6.0	2.0	18	64%	3%	10
	Point Pleasant	95	5.0	4.0	5.6	1.7	15	73%	3%	5
Well B	Point Pleasant	150	6.1	4.8	6.7	2.3	19	53%	6%	9
	Point Pleasant	170	5.3	4.2	5.8	1.6	13	68%	3%	9
	Point Pleasant	58	5.4	4.0	5.9	1.8	13	67%	2%	2
	Point Pleasant	128	4.2	3.3	4.9	1.2	7	87%	0%	16
	Point Pleasant	126	5.0	3.6	5.8	2.1	16	71%	5%	11
	Point Pleasant	62	5.4	4.2	6.3	1.6	11	56%	2%	4
Well C	Point Pleasant	102	3.8	2.7	4.7	1.5	10.0	83%	1%	19
	Point Pleasant	210	4.9	3.8	5.2	3.2	40	80%	2%	53
	Point Pleasant	160	5.6	4	6.2	2.4	17	67%	7%	10
	Point Pleasant	110	4.7	3.8	5.2	1.4	10	83%	2%	28
	Point Pleasant	497	3.8	2.8	4.5	1.4	11	91%	1%	124
	Point Pleasant	436	4	2.9	4.7	1.5	12	85%	0%	109
Well D	Point Pleasant	102	5	3.7	5.7	1.7	10	72%	2%	7
	Point Pleasant	100	4.2	3.3	4.8	1.3	8	83%	0%	6
	Point Pleasant	103	4.8	3.7	5.3	1.6	11	78%	3%	11
	Point Pleasant	103	3.8	2.9	4.3	1.2	7	85%	0%	25
	Point Pleasant	127	4	3.1	4.7	1.2	8	87%	0%	56
	Point Pleasant	100	4	2.9	4.7	1.6	12	87%	2%	66
	Point Pleasant	105	3.8	3	4.3	1.4	9	90%	0%	93
	Point Pleasant	100	4.7	3.4	5.6	1.8	10	73%	1%	13

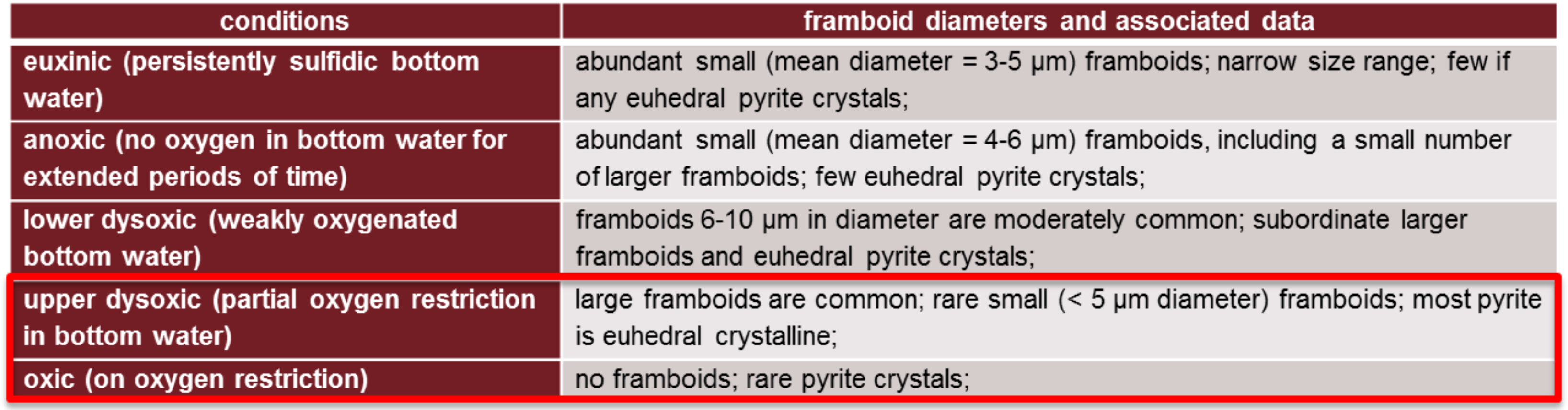




- Point Pleasant samples have a low occurrence of both bulk pyrite and framboids.
- Mean framboids are all very small, average 4.6 µm, with narrow size range (± 1.7 µm).
- While present, framboids >10µm are quite rare (average 2% of population).

Pyrite in the Point Pleasant

- Pyrite data tells two different stories.
- Overall paucity of pyrite, combined with euhedral pyrite being the most common form, would suggest a dominantly dysoxic to oxic water column.
- Small mean diameter of framboids (4.6 µm) and the low standard deviation (~1.7 µm) are consistent with framboids accumulating in an anoxic-euxinic water column.



conditions	framboid diameters and associated data
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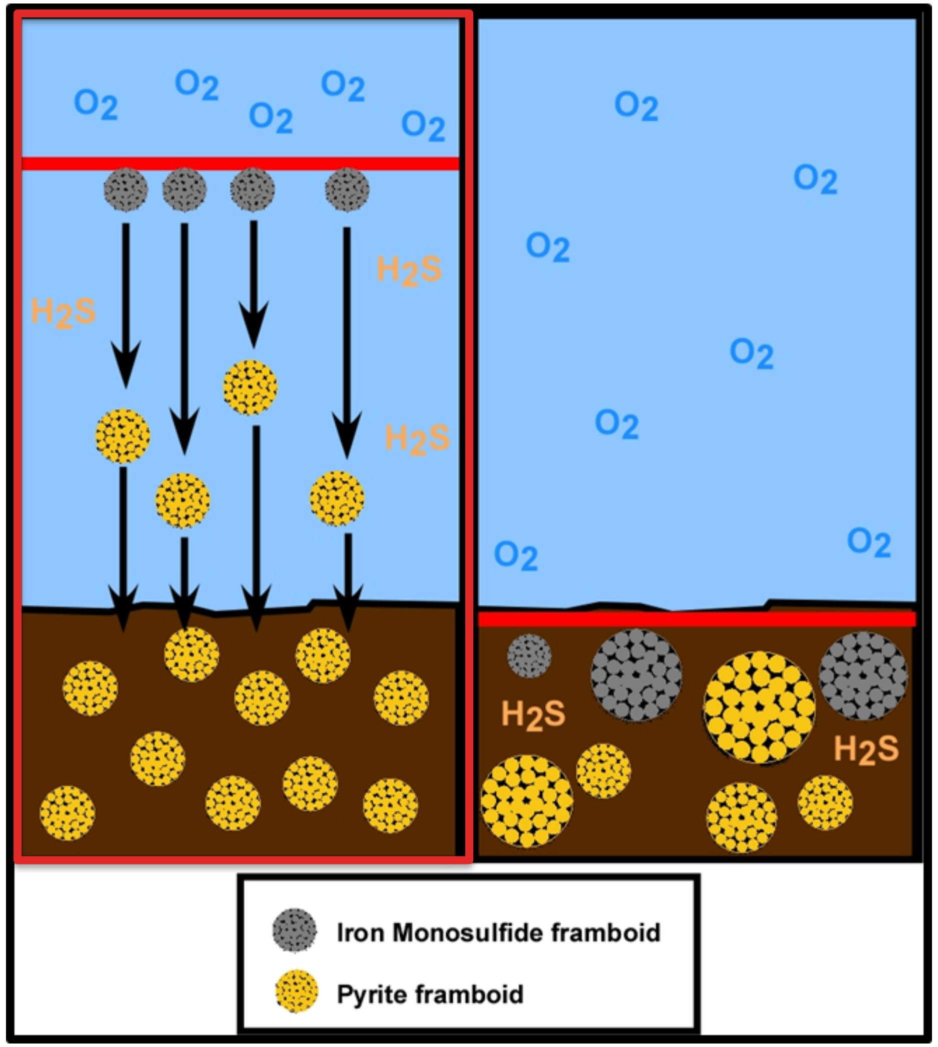


Pyrite in the Point Pleasant

Lack of Reactants

- **Lack of reactants**. If the system is subject to a lack of reactive iron or hydrogen sulfide then pyrite formation would be limited.
  - There is evidence for this in modern Santa Barbara Basin sediments off the coast of California, where Fe limitation is called on to explain framboids of a mean diameter of 4 µm accumulating under a suboxic water column (Schieber and Schimmelmann, 2007).

