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# The environmental fate of phosphorus locked away in iron minerals

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Iron oxides (FeOx) are minerals with a high capacity to bind and sequester phosphorus (P). In this way, FeOx help control the mobility and bioavailability of this key nutrient that is, in many terrestrial and coastal aquatic systems, a contaminant. Because P sorption in turn affects the structure and reactivity of FeOx, a complex and poorly understood interplay exists between the environmental fates of FeOx and P. Elucidating this interplay is important to constrain the role of FeOx in P burial under different depositional (redox) conditions. Here, we explore the structure of P-bearing FeOx and their environmental fate in a series of laboratory and field experiments. Synthetic amorphous and crystalline FeOx with sorbed P were exposed to the common dissolved reductants ferrous iron ($Fe^{2+}$) and sulfide ($H_2S$) in freshwater and salt marsh sediments as well as under controlled laboratory conditions. For the former, we used a novel diffusive sampler approach that allowed us to investigate in detail the transformation of target phases under fully natural conditions [1]. FeOx transformations and P release were tracked over several weeks with chemical and (micro)spectroscopic methods. Our results show that $Fe^{2+}$-catalyzed crystallization of P-bearing amorphous FeOx was strongly inhibited and P remained sequestered in the FeOx. This suggests a feedback whereby high P concentrations (for instance in eutrophic systems) result in the formation of poorly ordered, P-rich FeOx that have an extended lifetime, thus boosting the (short-term) sedimentary P retention capacity. Conversely, exposure to $H_2S$ resulted in extensive FeOx transformation (sulfidation) — even accelerated for P-bearing FeOx — and P release. Lastly, an inoculated incubation experiment using a mixture of natural sediment and synthetic FeOx showed that microbial FeOx reduction rates were higher for P-bearing FeOx compared to pure FeOx. Overall, we show diverging effects of P sorption on FeOx reactivity towards different reducing agents and our results underpin the profound impact of the anoxic-to-sulfidic transition on coupled Fe-P cycling.

[1] Kraal et al. (2020), Environ. Sci. Techn. 54, 12795-12802