Redox Conditions during Deposition and Early Diagenesis of the Upper Ordovician Point Pleasant Limestones of Southwestern Pennsylvania and Northern West Virginia*

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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 16 samples retrieved from three horizontal Point Pleasant wells were analyzed by SEM. 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. Two models can explain this apparent paradox:

1) Anoxia developing within marine snow aggregates suspended in the water column could have produced a micro-environment conducive to the precipitation of framboids in an otherwise dysoxic water column, or
2) The occurrence of small framboids may be explained by a lack of reactants necessary to sustain pyrite growth in anoxic pore waters

Indeed, the latter model is consistent with low production of H_2S inferred from low total organic carbon (TOC) content of the Point Pleasant. Further, total iron content below average shale values in the Point Pleasant indicates low delivery of reactive iron to the seafloor. Both models are consistent with the Point Pleasant 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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Eastern Section of the American Association of Petroleum Geologists 45th Annual Meeting September 24-28th, 2016

RANDY BLOOD

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OUTLINE

- Purpose of this work
- Background on pyrite in sedimentary environments
- Methods
- 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

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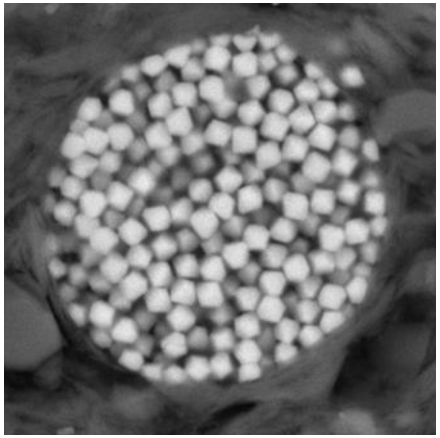
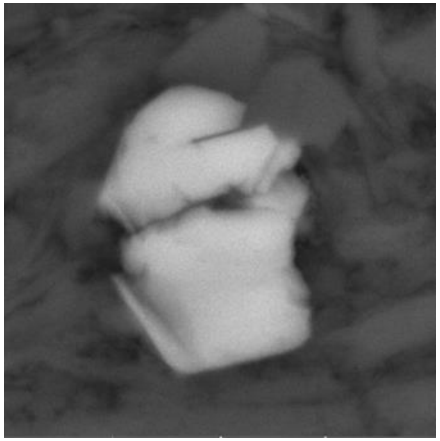
PYRITE

- 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.



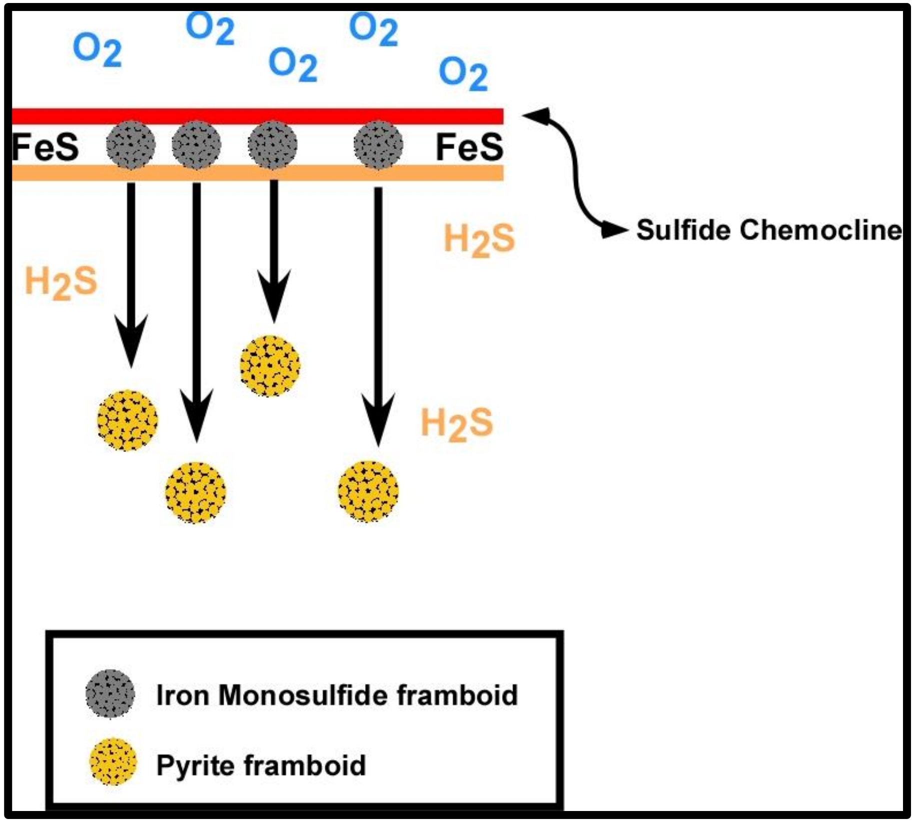
- types of pyrite of interest
  - **Framboids**: spherical aggregates of pyrite microcrystallites that **form at the chemocline** (the transition from sulfide bearing anoxic water and oxygen-bearing water). They can form suspended in the water column and sink to accumulate in the mud and can also form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

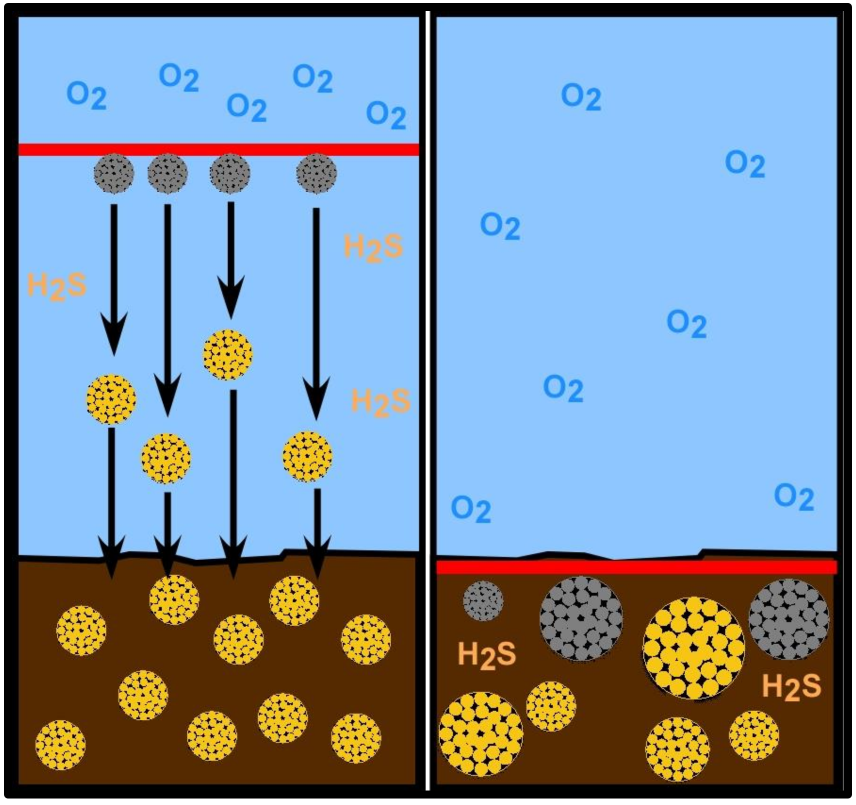


  - **Euhedral:** large individual grains of pyrite that form in the sediment at a much slower rate and can precipitate directly from the interaction of hydrogen sulfide with reactive iron.