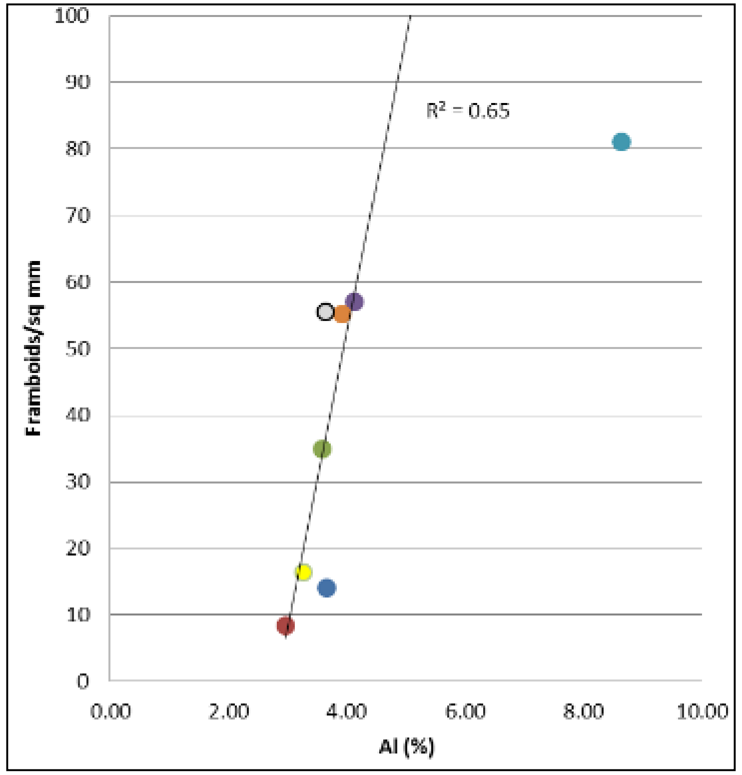
- A strong relationship exists between clastic influx (Al %) and number of framboids. Unsurprisingly, the Utica hosts more framboids given its higher Al content.
- The Utica however, does not contain as many framboids per Al content as would be expected given the Point Pleasant trend.
  - This may represent a shift in the balance of reactive versus detrital Fe where a larger component of Utica Fe is detrital and not available to the production of pyrite.

Average shale Fe/Al : **0.55** (Wedephol, 1971)
Average Upper Crust Fe/Al: **0.44** (Taylor and McLennan, 1985)

Well	Formation	Al (%)	Fe/Al
Scott's Run	Point Pleasant	3.59	0.41
Scott's Run	Point Pleasant	3.74	0.26
Scott's Run	Point Pleasant	3.43	0.35
Scott's Run	Point Pleasant	3.92	0.33
Pettit	Point Pleasant	3.82	0.36
Pettit	Point Pleasant	2.57	0.43
Pettit	Point Pleasant	2.69	0.48
Pettit	Point Pleasant	2.99	0.43
Pettit	Point Pleasant	2.80	0.41
Pettit	Point Pleasant		
BIG190	Point Pleasant	4.42	0.54
BIG190	Point Pleasant	3.27	0.52
BIG190	Point Pleasant	3.33	0.51
BIG190	Point Pleasant	4.03	0.42
BIG190	Point Pleasant	4.76	0.49
BIG190	Point Pleasant	5.04	0.41
Shipman	Point Pleasant	4.32	0.37
Shipman	Point Pleasant	2.80	0.46
Shipman	Point Pleasant	3.19	0.36
Shipman	Point Pleasant	4.01	0.35
Shipman	Point Pleasant	3.48	0.39
Shipman	Point Pleasant	3.34	0.37
Shipman	Point Pleasant	3.77	0.37
Shipman	Point Pleasant	3.86	0.37

- All samples depleted relative to average shale values and most are depleted relative to crustal values (average Fe/Al of all Point Pleasant data 0.45).

- Supply of Fe, namely reactive Fe to the basin, was limited.

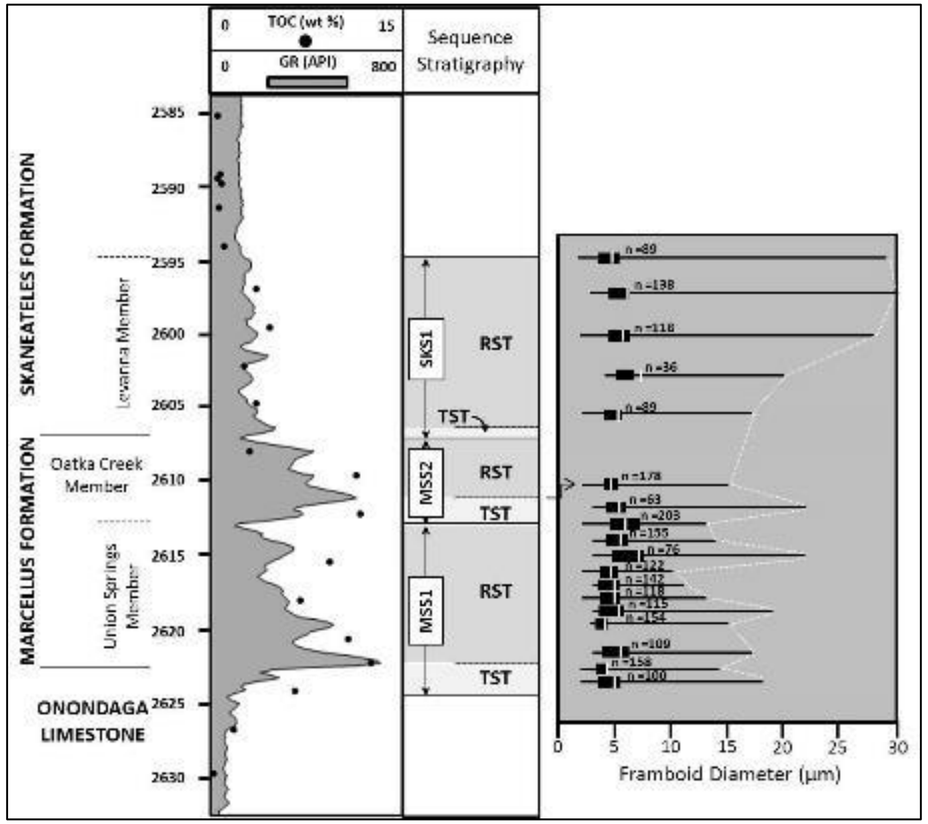


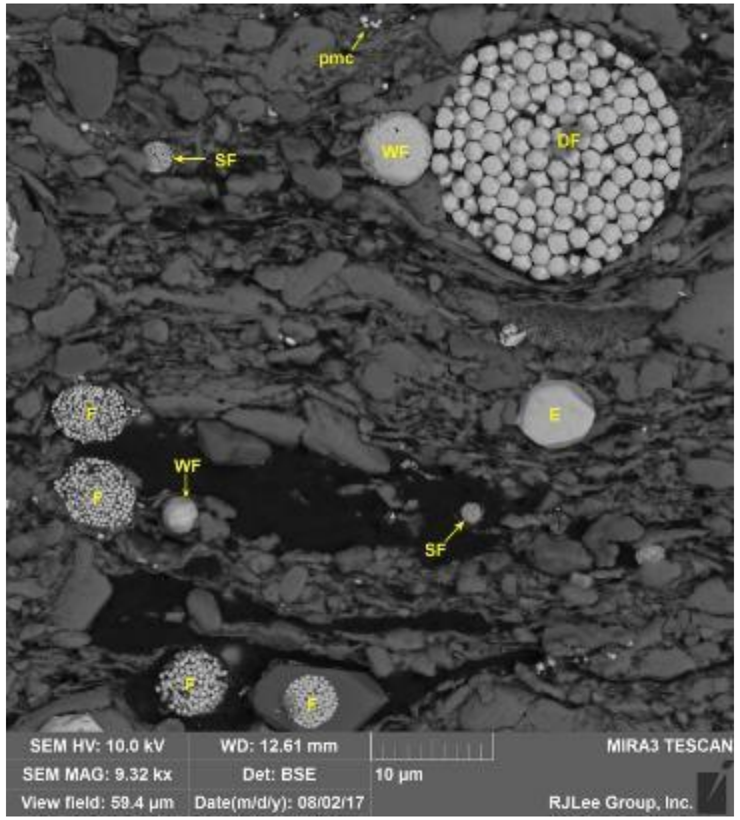
- Average Al in the Point Pleasant (n = 125) 6.5% (Range 3.8-15.0; STDEV 1.4%); ~25% below the average shale value of 8.8% suggesting limited clastic and attendant reactive Fe influx.

