Probing the Defect Structure and Chemistry of Environmental Nanoparticles with Micrometer-Sized X-Ray Beams

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Major goals of environmental science are to control mobility of toxic elements and to remediate contaminated soils, sediments, and subsurface waters. These goals cannot be met without first having in hand a fundamental understanding of the elemental composition, defect structure, and surface properties of environmental nanoparticles. Key problems are their short-range order and high density of defects, the multiplicity of reactive surface sites and bonding mechanisms of impurities, and the partitioning of elements into coexisting organic and inorganic phases. In most cases, the information sought can be obtained by application of synergistic synchrotron-based X-ray techniques, including microfluorescence (micro-SRXF), microdiffraction (micro-XRD), and microspectroscopy (micro-EXAFS), and data modelling with meaningful structure models. In this approach, micro-SRXF is used to map trace contaminants among coexisting constituents in a natural matrix, thus determining their distribution and relative abundance with unrivalled sensitivity. Then, micro-XRD is employed to identify nanocrystalline minerals and, more importantly, to determine the nature of structural and chemical defects (stacking faults, cationic and anionic vacancies and occupancies, site occupation of impurities, stoichiometry) through modelling of their scattering properties. Finally, micro-EXAFS gives the uptake and complexation mechanism of trace contaminants by individual constituents. Since the distribution of trace elements is heterogeneous on nanometer to micrometer length scales and nanoparticles are generally aggregated in environmental systems, the combination of these three microscopic techniques provides just the tool needed to scrutinize the nature and fundamental properties of environmental matter. This new kind of hybridization of experimental and modelling approaches to the characterization of natural nanoparticles will be illustrated using examples, under current investigation, of natural sequestration of trace metals in soils and the phytoremediation of contaminated solids.

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