Deposition and Diagenesis of the Upper Ordovician Point Pleasant Limestone, Appalachian Basin, USA: Insights into Organic Matter Production, Preservation, and Reservoir Development*

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Abstract

The mode and occurrence of sedimentary pyrite have often been used to assess the redox conditions of bottom and pore waters in ancient sediments. Framboids form rapidly in the zone of iron reduction immediately below the sulfide chemocline, while euhedral pyrite grains form at more protracted rates in hydrogen sulfide (H_2S)-bearing water. Sediments accumulating under dysoxic water are characterized by a low occurrence of pyrite which takes the form of euhedral grains with a subordinate occurrence of framboids. However, in anoxic pore waters, morphology shifts to framboidal pyrite of variable and often large (>10 µm) size. Further, sediments accumulating under an anoxic water column illustrate a framboid population that is small in diameter (<5-6 µm) and less variable in size. Pyrite in cuttings and core chips retrieved from vertical and horizontal Point Pleasant wells were analyzed by SEM. Where possible at least 100 framboids were measured, and statistics on the mean, maximum and standard deviation of diameters were analyzed. Results demonstrate a dearth of pyrite in the Point Pleasant (0.02-1.7% of area analyzed). While pyrite morphology is dominated by euhedral grains and masses (~80% of pyrite encountered), the framboids are uniformly small on average (4.7 µm), with just a few >10 µm. The lack of pyrite and its occurrence as mostly euhedral grains and masses suggest accumulation under a dysoxic water column. Conversely, the size of the framboids suggests they formed in a water column containing free H_2S. This apparent paradox may be explained by a model where the occurrence of small framboids resulted from a lack of reactants necessary to sustain pyrite growth in anoxic pore waters. Abundant nucleation sites competing for a finite amount of reactants would result in a population of many small framboids with few large examples. Indeed, the low total iron/aluminum (Fe/Al) content of the Point Pleasant (average Fe/Al 0.45), is below ~20% lower than total Fe/Al of average shale values (Fe/Al = 0.55), which would indicate a low delivery of reactive iron to the seafloor during Point Pleasant deposition. Further, primary productivity may have been limited by the lack of bio-limiting iron. This model is consistent with the sediment accumulating under a dysoxic water column, where TOC preservation was accomplished by its burial and removal from zones of oxidation and biologic degradation.

Selected References

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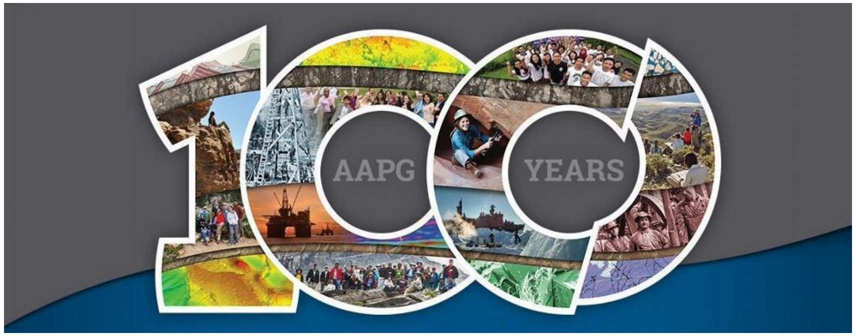

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OUTLINE

- Purpose of this work
- Background on pyrite in sedimentary environments
- Data and results
- Discussion
- Conclusions

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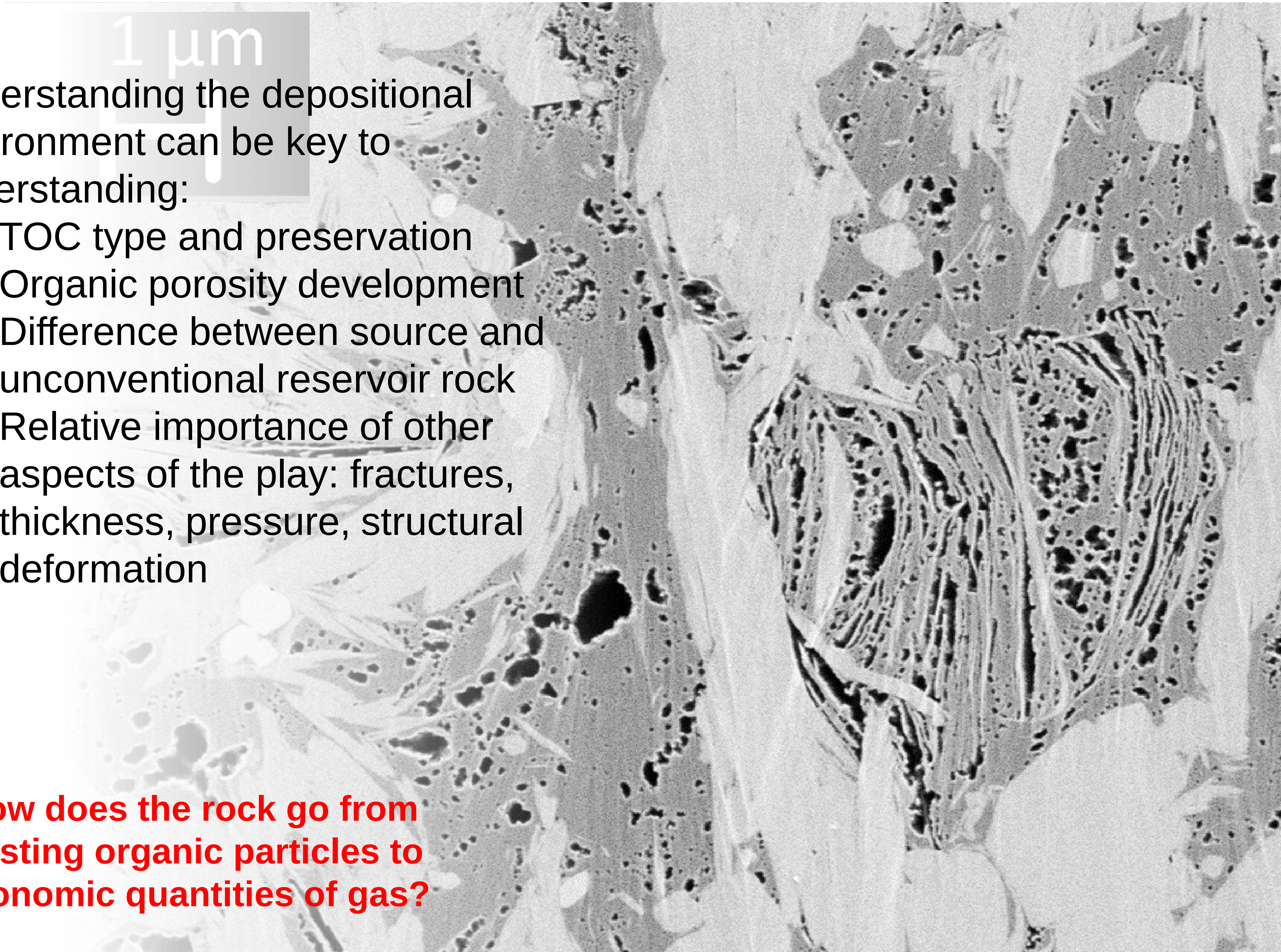
OUTLINE PURPOSE OF THE WORK



- Understanding the depositional environment can be key to understanding:
  - TOC type and preservation
  - Organic porosity development
  - Difference between source and unconventional reservoir rock
  - Relative importance of other aspects of the play: fractures, thickness, pressure, structural deformation

How does the rock go from hosting organic particles to economic quantities of gas?