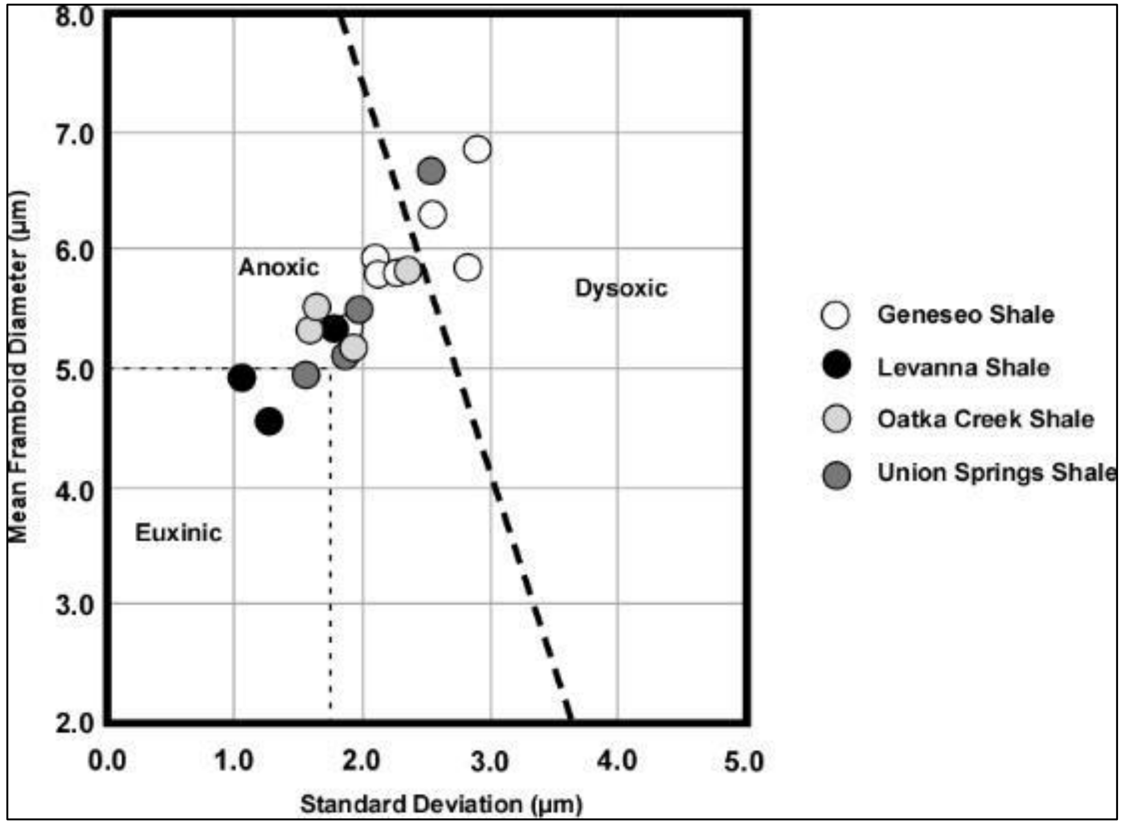
Pyrite in the Marcellus

Well	Formation	% BR Pyrite	% framboidal Pyrite
Huey	Oatka Creek	0.76%	70.70%
Huey	Oatka Creek	1.43%	42.98%
Huey	Oatka Creek	0.95%	58.95%
Huey	Oatka Creek	2.94%	34.75%
Huey	Oatka Creek	4.42%	28.73%
Huey	Oatka Creek	3.48%	54.81%
Huey	Union Springs	2.75%	52.43%
Huey	Union Springs	2.13%	13.01%
Huey	Union Springs	1.66%	61.75%
Huey	Union Springs	1.70%	65.39%
Huey	Union Springs	3.74%	55.66%
Huey	**Average**	**2.36%**	**49.01%**

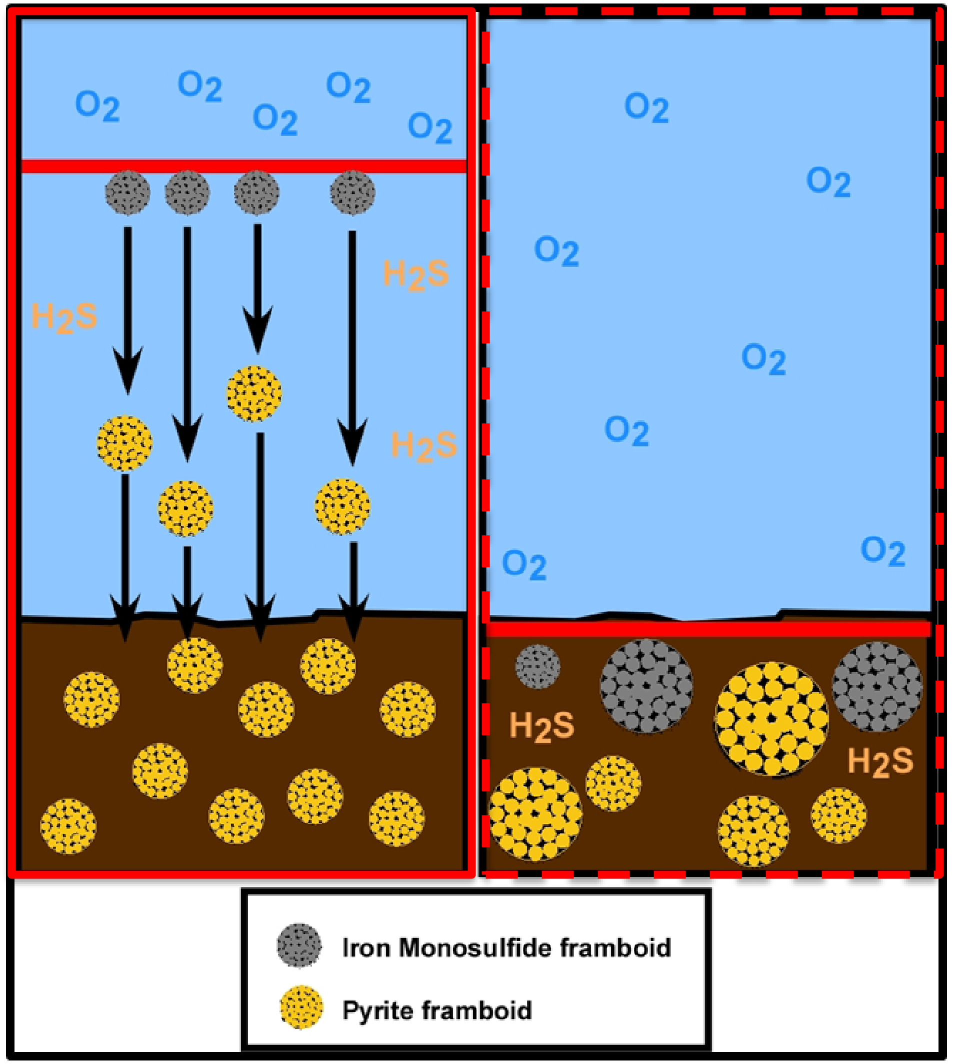
- Marcellus characterized by a high occurrence of bulk pyrite, much of which occurs as framboids.
- Mean framboids are generally small, >6µm.
- Framboids >10µm are commonly found in most samples.



