# $\delta^{34}S$ Study of Multiple Generations of Sulfide in the Bakken System by SIMS

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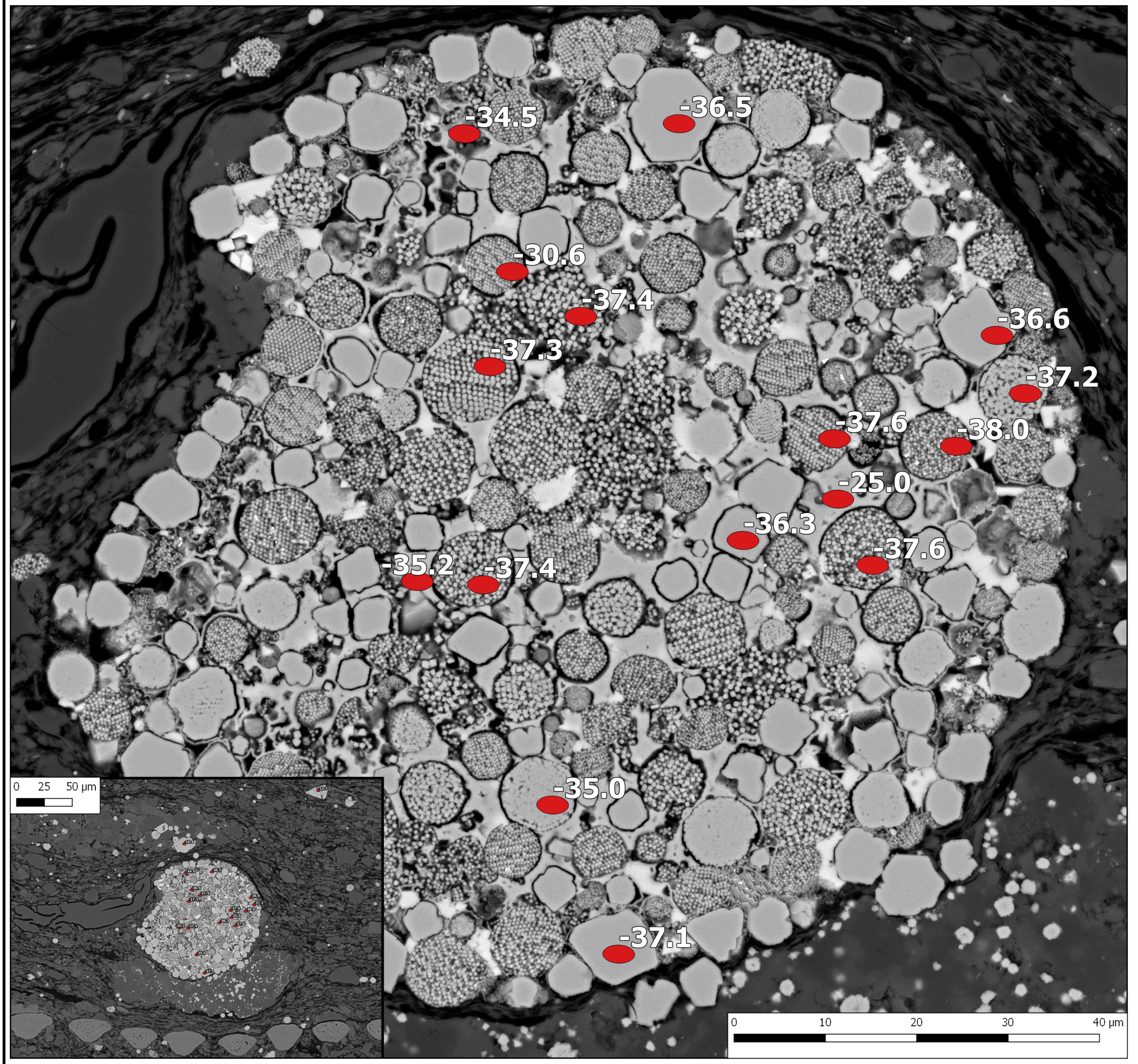