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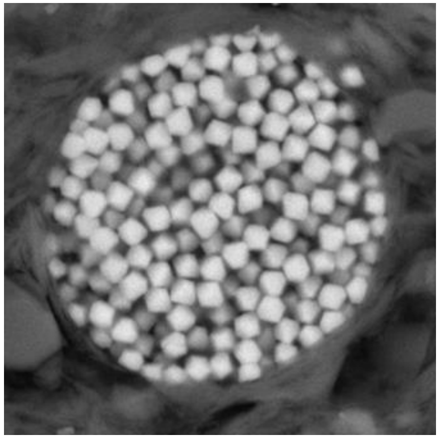
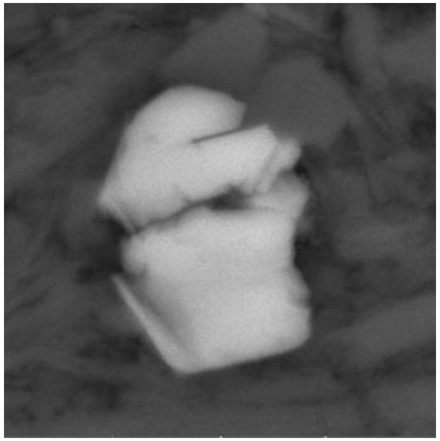
PYRITE

- 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.



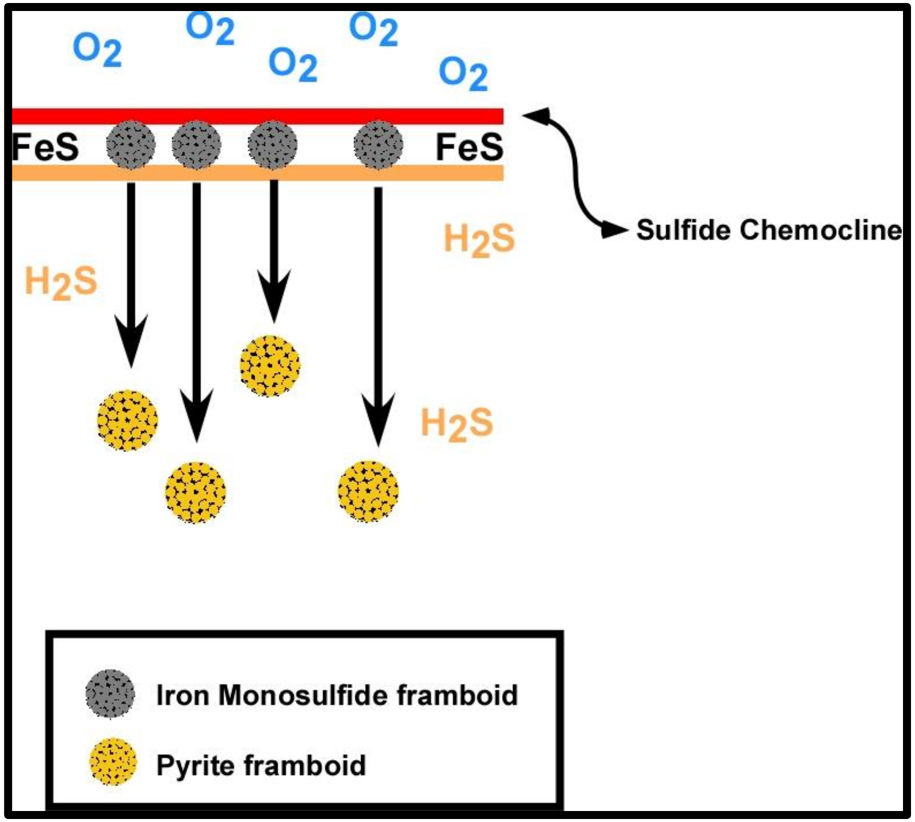
- types of pyrite of interest
  - **Framboids**: spherical aggregates of pyrite microcrystallites that **form at the chemocline** (the transition from sulfide bearing anoxic water and oxygen-bearing water). They can form suspended in the water column and sink to accumulate in the mud and can also form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

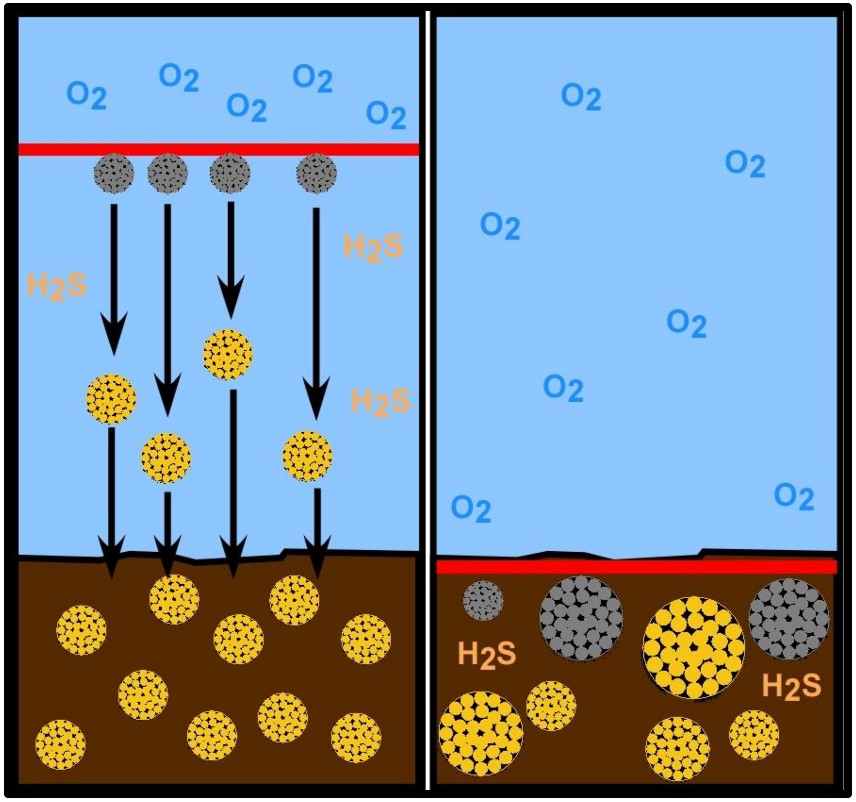


  - **Euhedral:** large individual grains of pyrite that form in the sediment at a much slower rate and can precipitate directly from the interaction of hydrogen sulfide with reactive iron.

