

The role of synchrotron radiation in advancing the frontiers of water-rock interactions

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ABSTRACT: This overview paper discusses the important role that synchrotron-based techniques play in addressing frontiers in water-rock interactions. Over the past decade, with the advent of cutting-edge molecular scale *in-situ* analytical techniques, significant advances have occurred in determining the speciation and sorption/release mechanisms of metals, oxyanions, and other contaminants in soil and water environments. These frontiers in molecular environmental science have major impacts on remediation efforts, development of predictive models, and bioavailability assessments. This paper will emphasize the use of synchrotron-based techniques, including micro-focused x-ray absorption fine structure (XAFS) and x-ray fluorescence (XRF) spectroscopies and micro-tomography to speciate and determine associations of metal(loid)s in soils and plants, and real-time Fourier transform infrared (FTIR) spectroscopy to investigate microbially mediated transformations of contaminants.

1 THE CRITICAL ZONE

The critical zone is “the heterogeneous, near surface environment in which complex interactions involving rock, soil, water, air and living organisms regulate the natural habitat and determine the availability of life sustaining resources” (NRC 2001). The critical zone is an interfacial region of mass and energy flux comprising terrestrial, lacustrine, and marine components of the continental crust and is one of two primary loci of life on Earth and for most of human activity. The other major locus of life is the sun (NRC 2001). The critical zone is comprised of an array of spatial scales, ranging from the atomic to the global, and temporal scales, ranging from seconds to eons. The physical, chemical, and biological processes within the critical zone mediate exchange of mass and energy which is required for biomass productivity, chemical recycling, and water storage. The critical zone is the most heterogeneous and abstruse portion of the entire Earth (NRC 2001). However, we must understand the physical, chemical, and biological processes and reactions in the critical zone over a range of spatial and temporal scales if we are going to sustain the planet for human habitation (Hochella 2002). Processes within the critical zone can be divided into four categories. Each of these affects the other and includes: biologic activ-

ity, weathering, fluid transport, and near-surface tectonics.

2 MOLECULAR ENVIRONMENTAL GEOSCIENCE

The research challenges and questions we face in the geosciences occur over multiple scales (Fig. 1) and at interfaces where complex reactions occur involving inorganic, organic and microbial components. While we ultimately want to make accurate predictions at the field/landscape scale, fundamental mechanistic information at smaller scales, i.e. microscopic, molecular, and atomistic is required. Small scale investigations, combined with macroscopic measurements, provides the level of chemical, biological, and physical detail to comprehend contaminant reactivity and bioavailability over a range of environmental conditions. This information then needs to be integrated into field scale hydrologic and geochemical models (O'Day 1999).

With the advent of state-of-the-art analytical techniques, some of which are synchrotron-based, one can elucidate reaction mechanisms at a small scale. This has been one of the major advances in the environmental sciences over the past decade. Undoubtedly, the molecular characterization of mi-

croenvironments and interfacial reactions will become increasingly significant in understanding the interactions between chemistry, physics, and biology in the environment. The use of small-scale techniques in environmental research has resulted in a new multidisciplinary field of study in which geoscientists are actively involved—molecular environmental science. Molecular environmental science can be defined as the study of the chemical and physical forms and distribution of contaminants in soils, sediments, waste materials, natural waters, and the atmosphere at the molecular level.

There are a number of areas in the geosciences and environmental sciences where the application of molecular environmental science is resulting in major frontiers. These include: speciation of contaminants which is essential for understanding release mechanisms, spatial resolution, chemical transformations, toxicity, bioavailability, and ultimate impacts on human health; mechanisms of microbial transformations; development of predictive models; effective remediation and waste management strategies; and risk assessment. The application of molecular environmental science will be illustrated throughout the remainder of this overview paper.

