Isotopic spatial patterns as biosignatures

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Minerals or organic carbon deposited in the presence of microbes can potentially preserve biosignatures. We investigated the sulfur isotopic composition of gypsum ($CaSO_4.2H_2O$) formed in the presence of sulfur-oxidizing microbes in the Frasassi cave system, Italy. Sulfur isotopic compositions ($\delta^{34}S_{V-CDT}$) of gypsum sampled from cave walls in contact with sulfidic air varied from -11 to -24‰. Over centimeter length scales, the $\delta^{34}S$ values of gypsum varied by up to 8.5‰. Gypsum precipitated both in the presence and absence of microbes is expected to have $\delta^{34}S$ values 1‰ more positive compated to dissolved sulfate. We therefore interpret the 8.5‰ variation in gypsum $\delta^{34}S$ (towards more negative values) to reflect the isotopic effect of microbial sulfide oxidation. This range is similar to that expected for abiotic sulfide oxidation to sulfate. However, at the meter length scale, reactive transport modeling showed that the ~13‰ variation we observed in gypsum $\delta^{34}S$ reflects isotopic distillation of circulating H_2S gas due to microbial sulfide oxidation along the flow path. Systematic variations of gypsum $\delta^{34}S$ along fluid flow paths can thus be interpreted as biogenic given that slow, abiotic oxidation cannot produce the same spatial patterns over similar length scales. We postulate that spatial isotopic patterns are recorded along fluid flow paths in a wide variety of environments that could potentially preserve biosignatures. The magnitude and spatial scale over which the biosignature is expressed depends on fluid flow parameters and biotic and abiotic process rates and isotopic fractionations. These interactions can be modeled with relative ease and could guide sampling schemes for biosignature detection in the rock record and on other planets.