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Oxygen and sulfur isotope effects governed by bacterial sulfate reduction

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Bacterial sulfate reduction is one of the most important processes in the sulfur cycle. The reduction of sulfate is described in the Rees model, where the cell internal sulfate reacts with ATP (adenosine-triphosphate) to form APS (adenosine-5'-phosphosulfate) which is thereafter reduced directly to sulfite. The final step of the biochemical reaction involves the reduction of sulfite to sulfide.

Bacterial sulfate reduction is accompanied by stable isotope fractionation and increasing δ^{34}S and δ^{18}O values of sulfate with decreasing sulfate concentrations. It is proposed that isotope fractionation occurs during the formation of APS and in the reduction of sulfite to sulfide due to the splitting of S-O bonds. So far, it is suggested that bacterial sulfate reduction rates as well as the type of the electron source control the isotope fractionation factor of δ^{34}S. Furthermore, concerning the isotope effects of oxygen, different authors suggest that the δ^{18}O of sulfate is additionally affected by cell internal processes such as an oxygen isotope exchange with water. We challenge the existing hypothesis that sulfate isotope fractionation depends on the reduction rate and the objective of this study is therefore to provide insight in the mechanism of isotope fractionation during BSR.

The bacterial strains *Desulfovibrio desulfuricans*, *Desulfobacca acetoxidans*, *Desulfonatronovibrio hydrogenovorans* as well as *TRM1* were used. These microorganisms show broad variations in their fractionation factors and metabolize different carbon sources (lactate, acetate, formate and toluene). To study oxygen isotope exchange and possible incorporation of water-oxygen into sulfate, enriched ($\delta^{18}O_{water}$ about +700‰) and depleted water ($\delta^{18}O_{water}$-40‰) was used in batch experiments. First results show surprising δ^{18}O values of the residual sulfate. The data sets can be grouped in two clusters: Group A (*Desulfobacca acetoxidans*, *TRM1*) shows δ^{18}O

of sulfate up to 700‰ in the attempts with enriched water. A complete exchange between δ^{18}O of water and the remaining sulfate was observed here. In contrast, group B *(Desulfovibrio desulfuricans, Desulfonatronovibrio hydrogenovorans)* revealed δ^{18}O values of sulfate near 60‰ in the experiments with heavy water. In the experiments with oxygen depleted water, the oxygen isotope values of the remaining sulfate show fairly constant δ^{18}O values. Based on these results we postulate that intermediates of the sulfate reduction pathway such as sulfite are reoxidised or maybe disproportionated during reduction. This reoxidation leads to an incorporation of oxygen from water in the sulfate which changes the isotopic composition of the remaining (or partly recycled) sulfate. It also leads to changing sulfur isotope values. This reoxidation does therefore strongly affect the stable isotope fractionation factors for oxygen and sulfur that can be measured during sulfate reduction. Furthermore, the reoxidation or disproportionation is probably dependent on the metabolic rate and therefore does also pretend to influence the stable isotope fractionation factor in a rate dependent manor. However, this effect is only indirect. The chemical isotope fractionation itself is probably not rate dependent.