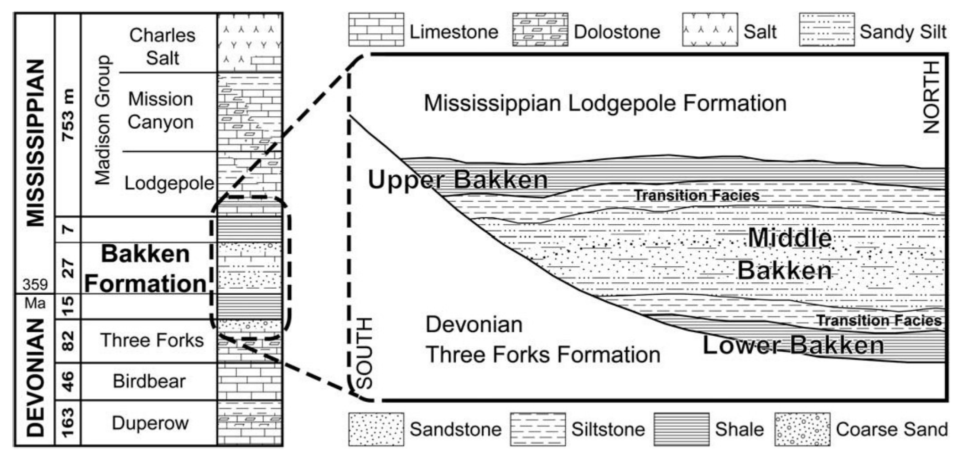

## Abstract

Sulfur isotope ratios provide insight into both redox conditions during deposition and biological processes in soft sediment. While it is accepted that traditional bulk $\delta^{34}S$ analyses often homogenize micron-scale (and larger) variability in sediment, a comprehensive understanding of what information these micron-scale records might contain is still being developed. Petrographic investigations into the Devonian Lower Bakken black shale in North Dakota reveal multiple generations of sulfide growth, including isolated framboids, polyframboids, euhedral pyrite, pyrite pseudomorphing dolomite, and sphalerite. Presented here is a preliminary SIMS $\delta^{34}S$ dataset ($\delta^{34}S$ values -38 to -10‰, spot size <3 microns) that, when integrated with petrographic observations, shows multiple lines of evidence of early active biological sulfate reduction. There is also evidence of a sulfate source driven to increasingly heavy $\delta^{34}S$ values by partially closed-system fractionation processes, as sulfate supply was depleted in sediments with restricted exchange to external reservoirs. Mass balance calculations on framboid populations are used to estimate rates of sulfate depletion, and possible causes of a bimodal distribution between pyrite framboids(-38 to -32‰ VCDT) and large (>10 µm) euhedral sulfides (-21 to -10‰) are discussed.

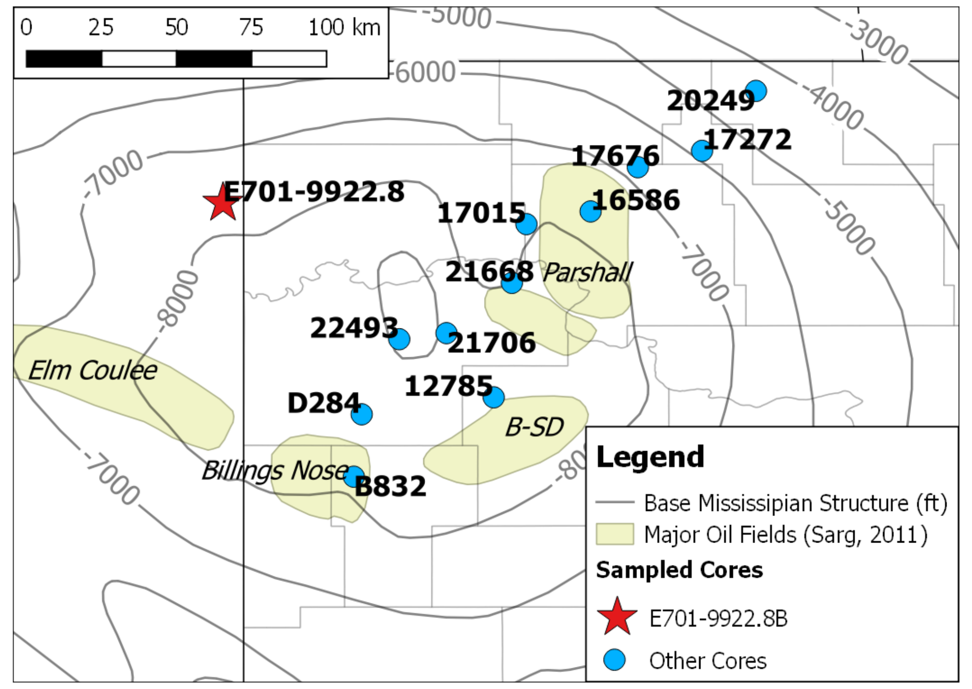
***At Left:*** *BSE image of a large pyrite polyframboid from the Lower Bakken, with SIMS $\delta^{34}S$ analyses in red. Polyframboids such as this one are most often found in particle-rich layers containing deformed clay pellets and apatite skeletal fragments. From E701-9922.8B*