FRAMBOID FORMATION

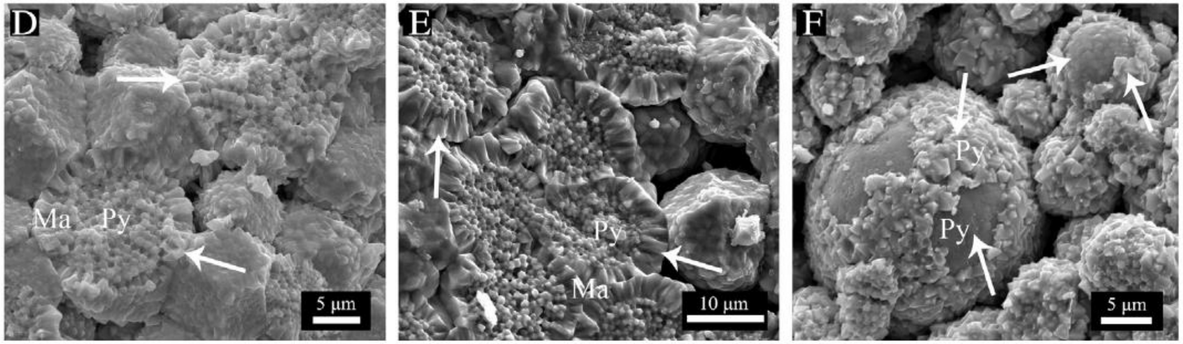
- Framboids composed of iron monosulfides (mackinawite, griegite) form in the zone of Fe reduction immediately below the sulfide chemocline where magnetic properties of the elements attract microcrystallites to each other to form spherical aggregates.
- Framboids that form in the water column can grow to ~5µm before the water cannot support their weight and they sink out of this zone arresting their growth and quickly reacting with H2S 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.



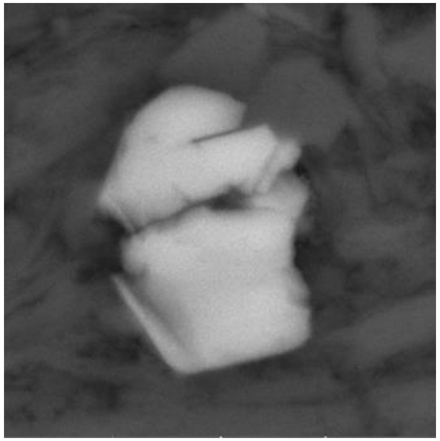


EUHEDRAL PYRITE FORMATION

- 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 also is some instances 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;

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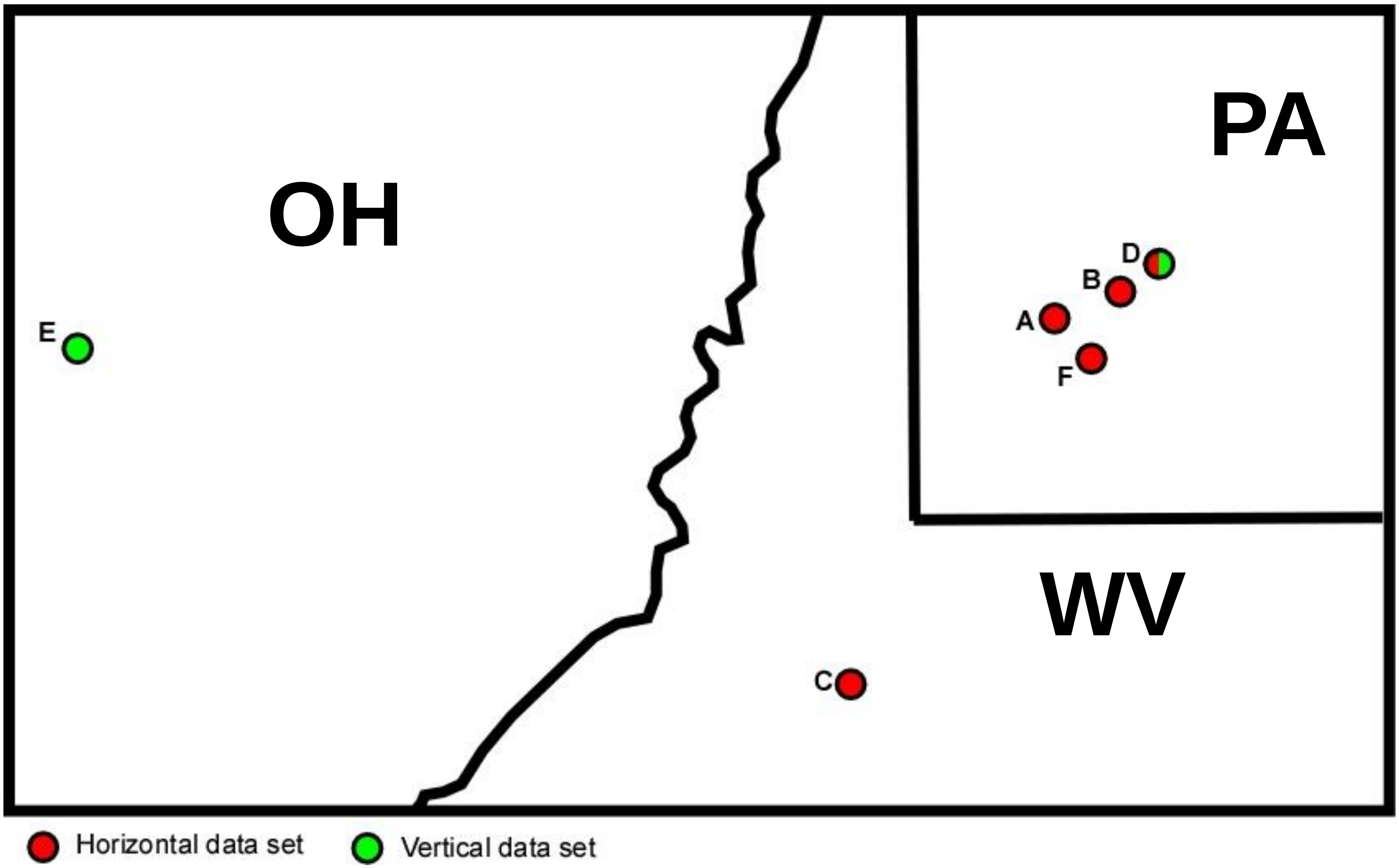
DATA SET

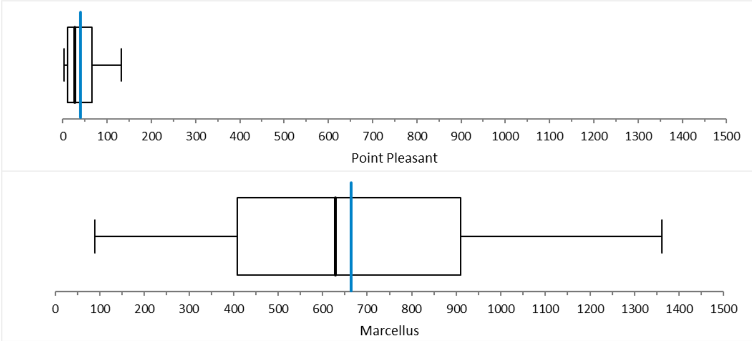


RESULTS: PYRITE COMPARISON BETWEEN MARCELLUS AND POINT PLEASANT

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%**

Well	Formation	% BR Pyrite	% framboidal Pyrite
Well A	Point Pleasant	0.56%	35.46%
	Point Pleasant	0.56%	33.89%
	Point Pleasant	0.53%	30.11%
	Point Pleasant	1.37%	8.56%
Well B	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%
Well C	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%**

- The Marcellus contains much more pyrite than the Point Pleasant. Roughly 5x as much pyrite.
- Further, a much larger proportion of that pyrite, more than double, occurs as framboidal pyrite in the Marcellus, where only ~20% of the pyrite present in the Point Pleasant is framboidal.