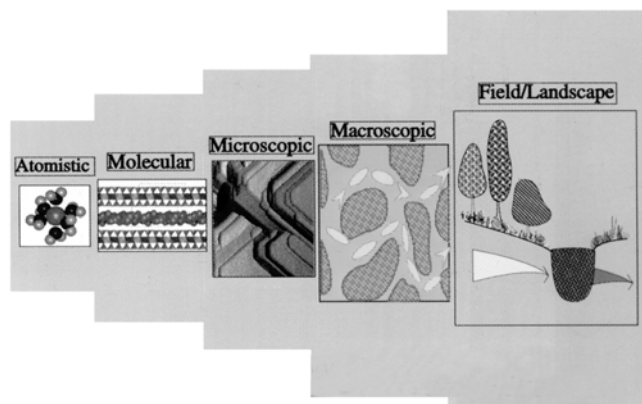


Figure 1. Illustration of the various spatial scales that geoscientists are interested in. From (Bertsch & Hunter 1998).

3 SYNCHROTRON RADIATION

The use of intense light to understand mechanisms of geochemical reactions and processes has revolutionized the geosciences. Intense light can be produced at a synchrotron facility. Synchrotron radiation is produced over a wide range of energies from the infrared region with energies <1 eV, to the hard x-ray region with energies of 100 keV or more. There are a number of synchrotron facilities throughout the world. In the USA major facilities are found at National Laboratories. One of the most

widely used synchrotron-based spectroscopic techniques is x-ray absorption spectroscopy (XAS). Its use has and will continue to revolutionize our understanding of important geochemical properties and processes. XAS can be used to study most elements in crystalline or non-crystalline solid, liquid or gaseous states over a concentration range of a few mg L^{-1} to the pure element. XAS can be used to probe structural sites ranging from those in crystals and glasses to those at interfaces such as the mineral/water interface. With second- and third-generation synchrotron light sources that provide X-ray energies ranging from the infrared to the hard X-ray regions, higher flux and higher brightness, beamline optics that produce micro-focused beams for spectromicroscopy and imaging studies, and state-of-the-art X-ray detectors, important advances in the geosciences will surely occur over the next decade (Sparks 2002).

XAS is also an *in-situ* technique, which means that one can study reactions in the presence of water. This is a major advantage over many molecular scale techniques, which are *ex-situ*, often requiring drying of the sample material, placing it in an ultra-high vacuum (UHV), heating the sample or employing particle bombardment. Such conditions can alter the sample, creating artifacts, and do not simulate most natural conditions. It is important to study geochemical reactions in water as it is the principal medium of transport of inorganic and organic species and biochemical reactions take place in aqueous media and across biological membranes that are water-based (O'Day 1999; Sparks 2002).

XAS is an element specific, bulk method that yields information about the local structural and compositional environment of an absorbing atom. It “sees” only the 2 or 3 closest shells of neighbors around an absorbing atom (0.6 nm) due to the short electron mean free path in most substances. Using XAS, one can ascertain important soil chemical information such as the oxidation state, information on next nearest neighbors, bond distances (accurate to ± 0.002 nm), and coordination numbers (accurate to ± 15 -20 %; Brown et al. 1995).

4 SORPTION PROCESSES AND *IN SITU* MOLECULAR SCALE TECHNIQUES

Over the past 15 years, major advances have occurred in elucidating sorption mechanisms at the water/rock interface. Based on pioneering studies by Stumm and Schindler and their coworkers, it was assumed that major adsorption complexes were outer-sphere (a water molecule is present between the surface functional group and the bound ion or molecule) and inner-sphere (no water molecule is present

between the ion or molecule and the surface functional group to which it is bound). However, until molecular scale studies were performed, conclusions about sorption mechanisms were purely speculative. With the advent of *in situ* molecular scale techniques such as Fourier-transform infrared (FTIR), nuclear magnetic resonance (NMR), and XAS spectroscopies, definitive information on sorption products and mechanisms have been gleaned. Numerous studies have appeared in the soil and geochemistry literature over the past 10 years employing XAS and other *in situ* spectroscopic techniques to elucidate metal/metalloid adsorption complexation mechanisms at the mineral/water interface. Many of the XAS studies are reported in Brown & Parks (2001), Brown & Sturchio (2002), and Sparks (2002). From these studies, one can conclude that sorption of alkali and alkaline earth elements primarily occurs via outer-sphere complexes while for most other cations and anions, such as most heavy metals and oxyanions (exceptions being sulfate and selenate in some cases), inner-sphere sorption complexes result. However, as others have recently shown, the type of sorption mechanism for a particular ion is greatly affected by environmental factors such as ionic strength and pH (Strawn & Sparks 1999).

