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Mobility of phosphorus regulated by microbial co-reduction of iron(III) and sulfate in mixed cultures

BIAO WAN[1], PRACHI JOSHI[2], JEREMIAH SHUSTER[2], STEFAN FISCHER[2], ANDREAS KAPPLER[3] AND MUAMMAR MANSOR[2]

[1]Eberhard-Karls-University Tuebingen
[2]University of Tuebingen
[3]University of Tubingen

Presenting Author: biao.wan@uni-tuebingen.de

Phosphorus (P) is an essential macronutrient and its interfacial chemistry and environmental behavior have been extensively investigated under oxic conditions. However, how microbial Fe(III) and sulfur (S) reduction influence the conversion of P-binding iron minerals and what the consequences are for the fate of P transformation under anoxic conditions are not fully understood. We therefore investigated the co-reduction of iron(III) minerals by *Shewanella oneidensis* MR-1 and sulfate (SO_4^{2-}) by *Desulfovibrio vulgaris*, and how it changes Fe, P, and S speciation during the reduction of phosphate-adsorbed ferrihydrite and $FePO_4$ minerals in the co-culture. We found that sulfate concentrations significantly influenced the release of dissolved phosphate and Fe^{2+}. The reduction of 4 mM of sulfate (i.e. relevant to freshwaters) led to a release of dissolved Fe^{2+} but not phosphate. In contrast, the reduction of 30 mM sulfate (i.e. seawater concentration) resulted in phosphate mobilization and Fe(II) precipitation due to the production of large amounts of sulfide. Solid phase characterization revealed that, in the presence of 30 mM sulfate, micrometer-sized iron sulfide aggregates were formed, including mackinawite and greigite, and adsorbed phosphate was mostly released into the solution and partially precipitated as Fe(II)-phosphate mineral (i.e. vivianite). In the presence of 4 mM sulfate, co-reduction of sulfate and Fe(III) led to the formation of nanometer rose-like iron sulfide phases (also as mackinawite and greigite), and surface-adsorbed phosphate was mainly precipitated as vivianite. These findings suggest that microbial sulfate reduction can significantly change Fe-P speciation and mobility, related to the extent and dominance of sulfate versus iron(III) reduction. This study provides a detailed understanding of the crucial roles of S and Fe biogeochemical cycles for the fate of P in freshwater and seawater aquatic environments.