

# **Fe(II)-catalyzed ferrihydrite transformation in the presence of phosphate during redox oscillations: mutual effects on iron mineralogy and phosphate sorption**

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Phosphate is an essential nutrient for plant growth and a potential source of eutrophication. In aquatic and terrestrial environments, phosphate is often strongly adsorbed onto iron (Fe) oxides. Therefore, the geochemical behavior of phosphate is strongly affected by Fe oxide transformation reactions. In suboxic and anoxic environments, elevated aqueous Fe(II) can catalyze the transformation of poorly-crystalline ferrihydrite into more crystalline Fe oxides such as lepidocrocite or goethite with lower sorption capacities. On the other hand, the transition to oxic conditions may oxidize dissolved  $\text{Fe}^{2+}$  and impede the transformation. To our knowledge, the combined effect of oscillating oxic and reducing conditions on phosphate sorption and secondary iron mineral formation has not yet been examined.

We investigated phosphate sorption under dynamic redox conditions at circumneutral pH using 25 mM synthetic ferrihydrite at three phosphate levels (0, 0.05 and 0.5 mM). The Fe(II)-catalyzed transformation was initiated by adding 1 mM  $\text{Fe}^{2+}$ . After 30h of anoxic period, aqueous phase was removed prior to the addition of phosphate-free oxic solution. After 15h, again, aqueous phase was removed and subsequent anoxic period was initiated by adding anoxic solution with  $\text{Fe}^{2+}$  and phosphate. Aqueous phosphate and  $\text{Fe}^{2+}$  concentrations as well as changes in Fe mineralogy were tracked over five redox cycles using photometric, spectroscopic and microscopic techniques.

Our first results show that ferrihydrite partially transformed to lepidocrocite in all phosphate treatments. Goethite formation was effectively inhibited even by low concentrations of phosphate. Based on X-ray diffraction analyses, repeated redox oscillations did not induce further changes in Fe mineralogy. Dissolved phosphate concentrations gradually decreased during the anoxic half-cycles, presumably due to vivianite precipitation and sorption reactions. Our study highlights that phosphate can stabilize low crystalline Fe oxides against Fe(II)-catalyzed transformation and thereby alter phosphate immobilization pathways in dynamic redox environments.