



Combined S-33 and O-18 Isotope Tracing of Intracellular Sulfur Metabolism during Microbial Sulfate Reduction

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Microbial sulfate reduction is a key player in the global carbon cycle, oxidizing nearly 50% of organic matter in marine sediments. The biochemical pathway of microbial sulfate reduction fractionates sulfur and oxygen isotopes and these fractionations can be used to reconstruct S cycling in sediments. Sulfur isotope fractionation during microbial sulfate reduction, which partitions lighter sulfur (^{32}S) into sulfide and heavier sulfur (^{33}S and ^{34}S) into the residual sulfate, can be as high as 72‰ for $^{34}\text{S}/^{32}\text{S}$. The availability and type of organic substrate control the magnitude of sulfur isotope fractionation by influencing the fluxes of and the transfer of electrons to different S species. The partitioning of oxygen in sulfate during microbial sulfate reduction appears to be strongly influenced by the oxygen isotopic composition of water in which the bacteria grow, but its magnitude also seems to correlate with the magnitude of $^{34}\text{S}/^{32}\text{S}$ isotope fractionation. In addition, the fractionation of $^{33}\text{S}/^{32}\text{S}$ is thought to reflect the reversibility of some intercellular fluxes. We wanted to investigate whether the $^{18}\text{O}/^{16}\text{O}$, $^{34}\text{S}/^{32}\text{S}$ and $^{33}\text{S}/^{32}\text{S}$ isotope fractionations in sulfate are controlled by the same intracellular processes and conditions. This was done by investigating the combined sulfur and oxygen isotope partitioning by a marine *Desulfovibrio* sp. grown in pure culture on different organic substrates and in water with different isotopic composition of oxygen.

The isotope fractionations of oxygen and sulfur correlated with the cell specific sulfate reduction rates (csSRR), where slower rates yielded higher sulfur fractionation (as high as 60‰,) and higher oxygen isotope fractionation. The trends in $^{33}\text{S}/^{32}\text{S}$ and $^{34}\text{S}/^{32}\text{S}$ with the changing csSRR was similar to the trends in $^{18}\text{O}/^{16}\text{O}$ with the csSRR, suggesting that the same intercellular pathways controlled both oxygen and sulfur isotope signatures during microbial sulfate reduction. The use of water with different isotopic composition of oxygen showed that the kinetic isotopic fractionation was negligible and that $\delta^{18}\text{O}$ in sulfate should be 22.5‰ higher than $\delta^{18}\text{O}$ in water (at 22°C). This relationship indicates that more intracellular sulfite may be oxidized back to sulfate when the flux of electrons from the electron donor to sulfite is low, allowing isotopic exchange of oxygen between sulfite and water. The use of our experimental results as constraints in a reactive transport model implies that the magnitudes of the oxygen isotope fractionation and sulfur isotope fractionation are correlated under a broad range of sulfate reduction rates in marine and marginal marine environments. This correlation suggests a strong role for the electron donor in controlling the intracellular redox fluxes of sulfur and the fractionation of oxygen isotopes in the natural environment.