FRAMBOID FORMATION

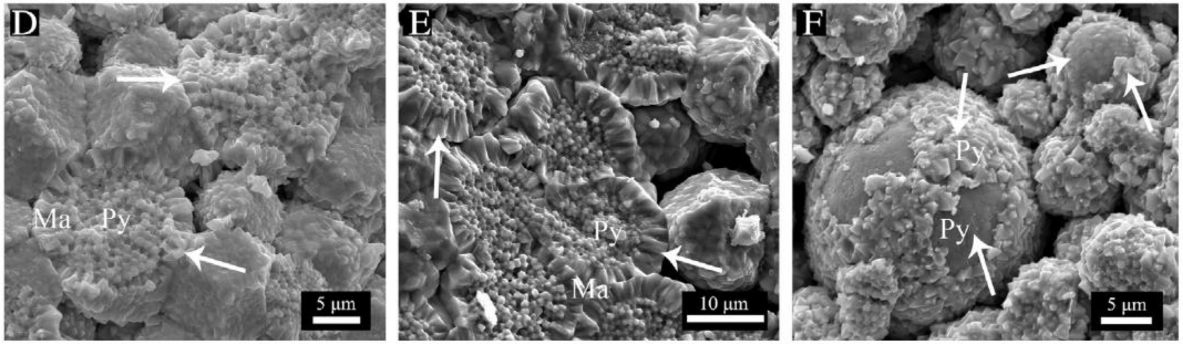
- Framboids composed of iron monosulfides (mackinawite, griegite) form in the zone of Fe reduction immediately below the sulfide chemocline where magnetic properties of the elements attract microcrystallites to each other to form spherical aggregates.
- Framboids that form in the water column can grow 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.



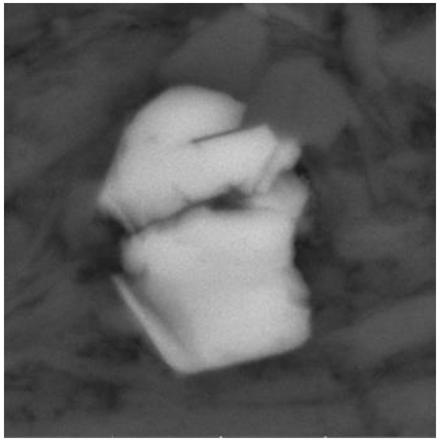


EUHEDRAL PYRITE FORMATION

- 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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METHODS

- Samples were selected from cuttings at roughly 1000’ intervals along the lateral portion of the well, and representative of all facies through the stratigraphic section on vertical wells.
- Samples were selected based on size in order to provide enough surface area for valid measurements.

- Automated SEM runs performed on cuttings provided by EQT.
- Pyrite identified in BSE images (appear brighter due to higher atomic density).
  - Can be differentiated from other high density minerals such as Barite ($BaSO_4$) and Rutile (TiO_2) using EDS.
- High resolution images of particles obtained are classified as framboidal or non-framboidal (euhedral) based on roundness and Euler number, and other (non-pyritic).
- Image data provides: area analyzed, maximum diameter, area, roundness, and additional data.

- Area of euhedral and framboidal pyrite and imaged sample are used to determine the occurrence in area of pyrite and the percentage of pyrite that occurs as framboidal pyrite.
- Statistics generated on framboids for n, maximum framboid diameter, mean diameter, standard deviation, %<= 5µm, and %>= 10 µm.

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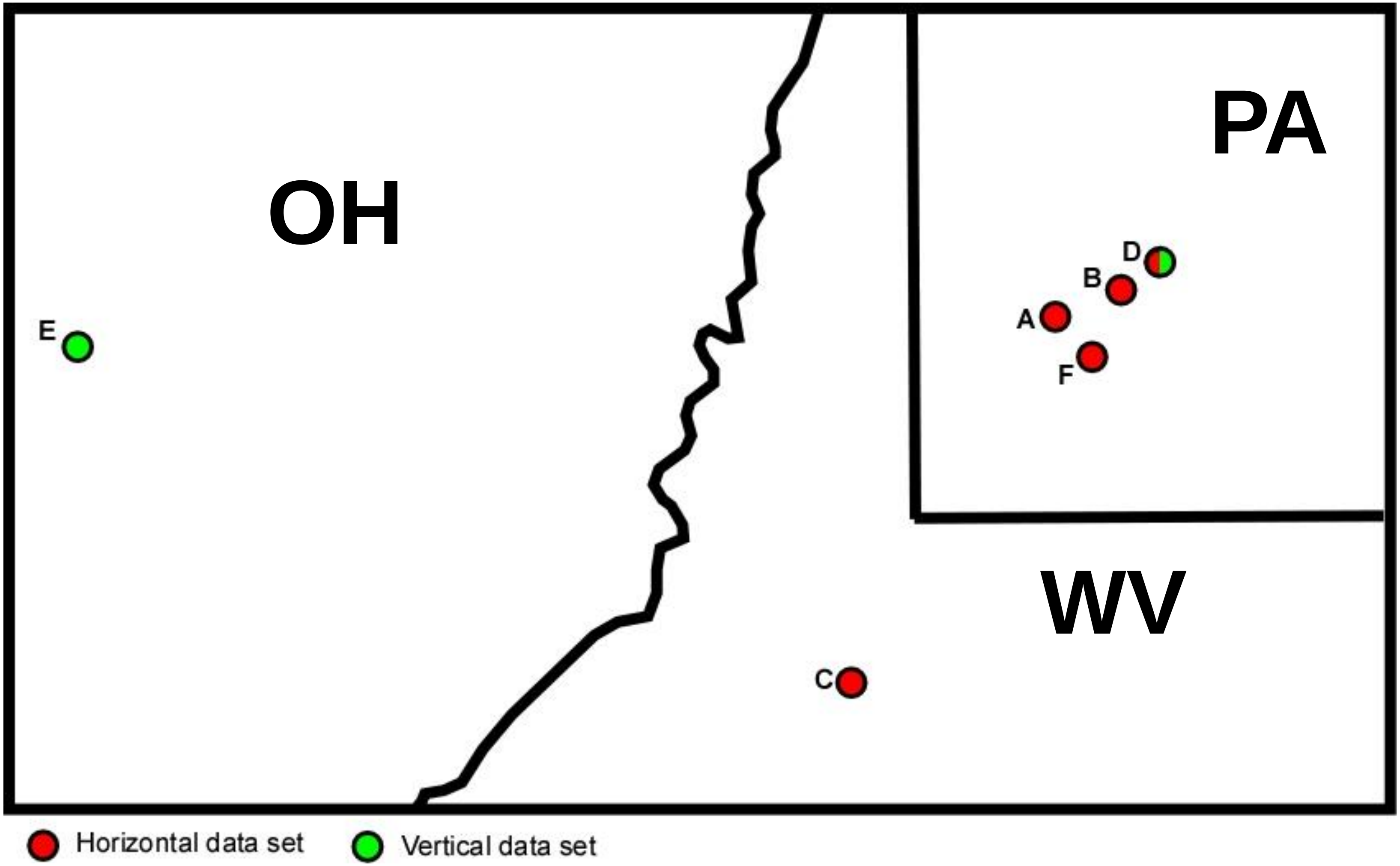
DATA SET