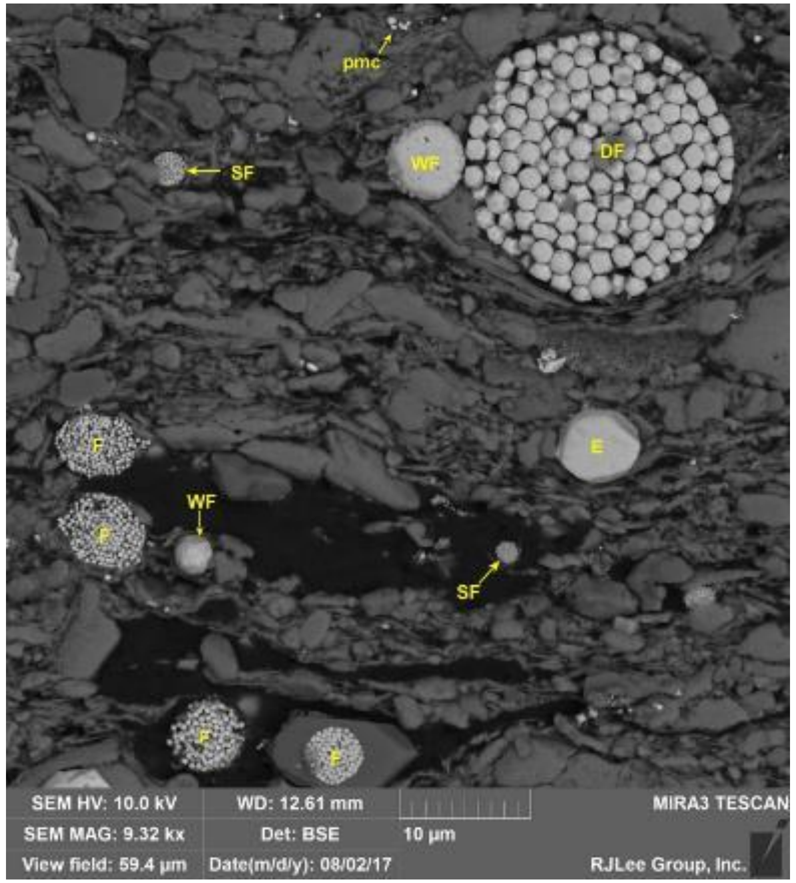




Pyrite in the Marcellus



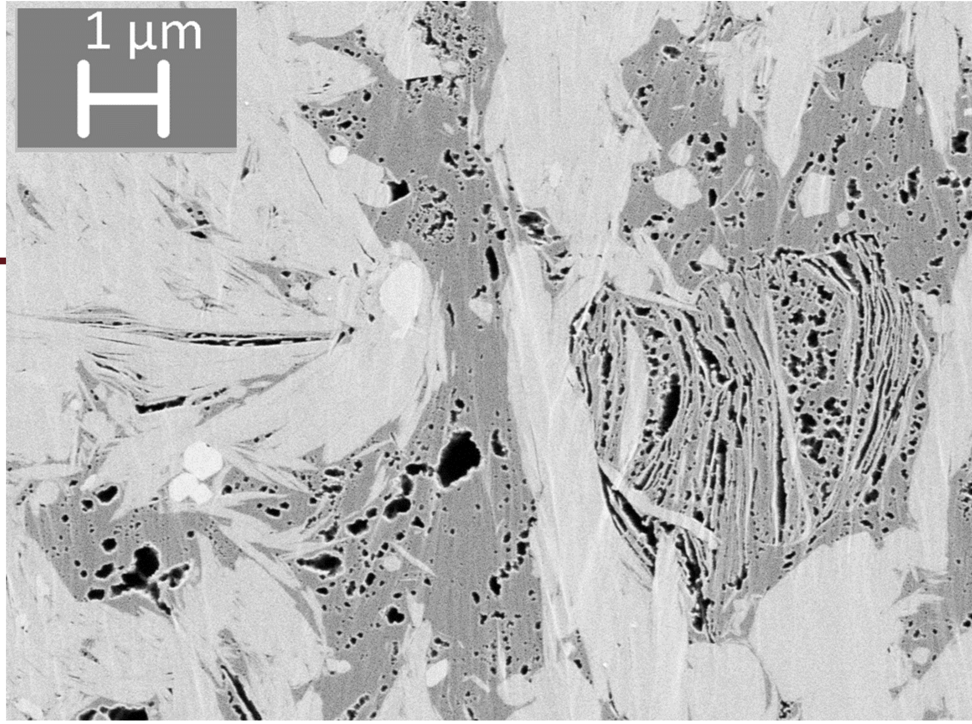
- Marcellus framboids record dominantly anoxic to euxinic conditions.
- Occasionally the chemocline is forced down to, or below, the sediment-water interface, promoting the growth of diagenetic framboids.
- Results in a time-averaged data set that records the dominant conditions. However it can be difficult to tease out annual or decadal fluctuations in the position of the redox boundary.

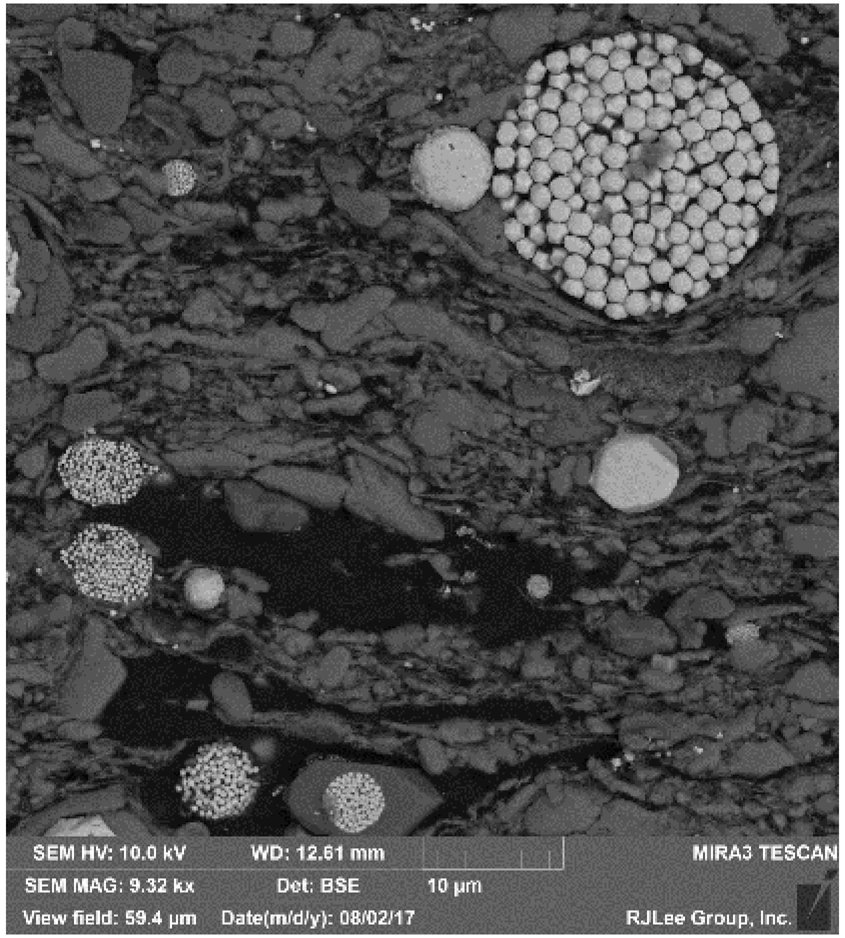


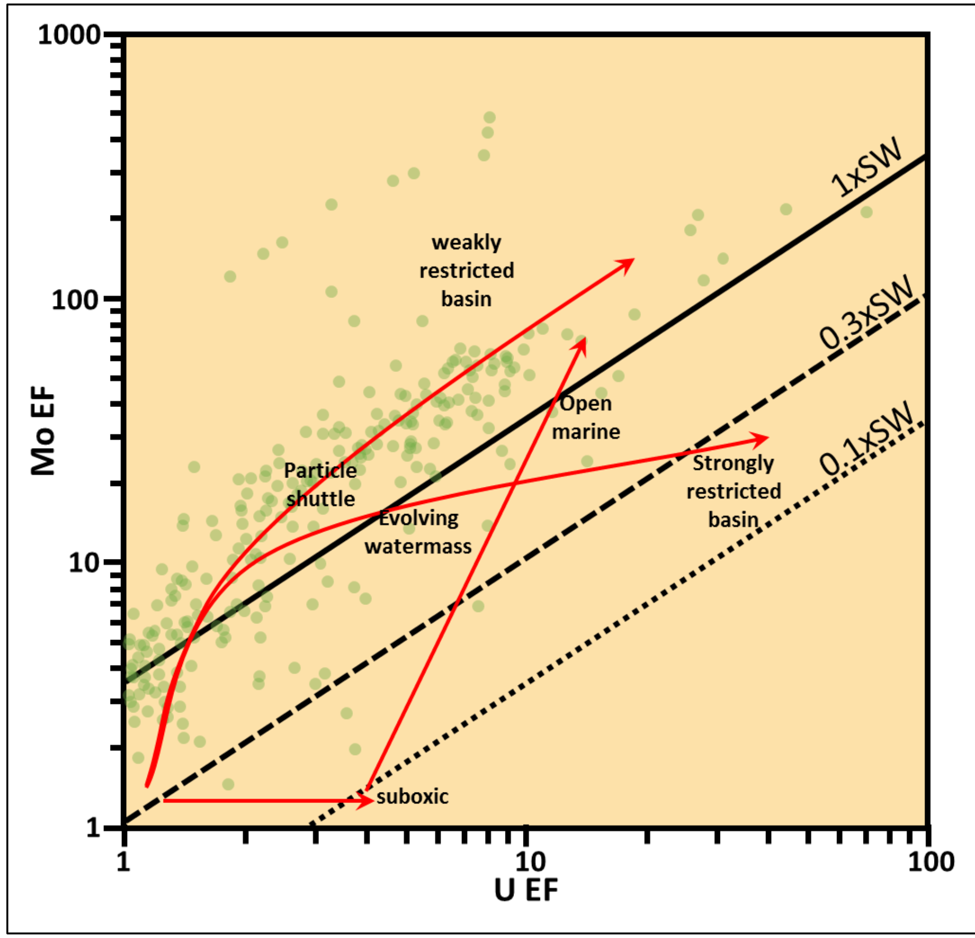
1. Small syngenetic framboids (SF) form in the water column.
2. Chemocline drops, to or below, the sediment-water interface and diagenetic framboids (DF) form.
3. Euhedral grains (E) form along with the welding of framboids.

