

Controls on iron sulfide multiple sulfur isotopic composition: unraveling the roles of sulfide oxidation and of variable fractionation factors during microbial sulfate reduction

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The variations in the isotopic values of sulfur bearing sedimentary archives (i.e., $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{FeS}_x}$) have often been used to deduce the long-term shifts in fluxes of oxidized and reduced sulfur species to and from the ocean. Further, the net fractionation factor $^{34}\epsilon_{\text{net}} = \delta^{34}\text{S}_{\text{FeS}_x} - \delta^{34}\text{S}_{\text{SWSO}_4}$ between co-eval sulfate and sulfide bearing minerals is generally calculated to approximate the isotopic fractionation expressed during microbial sulfate reduction MSR $^{34}\epsilon_{\text{MSR}} = \delta^{34}\text{S}_{\text{H}_2\text{S}} - \delta^{34}\text{S}_{\text{SWSO}_4}$. However, these types of isotopic archives are complex to interpret without ambiguity because they can be affected by several processes that have the potential to overprint each other isotopic signature.

For example, when sulfide pooling occurs, the observed isotopic difference between sulfide and co-eval sea water sulfate $^{34}\epsilon_{\text{net}}$ is smaller than the actual microbial sulfate reduction fractionation factor $^{34}\epsilon_{\text{net}}$. Some authors thus suggest that $^{34}\epsilon_{\text{MSR}}$ cannot vary significantly in natural environments and is always close to thermodynamic equilibrium, meaning that the variability in sulfur isotopic composition in the rock record is only due to variable degrees of sulfide pooling. In addition, while the occurrence of re-oxidative processes has the potential to further modify the $^{34}\epsilon_{\text{net}}$ from the initial $^{34}\epsilon_{\text{MSR}}$, their influence are often neglected when interpreting isotopic data.

Here, we measured the multiple sulfur isotopic composition of iron sulfides entrapped in gypsum layers deposited at the end of the Miocene in the Mediterranean. Our results show that iron sulfide relative enrichment can be, in certain cases, controlled by fractionation factors $^{34}\epsilon_{\text{MSR}}$ deviating significantly from the one predicted by thermodynamic equilibrium calculations. In addition, we demonstrated that an almost quantitative re-oxidation of sulfide back into sulfate was also occurring during the simultaneous formation of iron sulfide and gypsum in both deep and marginal basins of the Mediterranean. This intense recycling of sulfide have masked an extremely important MSR activity. Whereas, we calculated fluxes of organic carbon remineralized by MSR comparable to those measured in highly productive margins (3.8mm.cm-2.yrs-1), only a very low amount of hydrogen sulfide was ultimately scavenged by iron to form iron sulfide minerals, the vast majority of it being rapidly re-oxidized.