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Improving Interpretations of the S-Isotope Composition of Pyrite with Isotopic Measurements of Individual Pyrite Framboids

Katja M. Meyer, Department of Environmental Science, Willamette University, Salem, OR

I. Summary of Research Findings to Date

The goal of this project is to use high-resolution sulfur isotope measurements of pyrite framboids to improve the interpretation of $\delta^{34}S$ in the geological record, especially during intervals of ocean redox change. Changes in marine sulfur cycling during intervals of ocean anoxia/euxinia are often observed as widespread, rapid changes in the isotopic composition of sedimentary pyrite ($\delta^{34}S_{pyrite}$) and calcite-associated sulfate ($\delta^{34}S_{CAS}$). However, the underlying dynamics of these changes remain incompletely understood. In particular, $\delta^{34}S_{pyrite}$ records often show high variability over short stratigraphic ranges and cannot easily be correlated with other coeval sections worldwide. One difficulty in interpreting sedimentary $\delta^{34}S_{pyrite}$ records may result from the presence of both syngenetic and diagenetic sources in a bulk measurement. In this study, we examine the relationship between framboid diameter and $\delta^{34}S$ of framboids in a modern euxinic analog and in Early Triassic limestones. We hypothesized that the small framboids formed within the water column will show less variation in $\delta^{34}S_{pyrite}$ than bulk $\delta^{34}S$ and can be used as a proxy for water column $\delta^{34}S_{H2S}$. Larger framboids formed in the sediments, however, may display greater variability in $\delta^{34}S_{pyrite}$ due to closed-system behavior that is decoupled from the water column.

Since being funded by PRF, my research group has prepared both rock and lake sediment samples for SIMS isotope analysis to measure the $\delta^{34}S$ composition of individual pyrite framboids that span a range of sizes. In the first two years of the grant, we used density separation methods developed in the Fike Lab (Washington University, St Louis) to separate pyrite framboids from Fayetteville Green Lake (FGL) sediments from below and above the sulfidic monimolimnion. These mineral separates were embedded in 1" round epoxy disks, polished, and analyzed via SEM and SIMS. While SEM visualization revealed characteristic pyrite framboids in the samples, it was challenging to measure $\delta^{34}S$ of individual pyrites via SIMS because of the relatively small number of pyrites, wide spacing of mineral grains, and difficulty locating the pyrites after the samples were gold-coated. Since summer 2017 we have successfully improved the density separation, mapping, and analysis of framboidal pyrites, and we have added approximately 200 $\delta^{34}S$ measurements of individual framboids from FGL sediments from 3 different depths at and below the chemocline. We observe up to a 40 permil range in $\delta^{34}S$ of framboids isolated from a single sample with no clear relationship to framboid diameter. The range of isotope compositions reported in these initial data are similar to observations of modern microbial mats and sedimentary rocks and likely capture both pyrites formed in the water column and in the sediments. In 2018-2019 my group will continue our data analysis and interpretation, and we anticipate writing a manuscript for submission to the journal *Geobiology*.

Second, since 2016 my research group has also investigated the $\delta^{34}S$ – framboid diameter relationship in Early Triassic limestones that were deposited following the end-Permian mass extinction interval. Several undergraduates participated in using SEM to measure the diameter and map the position of pyrite framboids on 4 different 1" round thin sections of Early Triassic limestones from the Great Bank of Guizhou, Nanpanjiang Basin, South China. We have generated ~50 $\delta^{34}S$ measurements from one sample and have mapped the position of several hundred pyrites for future isotope analysis via SIMS. The initial $\delta^{34}S$ are similar to the FGL data: the isotope compositions within a single sample span a range of almost 30 per mil and do not show any relationship to framboid diameter. Furthermore, there is also no $\delta^{34}S$-diameter relationship after removing any framboids that are partially infilled or show signs of post-depositional alteration. We are continuing to generate data from other limestone samples to see if this observation holds true. Many of the limestone samples have few pyrites, and mapping and identifying them in a 1" round thin section is challenging. As a result, we plan to develop a method of separating pyrites from crushed limestone samples and will prepare them for SIMS analysis on epoxy disks similar to our work with FGL sediments. This project will form the basis of one undergraduate Chemistry senior thesis during 2018-19.

II. Impact of the research on field of study and career

To date, this research project has opened new collaboration (with David Fike's research group, Washington University, St Louis) and has led to networking opportunities with other researchers working on questions related to the production and preservation of $\delta^{34}S$ in pyrites and calcite-associated sulfate. I am working with two scientists in the Fike lab to continue to improve our pyrite isolation techniques and adapt them for smaller and lower pyrite samples. In collaboration with Clive Jones and David Fike, we also developed a method of measuring the true diameter of mineral grains in thin section; our manuscript entitled, "SIMS methodology for isotopic ratio measurements of micro-grains in thin sections: true grain size estimation and deconvolution of inter-grain size gradients and intra-grain radial gradients," was recently accepted (with revisions) for publication in *Geostandards and Geoanalytical Research*.

I presented this work at the Gordon Research Conference in Geobiology (January 2018) and at the US Kavli Frontiers of Science Symposium (February 2018). These meetings were productive opportunities to gather feedback on our work and expand my network. I anticipate this project leading to 2 peer-reviewed publications with undergraduate co-authors after analysis of FGL data and after collection of additional $\delta^{34}S$ data for the Early Triassic limestones.

III. Student mentoring and outcomes

Since 2016 four summer undergraduate students have been supported by ACS-PRF funding to work on this project, and two students have participated in the work informally (through independent study during the academic year). The grant has allowed my undergraduate team to gain research experience that is not otherwise available through our formal curriculum. They also were able to travel to the University of Oregon Center for Materials Characterization in Oregon (CAMCOR) to use the SEM. They report that this experience was valuable not only to visualize and map their samples, but also to be exposed to the range of interesting research going on at a major research university. Students participating in this project presented their work at the regional Murdock College Science Research Conference (November 2016 and November 2017). This regional undergraduate science meeting is an excellent opportunity to expose Willamette students to the breadth of undergraduate research in the Pacific Northwest; students attending this meeting also have access to representatives from major graduate programs in the area. Finally, two undergraduates presented this work at the Geological Society of America Meeting (October 2017, Seattle) in the session, *New Voices in Geobiology*. One student from our summer 2017 group has continued to work with me via an independent study and will focus his senior thesis in Chemistry on the Permian-Triassic portion of this project during 2018-2019.

Five students who contributed to this project have graduated from Willamette with degrees in Environmental Science or Biology. Three of the five students, all female, began graduate school in the sciences (Biological Oceanography, GIS, and Photovoltaics) this fall. The graduate student earning her master's degree in Photovoltaics is doing a majority of her graduate coursework in the CAMCOR facility at University of Oregon. The summer research supported by ACS-PRF funding gave these students valuable experience that helped them hone their disciplinary interests and motivated their decision to apply to graduate programs in the sciences.