Creating Giants: The depositional and diagenetic pathways to the Ordovician Point Pleasant Limestone and Devonian Marcellus Shale Unconventional Reservoirs

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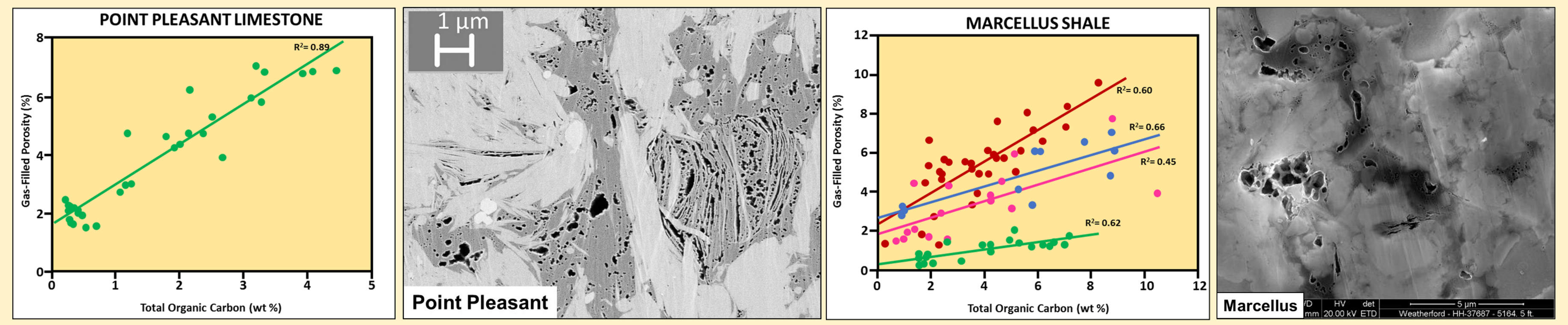
ABSTRACT

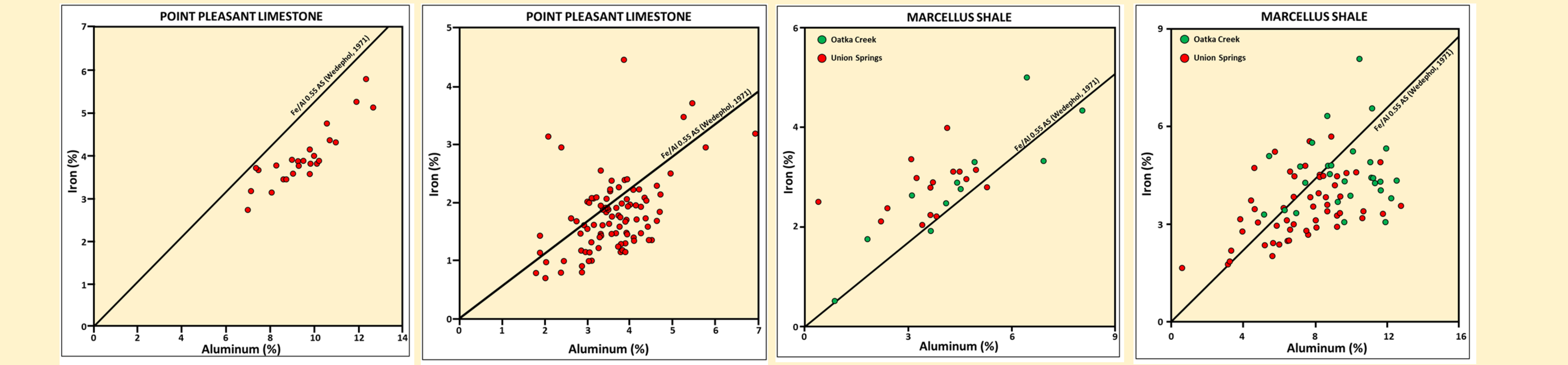
Appalachian Basin "shale gas", driven by the Devonian Marcellus Shale and Ordovician Utica/Point Pleasant has become a significant component of U.S. natural gas production. While they display similar production mechanisms, the conditions under which these deposits accumulated were markedly different. 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, 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 by rapid burial. However, despite the lower organic carbon content, locally the Point Pleasant hosts a pore pressure well 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.

PURPOSE OF THE WORK



Understanding the conditions under which organic carbon accumulate is paramount to understanding the development of many unconventional reservoirs. Indeed, a strong correlation exists between measured gas-filled porosity and total organic carbon (TOC) owing to the organic carbon providing the primary host to interconnected porosity.

