

Multiple Fe, Mn, and P mineral interaction pathways at the SWI of a shallow eutrophic lake revealed by K-edge XANES and multi-energy mapping across epoxy preserved sediment profiles.

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Phosphorus (P) is often the limiting nutrient governing timing, duration, and severity of harmful algal blooms (HABs). Release of internally loaded P sorbed to iron (Fe) and manganese (Mn) oxyhydroxide minerals is generally the most active form in sediments, and the fate of these minerals responding to redox fluctuations, is intimately linked to the speciation, mobility, and bioavailability of P. We hypothesize frequent redox cycling selects for an increased pool of P bound to amorphous metal oxyhydroxides that are either reduced under water column anoxia by sediment microbes or form by Fe²⁺ oxidation and ripen and recrystallize under oxidizing conditions over time. Sediments from Missisquoi Bay, VT were used in long-term mesocosm experiments (70 days), simulating endmember, and cycled redox conditions at the sediment-water interface (SWI). Bulk chemistry and electrochemistry allowed detailed observations of dissolved species in the water column and pore water. At specific intervals, mesocosm sediment was sampled via miniature freeze core and epoxy embedding, to preserve fine scale preservation across the SWI. We used X-ray spectromicroscopy to map the distribution of P, Fe, and Mn abundance across epoxy embedded experimentally manipulated sediment profiles. Multi-energy μ -X-ray Fluorescence (μ -XRF) mapping was combined with XANES spectroscopy and multivariate analysis to produce detailed maps of in situ chemical and mineral speciation and alteration. Results reveal significant mineralogical differences between endmember redox state sediments (oxic vs. anoxic) and oxic-anoxic cycled sediments. Fe and P K-edge XANES and μ -XRF mapping reveal crystalline Fe oxyhydroxides are concentrated just beneath the SWI under long-term oxidation, but are mostly absent under long-term reduction and redox cycling. Under cycling conditions, Fe oxyhydroxides forming, or deposited, at the SWI appear to undergo rapid conversion to amorphous Fe(II)-phosphate before subsequent conversion to strengite-like Fe(III)-phosphate mineral phases. Authigenic vivianite nucleation and growth was observed beneath the SWI in long-term reducing and redox cycled sediments and was closely colocalized with metal-

polyphosphates. Our results reveal detailed geochemical processes governing metal oxyhydroxide and metal phosphate mineral transitions that likely control the speciation, mobility, and bioavailability of P in HAB impacted freshwater settings.