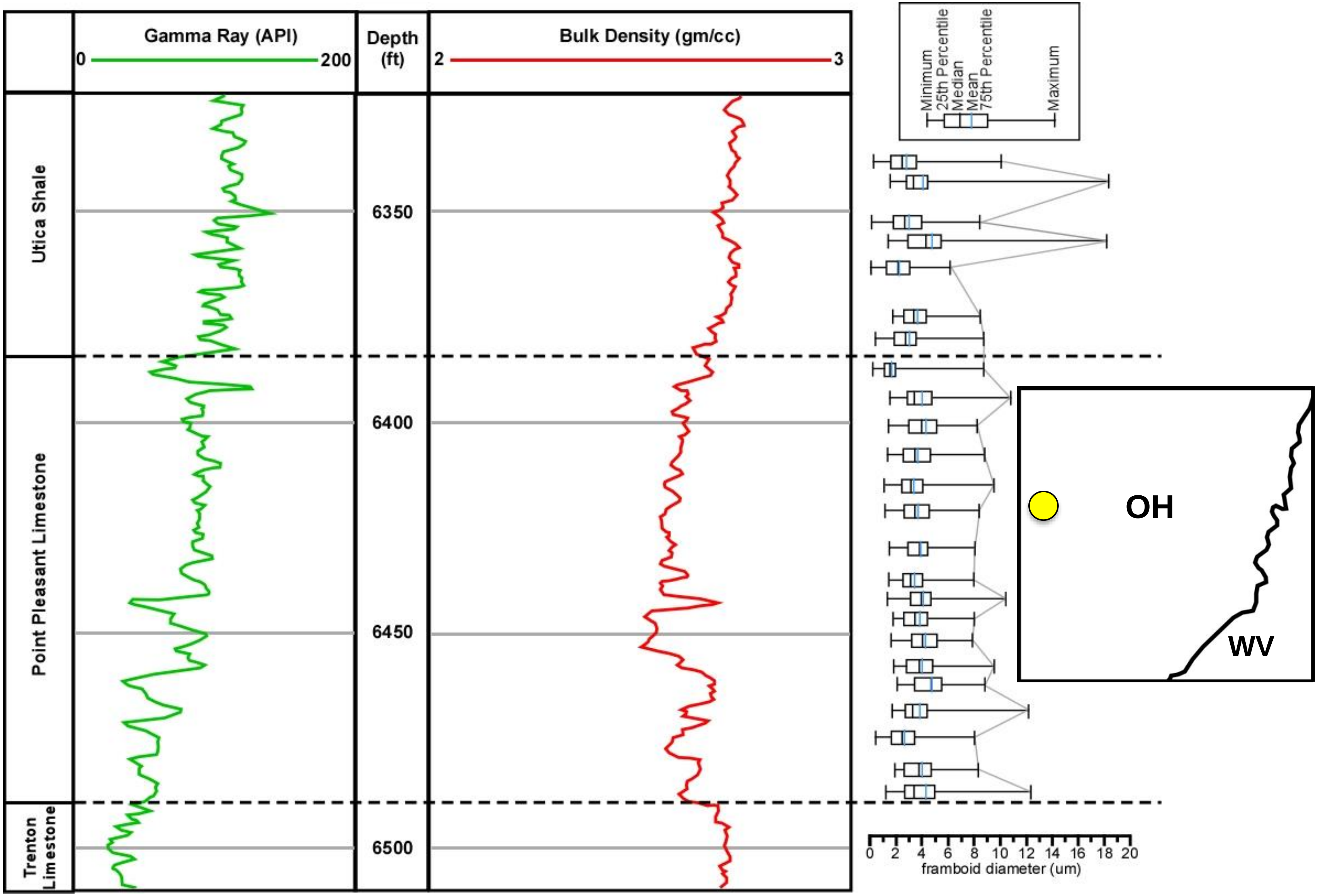


Framboid Density (framboids/mm^2)

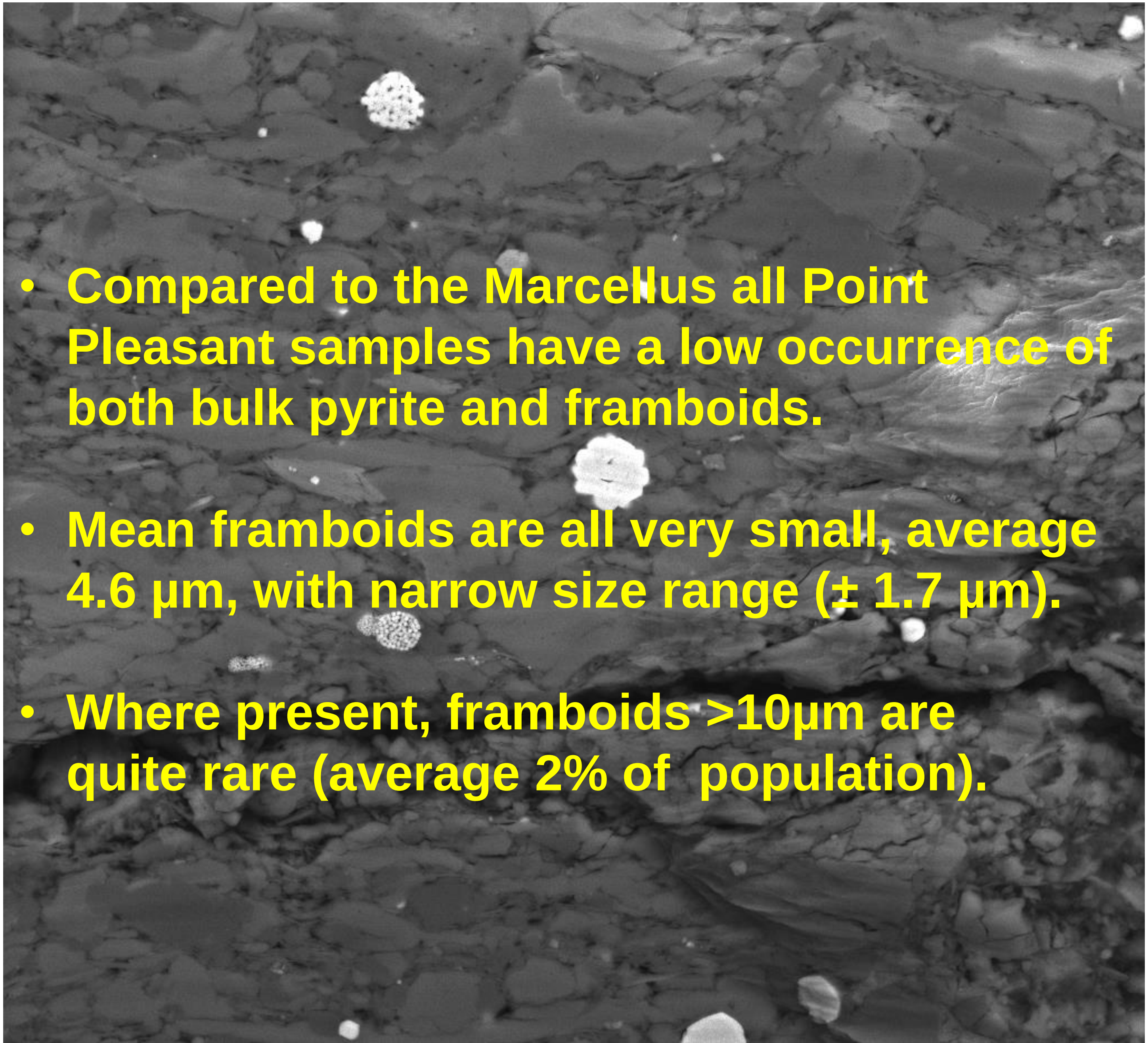
RESULTS: POINT PLEASANT

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

RESULTS: WELL E



SUMMARY OF OBSERVATIONS



- Compared to the Marcellus all 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).
- Where present, framboids >10µm are quite rare (average 2% of population).

