

## Oxidative sulfur isotope fractionation on sulfidic cave walls

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Chemotrophic sulfide oxidation to sulfate is a major step in the global sulfur cycle. S isotopic fractionation during this process is usually small [1] but can have a huge impact to the isotopic compositions of sedimentary sulfide and sulfate [2]. Determining the isotopic fractionation expressed during this process in nature is difficult mainly due to masking by the relatively large fractionations expressed during sulfate reduction. In the sulfidic Frasassi caves, Italy, microbial S oxidation dominates on the cave walls, leading to gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) formation. This system provides an excellent opportunity to determine the isotopic fractionation due to chemotrophic sulfide oxidation in the absence of other major S cycling processes. We sampled hydrogen sulfide gas ( $\text{H}_2\text{S}(\text{g})$ ) and gypsum from the caves for S isotopic analysis. Gypsum minerals were classified into two groups based on morphology: microcrystalline gypsum and elongated needles.  $\delta^{34}\text{S}$  values of microgypsum were between 0 to  $-9\text{‰}$  depleted relative to the  $\text{H}_2\text{S}$  source. Unexpectedly,  $\delta^{34}\text{S}$  values of both microgypsum and  $\text{H}_2\text{S}(\text{g})$  showed a decrease with height, suggesting that diffusive fractionation of  $\text{H}_2\text{S}(\text{g})$  may contribute to the large (6-8‰) fractionation in gypsum minerals observed over two meters of distance. Within small sections of the cave walls, microbial S oxidation expressed  $<5\text{‰}$  fractionation in microcrystalline gypsum, indistinguishable with values expected from abiotic sulfide oxidation with  $\text{O}_2$  [3]. In comparison, needle-shaped gypsum were between  $+4\text{‰}$  enriched to  $-4\text{‰}$  depleted relative to the  $\text{H}_2\text{S}$  source. Additionally, needle-shaped gypsum were consistently  $\sim 2\text{‰}$  enriched relative to associated microcrystalline gypsum. This signifies either a faster oxidation rate of  $\text{H}_2\text{S}$  or a different pathway of sulfide oxidation to sulfate around needles, possibly through an isotopically heavier sulfur intermediate such as elemental sulfur.

[1] Zerkle, Jones, Farquhar & Macalady (2016) *GCA* **173**, 373-386. [2] Habicht & Canfield (2001) *Geol* **29**, 555-558. [3] Fry, Ruf, Gest, & Hayes (1988) *Chem Geol* **73**, 205-210.