

# Imaging distribution and speciation of P across natural Fe oxides, clay minerals, microorganisms, and diatoms by Nano-XRF and Nano-NEXAFS

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The cycling of nutrients strongly depends on their speciation. We used a combination of XRF and P-NEXAFS to visualize distribution and speciation of P in soils and creek sediments. XRF maps were acquired at 580 eV and 2550 eV to optimize fluorescence excitation conditions for C, O and O, Fe, Na, Mg, Al, Si, P, and S, respectively. In samples with Fe-rich clay minerals, SEM or AFM images proved useful to identify clay minerals by their morphology. NEXAFS image stacks at the P K-absorption edge were collected to address P speciation on minerals, bacteria, and siliceous algae. For this study, we used the AnImaX STXM-endstation, set up at beamline P04 of PETRA-III at DESY, providing the necessary high energy resolution ( $< 0.5$  eV), spatial resolution ( $< 100$  nm), and fast acquisition times ( $< 5$  ms/pixel).

Our images show that a large part of C and P is associated with mineral surfaces, particularly with the Fe oxides. The distribution of P is heterogeneous and not always co-localized with C. Clay minerals are not associated with P and S. The extent of organic coatings on minerals varies between different samples. A patchy organic coverage on mineral surfaces, as often described from NanoSIMS measurements, could not be detected. In fresh creek sediments, a considerable part of the organic P was found in microbial exudates as well as in certain organelles of freshwater organisms. Particularly rich in P were synurophycean cysts. Linear combination fitting of P-NEXAFS spectra indicated that the P-rich material mainly consists of a mixture of inorganic and organic phosphates bound by inner-sphere P-O-Fe bonds to Fe oxides. Free (not bound to Fe) organic phosphate was found in bacterial cells, diatoms, and extracellular organic material. Separate Ca, Al, or Fe phosphate minerals did not occur.

Our observations confirm a high reactivity of Fe oxides towards organic matter and phosphate. Inorganic phosphate competes with organic phosphate and other organic matter for adsorption sites. All P on Fe oxides forms inner-sphere P-O-Fe bonds and presumably has very low bioavailability.

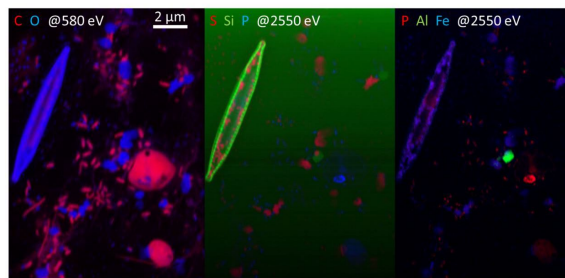


Figure 1: XRF maps collected at 580 eV and 2550 eV on creek material on a Si substrate; 190 x 333 pixel, step size 100 nm. □