A number of soil chemists and geochemists have shown that sorption of metals such as Co, Cr, Mn, Ni, and Zn on mineral components (Scheidegger et al. 1997; Thompson et al. 1999) and soils results in the formation of metal hydroxide precipitate phases. In the case of Al-bearing soil mineral sorbents, the precipitates are metal-Al hydroxides (hydroxalcite type, layered double hydroxide [LDH] structure) while with non-Al bearing soil minerals, the precipitate phases are metal hydroxides (Scheinost et al. 1999). The surface precipitates occur at metal loadings far below a theoretical monolayer coverage, in a pH-range well below the pH where the formation of metal hydroxide precipitates would be expected according to the thermodynamic solubility product, and at time scales as fast as 15 min (Scheidegger et al. 1998). Using XAS, in combination with diffuse reflectance spectroscopy (DRS) and high resolution thermogravimetric analysis (HRTGA), Ford et al. (1999) found that mixed Ni-Al (LDH) precipitates transform over time to a precursor Ni-Al phyllosilicate phase, which greatly enhances the stability of the metal. For example, Scheckel & Sparks (2001) investigated Ni sorption on several phyllosilicates, gibbsite, amorphous silica, and a mixture of gibbsite and amorphous silica for residence times of 1 h to 2 years and subsequent Ni release using an array of dissolution agents. As residence time increased from 1 h to 2 years, the amount of Ni released from the precipitates decreased from 98% to ~0%, indi-

ating an increase in stability with aging time regardless of sorbent and dissolution agent. This enhanced stability is due to a combination of substitution of Al for Ni in the octahedral layers of the LDH, Si incorporation into the interlayers of the precipitates due to weathering of the sorbent, and perhaps Ostwald ripening (Scheckel et al. 2000). The formation of metal hydroxide precipitates could be an important mechanism for sequestering metals in soil and water environments such that they are less mobile and bioavailable. It is also apparent that to accurately model metal retention/release in soil environments, one must employ sorption models that can describe both adsorption and precipitation phenomena since sorption is often a continuum. At low sorption densities, mononuclear, monodentate and bidentate inner-sphere complexes occur and at higher sorption densities, multinuclear clusters and surface precipitates can form.

5 NEW FRONTIERS IN WATER-ROCK INTERACTIONS

In the remaining section of this review, I want to focus on what I believe are some of the frontiers in the use of molecular scale spectroscopic techniques to investigate natural, heterogeneous materials such as soils and plants. In my view, the combination of advanced technologies and interdisciplinary research will dominate the geosciences field and lead to major discoveries. Molecular-scale investigations have and will open new frontiers concerning water-rock interactions. These include: speciation of contaminants in soils and other heterogeneous systems; cycling of trace elements and nutrients such as C, N, and S and impacts on global climate change; development of models that will accurately predict the rate, fate, and transport of contaminants in the subsurface environment; elucidation of mechanisms for microbial transformations of contaminants; unraveling the precise structure of humic substances; and understanding plant/soil interfacial reactions such as effects of plants on dissolution reactions and the chemistry of the rhizosphere. For the purposes of this review, I wish to focus on speciation of contaminated soils, mineral/bacterial and plant/soil interfacial processes.

5.1 Speciation of Metals in Soils

Standard XAS techniques probe an area of several square mm. However, the most reactive sites in soils have particle sizes in the micrometer range and metal speciation may vary over regions of a few 100 μm^2 . Therefore, the derived structural information

may be only an average of several contaminant species. With the advent of third generation synchrotron radiation facilities, which afford enhanced spatial resolution ($<5 \mu\text{m}$) and sensitivity, one can speciate metals in soils at the micro-scale. Thus, one can determine all potential species within a small area in the soil matrix. An example of this capability is shown in Fig. 2 where Zn and other metals were mapped (micro-synchrotron X-ray fluorescence spectroscopy, $\mu\text{-SXRF}$) and speciated (micro-extended X-ray absorption fine structure spectroscopy, $\mu\text{-EXAFS}$) in a contaminated subsoil sample collected around the Palmerton, Pennsylvania, USA smelting facility near that town (Roberts et al. 2002).