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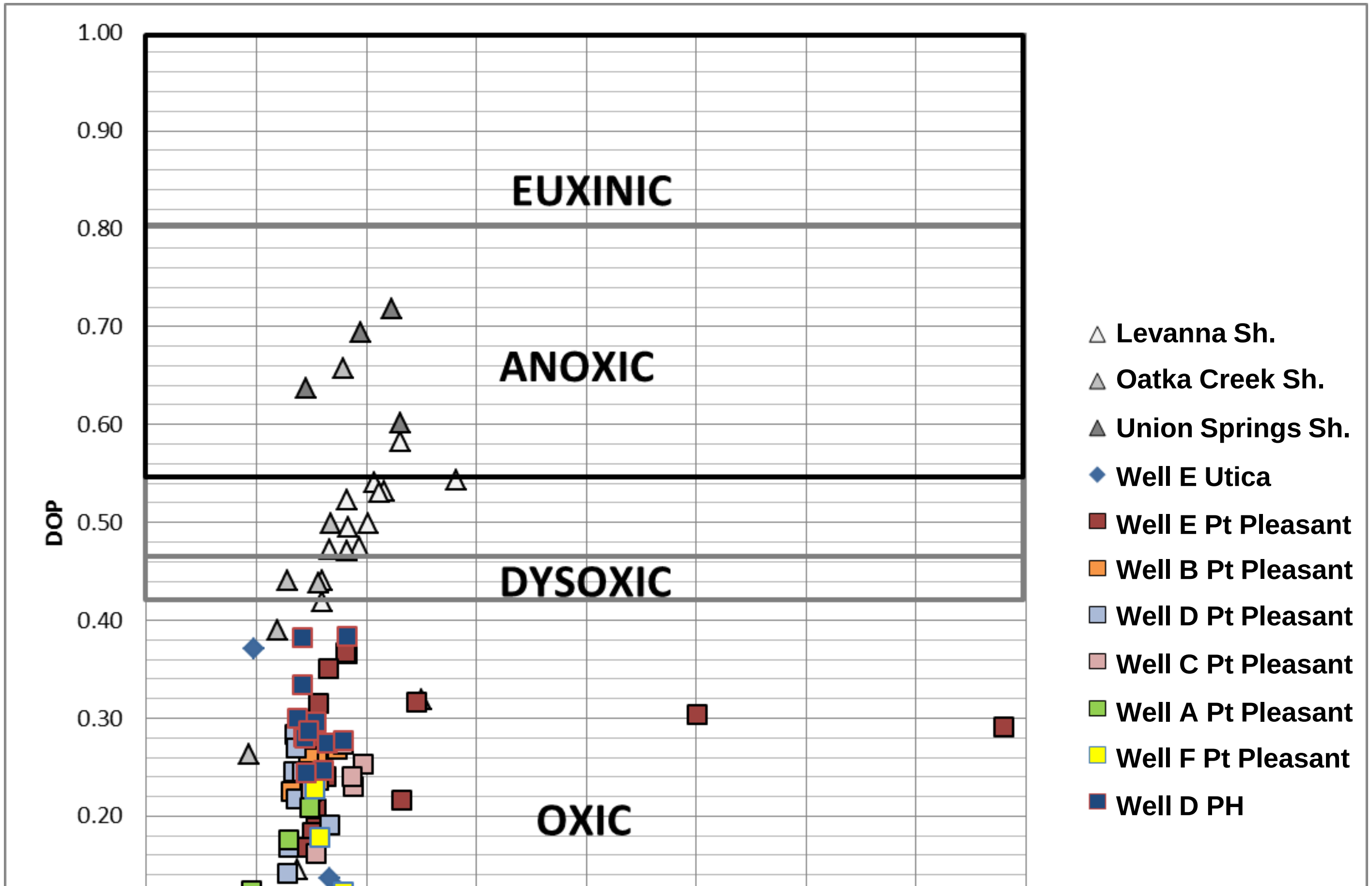
DISCUSSION

- 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.

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;

