☒ Talk ☐ Poster

Soft X-Ray Spectromicroscopy of P-O-Fe Bonds in Mineral-Organic Associations

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This study aims to visualize the distribution and composition of natural organic matter coatings on mineral surfaces, and provide evidence for the formation of inner-sphere Fe-O-P complexes between Fe oxides and organic matter. Synchrotron XRF imaging and NEXAFS spectroscopy were employed.

Analyses were conducted using AnImaX (Analytical Imaging with X-rays), a flexible and portable STXM end-station, installed at the XUV beamline P04 at PETRA III. Elemental mapping was performed using XRF at 320 eV and 2550 eV, while the chemical state of carbon and phosphorus was probed using NEXAFS.

In addition to synchrotron radiation-based NEXAFS spectroscopy, preliminary tests were carried out using a table-top spectrometer equipped with a laser-plasma source. NEXAFS spectra of hematite-goethite mixtures were analyzed to assess whether mineral ratios in unknown samples can be determined using this approach.

XRF maps revealed co-localization of Fe and C, while Al did not show such overlap. This suggests that Fe oxides are almost entirely coated with organic matter, whereas clay minerals are either bare or carry significantly less organic coverage.

NEXAFS at the C K-edge was used to characterize the organic matter associated with Fe oxides, especially near bacterial cells. The spectra differed from those of bacterial cells or extracellular polymeric substances, instead showing stronger signatures of alkyl and/or aromatic carbon. This indicates either a low affinity of fresh microbial exudates for Fe oxides or substantial chemical fractionation during sorption.

Phosphorus was detected on roughly half of Fe oxide surfaces. NEXAFS spectra exhibited a small pre-edge feature indicative of inner-sphere Fe-O-P bonding. The position of the absorption edge aligned with Fe-complexed organic P compounds. Orthophosphate adsorption appeared only in little quantities if at all.

In summary, mineral surfaces exhibited unexpectedly heterogeneous organic coatings and phosphate-mediated inner-sphere bonding plays an important role in the attachment of organic matter.