## Geologic Setting and Sampling

The Bakken Formation of the Williston Basin brackets the Devonian-Carboniferous boundary and is generally broken down into three members--an upper and a lower black shale bed, and a middle mixed siliciclastic carbonate unit. A suite of samples was collected from various locations within the basin in order to describe and study the sequential development of sulfides across the basin. This poster is focused on the sulfide petrography and $\delta^{34}S$ values within a single billet (E701-9922.8), in order to emphasize the significant variability present across small distances, but recent SIMS work has confirmed that $\delta^{34}S$ values are similarly distributed amongst sulfidic phases in other parts of the basin.



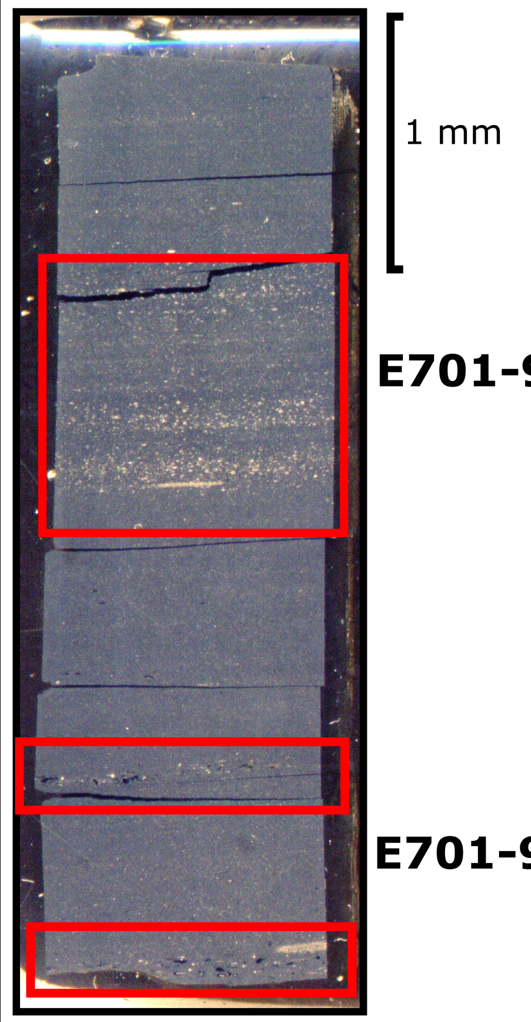

***Above:*** *Schematic stratigraphy of the Bakken at the end of the Devonian, emphasizing the smaller extent of the Lower Bakken.*




***At Right:*** *Map of the base-Mississippian structure throughout the Williston Basin. Major oil fields and sampled cores are denoted; sample core E701 is marked with a red star. Map is adapted from Sarg (2011).*

## Sample E701-9922.8

This sample was collected at the USGS core repository from a depth of 9,922.8 feet (~3km). Two mounts were made to examine the full range of features present in the billet.