DISCUSSION



Environment	DOP
Oxic	<0.42
Dysoxic	0.42-0.46
Anoxic	0.46-0.80
Euxinic	0.55-0.93

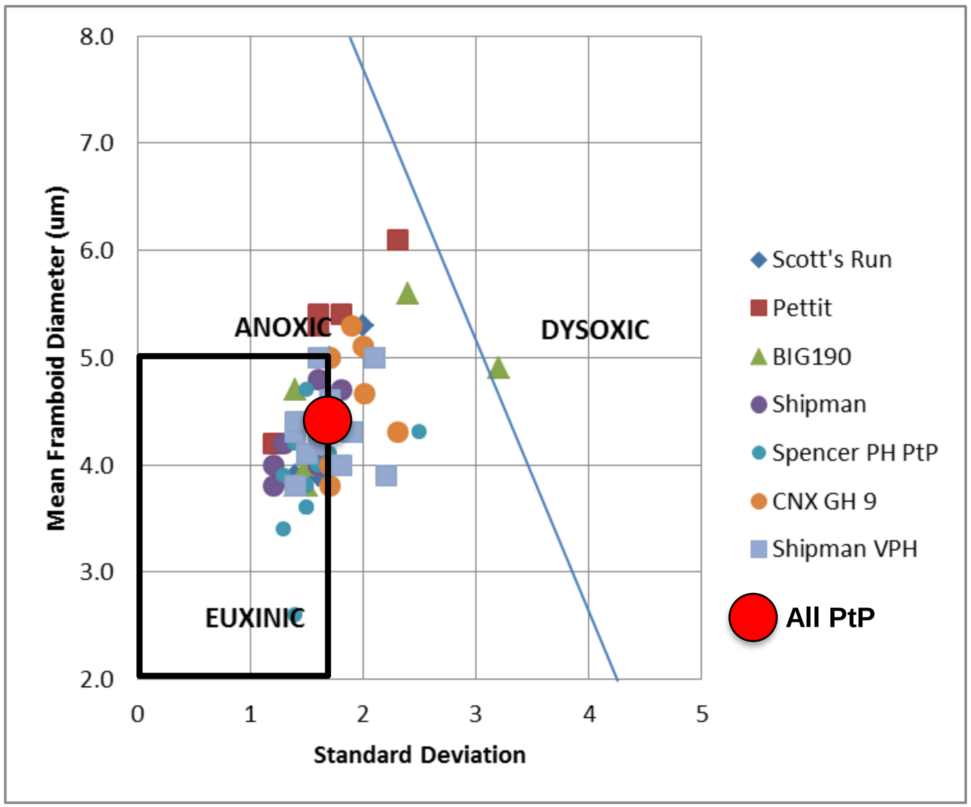
Rasiwell et al, 1987

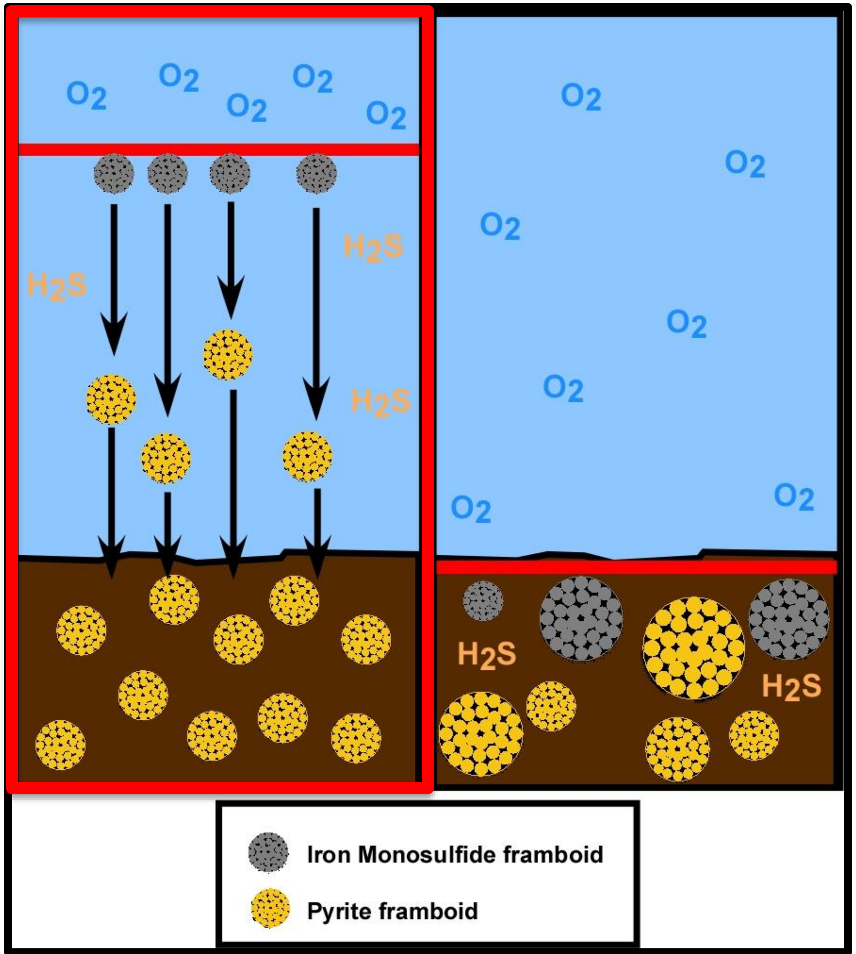
- This interpretation is supported by elemental data where Degrees of Pyritization (DOPs) are commonly <0.42, and redox sensitive element enrichments are at average shale values (AS) or below the level of detection (LOD).

$$DOP = \frac{Fe(pyrite)}{Fe\ (total)}$$

DISCUSSION

- Pyrite data tells two different stories.
- 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.





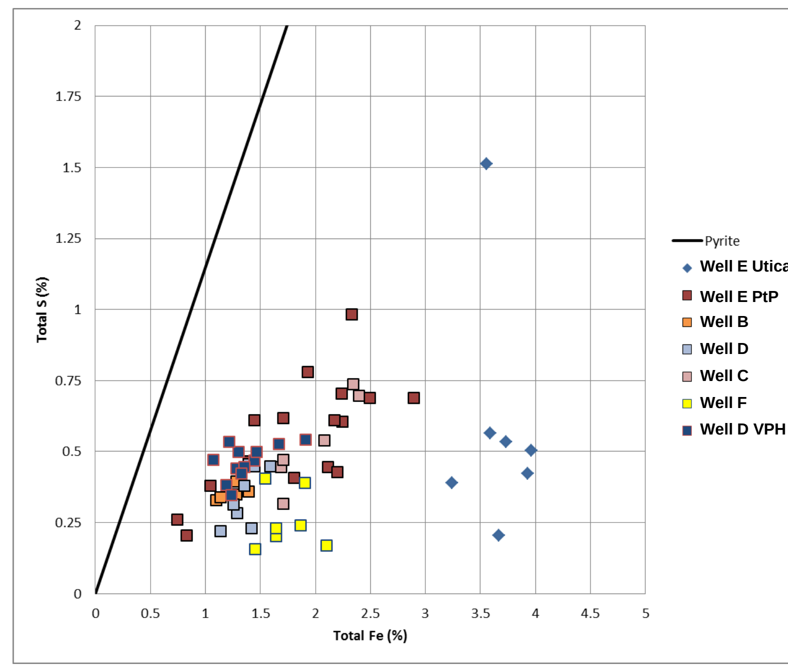
LACK OF REACTANTS

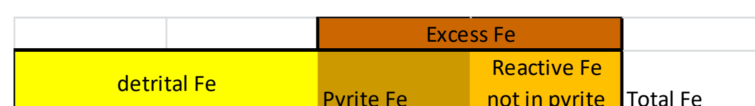
- **Lack of reactants**. If the system is limited due to a lack of reactive iron or hydrogen sulfide then pyrite formation would be limited. There is evidence for this in modern Santa Barbara Basin sediments off the coast of California, where Fe limitation is called on to explain framboids of a mean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

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

Well	Formation	Al (%)	Fe/Al
Well A	Point Pleasant	3.59	0.41
	Point Pleasant	3.74	0.26
	Point Pleasant	3.43	0.35
	Point Pleasant	3.92	0.33
Well B	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		
Well C	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
Well D	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

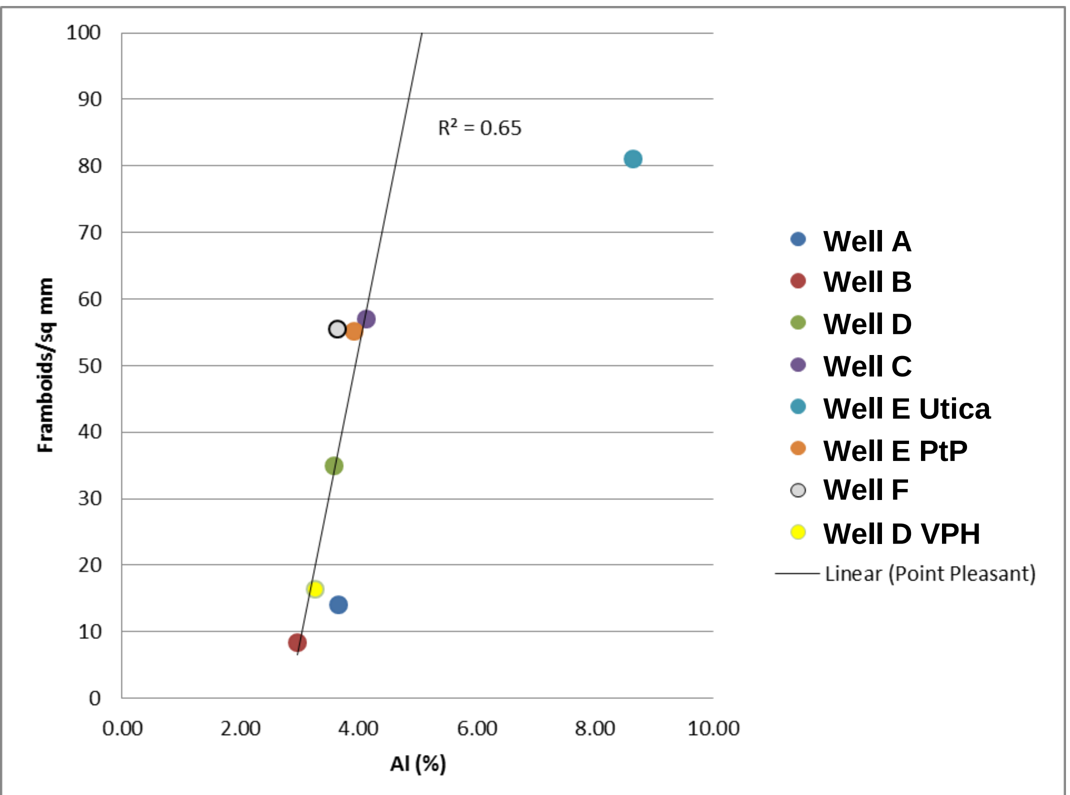
- All samples depleted relative to average shale values and most are depleted relative to crustal values (average Fe/Al of all Point Pleasant data 0.45).
- Supply of Fe, namely reactive Fe to the basin, was limited.
- Overabundance Fe relative to S is likely detrital Fe locked up in detrital minerals.