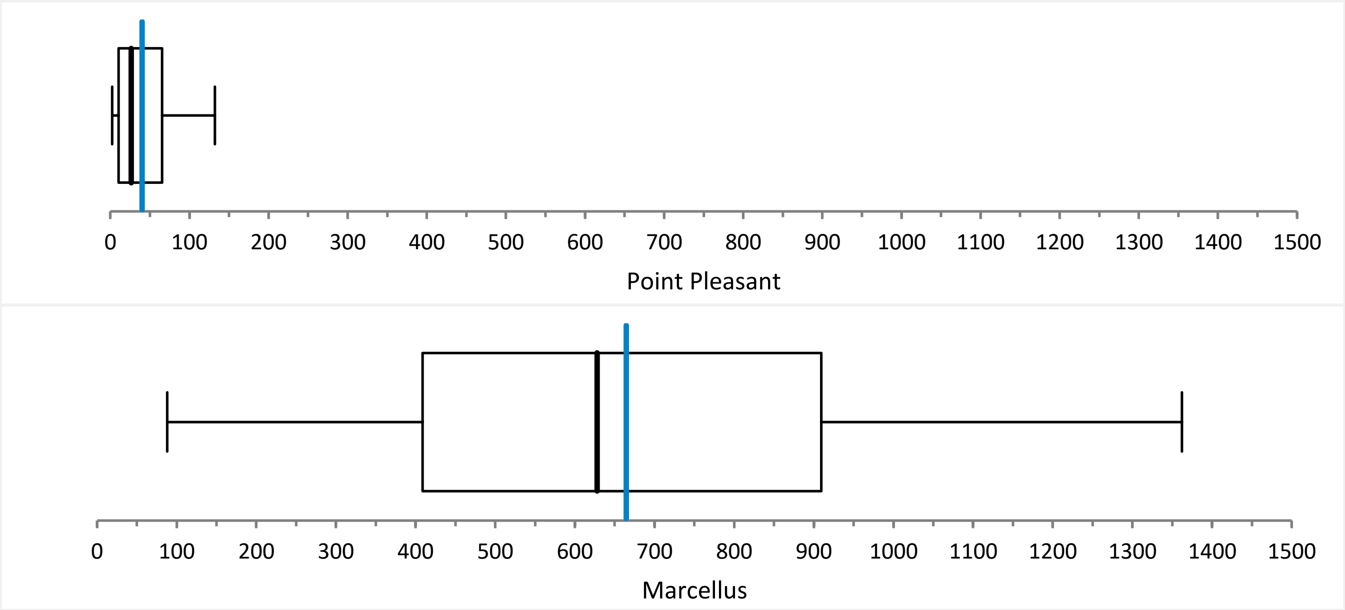
RESULTS: PYRITE COMPARISON BETWEEN MARCELLUS AND POINT PLEASANT

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.

RESULTS: FRAMBOID DENSITY COMPARISON BETWEEN MARCELLUS AND POINT PLEASANT



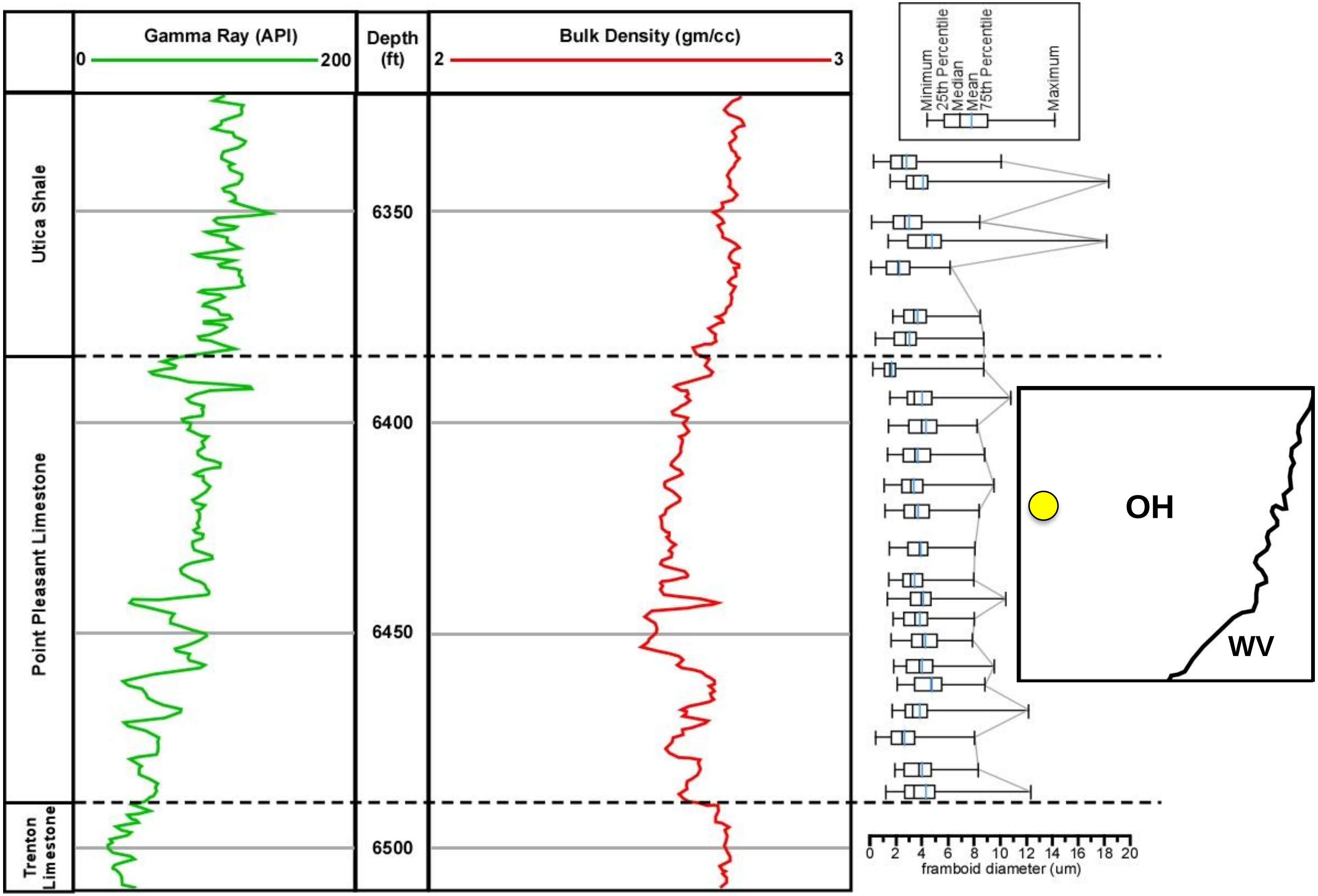
Framboid Density (framboids/mm^2)

- Indeed, there are many more framboids in the Marcellus than in the Point Pleasant. Mean occurrence in the Point Pleasant is less than 50 framboids per square mm, while the same is greater than 650 in the Marcellus.