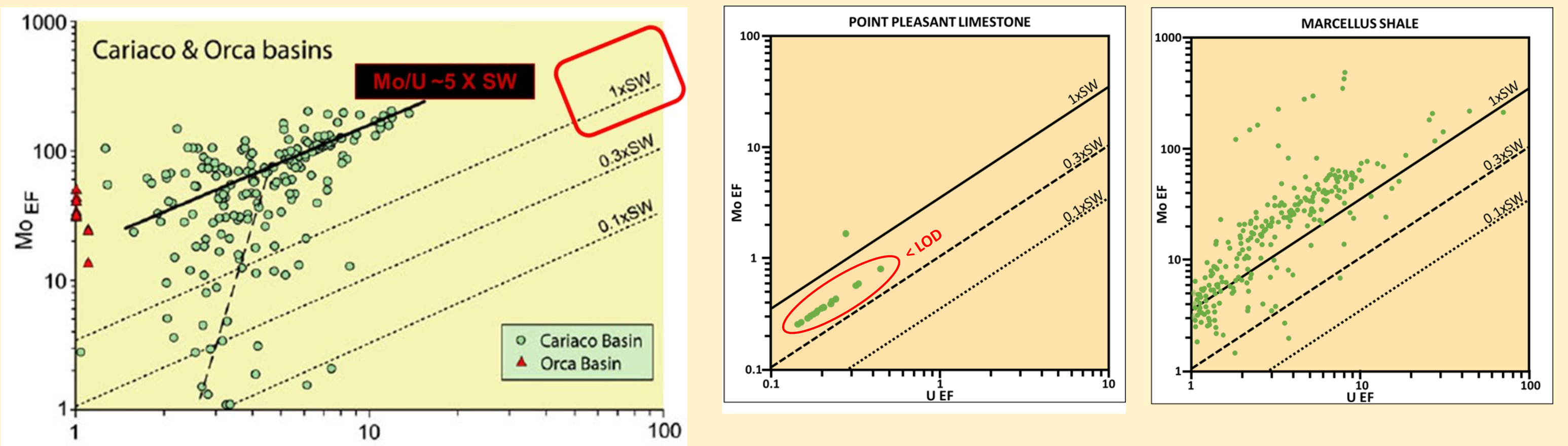
IRON AND ALUMINUM RELATIONSHIPS

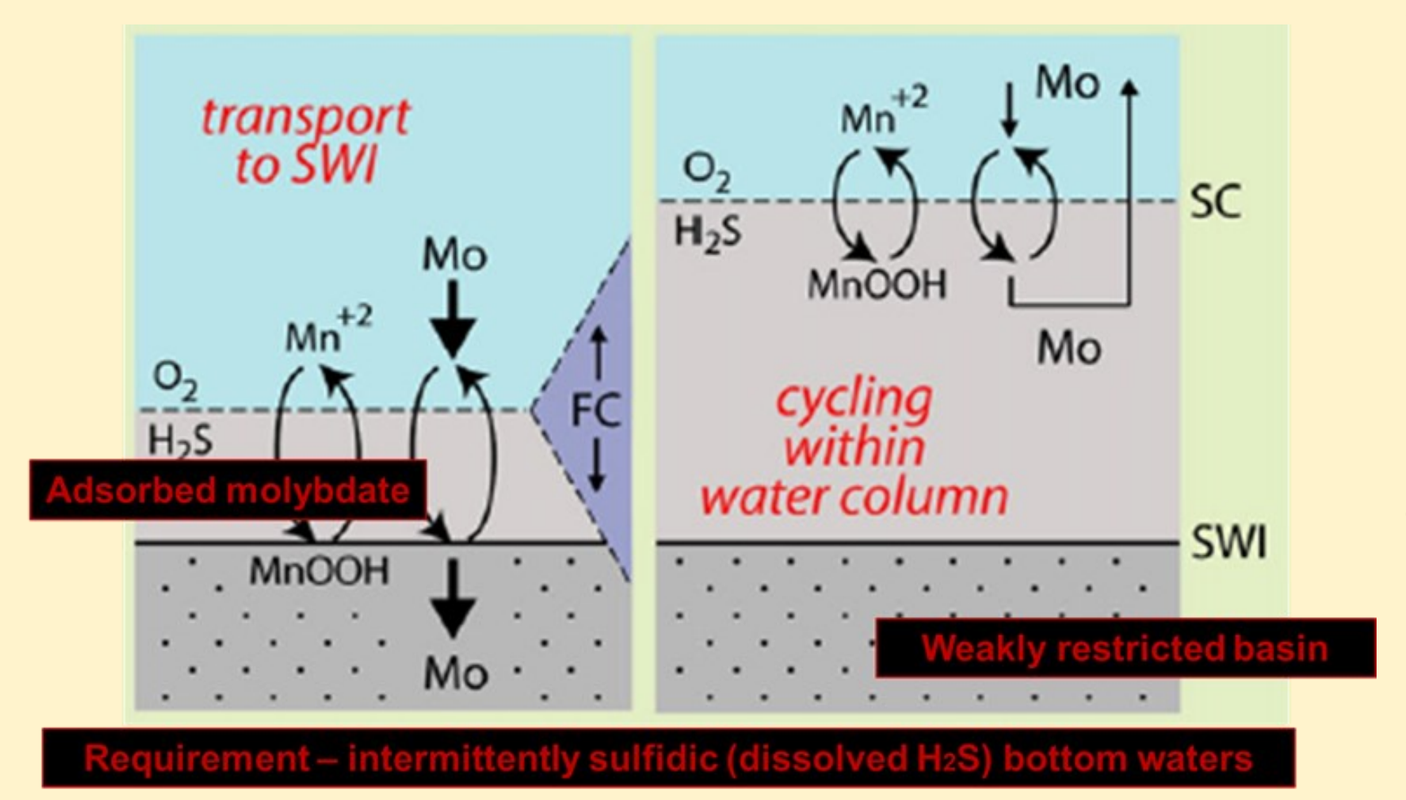


Aluminum (Al) acts as a proxy for clastic influx to the basin. The average ratio of clastic derived Iron (Fe) to Al is 0.55. Values in excess of 0.55 suggest the sequestering of reactive Fe as pyrite under anoxic/euxinic conditions. As a result Fe is often decoupled from Al. It should be noted that in areas of high clastic input, this influx can swamp reactive Fe with less reactive detrital Fe resulting in reduced Fe/Al more coincident with values observed in oxic environments.

Fe/Al ratios of 0.42-0.45 in the Point Pleasant suggest these sediments accumulated under an oxygenated water column. Fe/Al in the Marcellus range from 0.55-0.76. While the higher ratios strongly suggest anoxic/euxinic conditions, the lower ratios likely depict the swamping of the reactive Fe signal.