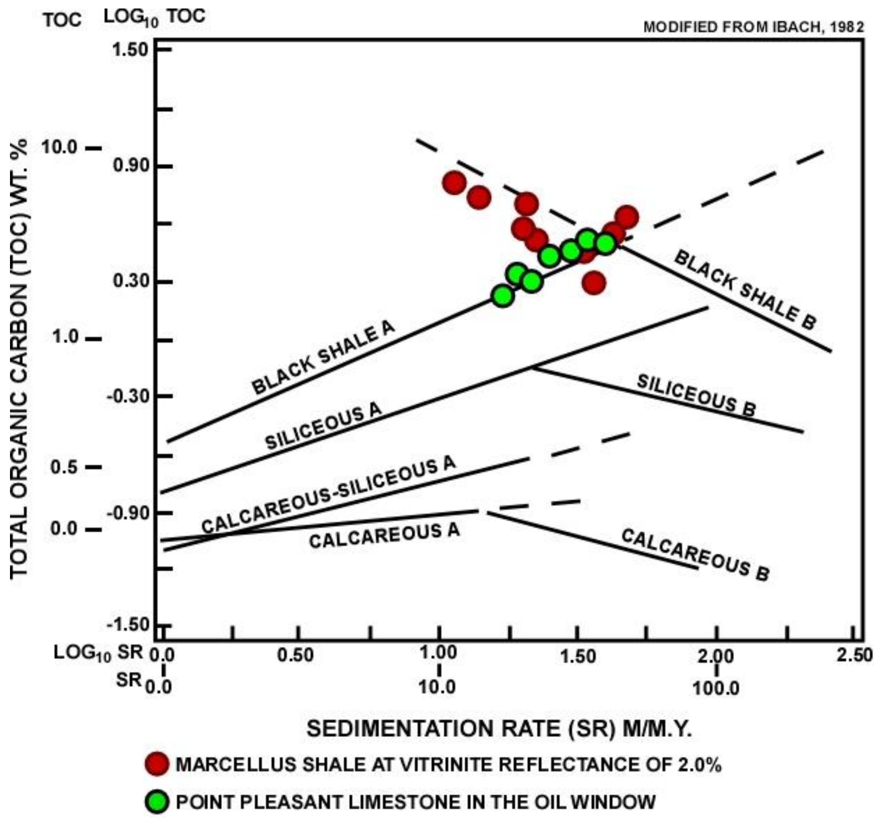
LACK OF REACTANTS - Fe INFLUX

- 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 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.

IMPLICATIONS-EXPLORATION TECHNIQUES

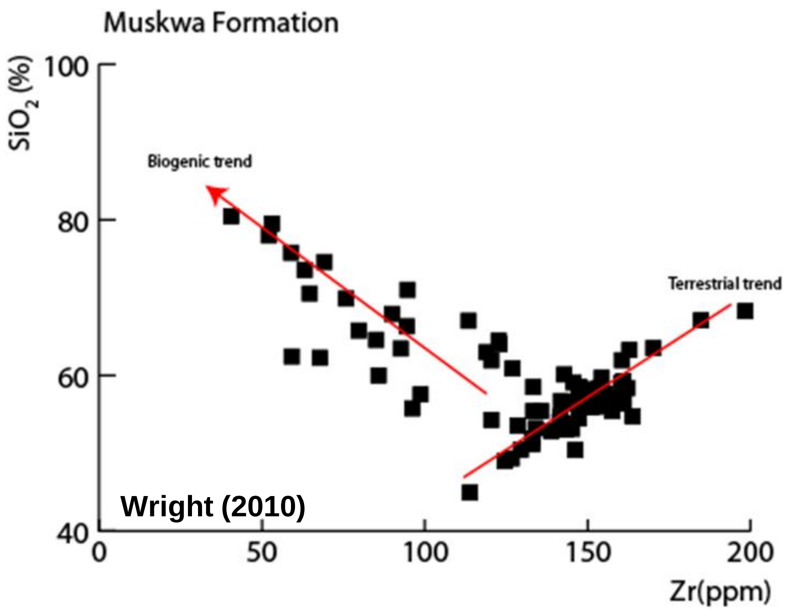


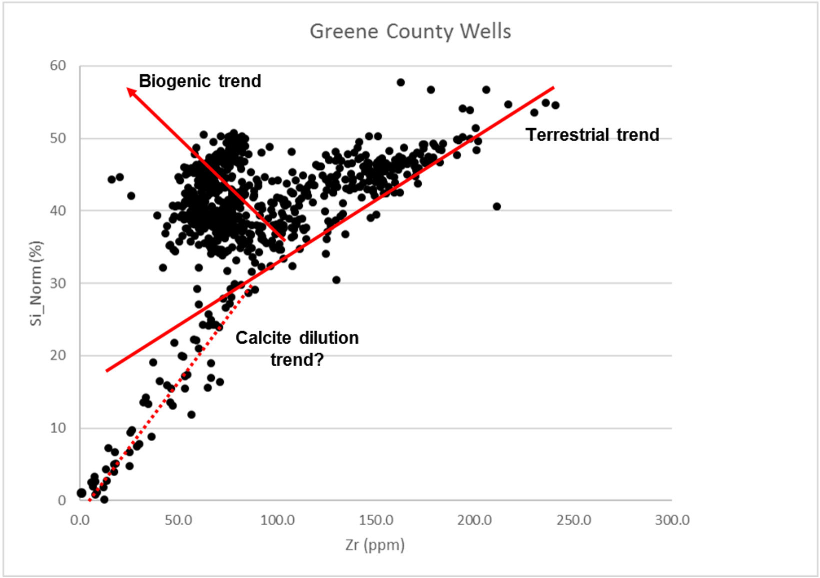
- Pyrite interpretation is consistent with Ibach's (1982) Type A Black shale where TOC accumulates under an oxygenated water column and is preserved by its removal from the zone of oxidation through rapid burial.