Outline

- Production Mechanisms
- Inorganic geochemistry considerations
- Pyrite morphology
- Discussion
- Conclusions

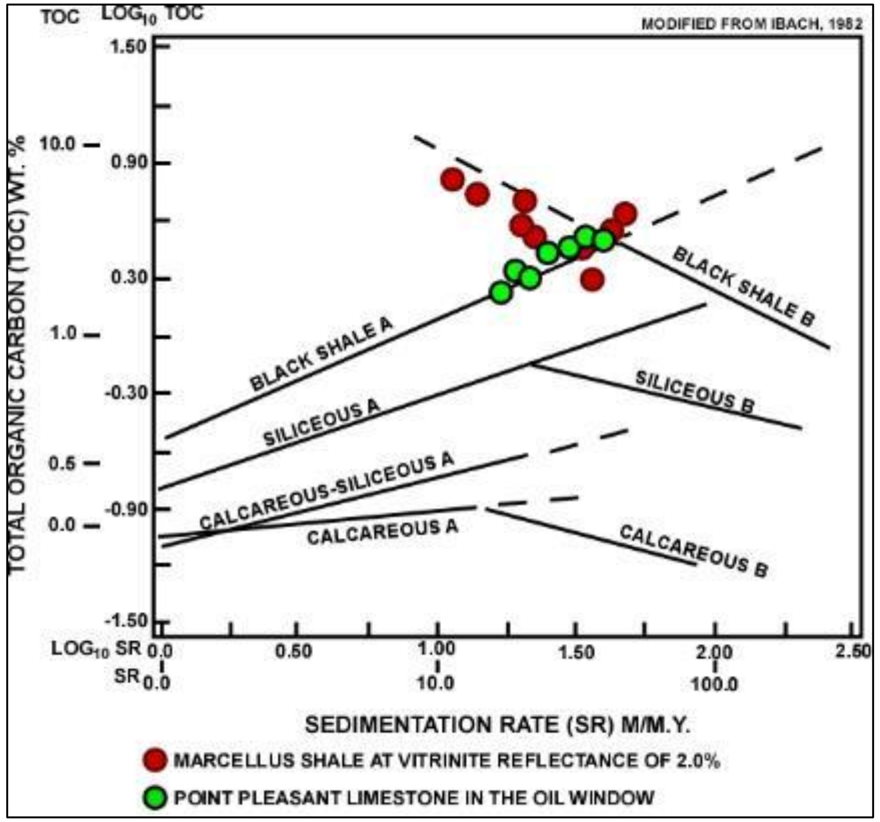






Pyrite in the Marcellus

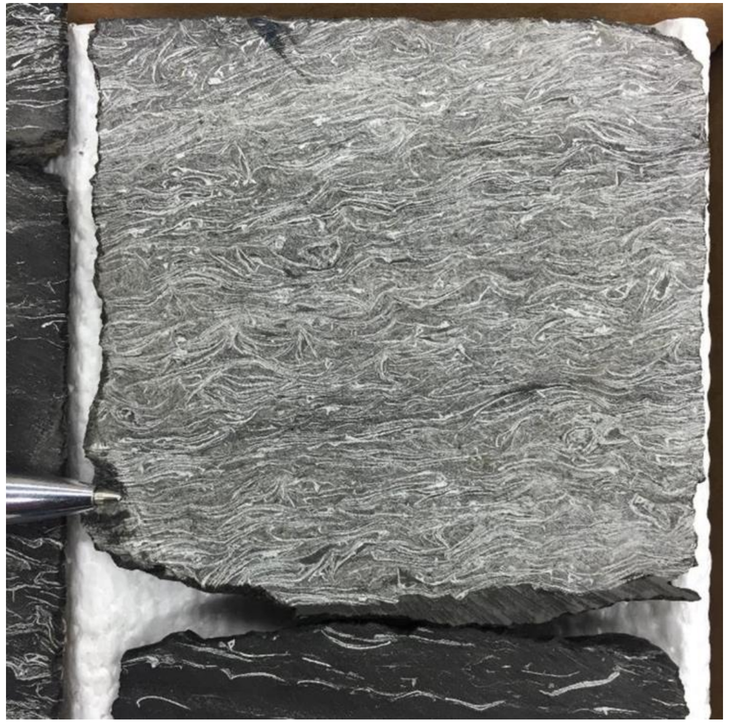
Formation	**Point Pleasant**	**Marcellus**
OM hosted pores	dominant	dominant
Iron Availability	limited	excess
U EF Mo EF	depleted	enriched
Biogenic Quartz	locally abundant	abundant
Framboids	small- Fe limited	small
Redox conditions	dysoxic/oxic	anoxic/euxinic

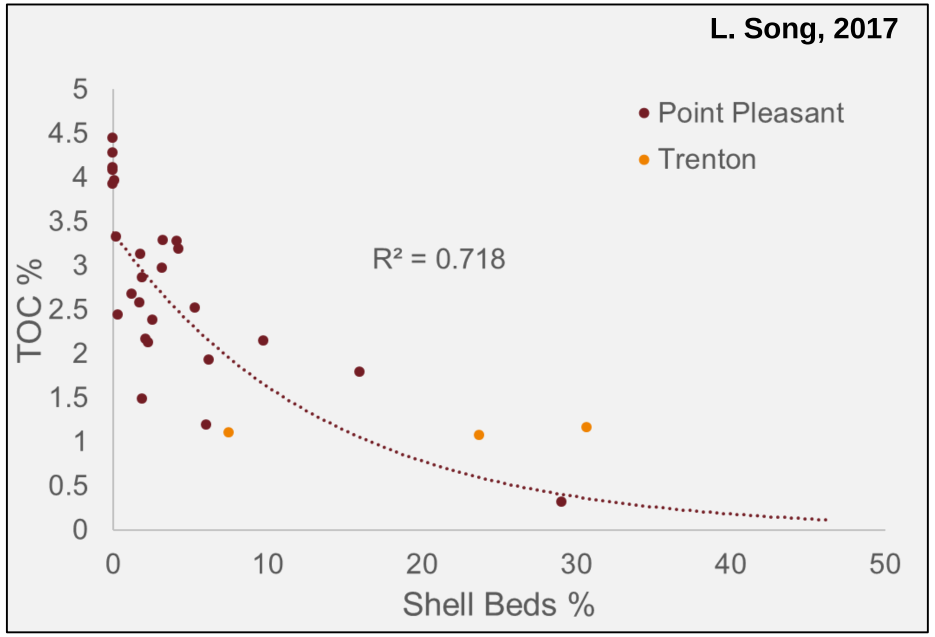


- From these observations we can deduce that the Point Pleasant and Marcellus accumulated under markedly different conditions.
- Exploration and production strategies, while sharing commonalities, may need to account for such diversity in rock types.