MOLYBDENUM AND URANIUM RELATIONSHIPS

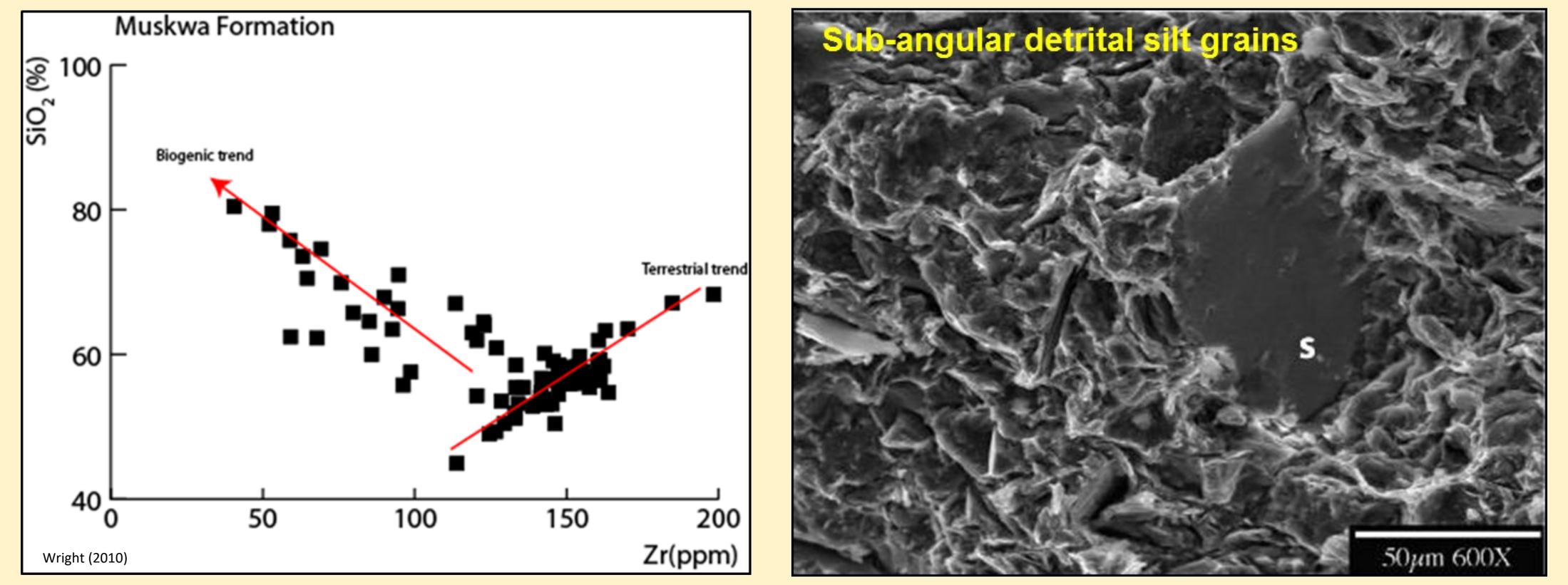


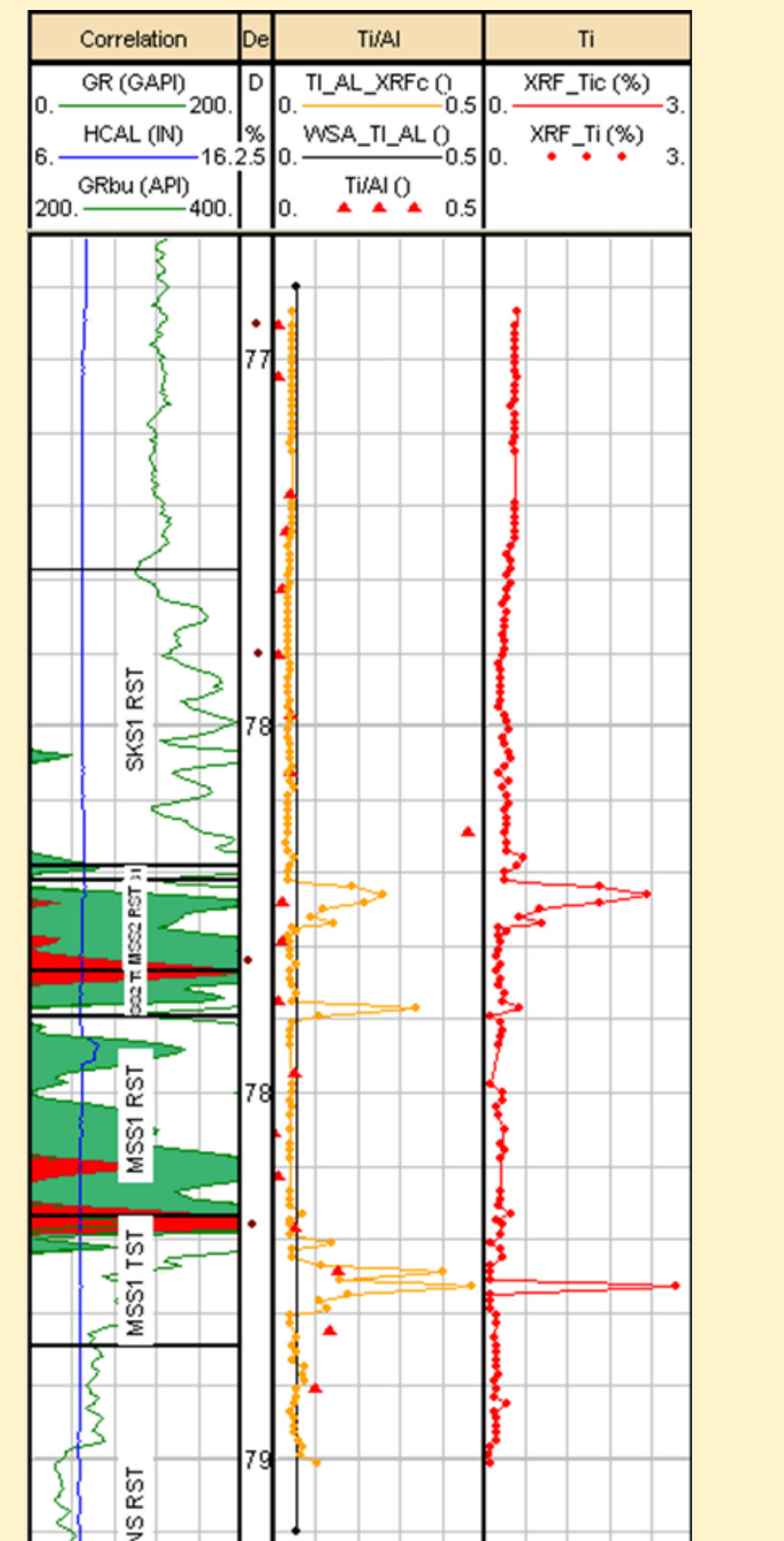


Algeo and Tribovillard (2009) demonstrated that the nature of molybdenum (Mo) and uranium (U) enrichment yields insight into the redox conditions under which sediments accumulate. Considerable enrichment of Mo relative to U suggest the operation of a particle shuttle by which Mo is transported from the oxygenated portion of the water column to euxinic bottom water. The process requires intermittently sulfidic bottom water in a weakly restricted basin that is occasionally reconnected to the global ocean.

