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Stable isotope fractionation during bacterial sulfate reduction is governed by reoxidation of intermediates

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Stable isotope fractionation is an important tool for assessing bacterial dissimilatory sulfate reduction. Isotope fractionation works on the principle that isotopes such as ^{32}S and ^{34}S react at slightly different rates, changing the ratio of the heavy to the light isotopes in the residual substrate fraction. During bacterial sulfate reduction, sulfate is reduced through several enzyme-mediated steps to sulfide. The sulfate reduction pathway is commonly described in the *Rees* model, where cell internal sulfate reacts with ATP (adenosine-triphosphate) to form APS (adenosine-5'-phosphosulfate), which is thereafter directly reduced to sulfite. The final step involves the reduction of cell internal sulfite to sulfide. Each individual step is accompanied by isotope fractionation, which in turn influences the isotope enrichment factor of sulfur and oxygen.

A systematic study with different sulfate-reducing bacterial strains (*Desulfovibrio desulfuricans, Desulfobacca acetoxidans, Desulfonatronovibrio hydrogenovorans* and *strain TRM1*) was performed with ^{18}O enriched water ($\delta^{18}O_{water}$= + 700 permil and depleted water ($\delta^{18}O_{water}$ = – 40 permil to follow the δ^{18}O shift in the residual sulfate during bacterial sulfate reduction. The experiments showed that the oxygen isotope composition of water clearly controls the oxygen isotope composition of residual sulfate. We suggest that the ^{18}O isotope exchange takes place in intermediates of the sulfate reduction pathway such as sulfite and the latter are partially reoxidized to form "recycled" sulfate. Moreover, we hypothesize that the reoxidation process of the intermediates also affect the isotope enrichment factor of sulfur, because bacterial strains with high sulfur enrichment factors (*Desulfobacca acetoxidans*, strain *TRM1*) showed high oxygen isotope exchange of water with residual sulfate, whereas low sulfur enrichment factors (by *Desulfovibrio desulfuricans, Desulfonatronovibrio hydrogenovorans*) were accompanied by small isotope exchange with water.

The *Rees* model assumes that the isotope fractionation is large, if the final reduction step of sulfite to sulfide is rate limiting because the first steps in the reaction pathway are either equilibrium reactions (APS reductase) or do not exhibit isotope effects (APS synthase). In contrast, when the intermediate sulfite, undergoes a fast transformation to the final product sulfide than the re-oxidation to sulfate would be smaller and small fractionation factors of sulfur are expected.

To verify this hypotheses batch experiments with the strain *Desulfovibrio desulfuricans* were performed in the presence of different nitrite concentrations. Dissolved nitrite inhibits the production of dissimilatory sulfite reductases and therefore governs the final reduction process of sulfite to sulfide. Our results showed an increase of the sulfur isotope enrichment factors from $\varepsilon = -12$ ‰ to up to $\varepsilon = -23$ ‰ with increasing nitrite concentrations. By the nitrite treatment we were able to convert a low fractionating organism into a high fractionating organism. This is in line with our expectation that, whenever the final reduction step of sulfate reduction is inhibited, it strongly influences the stable isotope enrichment factor of sulfur and in turn the $\delta^{18}O$ isotope exchange of water and residual sulfate. These novel results also show that the magnitude of the sulfur isotope fractionation is controlled by the kinetics and / or regulation of the enzymatic pathway of dissimilatory sulfate reduction and not by the physico-chemical features of the individual enzymes.