

Biogenic experimental pyrites record lighter isotopic signatures than inherited from microbial-sulfate reduction

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Sulfur is an essential element for life, in particular for dissimilatory sulfate-reducing micro-organisms (SRM) which gain energy from the multiple-steps reduction of environmental sulfate into sulfide. This microbial metabolism has been well studied in laboratory cultures and is known to produce isotope fractionation between sulfate and sulfide ranging from 5 to 45 ‰. In the geological record, sedimentary pyrites depleted in ³⁴S isotope are commonly assumed to result from SRM activity. However, fractionation between seawater sulfate and sedimentary pyrites are commonly larger and can reach up to 70 ‰. This is generally supposed to be inherited from specific environmental conditions with substrate limitation not reproduced in laboratory cultures, or the involvement of other sulfur based metabolism. Another explanation could reside in the formation process of pyrite. Indeed, due to the difficulty of producing biogenic pyrite in laboratory experiments, previous studies determined the isotope fractionation between sulfate and dissolved reduced S compounds rather than iron sulfide minerals.

Here, experiments forming biogenic pyrite were performed in pure culture of *Desulfovibrio desulfuricans* in a mineralizing medium containing nanoparticulate iron phosphate, supplied with lactate. After 1, 10 and 30 days, sulfur from acid volatile sulfide (AVS, mostly amorphous iron sulfide), chromium reducible sulfur (CRS, principally pyrite) and dissolved sulfate was chemically extracted to further analyze multiple sulfur isotopic compositions ($\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$).

The isotopic composition of both AVS and sulfate can be fitted by a Rayleigh distillation with a fractionation of -15 ‰ similarly to what has been reported in the literature between H₂S and sulfate in equivalent conditions. It suggests that no further fractionation occurs during the precipitation of iron monosulfide from dissolved sulfide produced by SRM, and therefore that the former directly record the isotopic signature of microbial sulfate-reduction. In contrast, sequentially extracted CRS were slightly lighter than the coexisting AVS by about -3 ‰. Although the magnitude of this isotopic shift is small in comparison with data reported in natural systems, it illustrates that a fractionation process occurs during the conversion of amorphous iron sulfide into pyrite which record lighter isotopic signatures than inherited from microbial sulfate-reduction step alone.