Zn concentrations were several thousand ppm in the soil. From the $\mu\text{-SXRF}$ maps one sees that Zn is strongly associated with Mn in the center of the samples, with Fe in other portions of the sample, and with neither Mn or Fe in some portions of the sample (Fig. 2a). This micro-scale heterogeneity in elemental associations suggests that Zn could be present in different phases over a small sample area. Bulk XAFS analyses suggested that Zn was bound as an inner-sphere complex to Al, Fe, and Mn oxides but the data interpretation was difficult (Fig. 2b).

$\mu\text{-EXAFS}$ data were collected on the three regions of the sample (labeled 1, 2, & 3 on the Zn map, Fig. 2a). Spot 1 on the map showed that Zn was octahedrally coordinated and sorbed to an Al-oxide phase (Fig. 2c). Spots 2 & 3, with Zn in a tetrahedral coordination, revealed that Zn was primarily sorbed to Fe-oxide (spot 2) and to Mn-oxide (Spot 3; Fig. 2c). These results suggest that Zn^{2+} could have been released from Zn-bearing mineral phases in the topsoil (containing mainly sphalerite, ZnS and franklinite, ZnFe_2O_4) and transported to the subsoil where the Zn^{2+} was partially re-adsorbed to both Al, Fe, and Mn oxides.

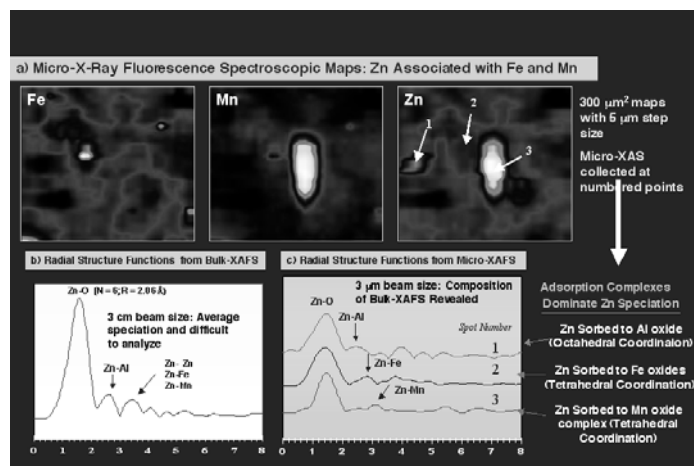


Figure 2. Synchrotron-based speciation of Zn in a smelter-contaminated subsurface soil using a) $\mu\text{-Synchrotron}$ x-ray fluo-

rescence ($\mu\text{-SXRF}$) spectroscopy, b) bulk XAFS, and c) $\mu\text{-XAFS}$ techniques. From Roberts (2001).

Nachtegaal et al. (2004) investigated the speciation and its relation to the mobility and bioavailability of Zn in a non-remediated and remediated smelter contaminated soil from Belgium. State-of-the-art electron and X-ray microscopic, in combination with $\mu\text{-EXAFS}$ spectroscopic, studies were conducted on the soils. No significant differences in Zn speciation were found between samples of the remediated and non-remediated soils. Thirty percent of Zn was in smelter related minerals, mainly willemite, 10% of Zn was chemisorbed to Fe- and Mn-oxides and 60% of Zn was incorporated into newly formed mixed Zn-Al layered double hydroxides (LDH) in the non-remediated and a Zn-phyllosilicate in the remediated soil. Macroscopic desorption and biosensor studies were conducted on the soils to assess bioavailability of Zn. At the pH of the soils (6.4-6.7), these studies showed that the presence of the LDH phases greatly diminished the bioavailability of Zn in the soils. Desorption of Zn, and consequently bioavailability, was enhanced at lower pHs. The results of this investigation indicate that at higher pHs the formation of (mixed) metal hydroxide precipitates could be an important means of sequestering toxic metals such as Zn in the soil environment.

