ABSTRACTS

Alphabetical by first author
Investigating changes in arsenic speciation through the combination of *in vitro* simulated gastric fluid extractions and EXAFS spectroscopy

Mining conducted throughout the state of California has left an environmental legacy of exposed mine wastes containing elevated levels of toxic metal(loid)s including arsenic (As), a known carcinogen. The relationships between speciation, bioaccessibility, location, and particle size of As are critical to calculating and predicting the As exposure risks associated with these wastes.

Bulk mine tailings, waste rock, and surface sediment samples were collected from a number of gold mine sites across California and separated through dry sieving to generate eleven distinct size fractions which were then analyzed to determine initial As concentration. Bulk EXAFS spectroscopic analysis using principal component analysis, target transform and linear combination fitting of size-separated samples from various mine sites in California were then used to quantify the speciation and distribution of arsenic (As) both before and after exposure to a simulated gastric fluid extraction.

Across a majority of samples analyzed, results show little change in speciation between pre- and post-extraction, particularly in samples with low bioaccessibility. However, certain samples show quantitative changes in speciation after extraction. In Tropico mine tailings samples, amorphous ferric arsenate is preferentially removed, correlating closely with bioaccessibility values. Expressing As speciation changes in terms of the mass of As lost shows distinct differences between expressing it simply as percent change in As phase. Analyzing only percent change in the surface sediment samples, scorodite is the predominant species removed post-extraction, while some released As appears to reprecipitate as sodium arsenate. Expressing this solely as percentage change in speciation shows a slight loss in percentage of scorodite, but expressing it as mass lost shows over 70% of As released as scorodite.

Other trends observed include that As bioaccessibility generally increases as particle size decreases, tailings samples generally have higher As bioaccessibility than waste rock samples, and As bioaccessibility decreases as time after a rain event increases. These calculations and trends observed help better understand the mechanisms of As bioaccessibility than simply calculating total As released. Using this information can help better understand which variables best predict As toxicity in mine waste samples, leading to more accurate and expedited calculations in predicting As exposure.
Synchrotron Environmental Sciences at ALS, CAMD, and SSRL: Present and Future

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Synchrotron-based techniques have profoundly influenced environmental sciences, soil sciences, and geochemistry research. This techniques provide the ability to peer inside of materials and to obtain unique information on the physical and electronic structures around atoms, nanoparticles, bacteria, and natural microstructures. For these reasons, they continue to gain momentum as essential tools to explore the cycling and speciation of metals, carbon and nitrogen, and in systems traditionally outside the scope of molecular scale techniques. The molecular scale information gleaned from synchrotron studies is being extrapolated to understand macro-scale processes and biogeochemical interactions ranging from the global ocean to the microbe-metal interface and over time scales spanning millions of years.

The Advanced Light Source (ALS), the Center for Advanced Microstructures and Devices (CAMD), and the Stanford Synchrotron Radiation Lightsource (SSRL) have played major roles in the development of synchrotron environmental sciences by providing world-class capabilities in x-ray spectroscopy, scattering, and imaging techniques. This talk will address current capabilities and plans to maintain and develop robust scientific programs that address DOE missions.
Iron Sulfide Particle Size Effects during pyrolysis in a Maya Vacuum Resid and an Illinois #6 Argonne Premium Coal

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Coal is, and will remain for the foreseeable future, a major source of energy worldwide. Despite advances in renewable and gas resources, the U. S. Energy Information Administration predicts that coal will provide the majority of fuel for the generation of electricity continuing up to at least 2035. An understanding of sulfur-based mineral behavior in coals is still needed for coal processing and mining.

The FeS$_2$ polymorph pyrite and marcasite were mixed together with a Maya Vacuum Resid coal model in known ratios, and a scheme was devised to deduce particle size. The behavior of these samples was then tracked with increasing pyrolysis. The results show that marcasite is much less structurally stable if the initial particle size is large. This will result in a sudden generation of H$_2$S and generation of pyrrhotite, Fe$_{(1-x)}$S, which is a coal gasification catalyst.