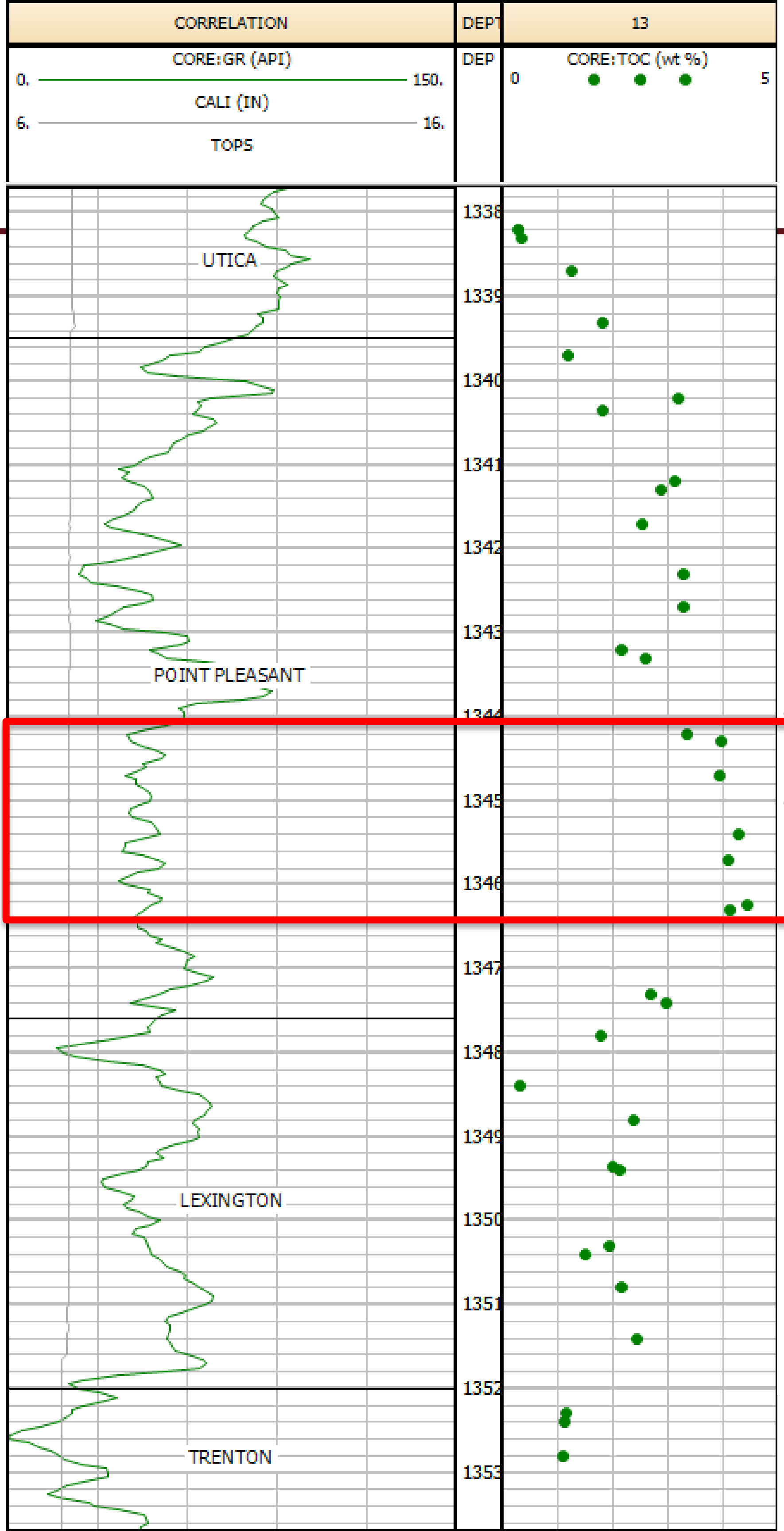
TOC and Sedimentation

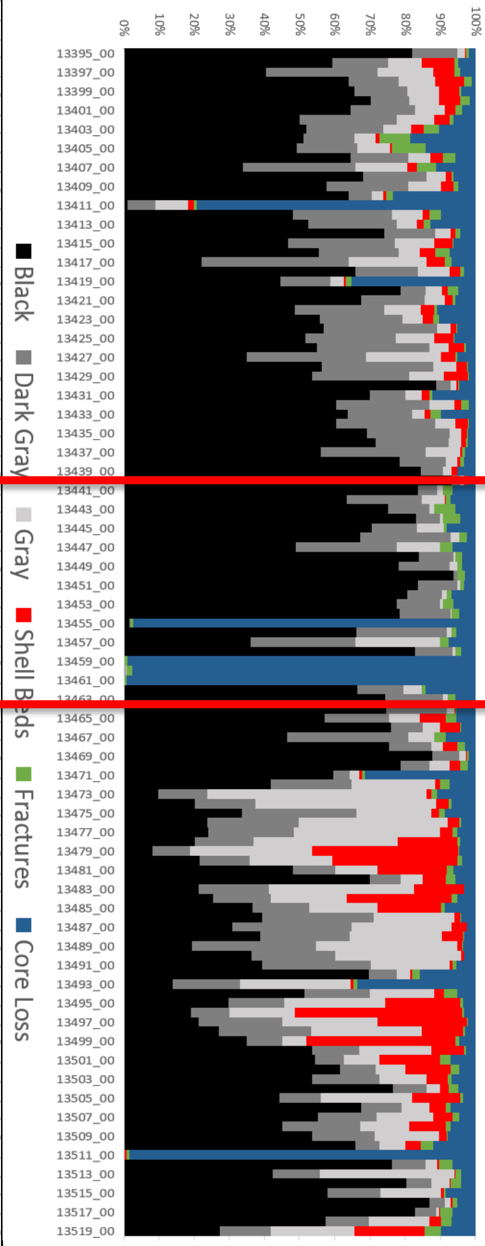
Point Pleasant





L. Song, 2017





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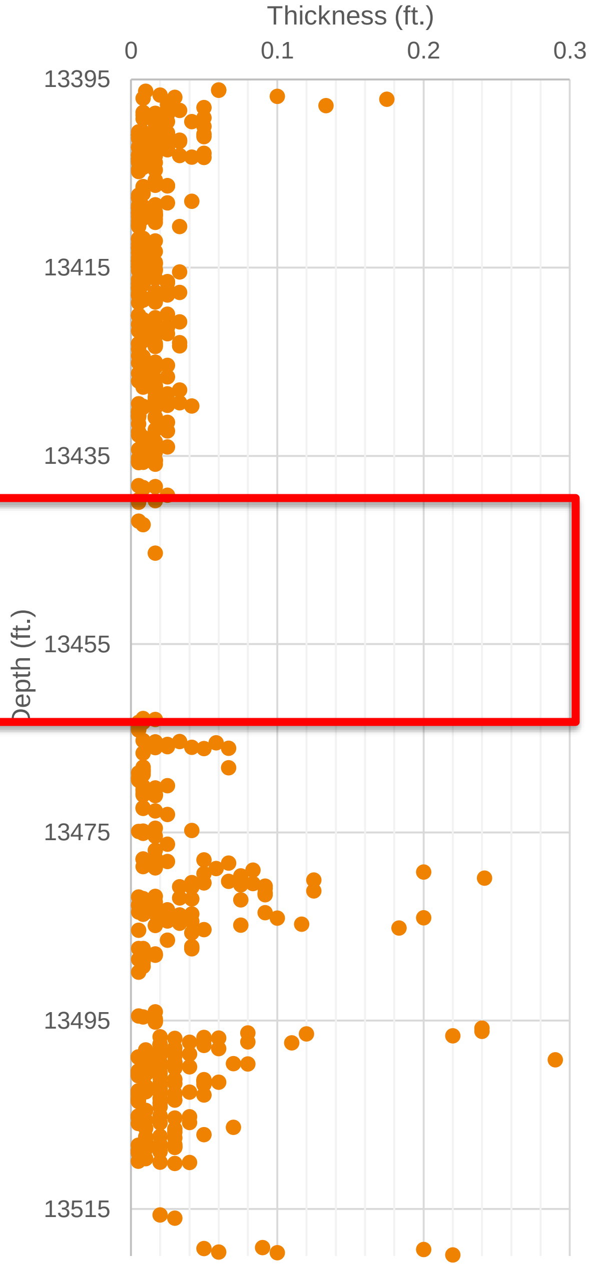
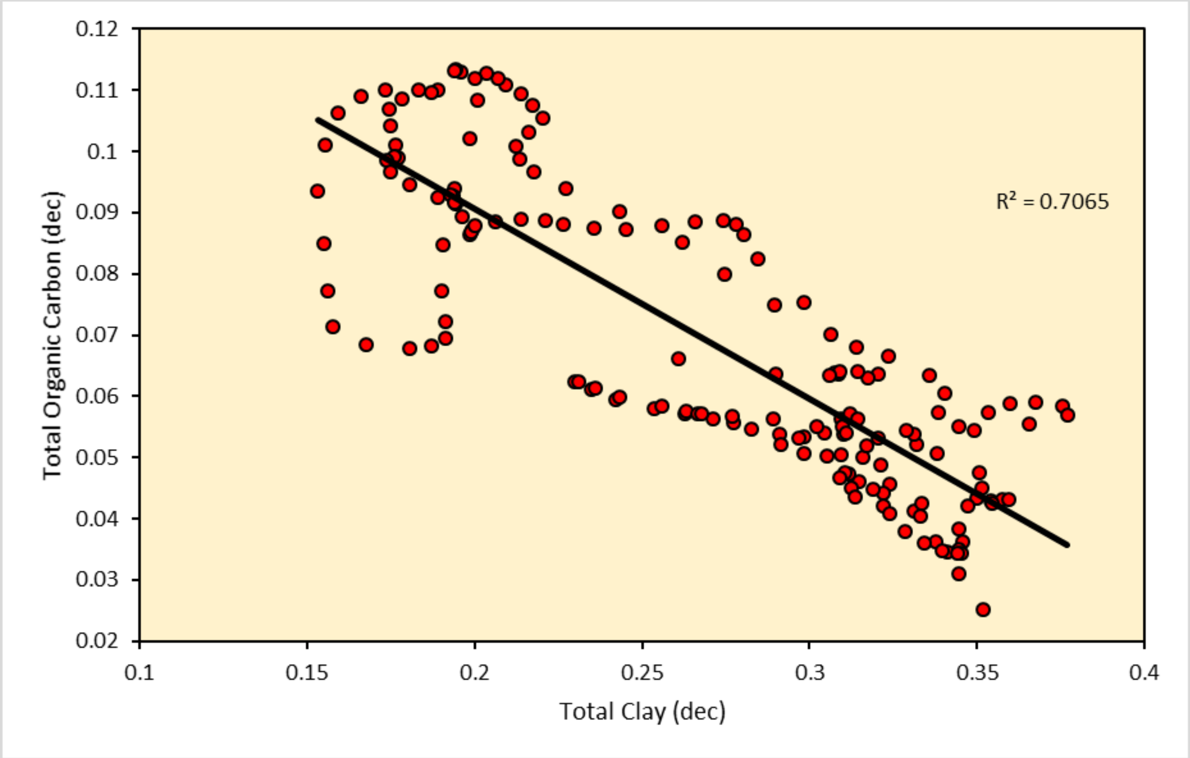
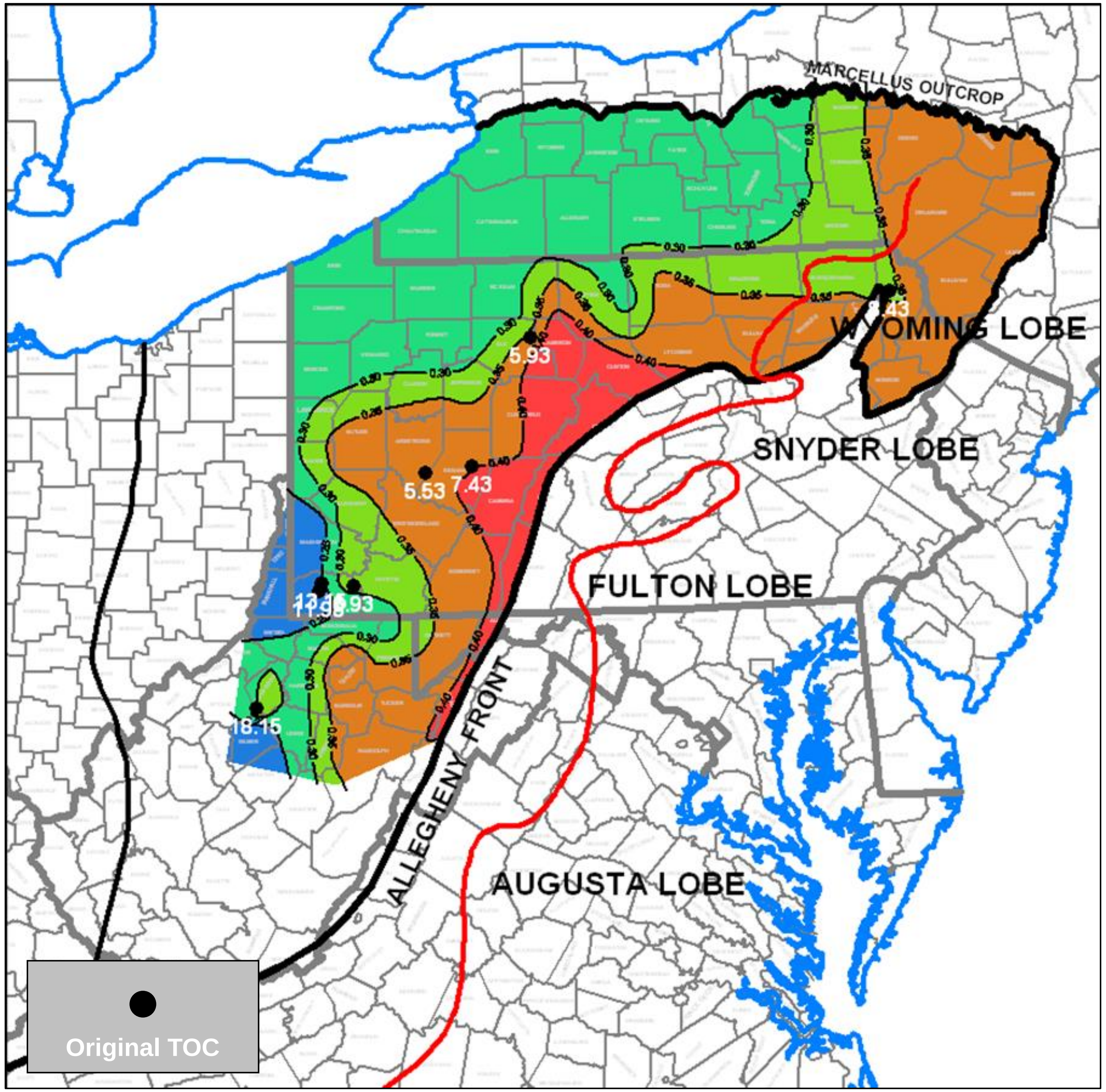