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



OBSERVATIONS: WELL E

- Point Pleasant framboids are uniformly small, on average 3.9 µm, standard deviation of 1.6 µm.
- With the exception of the basal sample, there are rare to no framboids exceeding 10 µm diameter and >85% are ≤ 5 µm.
- The greatest variability occurs in the basal Point Pleasant (Lexington) and uppermost Point Pleasant.
- Framboid density is low averaging 55 framboids per square mm.
- The Utica also hosts small, average 3.1 µm framboids, with a bit more variability in size (standard deviation of 1.8 µm).
- Uppermost samples analyzed have the highest variability with more examples > 10 µm.
- More framboids present than seen in Point Pleasant with an average of 93 framboids per square mm.

SUMMARY OF OBSERVATIONS

- **COMMONALITIES**
  - 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).
  - Well A and Well D more similar than Well B.

- **DIFFERENCES**
  - Lowest occurrence of pyrite in Well C and Well A is still nearly double the highest occurrence of pyrite in the Well B.
  - Well C has highest occurrence of framboids with some samples having >100 framboids per square mm.
  - Well B has consistently lowest occurrence of framboids, highest occurrence of large framboids, and greater variation.

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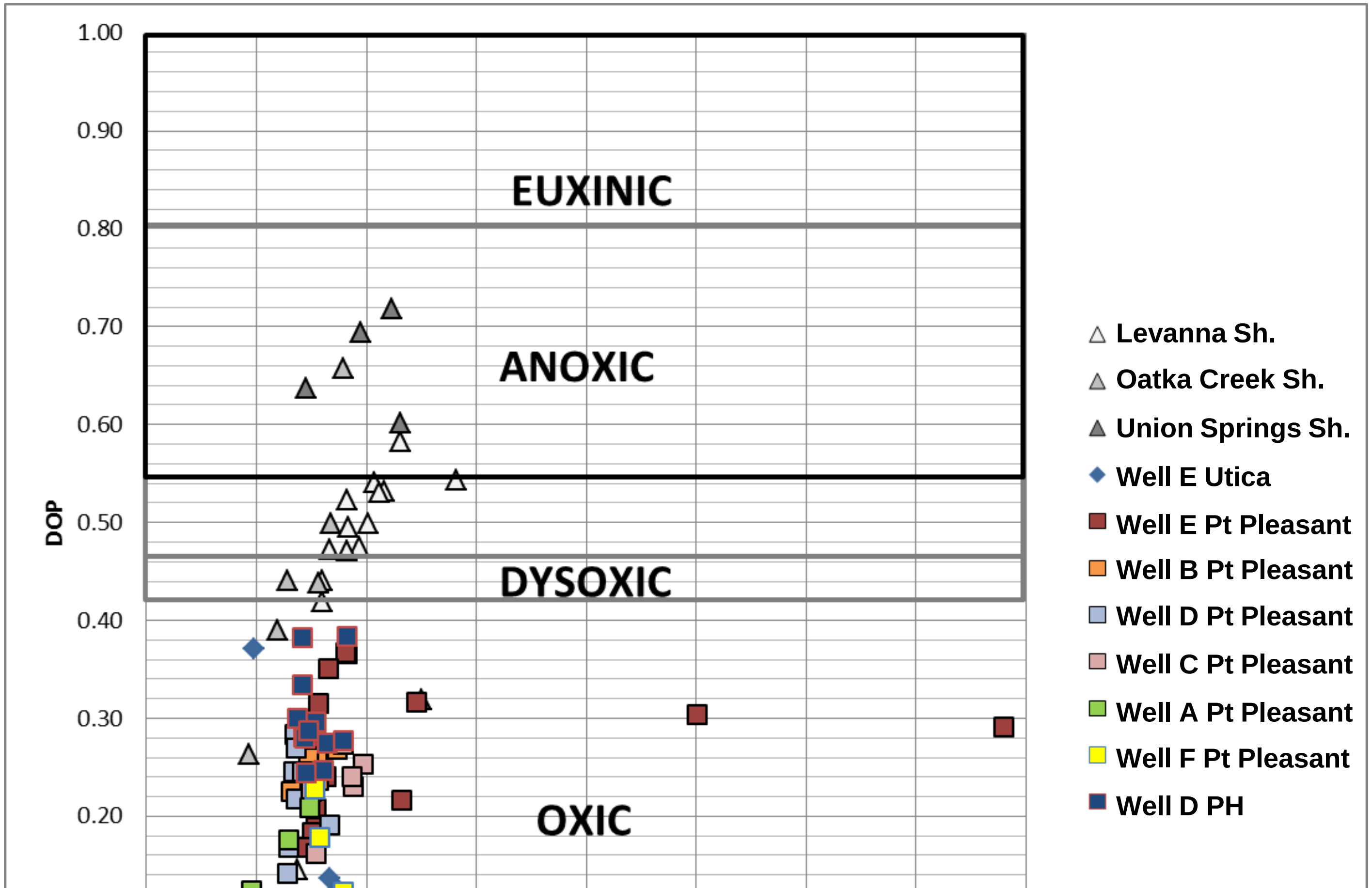
DISCUSSION

- Pyrite data tells two different stories.

- Overall paucity of pyrite combined with euhedral pyrite being the dominant 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