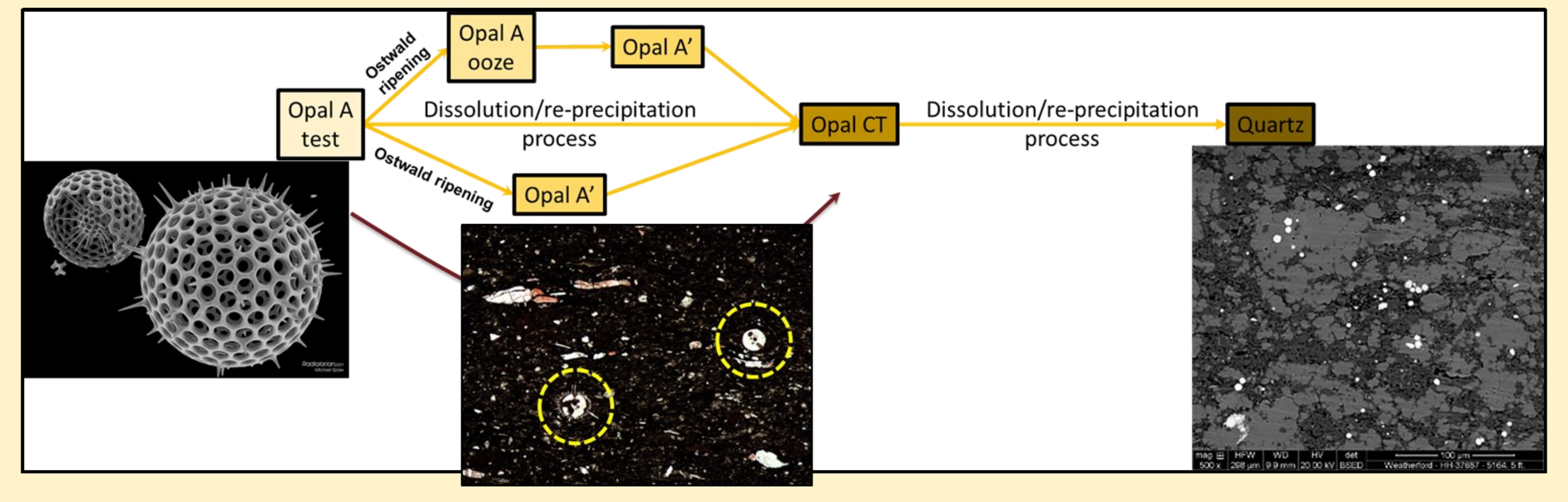
The Point Pleasant demonstrates minimal occurrences of Mo and U in quantifiable abundances using elemental dispersive x-ray fluorescence. This lack of redox sensitive elements suggest accumulation under oxygenated conditions. Conversely, Mo and U values in the Marcellus suggest the robust operation of a particle shuttle, and often euxinic conditions.

QUARTZ OCCURRENCE



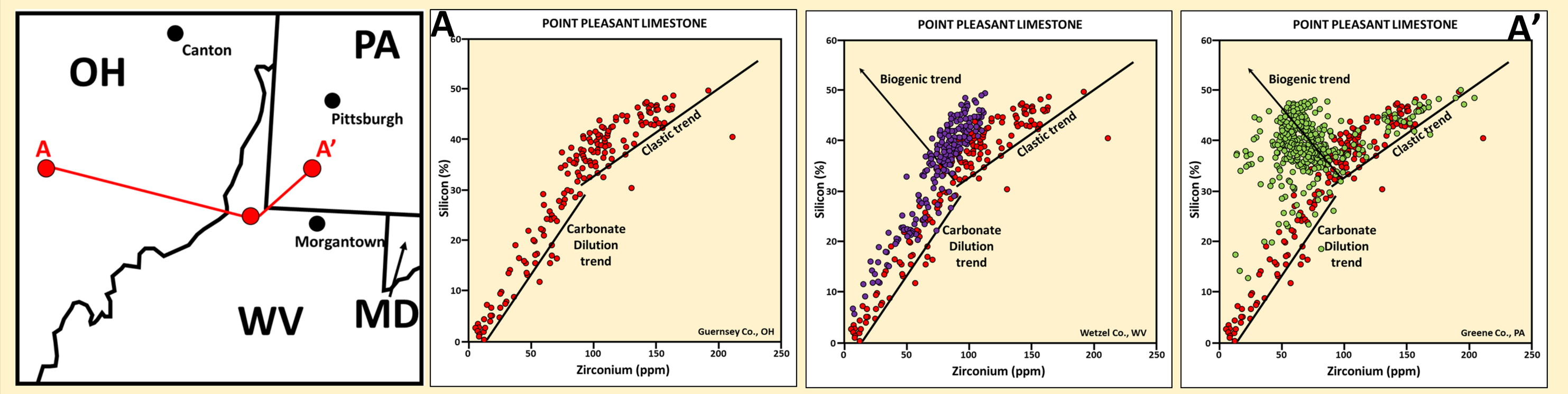


Wright (2010) demonstrated that Zr can be used to differentiate extrabasinal (detrital) quartz from intrabasinal (biogenic) quartz. Further, Titanium (Ti)/Al can distinguish eolian contributions to the quartz budget. Neither the Point Pleasant or the Marcellus demonstrate a significant eolian input.

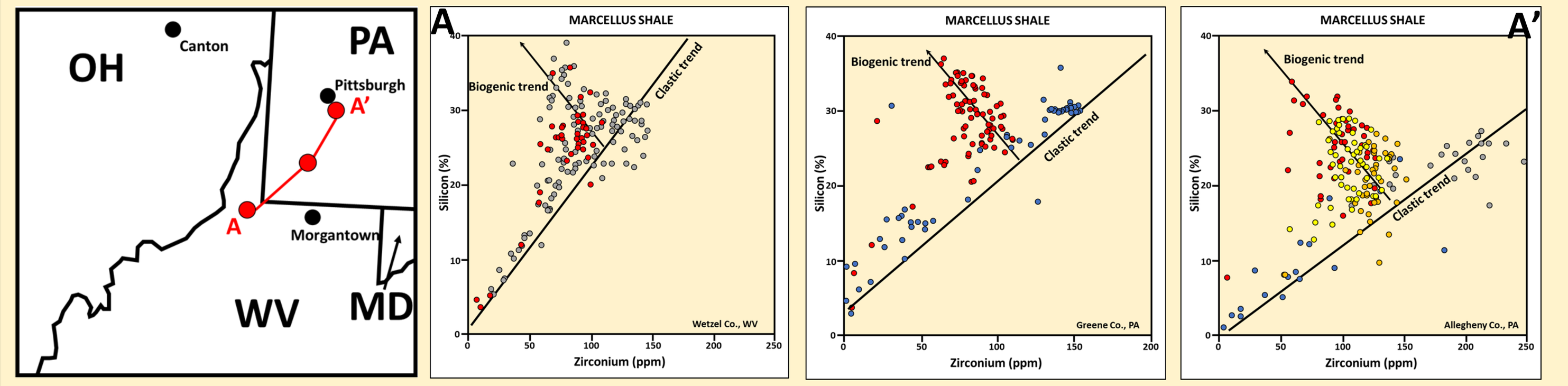


Through a series of steps, biogenic silica tests dissolve and re-precipitate to ultimately form a stable skeletal-like framework of quartz. This quartz frame work adds a structural rigidity and brittleness to the mudstone which is often conducive to hydrocarbon exploitation in terms of drilling rates and hydraulic fracture initiation and maintenance.