TOC and Sedimentation

Marcellus



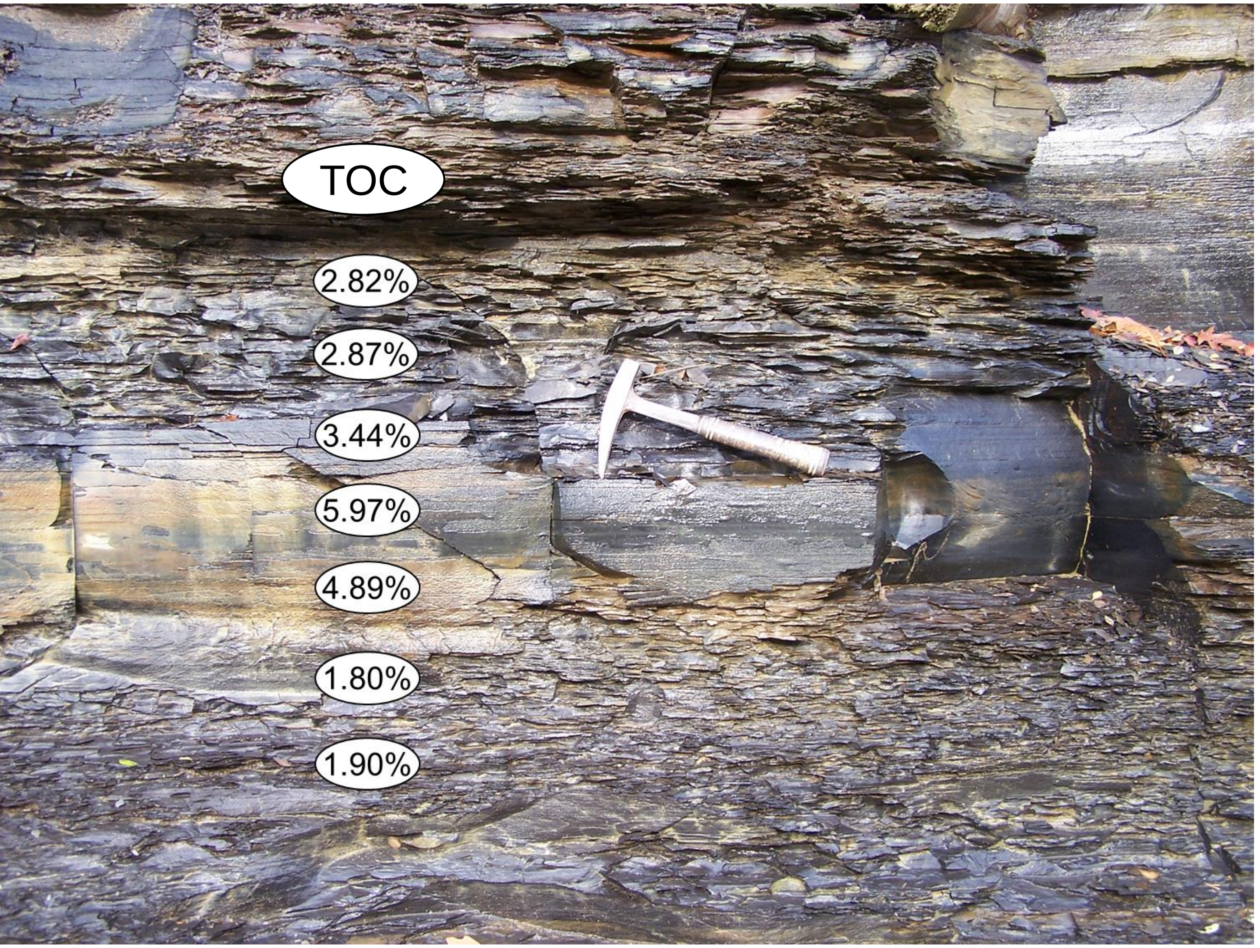


- At the log scale we can observe an inverse relationship between clay content and TOC.
- The same holds true at the basin scale when comparing clay distribution to original TOC calculations.

Reservoir Pressure

Point Pleasant vs Marcellus

- In SW PA, the pore pressure gradient in the Point Pleasant is ~30% higher than in the Marcellus.
  - How is this possible considering the preservation and generative potential of the Point Pleasant is so much lower?
- Perhaps the answer lies in expulsion of hydrocarbon through catagenic fractures.



The catagenic fracture exists in the highest TOC rock.

Higher occurrence of TOC generates more hydrocarbon.

Low permeability means the gas can’t escape (sealed).

