

XRF and P K-edge XANES on natural mineral-organic associations

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In soils and sediments, the association of organic molecules with mineral surfaces is a major mechanism to stabilize soil organic matter against biodegradation. Particularly strong inner-sphere P-O-Fe bonds are formed between organic phosphates and Fe oxides, whereas inorganic phosphate will compete with organic phosphates for the same mineral surface sites. Well known are such P-O-Fe bonds for the attachment of microorganisms to iron oxides, either by exudation of biopolymers, or by interactions of cell membrane molecules with the mineral surface. Even in complex matrices, iron-phosphate complexes can be identified by a small pre-edge peak at 2149 eV in the P K-edge XANES signal.

As the spatial distribution of P in soils and sediments is heterogeneous, XRF maps and XANES image stacks at the K-absorption edges of carbon and phosphorus have been measured on natural samples originating from creek sediments (pH 6) using the AnImaX STXM-endstation set up at beamline P04 of PETRA-III at DESY. The goal was to determine whether P-O-Fe bonds exist on pedogenic iron oxides and whether C-O-Fe bonds from carboxylic groups are overrated with respect to mineral binding. XRF maps allow to differentiate between clay minerals and Fe oxides and help to locate C-rich and P-rich regions on these mineral-organic associations. These maps showed that almost all Fe oxides are covered by organic matter, while organic coverages on clay minerals are sparse. The material on about 1/3 of the Fe oxides was rich in P. All XANES spectra on Fe oxides showed significant pre-edge peaks. First fitting results indicated that P-rich material mainly consists of a mixture of inorganic and organic phosphates. Free organic phosphates were found in bacterial cells, diatoms, and extracellular organic material. Separate Ca or Fe phosphate minerals or surface precipitates did not occur.

In summary, P-O-Fe bonds were common in our samples, but the majority of the organic material must have been attached to minerals by different interaction mechanisms. Fe oxides were more important for organic matter adsorption than clay minerals. As the Fe oxides were almost saturated by organic matter, adsorption of new material will involve desorption.