

**Peculiarly large sulfur isotope
fractionation during sulfide
oxidation by the nitrate-reducing
bacterium *Desulfovibrio alkaliphilus***

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Past and contemporary measurements of the sulfur isotope fractionation associated with sulfide oxidation report small fractionations for all pathways tested (phototrophic, chemotrophic, abiotic). Consequently, isotopic interpretations of sulfur and carbon cycling in modern marine sediments, as well as reconstructions of past sedimentary biogeochemistry, assume that large sulfur isotope fractionations reflect other microbial metabolisms like dissimilatory sulfate reduction and sulfur disproportionation.

We measured S isotope fractionation produced during the chemolithotrophic growth of *Desulfurivibrio alkaliphilus* (DA). DA is an alkalophile whose most vigorous growth occurs at pH >9 and, in the presence of excess nitrate and sulfide, produces ammonia and sulfate as metabolic waste products. The only enzymatic pathway in DA connecting sulfide and sulfate operates via a reversal of the dissimilatory sulfate reduction pathway. Essential genes of other sulfide oxidation pathways are absent from its genome.

In batch culture assays, we observed a consistent net isotope fractionation between sulfate and sulfide of +26‰ +/- 2‰. This is the largest sulfur isotope fractionation yet reported for sulfide oxidation under any circumstances. It is also larger than sulfur isotope fractionations reported for DA during elemental sulfur disproportionation [1]. These results suggest that sulfide oxidation is not a low-cast fractionating process and raises the possibility that, in the environment, associating large fractionations solely to sulfur disproportionation or sulfate reduction may be erroneous. Although the ubiquity of such a high isotopic fractionating sulfide oxidation pathway is unclear as DA was isolated from an alkaline environment, these findings may require a significant revision of sulfur isotopic interpretations of marine biogeochemical processes today and in Earth's past.

[1] Poser et al. (2016) *Geomicrobiol J.*, **33** 934-941