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Stable Isotope Fractionation During Anaerobic Bacterial Disproportionation of Elemental Sulfur: The Influence of Fe(II), Fe(III), and Mn(IV) Compounds

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Sulfate reduction is the main pathway for the oxidation of organic matter in coastal marine sediments. Hydrogen sulfide which is produced during this microbial dissimilatory process is not completely buried in the sediment but oxidized to a significant extent. These sulfur intermediate may be further oxidized, reduced or disproportionated. Particularly the latter process is associated with significant sulfur isotope fractionation (e.g., Canfield & Thamdrup, 1994; Cypionka et al., 1998). Bacterial disproportionation of elemental sulfur is an important process in the sulfur cycle of natural sediments and leads to the formation of hydrogen sulfide and sulfate according to the overall reaction (Bak & Cypionka, 1987):

$$4H_2O + 4S \text{ --> } 3H_2S + SO_4^{2-} + 2H^+ \quad (1)$$

To keep the disproportionation reaction exergonic, H_2S must be removed from solution, for instance, by reaction with iron and manganese (oxyhydr)oxides (e.g., Thamdrup et al., 1993). In the present study, stable sulfur and oxygen isotope fractionation during formation of sulfate according to reaction (1) was experimentally investigated during growth of a pure culture of *Desulfocapsa thiozymogenes* and an enrichment culture at 28°C. Synthetic $FeCO_3$, FeOOH or MnO_2 were used as scavengers for H_2S to keep the disproportionation reaction exergonic, and to suppress polysulfide formation and isotope exchange between S and H_2S. The oxygen atoms in sulfate during the anaerobic process (equation (1)) are completely derived from water (Böttcher et al., 2000). In the presence of iron compounds, dissolved sulfate was enriched in ^{18}O compared to water by about +17 per mil. Oxygen isotope fractionation was not influenced by the type of iron-bearing scavenger used, indicating that H_2S oxidation by FeOOH yields S as the dominant oxidation product. Sulfite is suggested to be formed as a metabolic intermediate to facilitate isotope exchange with water. Due to bacterial disproportionation, dissolved sulfate was enriched in ^{34}S compared to elemental sulfur by +11 to +18 per mil in the presence of FeOOH or $FeCO_3$. In agreement with mass balance considerations, reduced sulfur was enriched in ^{32}S.

In the presence of Mn(IV)oxide the measured sulfur isotope effects (-0.6 to +2.0 per mil) are much smaller than those measured for Fe(III) and Fe(II) compounds, indicating that microbial isotope fractionation was superimposed by chemical re-oxidation of hydrogen sulfide by MnO_2 to sulfate. This is confirmed by the oxygen isotope composition of sulfate, which was enriched in ^{18}O compared to water by only +8 to +12 per mil. Our results on the re-oxidation products in the presence of metabolizing micro-organisms are in general agreement with experiments on inorganic reactions in seawater (Yao & Millero, 1996). These new experimental results imply that the overall influence of bacterial disproportionation on stable isotope partitioning in natural surface sediments depends on the proportion of available reactive Fe(III) to Mn(IV) (oxyhydr)oxides.

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