QUARTZ OCCURRENCE

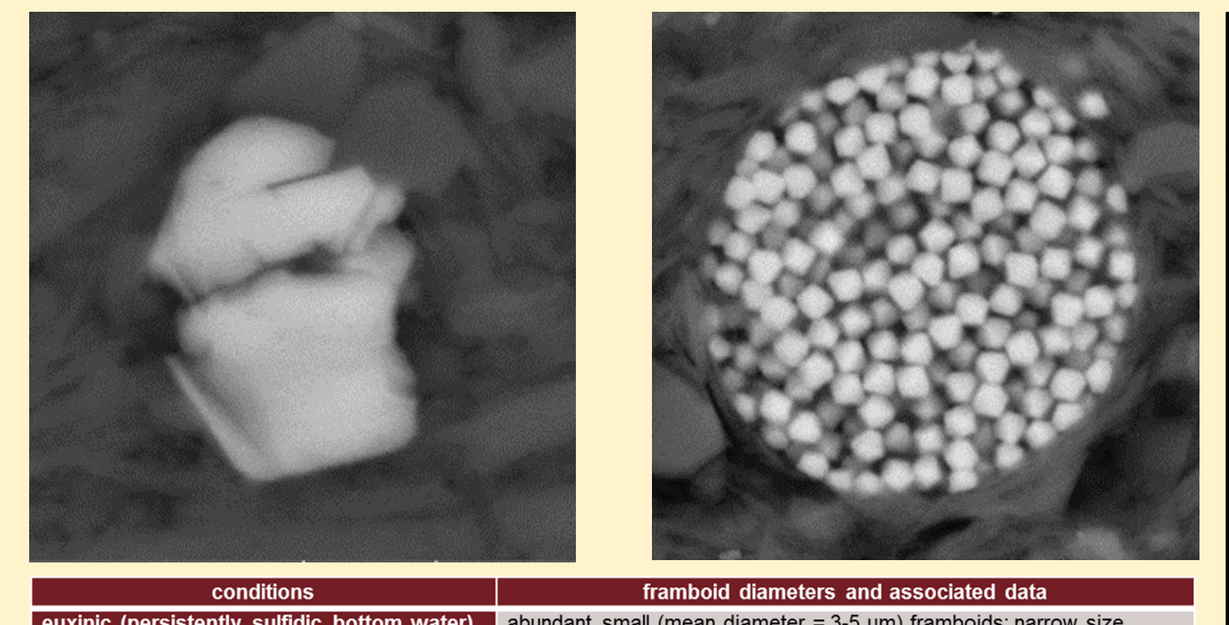


The Point Pleasant is dominated by clastic quartz to the west. The Si/Zr in WV may reflect changes in the role of clastic delivery versus carbonate production. However, the data demonstrates very robust production of biogenic quartz in western PA.

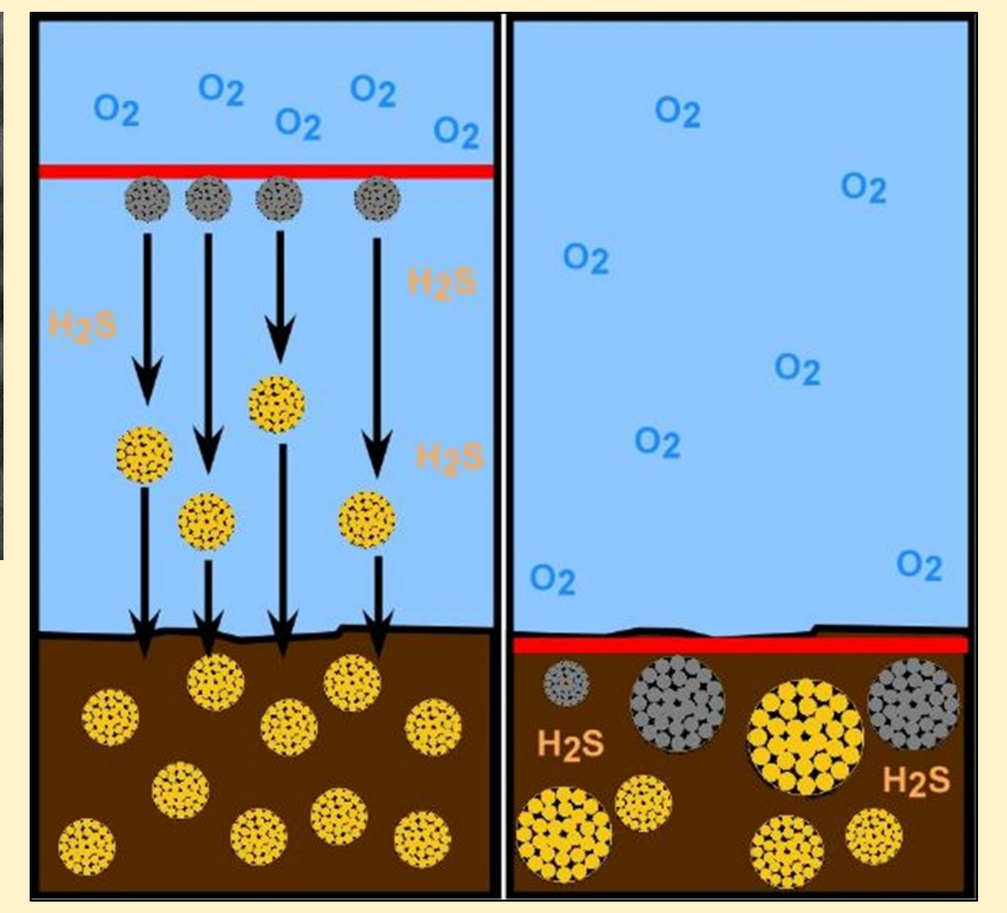


The Marcellus Shale demonstrates robust biogenic quartz production throughout the study area.

PYRITE MORPHOLOGY



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;