A large-particle and a small-particled Illinois #6 coal Argonne Premium Coal was also pyrolyzed to various degrees. The iron sulfide behavior in this sample showed that there was a difference in transformations from pyrite to pyrrhotite and then to troilite dependent on the particle size. One explanation is the shrinking-core model, in which escaping sulfur gas eventually weakens the particles’ outer sulfur-poor matrix, which breaks away, exposing the inner pyrite core.
LCLS and its potential applications to environmental science

Sebastien Boutet

Linac Coherent Light Source

SLAC National Accelerator Laboratory

The Linac Coherent Light Source is the first hard x-ray free electron laser user facility in the World. It provides some very unique x-ray beam properties and unique instrumentation and capabilities. In this talk I will introduce LCLS and its available beamline/instruments. I will specifically focus on capabilities with potential use to the environmental sciences, highlighted results from recent experiments.
Uptake, reduction, and reoxidation mechanisms of uranium in biogeochemical systems studied by x-ray absorption spectroscopy

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Uranium (U) is a contaminant of concern at several DOE sites such as the Hanford site at Pacific Northwest National Laboratory, WA (PNNL); the former U mine at Rifle, CO; and the former nuclear fuel production site at Oak Ridge National Laboratory, TN (ORNL). The chemical or biological reduction of U(VI) to U(IV) has been studied extensively as a way to contain groundwater plumes existing at these locations. The approach relies on the decrease in dissolved uranium concentrations when U(VI) in oxidized groundwater is reduced to the sparingly soluble uraninite (U\textsubscript{IV}O\textsubscript{2}) form. While both laboratory and field tests indicate that dissolved U concentrations decrease under reducing conditions, the mechanisms of uptake and the speciation of reduced U in complex biogeochemical systems remain under investigation. Synchrotron techniques such as x-ray absorption near-edge spectroscopy (XANES) and extended x-ray absorption fine-structure spectroscopy (EXAFS) are indispensable in probing these mechanisms, by providing the molecular level speciation of U in unaltered, wet samples.

Using U L\textsubscript{III}-edge EXAFS, we have shown that uraninite is not the predominant species when U(VI) in contaminated field-site sediments is reduced to U(IV). This finding draws into question the current use in models of thermodynamic and kinetic parameters derived for uraninite. To provide refinements for these models we have investigated the speciation of U(IV) in several laboratory systems relevant to the composition of subsurface sediments. In batch culture U(VI) bioreduction experiments, we find that the mechanism of bacterial respiration (e.g., cell wall reductase vs. electron shuttle mediators) or the presence of phosphate are factors contributing to non-uraninite U(IV) speciation. In suspensions of TiO\textsubscript{2} and Fe\textsubscript{3}O\textsubscript{4}, we find that mineral surface sites can stabilize adsorbed, non-uraninite U(IV) species for extended periods under reducing conditions. Stabilization of non-uraninite U(IV) occurs only at lower U surface coverages, which are more typical of natural environments. When the U surface coverage exceeds a mineral-specific threshold the predominant fraction of reduced U(IV) atoms form uraninite nanoparticles. These results suggest that in addition to biological factors, the high-affinity surface sites on various minerals found in sediments may inhibit the formation of uraninite following U(VI) reduction. The significant control of biological and abiotic factors on the resulting U(IV) speciation suggests a need to re-examine current geochemical transport models and underscores the importance of utilizing synchrotron-based speciation techniques in the study of environmental processes.
Synchrotrons and the Environment – A Marriage Made in Heaven