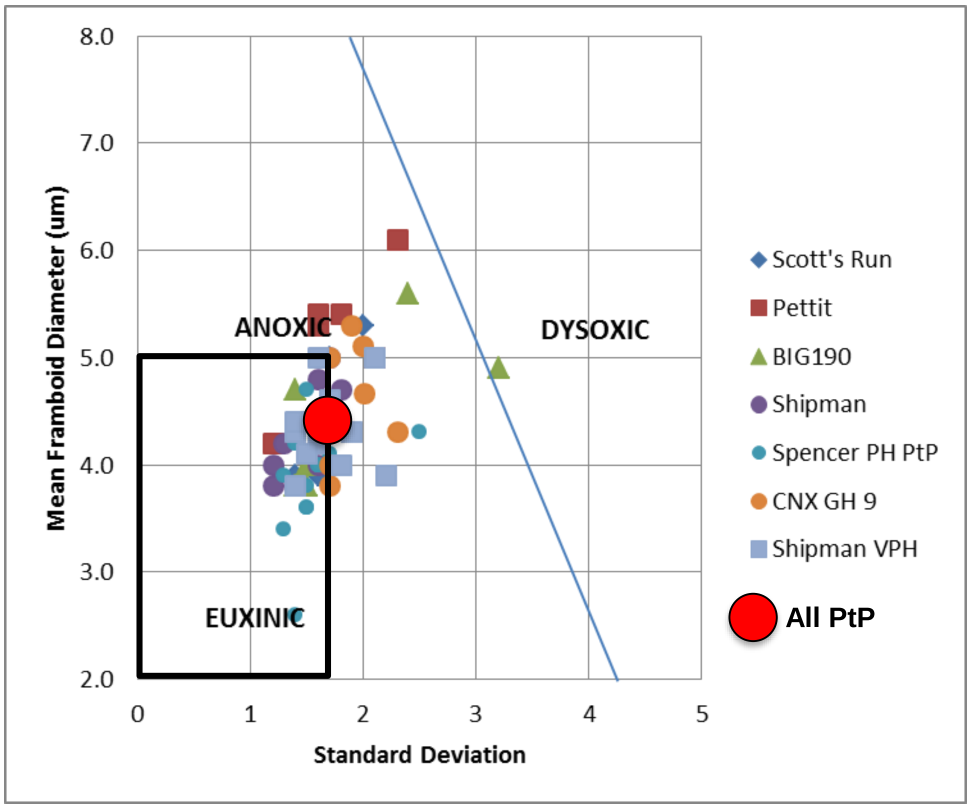
Rasiwell et al, 1987

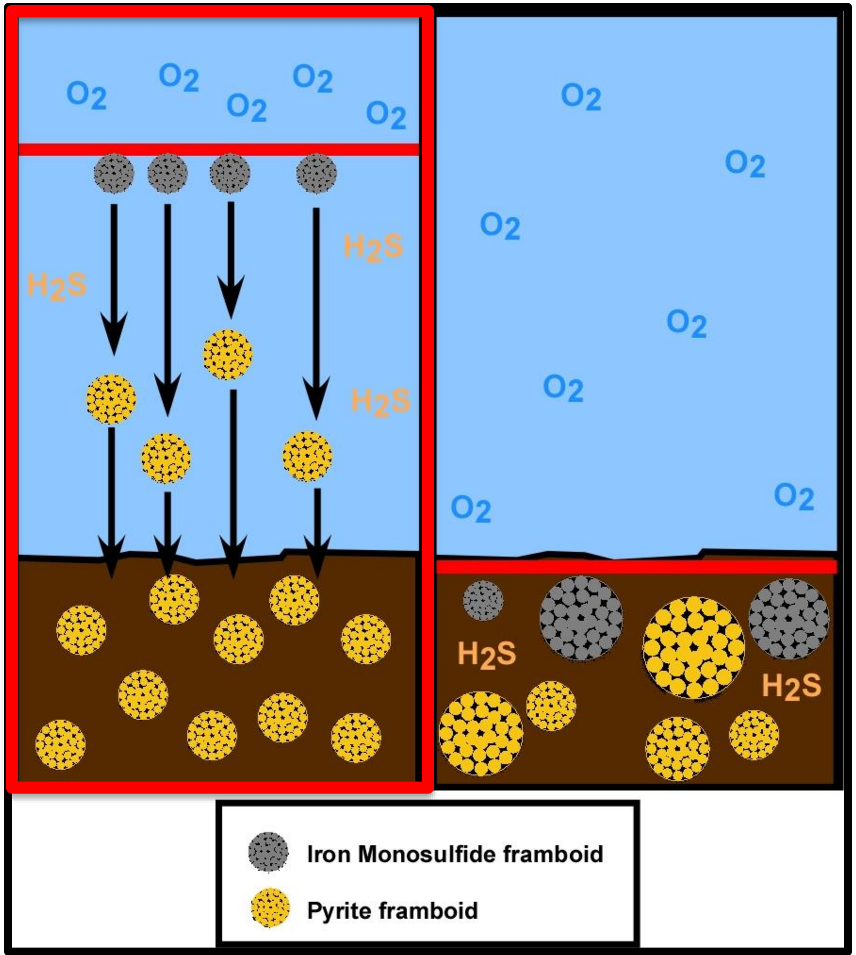
- This interpretation is supported by elemental data where Degrees of Pyritization (DOPs) are commonly <0.42, and redox sensitive element enrichments are at average shale values (AS) or below the level of detection (LOD).

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

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.





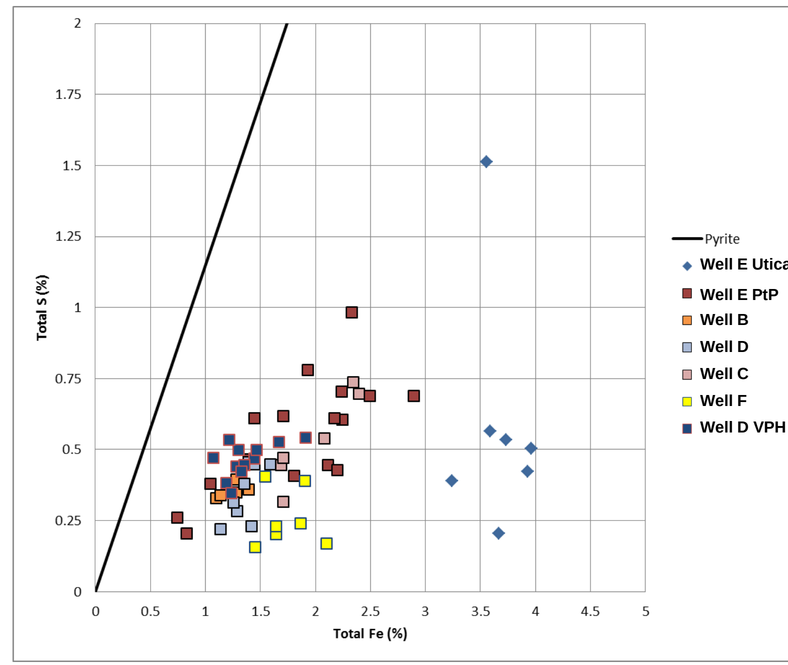
LACK OF REACTANTS

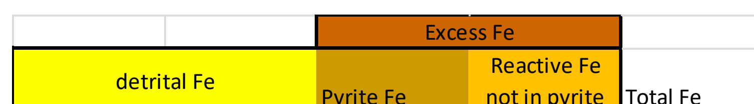
- **Lack of reactants**. If the system is limited due to a lack of reactive iron or hydrogen sulfide then pyrite formation would be limited. There is evidence for this in modern Santa Barbara Basin sediments off the coast of California, where Fe limitation is called on to explain framboids of a mean 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)

- 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.