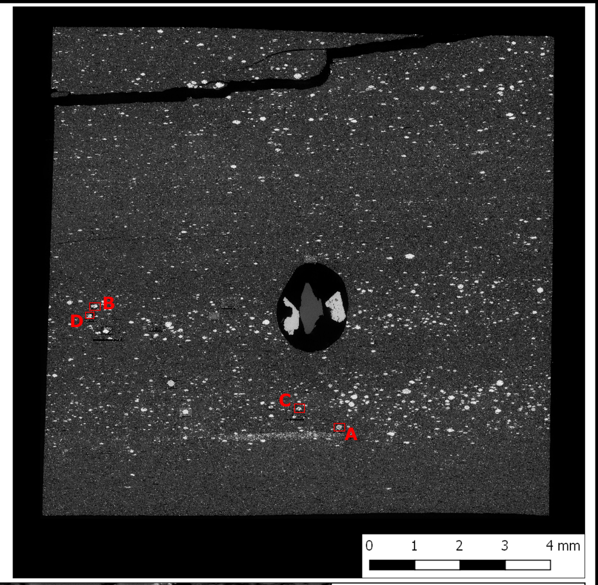

**E701-9922.8A**

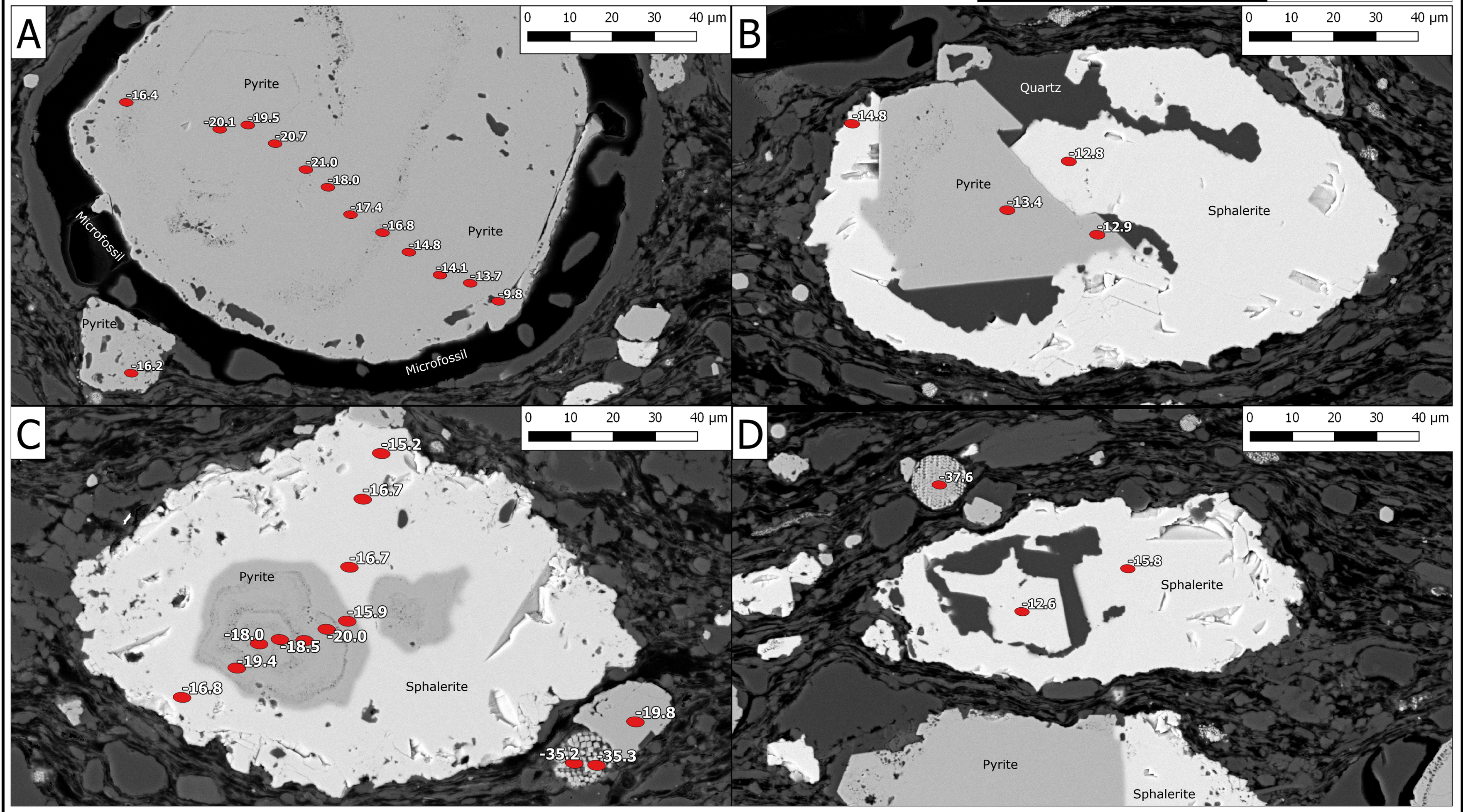
**E701-9922.8B**

## Sulfidic Phases: E701-9922.8A

The dominant pyrite phases present in E701-8822.8A are large euhedral pyrites and sphalerites replacing or filling in microfossils. There are minor framboids and pyrite replacing dolomite; there are no polyframboids present.