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The first synchrotron user facilities, primitive by today’s standards, signaled the beginning of a revolution in the way we characterize and study matter and molecular-level processes. These extremely intense x-ray sources have impacted many areas of science and technology in ways we could not imagine back in 1977 when I first used SSRL, a 1st generation synchrotron radiation source, to examine the local coordination environment of Fe in amorphous silicates using x-ray absorption fine structure spectroscopy. If we fast forward to 2014, 37 years later, we find 3rd generation x-ray sources with 8-10 orders of magnitude greater average brightness and 4th generation x-ray sources based on the free electron lasers with 17 orders of magnitude greater brightness and pulse lengths of femtoseconds. These powerful sources have led to new methods that allow measurements of complex samples and processes, including (1) environmental interfaces where most of the chemistry that controls natural environments takes place, (2) phase transitions at very high pressures and temperatures, (3) liquids such as water and aqueous solutions, (4) aluminosilicate melts at high temperatures and pressures, (5) nanomaterials, (6) natural organic matter, (7) microbial-mineral systems, and (8) metal-plant interactions organisms, just to name a few. I will review the results of some of these past studies and discuss the new types of measurements on complex environmental samples that will be made possible by new diffraction-limited and ultrafast sources of synchrotron radiation.
Black shales underlying the areas from Eastern Ohio, through Pennsylvania, and into Central New York State have become of economic interest lately due to the recent economic viability of shale gas extraction. Sulfide minerals such as pyrite and marcasite occur in these shales and are formed in anoxic, reducing conditions during deposition. Trace metals can be incorporated into these sulfides via various pathways: (1) cobalt (Co) and Nickel (Ni) tend to substitute stoichiometrically for iron (Fe) into iron sulfides, (2) copper (Cu) and Zinc (Zn) tend to form Cu- or Zn-sulfide phases separate from the iron sulfide, and (3) arsenic (As) and selenium (Se) can be incorporated into the iron sulfide by substituting for S. The manner in which these trace metals are incorporated directly influences how they are released into the environment during sulfide oxidation following shale weathering. The aim of this research is to examine the distribution of trace metals in iron sulfides from black shales to gain a better understanding of how they may enter the environment as the sulfides weather. This research was conducted by analyzing pyrite grains in thin section using Synchrotron-based X-ray microprobe (XMP) techniques including micro-X-ray fluorescence (micro-XRF) and micro-X-ray diffraction (micro-XRD). XMP data were collected at beamline 13-ID-E at the Advanced Photon Source, Argonne National Laboratory. Marcellus Shale samples collected in outcrop from the Oatka member in Leroy, NY and Jersey Shore, PA and the Union Springs member in Lewiston, PA along with a core sample from Beaver Meadow, NY were analyzed. A core sample from the Chattanooga Shale in Hancock Co, TN was also used. Micro-XRD analysis has shown that the sulfide grains are composed of some combination of pyrite and marcasite; other species such as arsenopyrite are absent even in areas where As is present. Micro-XRF analysis shows As and Se to be spatially correlated with each other and within the pyrite grains. Preliminary analysis of Co and Ni shows Co spatially correlated only with Fe, whereas Ni is spatially correlated both with Fe and without it. Preliminary analysis of Cu and Zn shows that they are not spatially correlated with the pyrite and instead form separate Cu- and Zn- sulfides. As these samples weather, these differences in distribution of trace metals will affect the manner in which they are released into the environment.
Heavy metals are common pollutants that pose a threat to human health and the environment, and their transport in surface waters and groundwater is controlled in part by reactions at mineral surfaces. Calcite is a ubiquitous mineral and has reactive surfaces that interact with heavy metals, attracting extensive research on metal-calcite interactions. However, numerous questions remain unanswered, specifically about the sorption mechanisms (e.g., adsorption vs. incorporation) and the composition and structure of incorporated metal phases. The interaction of Pb$^{2+}$ and Cd$^{2+}$ with the calcite (104) surface was investigated through in situ observations, using high-resolution X-ray reflectivity (XR), resonant anomalous XR (RAXR), X-ray reflection interface microscopy (XRIM), and atomic force microscopy (AFM). Specular XR and RAXR reveal that Pb incorporates in several unit-cell depths of the calcite surface [1]. Its location is similar to that of Ca in the crystal lattice with some displacement, indicating a presumed epitaxial, but strained, Pb-Ca carbonate solid solution. In situ AFM images show that this incorporation occurs by a dissolution-regrowth mechanism. Similar results were observed for Cd using XR and AFM, while XRIM maps reveal Cd-rich domains on the calcite surface. These results imply that this type of phase may play an important role in determining the mobility of Pb and Cd in carbonate-rich environments.

Integrated spectroscopy, microscopy, and aqueous chemistry investigation of heavy metal contamination in abandoned mine wastes in the Southwest

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Heavy metal contamination in an abandoned mine waste site located in the Navajo Nation in Northeastern Arizona was assessed by integrating spectroscopy, microscopy, and aqueous chemistry techniques. Uranium (U) concentrations collected from a spring located in the vicinity of these abandoned mine wastes exceeded the EPA maximum contaminant of 30 µg/L. Solid sample analyses performed by X-ray fluorescence resulted in concentrations of 0.6% U, 0.4% V, and 0.3% Fe by weight. X-ray photoelectron spectroscopy analyses confirmed the presence of 73% Fe(II), 27% Fe(III), and the predominance of U(VI), V(V), and As(0) in these abandoned mine wastes. Amorphous carnotite [K₂(UO₂)₂(VO₄)₂·3H₂O] was detected using transmission electron microscopy and X-ray absorption spectroscopy. The proportional release of U and V into solution was observed for chemical extractions using 10 mM ascorbic acid (~pH 3.5) after 96 hours of reaction. A similar proportional release of As and Fe after 2 hours of reaction was observed for chemical extractions using the same conditions mentioned previously. Lower concentrations of U, V, As, and Fe were released from chemical extractions using 10 mM bicarbonate (~pH 8.3). Our results suggest that mineral phases such as carnotite and an As-Fe-bearing mineral phase control the mobility of U and As in these abandoned mine wastes. This study has important implications related to heavy metal contamination in communities located close to abandoned mine wastes.
Sub-micron Resolution X-ray Spectroscopy (SRX) Beamline at National Synchrotron Light Source II