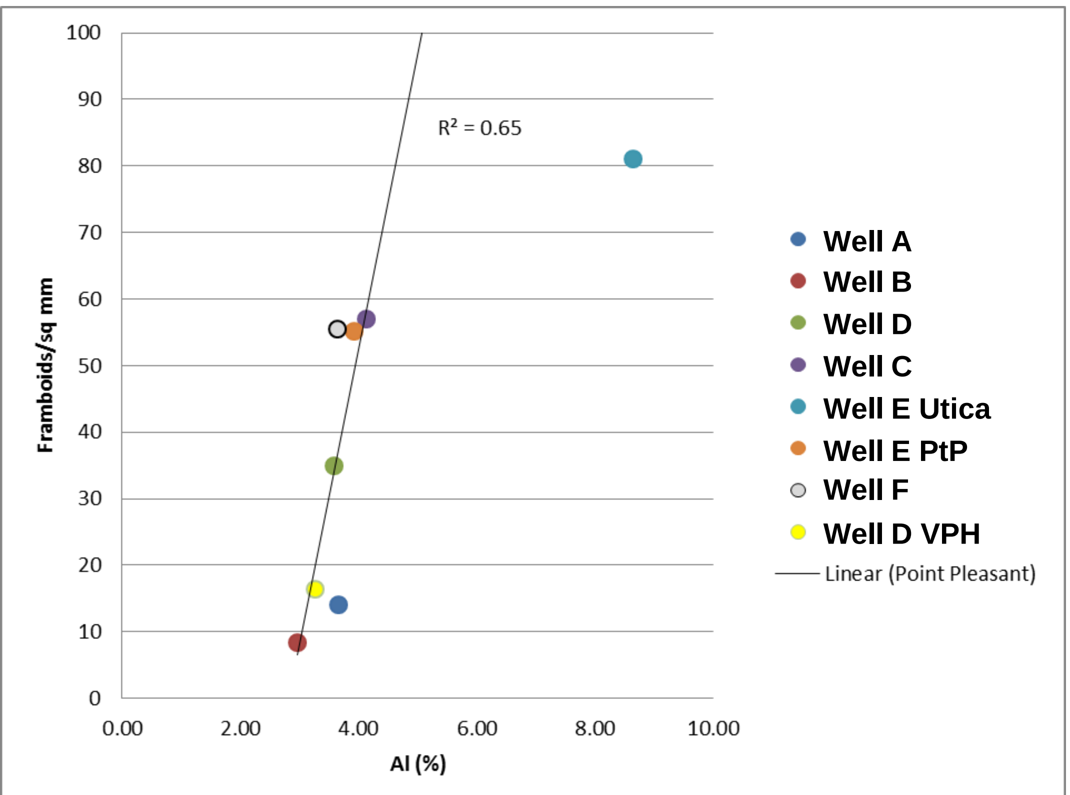
Well	Formation	Al (%)	Fe/Al
Well A	Point Pleasant	3.59	0.41
	Point Pleasant	3.74	0.26
	Point Pleasant	3.43	0.35
	Point Pleasant	3.92	0.33
Well B	Point Pleasant	3.82	0.36
	Point Pleasant	2.57	0.43
	Point Pleasant	2.69	0.48
	Point Pleasant	2.99	0.43
	Point Pleasant	2.80	0.41
	Point Pleasant		
Well C	Point 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





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.

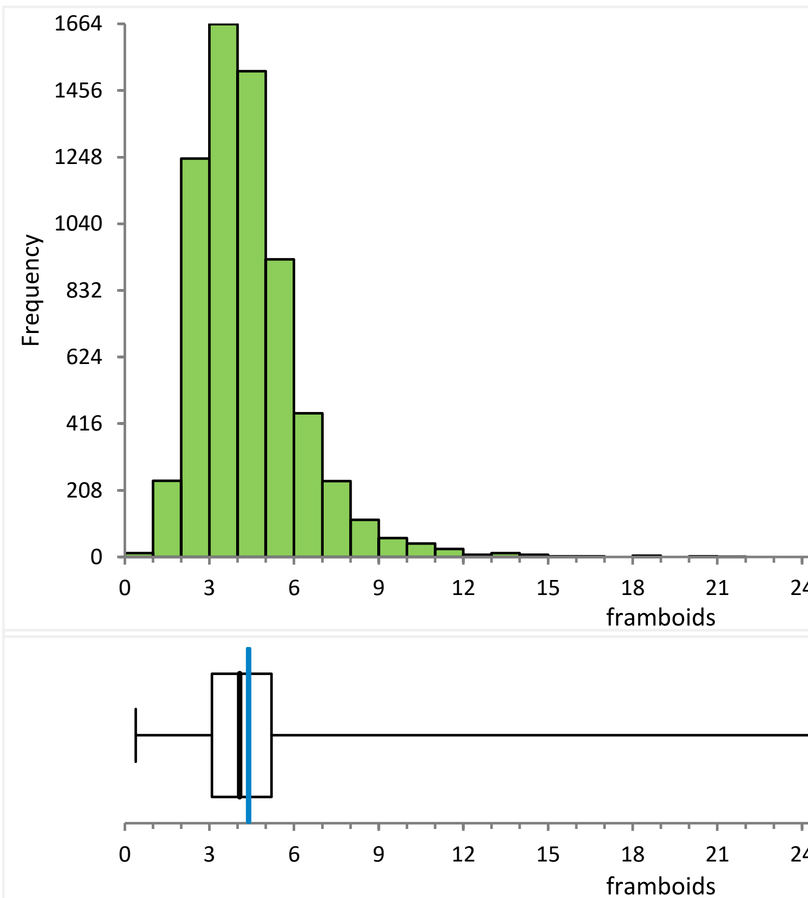


- Average Al in the Point Pleasant (n = 125) 6.5% (Range 3.8-15.0; STDEV 1.4%); ~25% below the average shale value of 8.8% suggesting limited clastic and attendant reactive Fe influx.

LACK OF REACTANTS - Fe INFLUX

- This theory has to be able to explain two observations about the framboids:
  1. The uniform size distribution of the framboids,
  2. The small size of the framboids.

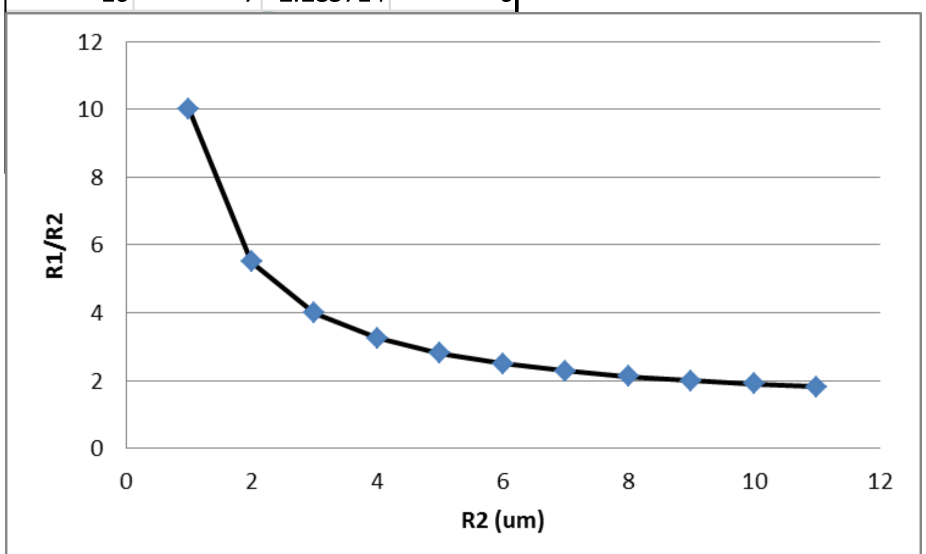
n=	6568
MFD=	37
%<= 5um	79.48%
%>= 10um	2.07%
Mean Diameter	4.4
Standard Deviation	1.7
25th Percentile	3.1
75th Percentile	5.2



HYPOTHESIS 3: LACK OF REACTANTS- NARROW FRAMBOID SIZE DISTRIBUTION

- Below in the simple case of two grains that grow at the same rate, but where one is a greater size than the other, their difference in size reduces through time.