***BSE-SEM images below:*** *A) Transect across a large zoned pyrite inside of a microfossil. Note that $\delta^{34}S$ values rise towards edge. Also note the partially replaced dolomite crystal in the lower left. B) Pyrite and sphalerite replacing quartz. C) Zoned pyrite surrounded by sphalerite, implying that sphalerite post-dates pyrite. Note the framboid in the lower right. D) Sphalerite replacing quartz, with pyrite framboid in upper left.*

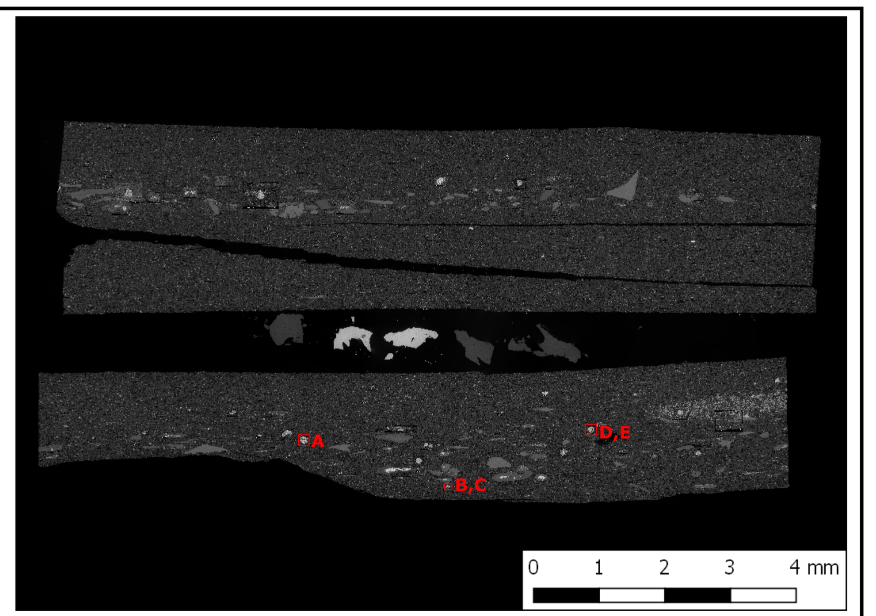


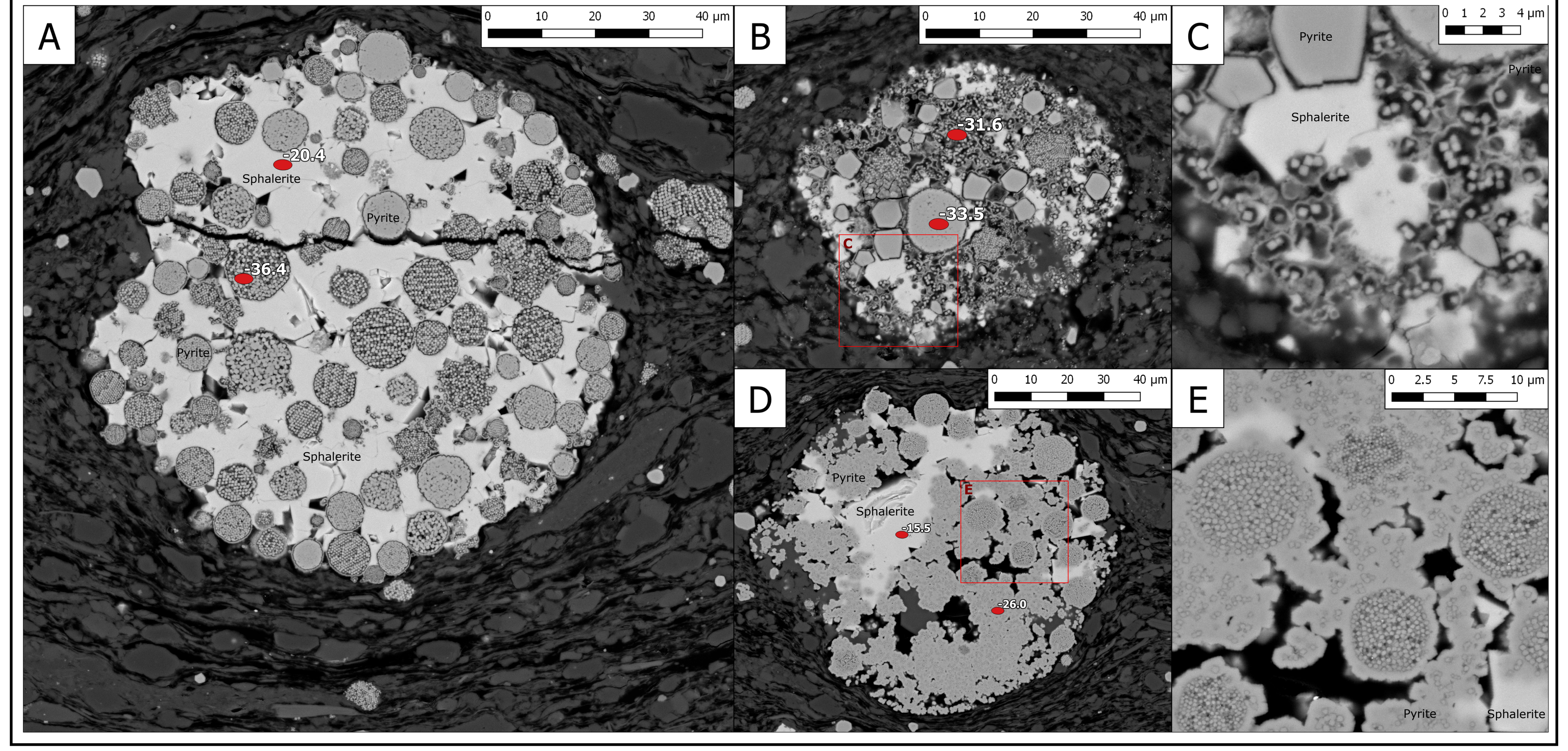



## Sulfidic Phases: E701-9922.8B

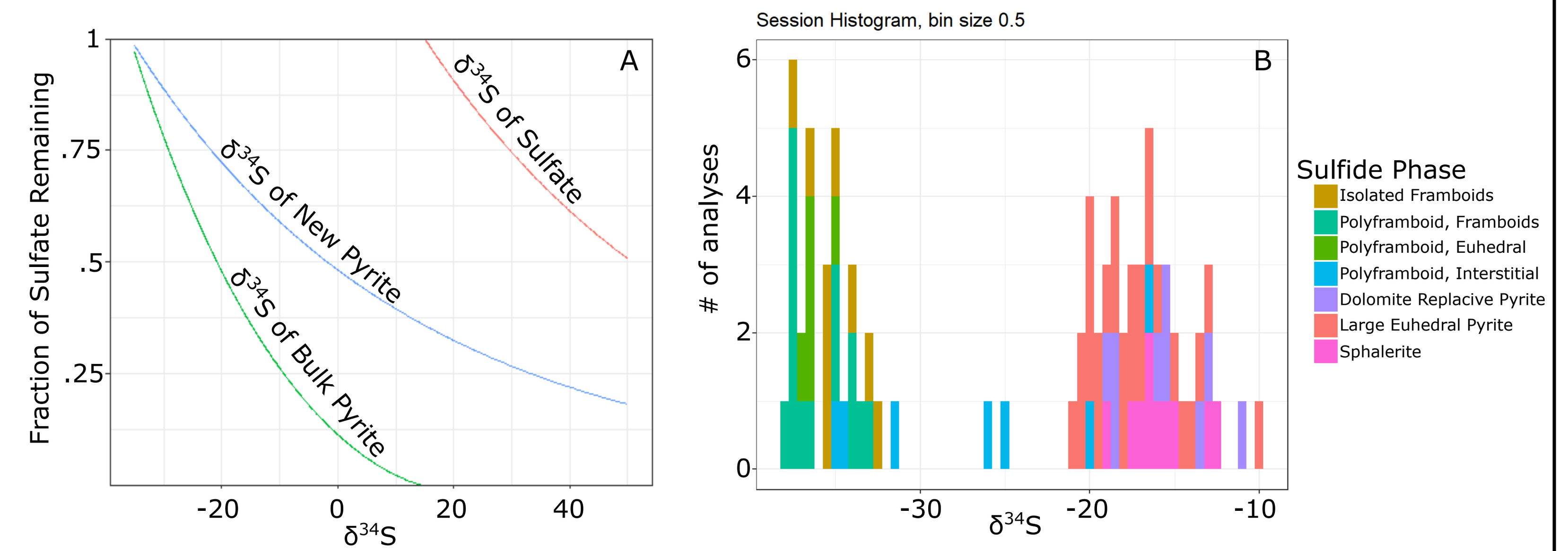
The dominant pyrite phases present in E701-9922.8B are polyframboids and framboids, with minor pyrite replacing dolomite, minor large euhedral pyrite, and minor sphalerite.

