# Effect of the energy status on multiple-S isotope fractionation during the microbial sulfate reduction

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Microbial sulfate reduction is the main fractionation mechanism responsible for the variation of sulfur isotopes in the sedimentary sulfur species through geologic time; however, the principal factors determining the magnitude of enrichment factors are yet to be determined. Because microbial sulfate reduction is the result of multistep enzymatic processes, the total isotope effect depends not only on the isotope effect but also on the reversibility of each reaction step. In general, the reversibility is predicted to be influenced by the free energy of the reaction [1]. Until now, only one study investigated the influence of $\Delta G$ on the S isotope fractionation by the same microbes, but it did not report a clear trend between the isotope fractionation and the Gibbs free energy yield of respective reactions [2]. In this study, we investigated multiple-S isotope fractionation using a sulfate reducing bacterium (*Desulfovibrio* sp.) isolated from a tidal flat in Cape Cod, Massachusetts, USA that grew on various electron donors. Grown on the same electron donor, we observed a larger fractionation with a lower cell specific sulfate reduction rate. When the enrichment factors were measured in the log-phase cultures grown on different electron donors, they changed with the calculated rates of ATP synthesis rather than the cell specific sulfate reduction rate. We hypothesize that a decrease in the energy released from sulfate reduction increases the reversibility of the reactions, yielding a larger isotope fractionation. Our data suggest that the isotopic fractionation can be correlated with the actual energy conservation through the synthesis of ATP rather than the Gibbs free energy yield of the reactions. We will also discuss the relationship between $^{33}S$ and $^{34}S$ fractionation to better constrain the biological flow networks of sulfate reduction [3].

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# Hydrolysis of desferrioxamine-B at the surface of goethite in the dark at pH 6

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Siderophores are Fe (III)-specific chelators that play an important role in the biogeochemical cycling of iron. Under conditions of iron stress, many plants and microorganisms facilitate iron uptake by secreting siderophores, which solubilize iron-bearing minerals. Numerous previous studies on siderophore-promoted dissolution have focused on a commercially available trihydoxamate siderophore, desferrioxamine-B (DFOB). However, the manner in which DFOB adsorbs and the mechanism by which it promotes mineral dissolution are still under discussion.

The goal of the present study was to investigate adsorption and dissolution processes at the surface of goethite in the presence of DFOB at a total ligand concentration of 1 $\mu$mol/m$^2$ at pH 6 in the dark. We performed an *in situ* infrared spectroscopic study to explore the reactions taking place at the goethite surface over a 4-day reaction period. We also carried out an independent macroscopic experiment to monitor the concentrations of the species in solution as a function of time. The DFOB hydrolysis products [1], acetate and $H_3O^+$, were produced at a rate even larger than the rate of iron dissolution. We also detected a nitroso-DFOB fragment, which is an oxidized form of the third product of DFOB hydrolysis, a hydroxylamine-DFOB [2]. The concentration of nitroso-DFOB increased linearly with time. The presence of this fragment is indirect evidence for Fe (III) reduction.

While hydrolysis of DFOB in the presence of Fe (III)-hydroxides has been speculated previously under visible light and pH 3 [3], it has not to our knowledge been reported in the dark at circumneutral pH. We propose that hydrolysis could play an important role in the dissolution of iron-bearing minerals by hydroxymate siderophores.

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