Pressure builds until it exceeds the confining stress and tensile strength of the rock.

Rock fractures and the seal ruptures, gas is allowed to escape and an equilibrium is reached.

Formation	wells analyzed	Average joints/ft
Marcellus	6	0.27
Point Pleasant	2	0.03

- The Marcellus has an order of magnitude more joints than the Point Pleasant.

- **It is possible that the Point Pleasant never generated enough pressure to fracture the rock and expulse hydrocarbon.**

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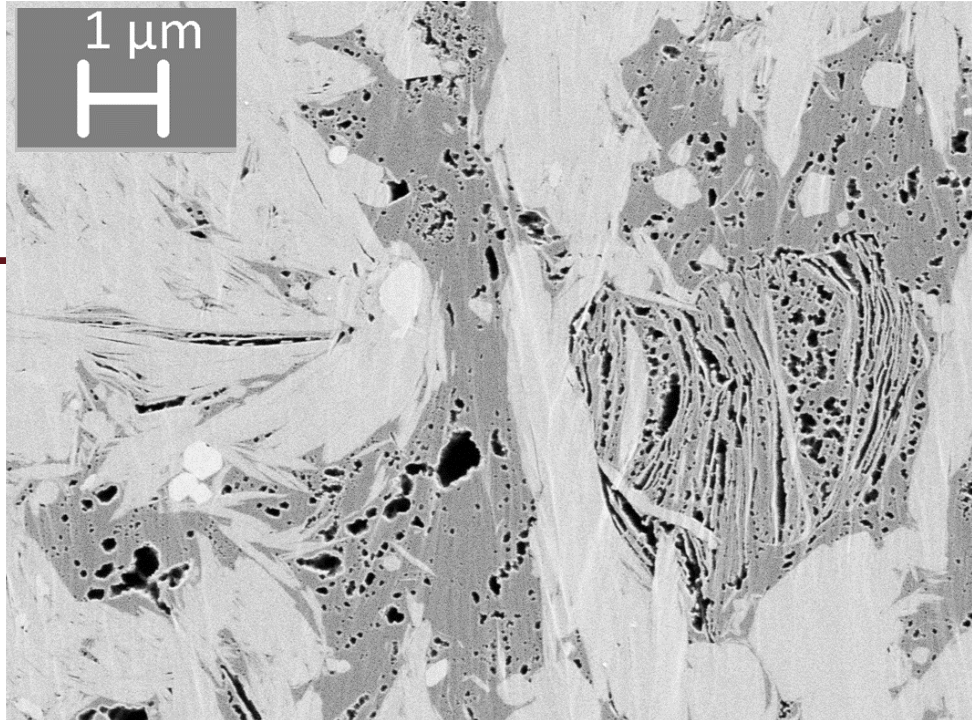

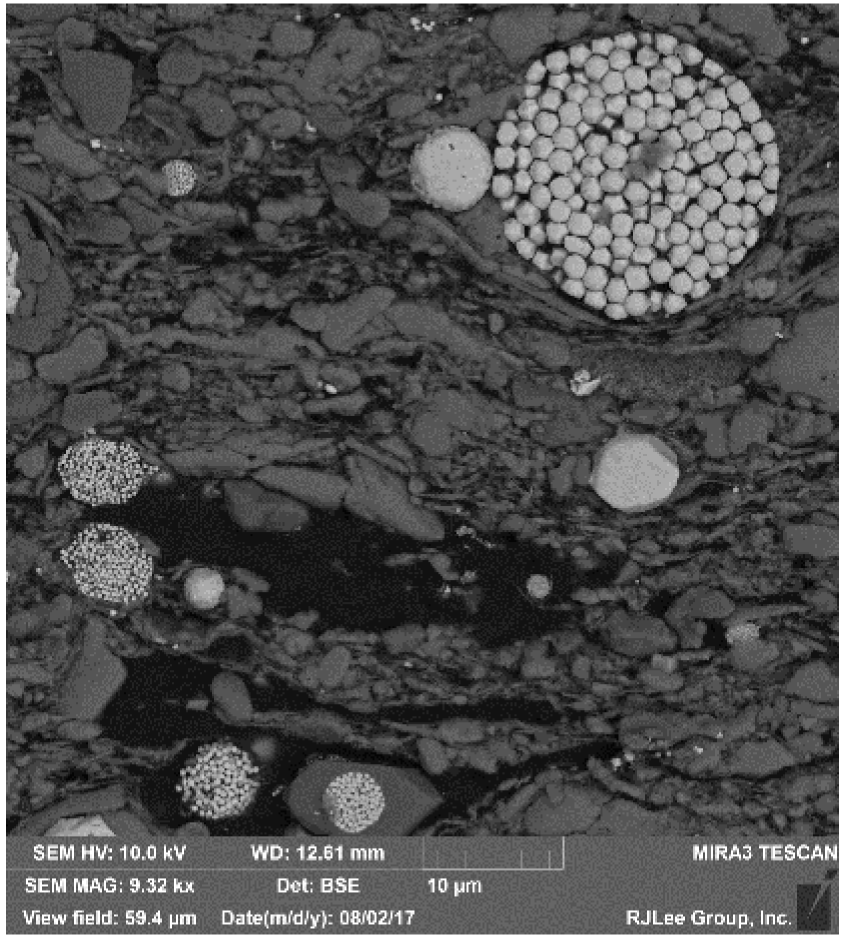

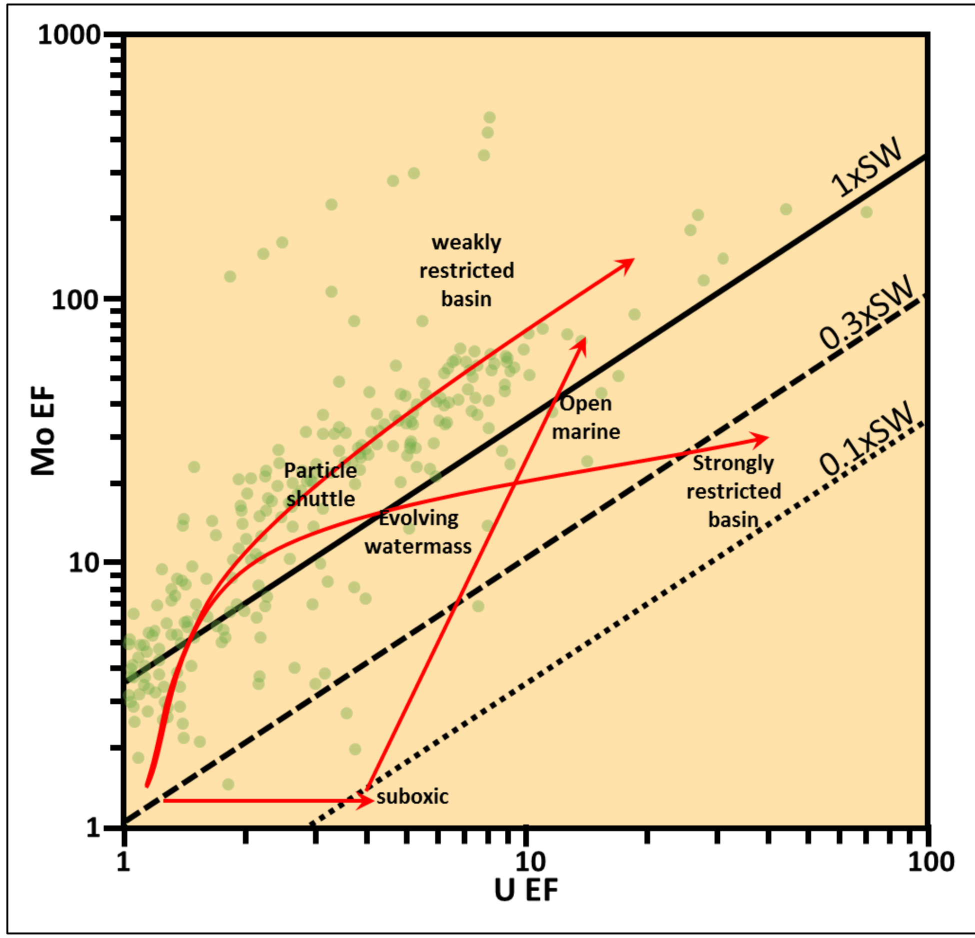

Conclusions

- The Point Pleasant and Marcellus accumulated under very different circumstances.

- The Point Pleasant:
  - Accumulated under dys(oxic) conditions where TOC preservation was accomplished by rapid burial.

- The Marcellus:
  - Accumulated under dominantly euxinic conditions where TOC concentration is controlled by dilution from clastic influx.

- The greater reservoir pressure observed in certain parts of the Point Pleasant may be due to the lack of catagenic fracturing and attendant expulsion of hydrocarbons.