The role of soluble Fe(III) in the cycling of iron and sulfur in coastal marine sediments

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ABSTRACT: In marine sediments, Fe(III) is found predominantly as a solid. Recently, however, soluble species of Fe^{3+} complexed by natural organic ligands have been detected in coastal marine sediments with voltammetric microelectrodes. The role of soluble Fe^{3+} complexes in diagenesis is unknown. In anoxic conditions, soluble Fe^{3+} can effectively oxidize FeS_2 and recycle iron and sulfur for use as terminal electron acceptors during natural organic matter (NOM) degradation. Alternatively, soluble Fe^{3+} complexes can catalyze the formation of FeS and FeS_2 through the rapid chemical reduction of Fe^{3+} by dissolved sulfide. To better understand the role of soluble Fe^{3+} in the transformation of iron and sulfur in marine sediments, we incubated the first few centimeters of unvegetated salt marsh sediment in plug-flow reactors. Microbial iron reduction seemed to prevail in suboxic conditions, but sulfate reduction outcompeted microbial iron reduction in the presence of reactive organic metabolites. The dominance of sulfate reduction led to the complete removal of reactive iron oxides by precipitation of FeS. Experiments mimicking the enrichment of soluble Fe^{3+} complexes in reduced sediments show that soluble Fe^{3+} does not reoxidize FeS and pyrite; rather, it promotes pyrite precipitation by enhancing sulfate reduction via complex bacterial interactions. The rate of pyrite formation in the presence of soluble Fe^{3+} is much higher than previously reported in the literature, suggesting that soluble Fe^{3+} might promote alternative pathways for microbial degradation of NOM that ultimately results in the immobilization of Fe and S as reduced iron sulfide minerals.

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