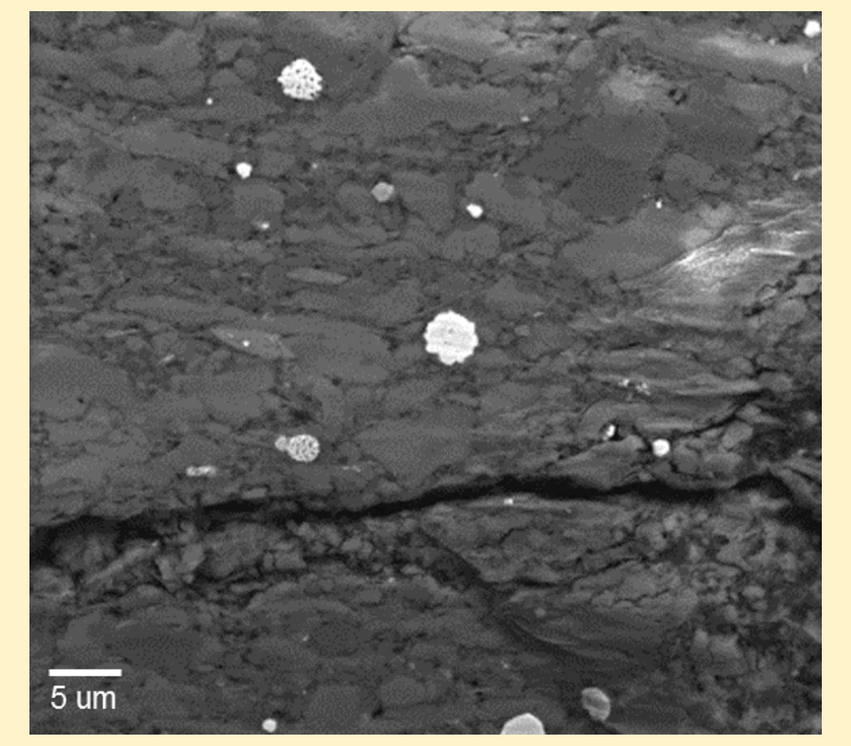


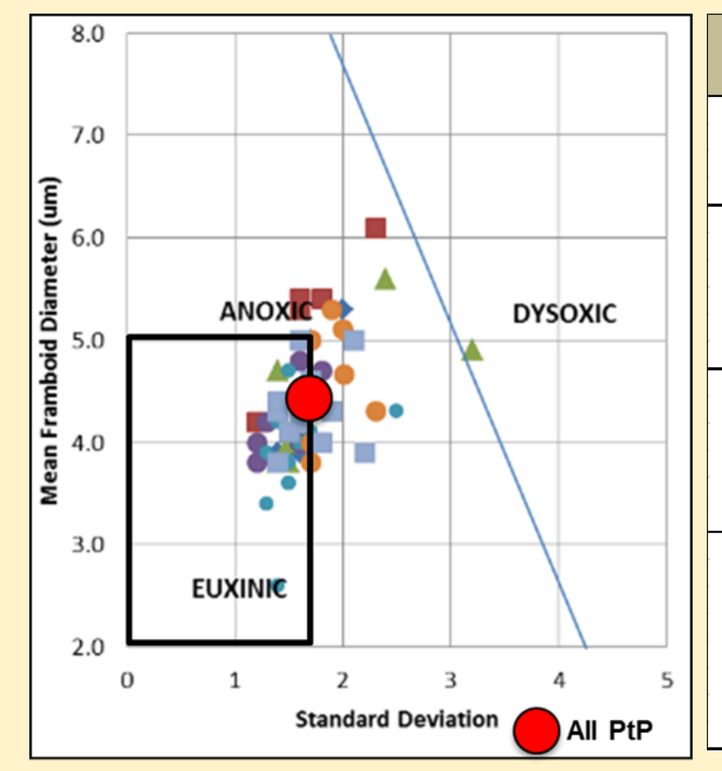
Euhedral and framboidal pyrite grains provide insight into the position of the sulfide chemocline at the time of deposition. Abundant small framboids are generally indicative of sediments accumulating under a dysoxic water column. Larger, and more variable sized framboids along with euhedral grains imply accumulation under a dysoxic water column.

PYRITE MORPHOLOGY – POINT PLEASANT

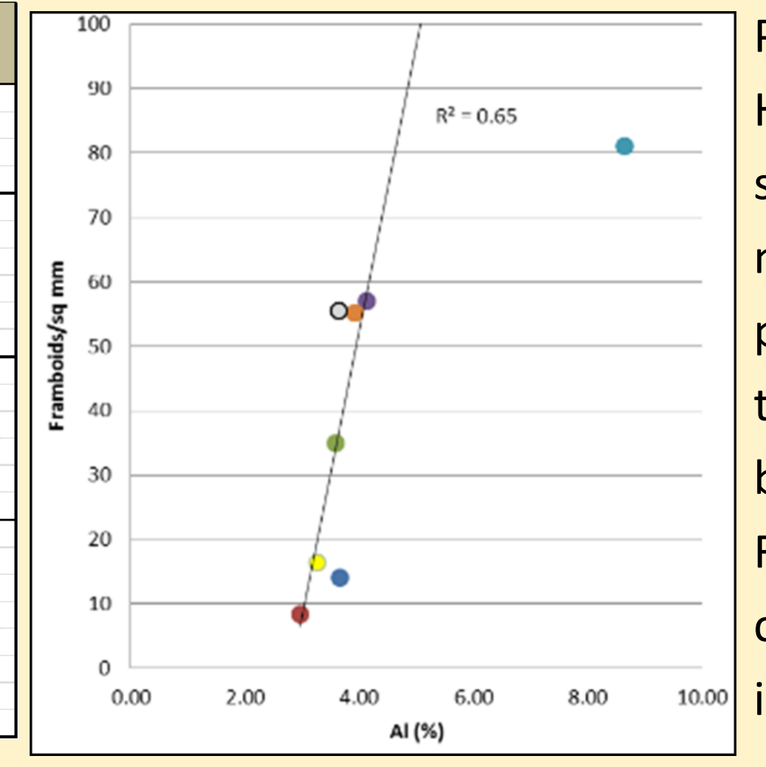
Well	Formation	% BR Pyrite	% framboidal Pyrite
	Point Pleasant	0.56%	35.46%
	Point Pleasant	0.56%	33.89%
	Point Pleasant	0.53%	30.11%
	Point Pleasant	1.37%	8.56%
	Point Pleasant	0.09%	4.79%
	Point Pleasant	0.02%	66.28%
	Point Pleasant	0.19%	6.96%
	Point Pleasant	0.18%	16.13%
	Point Pleasant	0.09%	16.60%
	Point Pleasant	0.27%	7.22%
	Point Pleasant	0.64%	19.25%
	Point Pleasant	0.44%	9.34%
	Point Pleasant	0.33%	3.98%
	Point Pleasant	0.44%	17.63%
	Point Pleasant	1.73%	23.09%
	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