R1 (um)	R2 (um)	R1/R2	Time
10	1	10	0
11	2	5.5	1
12	3	4	2
13	4	3.25	3
14	5	2.8	4
15	6	2.5	5
16	7	2.285714	6



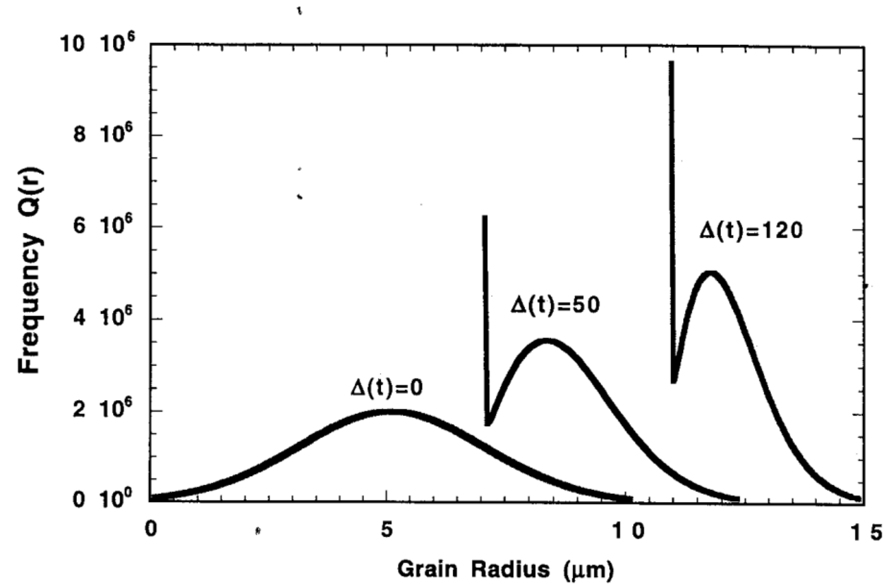


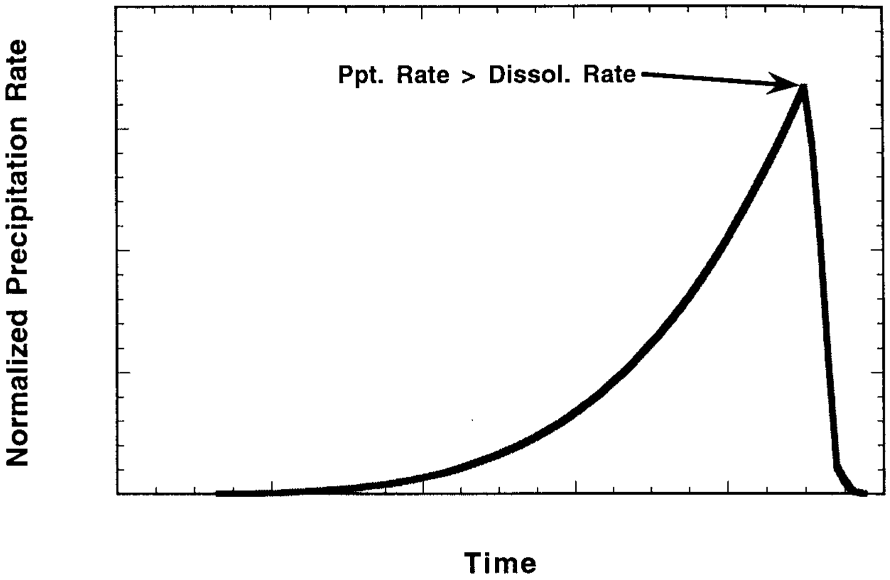
Fig. 4. Grain size frequency distribution versus grain radius for transport controlled growth at *different extents of reaction*, Δ(*t*).

- The same is observed when looking at data populations

Morse and Wang, 1996

HYPOTHESIS 3: LACK OF REACTANTS- NARROW FRAMBOID SIZE DISTRIBUTION

- For similar reasons, grain size distribution should become narrow even at constant nucleation.
- Although growth rate is constant and older grains will get larger, once saturation falls and nucleation ceases, all grains will grow at the same rate until equilibrium is reached, and as a result difference in size will be reduced.



