Ferrihydrite dissolution in phosphorus/siderophore system: synergism or antagonism?

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Abstract: Synergisms between microbial exudates on iron (hydr)oxide dissolution as an effective Fe acquisition pathway have been addressed recently. However, the process of Fe liberation, surface speciation and mechanisms where siderophores and phosphorus coexist have received little attention. This research systematically investigated the dissolution of ferrihydrite in the presence of desferrioxamine B (DFOB) and inorganic/organic phosphorus (P; orthophosphate, Pi; myo-inositol hexaphosphate, IHP) using zeta (ζ) potential measurement, sequential extraction (SEDEX) method, wet chemical analysis, field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), powder X-ray diffraction (pXRD), X-ray photoelectron spectroscopy (XPS), micro-Raman spectroscopy (μ-Raman), attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and two-dimensional correlation spectroscopy (2D-COS). Upon reaction with P-only or DFOB + P systems, the interfacial complexation partially switched from monolayer bidentate-binuclear surface complexes to ternary complexes, or then to amorphous Fe-P precipitates sequentially under environmentally relevant conditions. We observed Fe-Pi precipitated more readily in acidic condition whereas Fe-IHP precipation prefered neutral-alkaline environment. We also found phosphorus slightly promoted Fe release and re-fixation to leached layer and/or interfacial liquid zone initially, but subsequently prevented attacks from protons and DFOB through surface passivation. The co-effects of P and DFOB correspond to two distinct scenarios: 1) DFOB can be attracted to ferrihydrite surfaces via the negative electrical field induced by adsorbed phosphorus and acts synergistically with labile P-Fe complexes, resulting in temporal intensive dissolution; 2) further Fe shuttling to DFOB are prohibited by stabilized passive P/Fe-P layer. The new insights on the substantial antagonism between phosphorus and siderophores on Fe liberation improve our understanding of natural Fe cycling processes during bio-weathering.