5.2 Environmental Molecular Biology

The field of environmental molecular biology could significantly advance efforts to enhance environmental quality. The uptake and biochemical transformations of trace elements by plants are important in the production of food and fiber and in soil remediation. One area that will continue to be of great interest to soil and environmental scientists is the study of phytoremediation processes in hyperaccumulating plants. These plants may transform a toxic species into a less toxic form or produce a volatile species of the toxic element. However, we do not understand the chemical composition of metal binding sites within the plant materials. The speciation of the trace elements within the plants and the chemical structure of metal binding proteins are needed. These are areas where soil biochemists, soil chemists, and geochemists, using synchrotron-based techniques, and plant physiologists can work closely with plant molecular biologists, who are employing state-of-the-art genomic, proteomic, and bioinformatic approaches, to produce better metal accumulating plants, enhancing remediation efforts (Tonner & Traina 1998). Such collaborations can also advance our understanding of biogeochemical interac-

tions and cycling among organisms, ecosystems, and the environment.

A fine example of using *in-situ* synchrotron based techniques to study metal speciation on plant roots is the study by Hansel et al. (2002). They investigated spatial and temporal associations of As and Fe species on aquatic plant roots. The soil/root interface is very complex, containing both reduced and oxidized mineral species and organic-metal complexes. It is known that Fe (hydr)oxide precipitates, or plaques, appear on the surfaces of aquatic plants. These probably result from radial oxygen diffusion and subsequent oxidation of Fe^{II}. The Fe-plaques could serve as a substrate for metalloid retention and sequestration. Associated with the plaques are Fe-oxidizing bacteria. However, the role of bacteria in Fe oxidation within the rhizosphere is not well understood. The nature of the plaque mineralogy should indicate the biochemical conditions within the rhizosphere which may depend on plant species and/or site specific soil and aqueous chemistry (Hansel et al. 2002).

Hansel et al. (2002) used x-ray fluorescence microprobe and microtomography to study Fe plaque mineralogy and As speciation on the roots of two aquatic plant species, *P. arundinacea* (reed canarygrass) and *T. latifolia* (cattail). The microprobe analyses provides a vertical average of As and Fe through the plaque, and microtomography gives a cross-sectional slice through the plant root- from the interior of intact roots through the epidermis and plaque. Figure 3a and b shows microtomographic images of reed canarygrass roots.

As exists as isolated hot spots on the root surface and interior. High levels of As do not seem to correspond to higher levels of Fe (Figs. 3a and b). X-ray microprobe images of the plaque show heterogeneous precipitation of As and Fe on the surface of the plant root and elevated levels of As correspond with higher Fe concentrations (Fig. 3b). Using linear combination analyses, the Fe plaque on reed canarygrass was 63% ferrihydrite, 32% goethite, and 5% siderite (Hansel et al. 2002). XANES analyses of As in the plaque of reed canarygrass showed that As^V predominated with some As^{III}. The As appeared to be a sorbed species on Fe^{III} hydroxides.

Other soil chemical-biological research areas that will be prominent in the future include: understanding the transport and sorption kinetics and mechanisms of contaminants on nanoparticles; mechanisms of microbial-mineral interactions using *in-situ* nanoscale techniques such as biologic force microscopy (BFM; Lower et al. 2002); elucidating microbially mediated redox reactions; effect of biofilms on soil minerals, and metal and oxyanion speciation and retention; the role of biogenically derived min-

erals on contaminant transport and solubility; redox transformations of C, N, P, and S over different redox boundaries; and real-time biodegradation mechanisms of contaminants.