- This is very different from the Marcellus which plots along the "Black Shale B" trend.

- This raises concerns about applying a Marcellus model to the Point Pleasant as they accumulated under opposite preservation conditions.

IMPLICATIONS-BIOGENIC SILICA

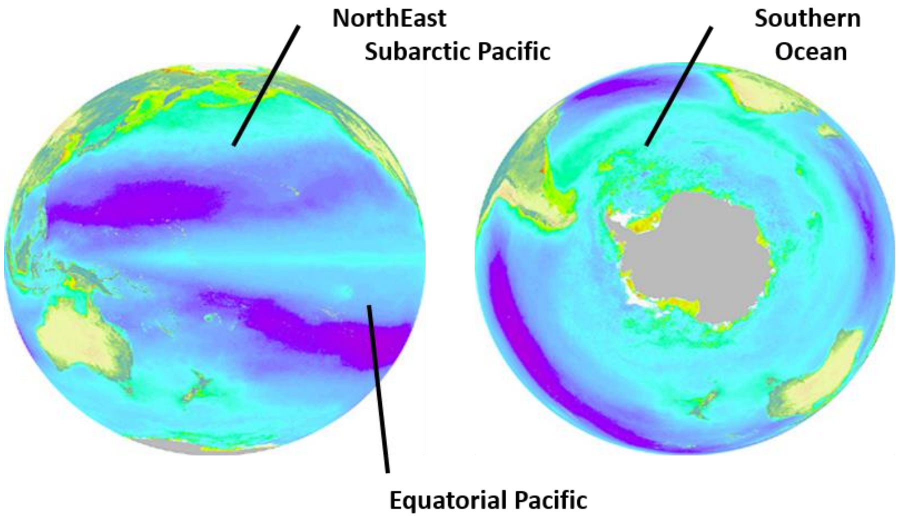




- Wright (2010) demonstrated that Zr can be used to differentiate detrital (extra-basinal) vs biogenic (inter-basinal) quartz.
- Greene county Point Pleasant clearly exhibits a trend suggesting a significant portion of quartz is biogenic in origin.

IMPLICATIONS-BIOGENIC SILICA

- **Low TOC is common to the Point Pleasant (and many Ordovician and Cambrian source rocks).**
  - A reduced influx of Fe (bio-limiting nutrient) to the system would slow primary productivity and offers another explanation for low TOC observed in the Point Pleasant.
    - Fe is required by phytoplankton to produce an enzyme that reduces NO3- to ammonium before it can be incorporated into protein synthesis.
    - Many examples of Fe limitation in modern oceans in so-called High Nutrient Low Chlorophyll (HNLC) zones including the Southern Ocean, Subarctic and equatorial Pacific, and coastal areas off northern California and Peru.
    - Fe fertilization of HNLC zones is currently considered as a method to sequester atmospheric carbon from carbon dioxide in deep ocean sediments, thus indicating it plays a major role in the accumulation of organic carbon in marine environments.



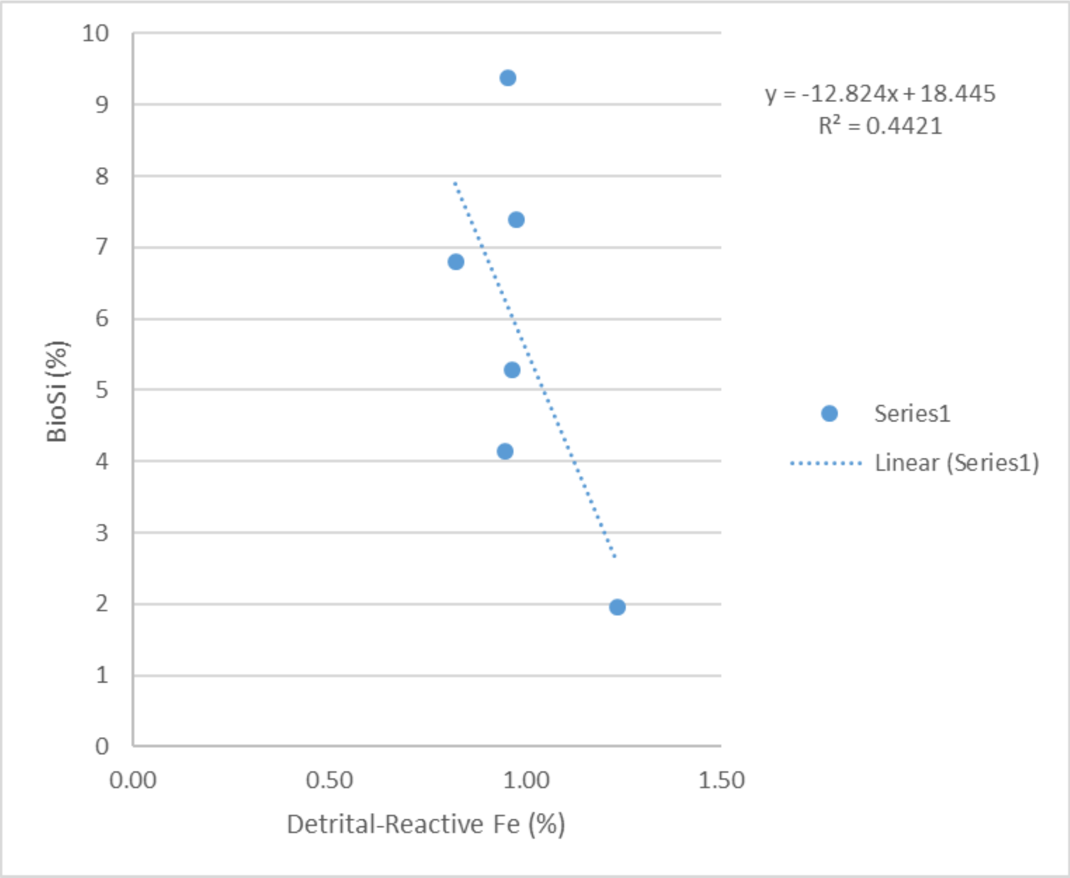
Regions of iron limitation (HNLC areas)

HNLC = High-macronutrient, low-chlorophyll (biomass)

Source: http://www.environmentalproteomics.org

IMPLICATIONS-BIOGENIC SILICA

- Hutchins and Bruland(1998) reported greater silicification of diatoms accumulating under Fe limitation.
- Point Pleasant demonstrates a negative relationship between biogenic Si and total Fe, perhaps for the same reason.



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CONCLUSIONS

- The Point Pleasant accumulated under dysoxic bottom waters.
  - Redox conditions remained largely constant throughout deposition.

- Most likely explanation for framboid size is a limitation of reactants, probably Fe.

- Low TOC of the Point Pleasant is consistent with deposition under dysoxic conditions.

- Biogenic Si enrichment may be linked to Fe limitation.

IMPLICATIONS

- **Often, the excellent quality of the Marcellus can more than make up for issues with less overpressure, and faulting leaking gas and/or stealing frac energy.**

- **In the Cambrian and Ordovician, reservoir quality alone may not be enough, and reservoir pressure and containment may play a much greater role. This makes the success of the play more dependent on understanding the burial, exhumation, and structural history of the Point Pleasant.**

Where energy meets innovation.