

Effect of phosphate and sulfate on Fe(II)-catalyzed trace metal incorporation into and release from Fe(III) oxides

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Trace element concentrations in natural systems are often controlled by adsorption-desorption reactions on iron oxide surfaces [1]. Biogeochemical iron cycling leads to the coexistence of aqueous Fe(II) with solid Fe(III) oxides, which undergo Fe(II)-Fe(III) interfacial electron transfer and atom exchange (ET-AE) reactions [2]. These reactions result in Fe(III) oxide recrystallization, causing the incorporation of structurally compatible adsorbates, e.g. Ni(II), into solid Fe(III) oxides as well as the release of preincorporated ions into solution [3-5]. Recent research has shown that oxoanions common to natural systems, such as phosphate, do not affect the rate or extent of Fe(II)-Fe(III) atom exchange reactions [6]. However, these species may still potentially alter trace metal incorporation and release by complexing with metals at the iron oxide surface or by changing growth and dissolution mechanisms via processes such as step pinning.

We have investigated the interaction of phosphate and sulfate with Fe(II) on goethite and hematite surfaces and the resulting impact on Ni incorporation and release. Macroscopic adsorption and ATR-FTIR studies demonstrate that oxoanions enhance Fe(II) adsorption through a direct interaction on the mineral surface. XAFS spectroscopy indicates that both phosphate and sulfate decrease Fe(II)-catalyzed Ni(II) incorporation into goethite and hematite; the effect of phosphate was more substantial. Ni(II) release from these minerals during Fe(II)-catalyzed recrystallization was also suppressed by phosphate and sulfate, with the former again producing the larger inhibitory effect. This research suggests that phosphate and sulfate affect trace element partitioning between aqueous solutions and Fe(III) oxides during Fe(II)-Fe(III) ET-AE reactions, potentially impacting contaminant fate and micronutrient bioavailability in soil and aquatic environments.

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The future of lipids as tools to study microbes and biogeochemical processes in the deep biosphere

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Recent work has demonstrated that the predominant microbial intact polar lipids (IPLs) in marine sediments, i.e., glycerol-based ether lipids with a glycosidic polar headgroup, are impacted by a considerable fossil fraction derived from past microbial generations [1]. Although IPL concentration profiles provide useful quantitative constraints on slowly growing archaeal communities [1], their use as direct markers of live biomass in deeply buried sediments is compromised. Hence lipid-based investigative strategies will have to be modified in order to sustain a central role of microbial lipids in future studies of seafloor life.

Future avenues will need to focus on IPLs that have little or no fossil bias, such as phospholipids [cf. 1] or new target compounds that are diagnostic for actively growing cells as identified by culture studies. Detection of these often far less abundant compounds will require implementation of more sensitive approaches [2]. Some novel groups of orphan lipids are concentrated in the seafloor [3]; the elucidation of their biological sources and function will likely provide important clues on the deep biosphere. Novel, minimally invasive stable isotope probing assays that target microbial lipids will have a key role in quantifying microbial growth and substrate specificity [4]. This paper will review the state-of-the-art and provide new examples that illustrate future directions of lipid-based research of seafloor life.

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