***BSE-SEM images below:*** *A) Large polyframboid with sphalerite infill. Note the wide variability in framboid microcrystal size, framboid diameter, and degree of microcrystal ordering. B) Pyrite polyframboid with sphalerite infill. C) Zoomed-in image of region in B. The thin-walled oval shapes may have once been the cell walls of sulfate-reducing microorganisms. D) Another polyframboid with sphalerite infill. E) Zoomed-in image of region in D. Note that both framboids and pyrite microcrystals are themselves surrounded in an unusual thick layer of pyrite.*




## Results: A Bimodal Distribution




*A) Modeled Rayleigh fractionation curves for $\delta^{34}S$ behavior in a depleting sulfate reservoir, assuming an alpha value of 0.95 and Devonian ocean $\delta^{34}S_{(sulfate)}$ = +15‰. **B)** Histogram of $\delta^{34}S$ values compiled from both E701-9922.8 SIMS mounts. Note that the simple Rayleigh fractionation model predicts a smooth distribution, but two populations are apparent in this sample.*

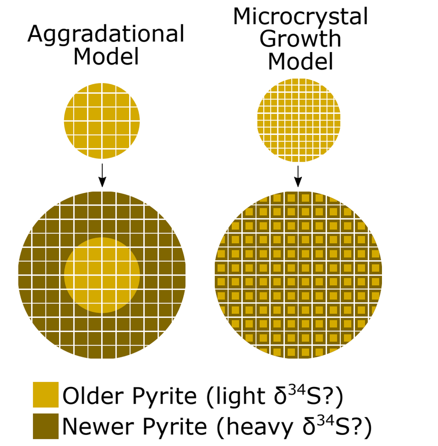
Compilation of $\delta^{34}S$ data of all sulfide phases in E701-9922.8 reveals two clusters of data (-40 to -30‰ and -20 to -10‰) with a significant gap (-30 to -20‰) in between. This distribution requires two sulfide generation events separated in space and/or time. The first event produced all of the framboidal pyrite and the -40 to -30‰ values. The second event produced the large replacive sulfides and the -20 to -10‰ values. Given our current petrographic and geochemical understanding of these rocks, there are three possible explanations for this distribution:

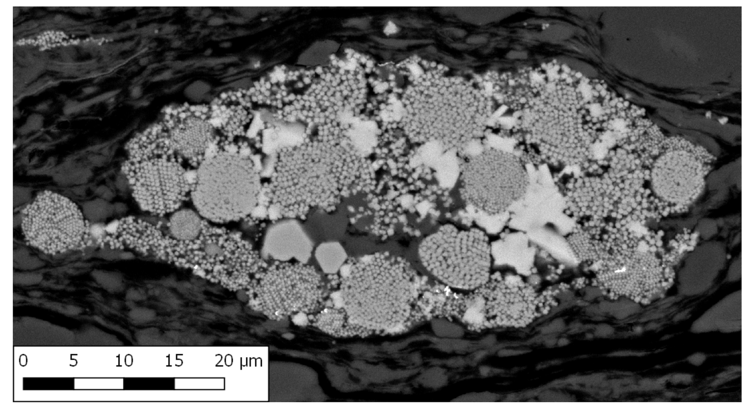
1) Framboidal pyrites formed in the water column and replacive sulfides formed in the sediment, both by Microbial Sulfate Reduction (MSR). This explanation requires that polyframboids aggregate on the sea floor.
2) Framboidal pyrites formed in very shallow soft sediment and replacive sulfides formed deeper down. All sulfides formed via MSR, but different rates of sulfide production in turn produced different fractionations.
3) Framboidal pyrites formed by MSR, and replacive euhedral sulfides formed much later at high temperatures by Thermochemical Sulfate Reduction (TSR)