A recent example of the use of synchrotron radiation to follow the real-time biodegradation of organic chemicals is the research of Holman et al. (2002). It was hypothesized that humic acid accelerates the degradation of polyaromatic hydrocarbons (PAHs) by enhancing the solubility of the PAH, thus increasing PAH bioavailability to microorganisms. However, there was no direct evidence that this indeed occurred until the research of Holman et al. (2002). In this study, the researchers employed synchrotron radiation-based Fourier transform infrared (SR-FTIR) spectromicroscopy to study the effect of HA (Elliott soil HA; abbreviated ESHA) on the degradation kinetics of pyrene by *Mycobacterium* sp. JLS on a magnetite surface.

With the bacteria present there was a reduction in the amount of pyrene on the surface. For samples without ESHA, the degradation of pyrene was slow at first and about 168 hours passed before changes in the spectra were noted. Then, biodegradation increased rapidly and all the pyrene was degraded in nearly 35 hours. Biodegradation of pyrene on samples with ESHA began immediately (about 1 hour) after the bacteria were added and was complete in 4 hours. During the latter part of the pyrene

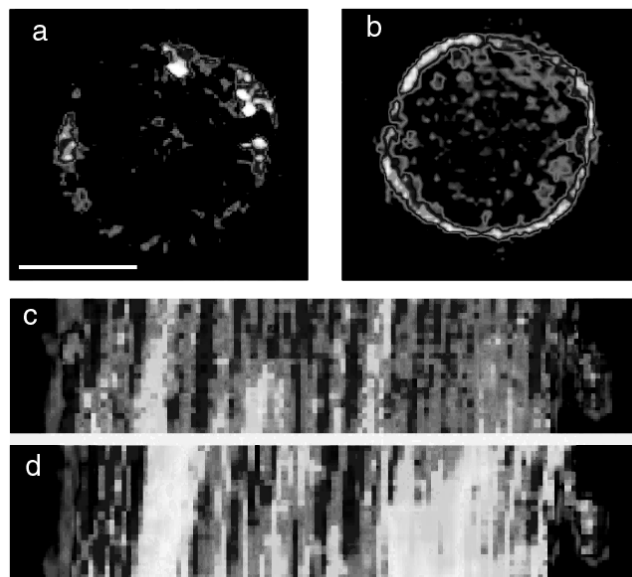


Figure 3. X-ray fluorescence microtomographic images of (a) As and (b) Fe distributions within *P. arundinacea* root cross-sections (slices). X-ray microtomography images were obtained by translating an unaltered (intact) root through an X-ray beam and collecting the fluorescence in order to reconstruct the root cross-section. X-ray microprobe image of (c) As and (d) Fe distributions on the surface of *P. arundinacea* roots. (X-ray microprobe analysis was conducted by physically slicing off a thin film of the Fe plaque from the surface of the root and ob-

taining a vertical average of the As and Fe concentrations within the plaque.) Scale bar represents 300 μm . From Hansel et al. (2002).

degradation, an increase in biomass absorption was noted, again indicating that biomass formation occurs at the same time as pyrene consumption. At the end of the time resolved studies (about 460 hours), the spatial distribution of pyrene, bacteria, and the ESHA were determined by taking spectra every 5 μm across the center of the bacterial colony containing ESHA. The center of the maps showed a region that contained a high population density of the bacteria and a high concentration of ESHA. Also, at the initiation of the experiment there was a high concentration of pyrene in this central region (the reason this region was studied). At the end of the study, pyrene in the central region was entirely degraded. Where pyrene was present without the bacteria, degradation was insignificant.

6 NEED FOR MULTIDISCIPLINARY, INTERDISCIPLINARY AND MULTIFACETED APPROACHES

The future of basic research in the geosciences is exceedingly bright. However, to successfully address and fund the major research needs that have been alluded to, and others that were not mentioned, multidisciplinary and interdisciplinary and multifaceted approaches must be carried out. Geoscientists, soil scientists, chemists, physicists, biologists, material scientists and engineers must and will increasingly collaborate. I predict that one of the major leitmotifs of the field in the 21st century will be the study of biological effects on chemical and physical reactions and processes. This provides geoscientists with a unique opportunity to combine their expertise with that of molecular biologists. We must also employ an array of multiple, molecular-scale techniques over a range of temporal scales in combination with macroscopic approaches and computational modeling to solve complex questions concerning geochemical properties and processes.

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