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Microscale iron and sulfur isotope signatures of early diagenetic pyrite formation

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Given the application of sedimentary pyrite iron and sulfur isotope compositions ($\delta^{56}Fe_{PYR}$, $\delta^{34}S_{PYR}$, $\Delta^{33}S_{PYR}$) to reconstruct global ocean properties and the evolving oxidation state of Earth’s surface, diagenetic impacts on pyrite-based proxies must be explored. Along with auxiliary petrographic and porewater data, we present coupled microscale $\delta^{56}Fe_{PYR}$-$\delta^{34}S_{PYR}$-$\Delta^{33}S_{PYR}$ in accumulating sediments on the oxic margin of the Black Sea. The coevolution of microscale $\delta^{56}Fe_{PYR}$-$\delta^{34}S_{PYR}$-$\Delta^{33}S_{PYR}$ distributions provides insight into the effect of porewater S species production, consumption, and buildup on the pyritization pathways. “Background” pyrite is characterized by low $\delta^{56}Fe_{PYR}$ and $\delta^{34}S_{PYR}$ values consistent with microbially-mediated iron and sulfate reduction and iron (oxyhydr)oxide sulfidization at low sulfide to iron ratios. In contrast, “sulfidic zone” pyrite displays distinct late-stage morphologies and higher $\delta^{56}Fe_{PYR}$ and $\delta^{34}S_{PYR}$, which reflect sulfide pooling at the sulfate-methane transition zone and direct sulfidization of residual iron phases. We propose that coupled $\delta^{56}Fe_{PYR}$-$\delta^{34}S_{PYR}$-$\Delta^{33}S_{PYR}$ distributions constrain the pyritization pathway and microbial and physico-chemical aspects of the depositional environment.