Depositional conditions control marine sedimentary pyrite isotopes

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Controls on the sulfur isotope ($\delta^{34}S$) composition of sedimentary pyrite are poorly understood and changes in bulk $\delta^{34}S$ values can be attributed to multiple biological and/or environmental causes. To address this, we performed grain-specific sulfur isotope analyses on pyrites extracted from samples from marine isotope stages 6 to 4 in the PRGL 1-4 core in the Gulf of Lion, using Secondary Ion Mass Spectrometry (SIMS). Previous analysis from this core revealed large amplitude (up to 70‰) changes in bulk $\delta^{34}S_{pyrite}$ that were coherent with glacial-interglacial sea level changes [1]. Here, we demonstrate that samples from interglacials feature a narrow inter-grain distribution in $\delta^{34}S_{pyrite}$, generally close to −45, whereas samples from glacials feature a large inter-grain range in $\delta^{34}S_{pyrite}$, from ~−50 to ~110‰; little to no intra-grain $\delta^{34}S$ variation was detected in grains large enough for multiple analyses. Our results suggest that throughout this interval the biological fractionation (ε_{bio}) from microbial sulfate reduction (MSR) was invariant and close to the thermodynamic equilibrium fractionation between sulfate and sulfide (~70‰). Moreover, the results indicate that closed-system pore water evolution increased in glacial times, and was the cause of the ^{34}S-enriched bulk pyrite from these intervals. The switch to more closed-system behavior during glacials was most likely driven by increased rates of sedimentation associated with marine regression. The observation that depositional conditions can control bulk pyrite $\delta^{34}S$ brings into question prior interpretations of the ancient pyrite $\delta^{34}S$ record.

[1] Pasquier *et al.* (2017) *PNAS* **114**, 5941-5945.