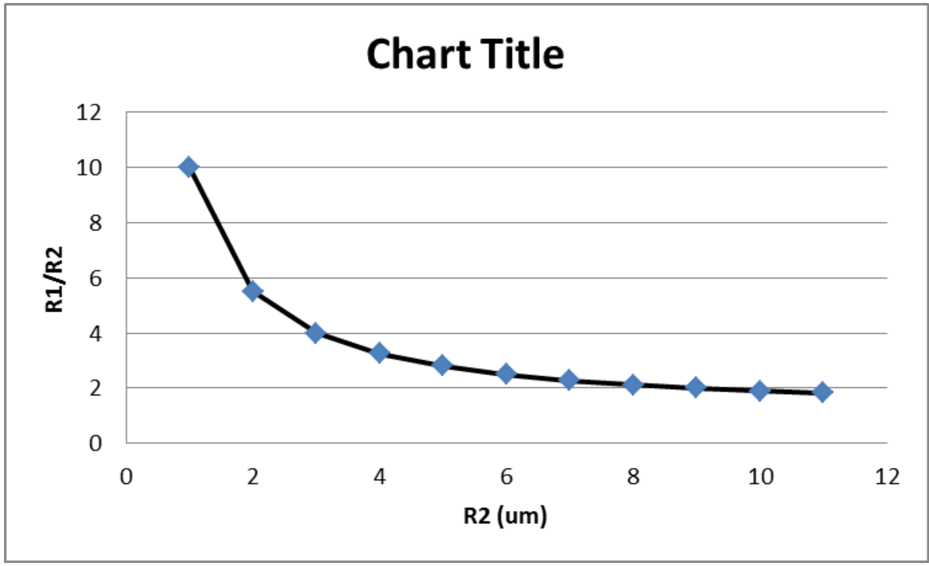


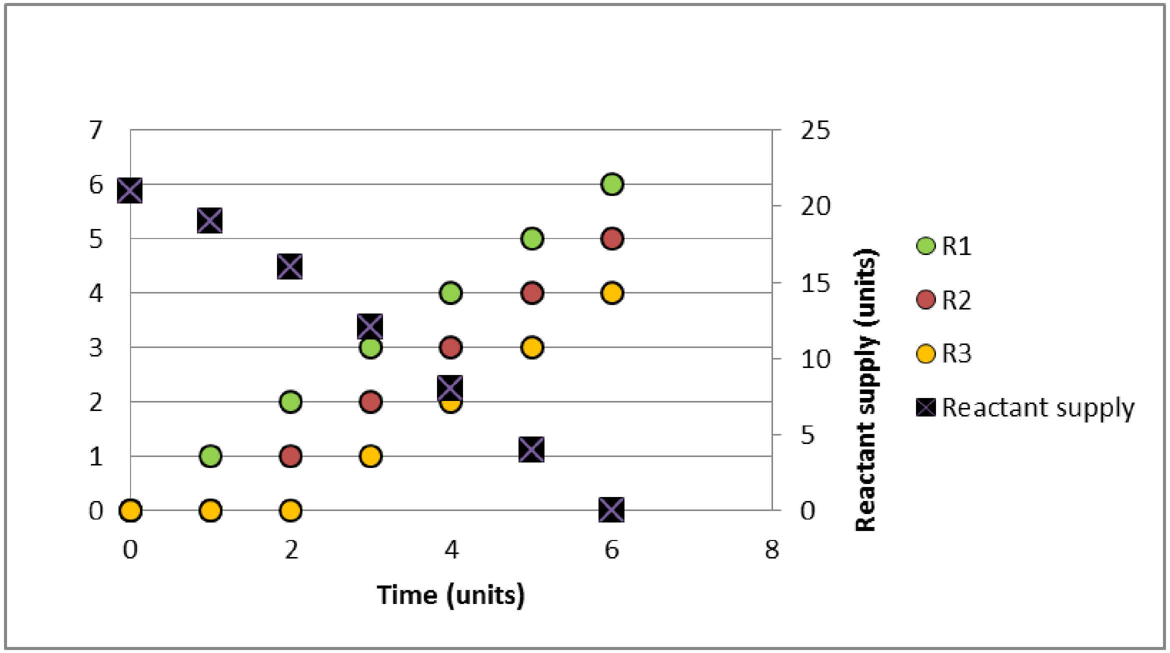
Fig. 7. Schematic representation of normalized (initial rate = 1) precipitation rate with time in arbitrary units.

- Wilkin and Barnes (1997) suggest that anoxic conditions promote higher nucleation density
  - This results in many small framboids rather than a few large framboids.

Morse and Wang, 1996

HYPOTHESIS 3: LACK OF REACTANTS- SMALL SIZE

- Possible reason for small framboid sizes:
  - 1. Sphere of Influence: when many small crystals are present they become limited over the area where they do not have to compete for dissolved reactants. As such, that competition can limit the size to which crystals can grow.
  - 2. Many nuclei competing for a finite amount of reactants will result in many small crystals.



Morse and Wang, 1996

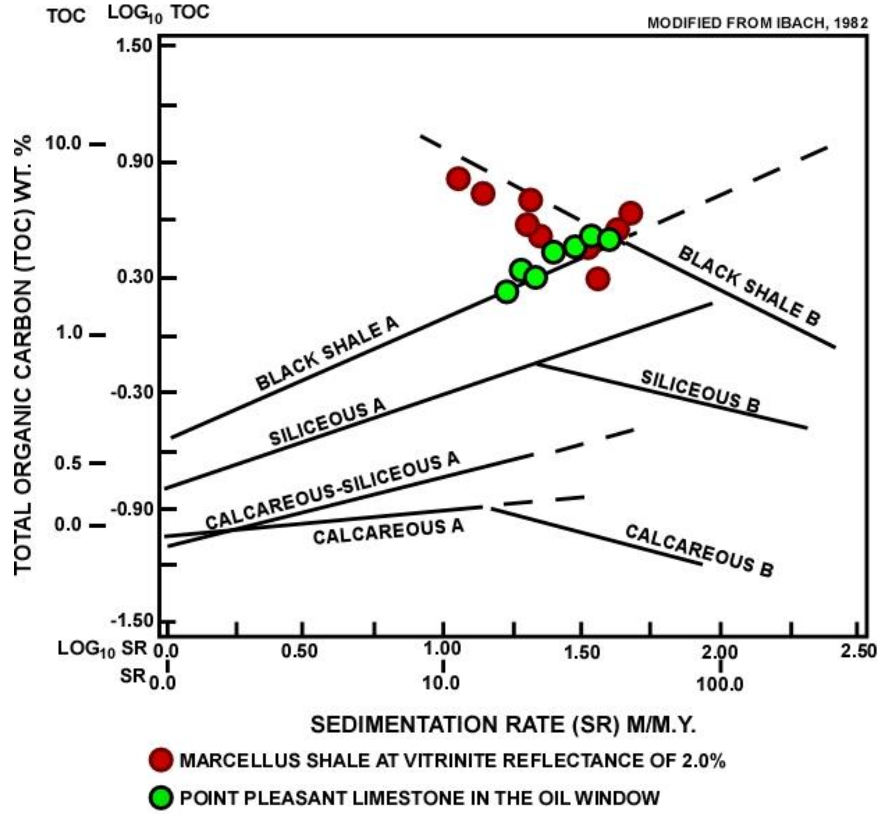
OUTLINE

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

CONCLUSIONS

- The Point Pleasant accumulated under dysoxic bottom waters.
  - Redox conditions remained largely constant showing minor variability at the onset and exit of Point Pleasant time and during Utica deposition.
- Most likely explanation for framboid size is a limitation of reactants, probably Fe.
  - Crystal nucleation theory explains the apparent small and narrow size distribution of pyrite framboids.
- Low TOC of the Point Pleasant is consistent with deposition under dysoxic conditions.

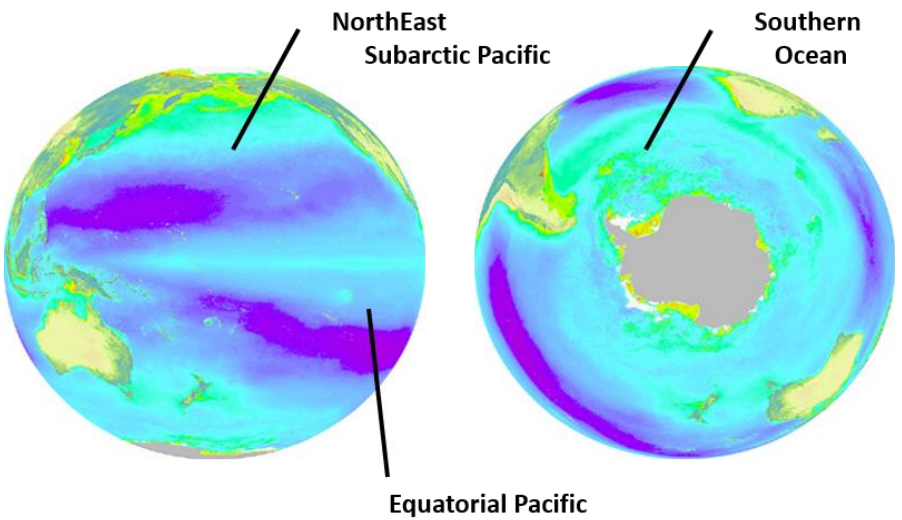
IMPLICATIONS



- 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

- **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

- **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.**

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