## Ongoing/Future Work: Can Framboid Populations Reveal $\delta^{34}S$ Depletion Rates?

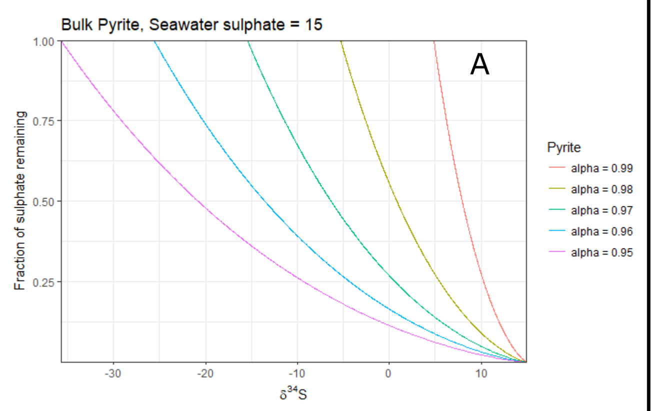
Though they have been studied for a century, the mechanism of pyrite framboid formation remains elusive.

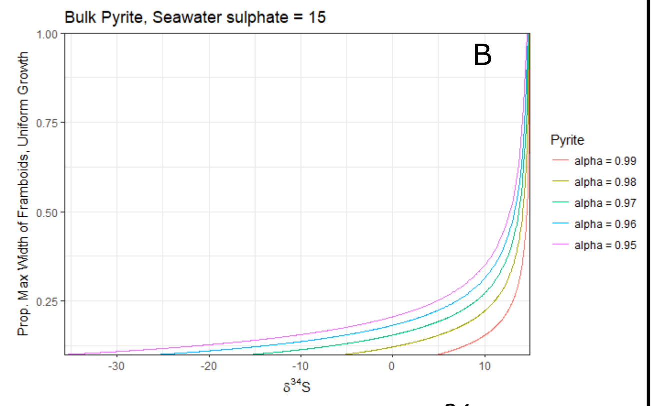
***Below:*** *Recent models of framboid formation can generally be grouped into two categories; those models in which framboids only grow along their outside edge ("aggradational" model), and those models that invoke the growth of all the framboid's microcrystals in tandem with each other. Determining which, if not both, of these mechanisms is at work from imagery is often ambiguous.*



While many microcrystals are too small even for SIMS, different sized framboids are likely to have different $\delta^{34}S$ values so long as they grow as sulfate is being depleted; therefore, useful information can still be extracted from the homogenized bulk value of a framboid. Preliminary results suggest a lack of $\delta^{34}S$ zonation within framboids, but there is a faint positive correlation between microcrystal size and bulk $\delta^{34}S$ value, lending strength to the microcrystal growth model. In the coming months this dataset will be expanded and interrogated further to see how robust this trend is, and with what accuracy this approach can estimate sulfate depletion rates in the geologic past.




***A)*** *Modeled bulk pyrite $\delta^{34}S$ behavior under Rayleigh fractionation conditions for a range of fractionation factors, and assuming ocean $\delta^{34}S_{(sulfate)}$ = +15‰.* ***B)*** *Same range of fractionation factors as in A, but instead of plotting bulk $\delta^{34}S$ composition against fraction of sulfate remaining, plotted on the y-axis is the fraction of a framboid microcrystal's maximum width at the time of sulfate exhaustion.*

**References**

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Poster created by Adam Denny for HiRes 2017 conference at the UW-Madison, June 19th, 2017