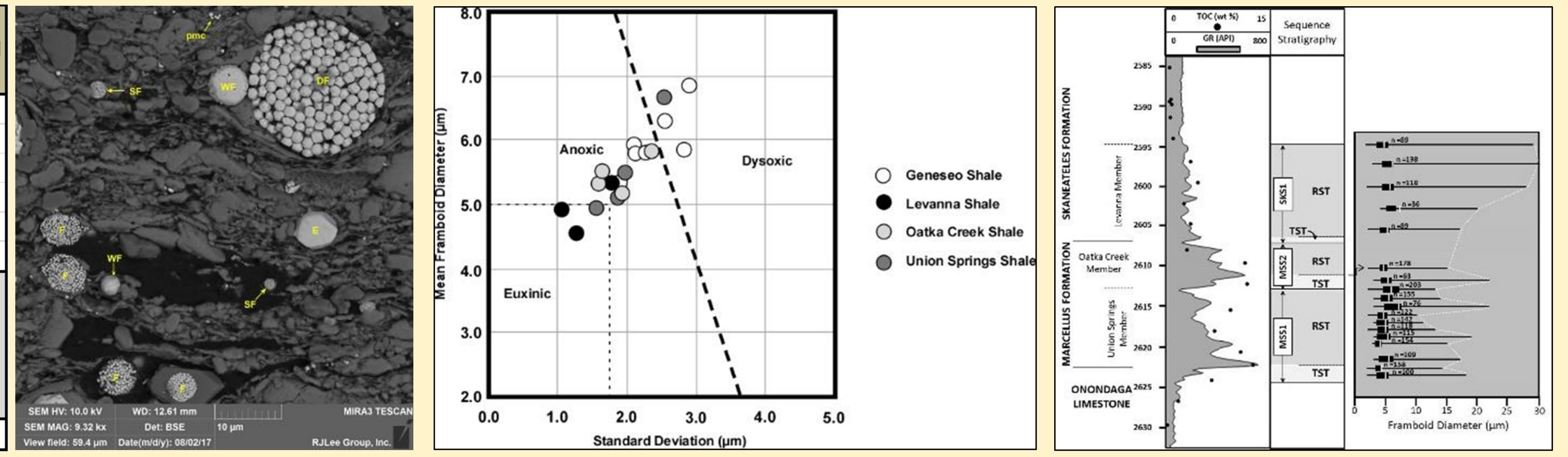
Well	Formation	Al (%)	Fe/Al
	Point Pleasant	3.59	0.41
	Point Pleasant	3.74	0.26
	Point Pleasant	3.43	0.35
	Point Pleasant	3.92	0.33
	Point Pleasant	3.82	0.36
	Point Pleasant	2.57	0.43
	Point Pleasant	2.69	0.48
	Point Pleasant	2.99	0.43
	Point Pleasant	2.80	0.41
	Point Pleasant		
	Point Pleasant	4.42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



Pyrite is relatively uncommon in the Point Pleasant. However, what few framboids exist are uniformly small implying sediment accumulation under an euxinic water column, an interpretation at odds with previously discussed data. This paradox likely owes to a limitation of reactants, specifically Fe. Framboids nucleate and grow but exhaust the supply of Fe before achieving sizes much larger than a few microns. Indeed framboid abundance is tied to clastic influx and the supply of Fe to the basin.

PYRITE MORPHOLOGY – MARCELLUS

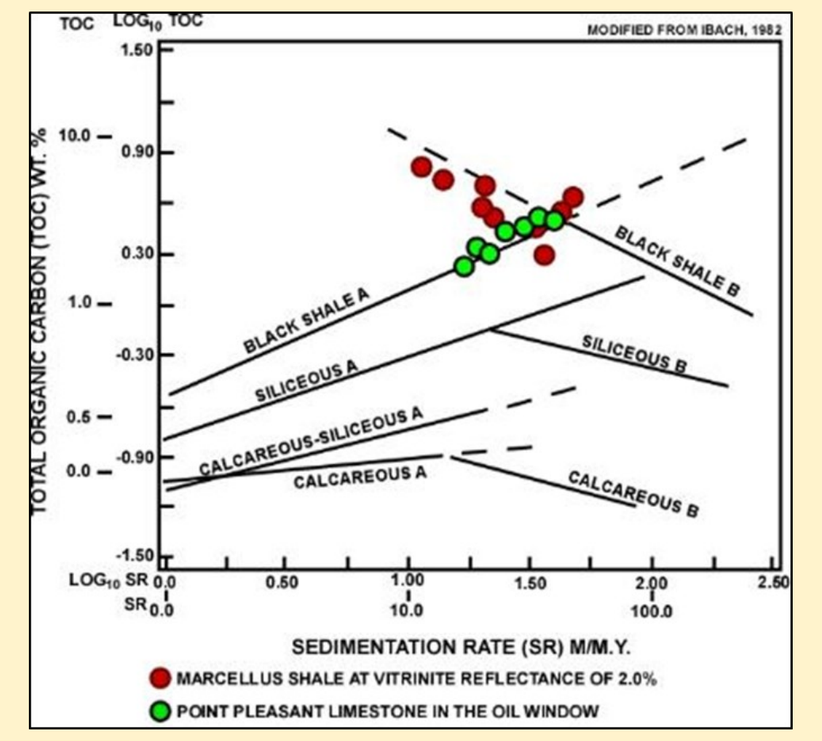
Well	Formation	% BR Pyrite	% framboidal Pyrite
	Oatka Creek	0.76%	70.70%
	Oatka Creek	1.43%	42.98%
	Oatka Creek	0.95%	58.95%
	Oatka Creek	2.94%	34.75%
	Oatka Creek	4.42%	28.73%
	Oatka Creek	3.48%	54.81%
	Union Springs	2.75%	52.43%
	Union Springs	2.13%	13.01%
	Union Springs	1.66%	61.75%
	Union Springs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


SF
WF
SEM HV: 10.0 kV
WD: 12.61 mm
SEM MAG: 9.32 kx
Det: BSE
10 µm
View field: 59.4 µm
Date(m/d/y): 08/02/17
MIRA3 TESCAN
RJLee Group, Inc.
Anoxic
Dysoxic
Euxinic
Standard Deviation (µm)
Geneseo Shale
Levanna Shale
Oatka Creek Shale
Union Springs Shale
ONONDAGA LIMESTONE
RST
TST
MSS1
Framboid Diameter (µm)

