Controls on sulfur isotope ratios in modern marine and geologic pyrite

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Sulfur isotope ratios (δ^{34}S) in modern marine and sedimentary pyrite have seen extensive use in investigations of sub-seafloor microbial activity and C-S cycling, in reconstructions of past reservoirs and fluxes in the biogeochemical S cycle and the tightly coupled cycles of C and O_2, and in reconstructions of the redox evolution of Earth's surface environment. These applications are guided by the assumption that variation in pyrite δ^{34}S values is related to drivers in the global S cycle and the aggregate fractionation imparted by microbial S metabolisms. A growing number of observations from a wide range of natural environments, however, suggest that major variation in pyrite δ^{34}S values is often related to neither of these factors. To address this, we developed a coupled microbial-diagenetic model, which accounts for the transport and reaction of oxidized and reduced S and Fe species, and which is capable of predicting the fractionation imparted by microbial sulfate reduction (ε_{mic}).

Using gridded ($1° \times 1°$) datasets of required model parameters (e.g., sedimentation rate, organic loading, porosity), we reproduce pyrite δ^{34}S distributions compiled from studies of modern marine sediments. We find that ε_{mic} remains uniformly large under the vast majority of modern marine conditions, and that the main determinant of pyrite δ^{34}S values is the sedimentation rate, which controls the relative importance of reaction and transport ("openness"). The abundance and reactivity of organic matter and iron are important secondary controls on pyrite δ^{34}S values.

Accounting for the preferential preservation in the marine sedimentary record of shallow-water environments, we explored the effects of evolving sulfate concentrations over Earth history on the range and average of δ^{34}S values preserved in pyrite. We suggest that the trend of increasing Archean-Proterozoic-Phanerozoic sulfate-pyrite δ^{34}S offset arises from the effect of increasing sulfate concentrations not on ε_{mic}, but on the openness of the sedimentary system.

With this new quantitative framework, we understand the tectonic, biological and oceanographic factors that have governed pyrite δ^{34}S values in marine sedimentary rocks through time.