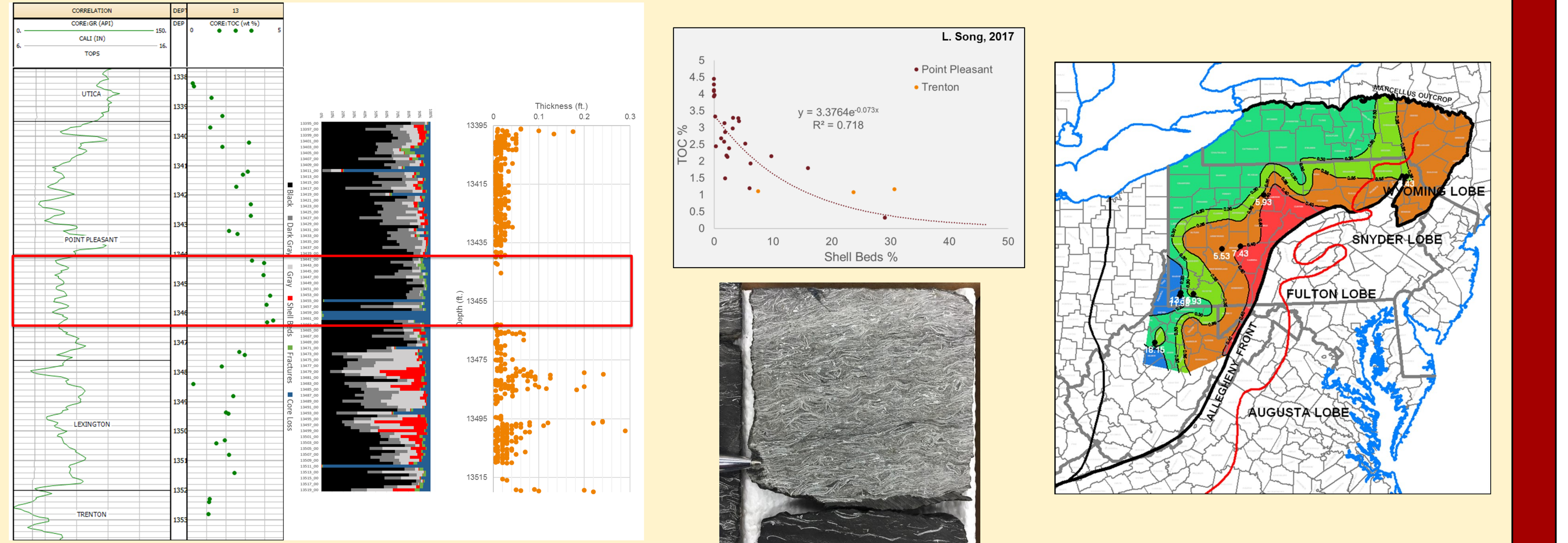
The Marcellus hosts an abundance of pyrite, much of which is framboidal. Inasmuch as the size of framboids suggest a dominantly anoxic to euxinic environment, subordinate large framboids and euhedral grains bear mention. The close spatial association of all three morphologies speaks to a time averaged window where the sample records a fluctuation in the position of the chemocline at a higher resolution than can be observed in a thin section-sized sample. Such fluctuations are consistent with Mo and U profiles discussed previously.

CONCLUSIONS

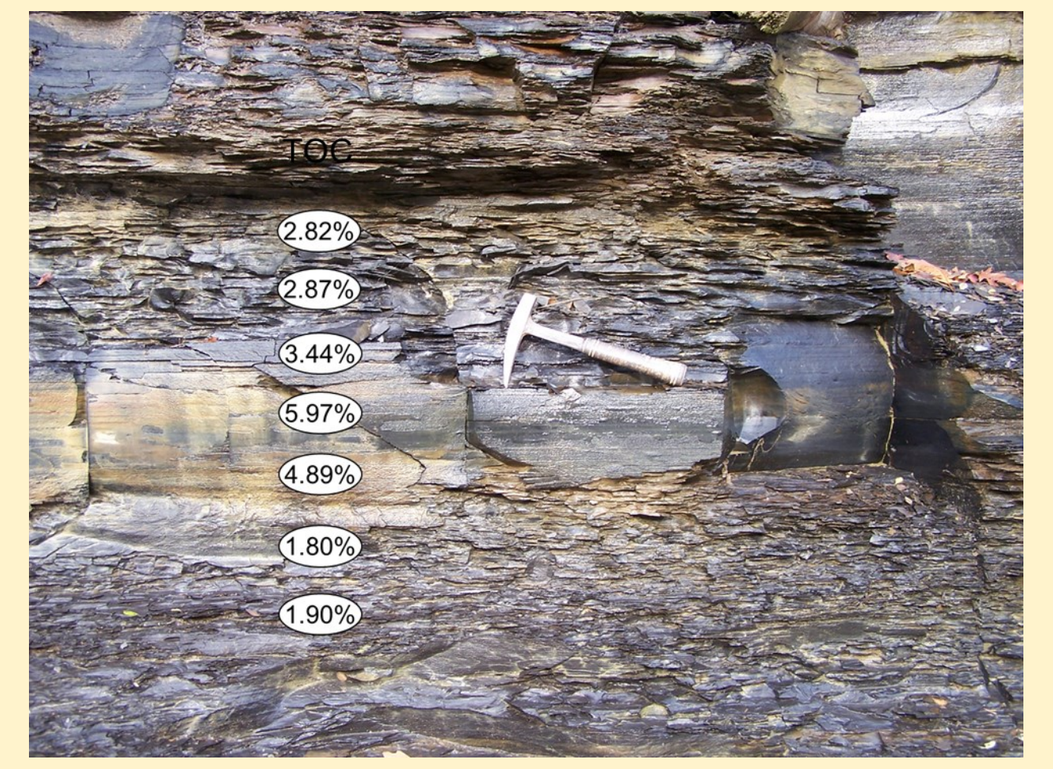
Formation	Point Pleasant	Marcellus
OM hosted pores	dominant	dominant
Iron Availability	limited	excess
U EF Mo EF	depleted	enriched
Biogenic Quartz	locally abundant	abundant
Framboids	small- Fe limited	small
Redox conditions	dysoxic/oxic	anoxic/euxinic



The Point Pleasant and Marcellus accumulated under disparate conditions. Organic-matter accumulation was accomplished by its rapid burial and removal from oxidizing agents in the Point Pleasant. Conversely, the dominantly anoxic/euxinic conditions of the Marcellus allowed for enhanced preservation of organic matter while its concentration was controlled by the dilution of incoming clastic material.



Indeed, investigation of a Point Pleasant core reveals that organic-carbon concentration is highest in those beds where detrital input is highest. Further, organic-carbon concentration shows a negative correlation with the occurrence and thickness of *in situ* shell beds. Conversely, basin-scale maps of the Marcellus depict the highest organic-carbon concentrations in areas of lowest clastic input, namely clay.



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

Finally, it is worth mentioning that the reservoir pressure of the Point Pleasant in southwestern PA is ~30% higher than the Marcellus, an observation that is odd considering the lower preservation and generative potential of the Point Pleasant.

However, it is noteworthy that while catagenic (hydrocarbon expulsion) fractures are very common to the Marcellus, they are virtually absent in the Point Pleasant.

Therefore, it is possible that hydrocarbons generated from the thermal breakdown of organic matter in the Point Pleasant never generated a high enough pore pressure to fracture the rock. As such, the majority of the hydrocarbon generated in the Point Pleasant may have never left the system thus preserving its higher reservoir pressure.

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