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National Synchrotron Light Source II (NSLS-II) will start commissioning with x-ray beam in the fall of this year (2014). The Sub-micron Resolution X-ray spectroscopy (SRX) beamline, part of the NSLS-II project, will benefit from the ultra-low emittance of the NSLS-II to address a wide variety of scientific applications studying heterogeneous systems at the sub-micrometer down to sub-100 nm length scale. The energy range, techniques and spatial resolution that SRX will provide are highly relevant to the applications in environmental science as described below:

The design of SRX (Figure) shows a canted in-vacuum undulator beamline, optimized to access an energy range of \(E = 4.65\) keV to \(E = 25\) keV. Its main optical components consist of a horizontally focusing mirror, a horizontally deflecting monochromator and two sets of Kirkpatrick-Baez (KB) mirrors as focusing optics. These KB mirrors will provide two distinct end-station capabilities - focusing the beam to either a sub-micrometer sized focal spot at high flux \((10^{13} \text{ photons/s} - \text{high flux mode})\) or a sub-100 nm spot at moderate flux \((10^{11-12} \text{ photons/s} - \text{high resolution mode})\), at the sample position. The overall higher flux at SRX will enable faster scan on larger area and potential for \textit{in situ/in operando} experiments.

The horizontally focusing mirror and high-flux KBs are capable of operating in collimating mode, thereby providing a higher energy resolution particularly suitable for absorption spectroscopy. The design of sample stages will enable fast 2D scanning and tomography capabilities. X-ray fluorescence imaging and tomography will provide elemental mapping in 2D and 3D, respectively. Spatially resolved X-ray Absorption Near Edge Structure (XANES) spectroscopy can be performed in fluorescence or transmission mode. Full-field imaging and tomography are also possible to provide morphology information. SRX will be equipped with a customized three-element energy dispersive detector and MAIA detector for fluorescence experiments. The design of the beamline, early commissioning plan, along with the scientific mission in environmental science it possesses will be presented.

\[\text{Figure} – \text{SRX beamline layout}\]
Abstract

The hydrophobic effect plays a key role in water treatment, membrane function and protein folding. However, this effect is not fully understood. One of the most debatable topics is whether the density depletion region between water and hydrophobic surface exists or not? We performed an X-ray reflectivity study on fluoroalkysilane self-assembled monolayers in contact with water and optimized the merit-function by exhausting the fitting model in parameter-space. Our result indicates the existence of low density region when the hydrophobic monolayer is packed densely.

What x rays can tell us about the interfacial profile of water near hydrophobic surfaces

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New Facility for Long Duration Experiments at Diamond Light Source

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Beamline I11 at Diamond Light Source is a dedicated powder diffraction instrument specialized for high-resolution and time-resolved experiments [1-3]. Recently, the beamline has undergone an extensive upgrade to add a new facility for long duration experiments (LDE). The LDE facility is the first of its kind, housing experiments which require periodic monitoring of “slow” changes occurring over a few weeks up to two years.

Now approaching completion, and welcoming first users in Oct 2014, the new endstation will contain the necessary hardware and environmental controls, to allow multiple, non-ambient, experiments to run simultaneously. These experiments will be mounted onto individual, adjustable linear drives to automatically and periodically move samples in and out of the beam, while a pre-programmed data collection routine will allow automated data acquisition. Data from each experiment will be collected once a week using a Pixium area detector. Parametric data (e.g. temperature, pressure, humidity) for each experiment will be recorded on an hourly basis.

This facility will be of particular benefit to research areas, particularly within the environmental sciences, where chemical and/or physical changes occur over long periods of time and important information relating to the development of phases cannot be obtained via ex-situ methods. Sample environments such as electrochemical cyclers, incubators, heating and cooling stages, environmental chambers and high pressure gas cells will be accommodated for user operation. These sample environments, when used alone or in conjunction with each another, provide the means to simulate the conditions found in a variety of terrestrial, and non-terrestrial, environments. Areas that will benefit from this include studies of crystallization, gas storage, hydrocarbon extraction, mineral evolution, seasonal effects, thermal and electrical cycling and hazardous waste storage.

With a versatile design and extensive automation, such as robotic sample changers and programmed thermal cycling, this novel facility has already attracted the attention of many academic researchers from diverse scientific backgrounds including the nuclear, environmental pharmaceutical, nanotechnology, defence, and speciality chemical industries.

An in-depth introduction to this new facility and its extensive capabilities will be presented, followed by examples of relevant research that is currently being undertaken on the Beamline.


Keywords: Synchrotron Instrumentation, Long Duration Studies, Environmental
Tackling nanoscience challenges with the new TXM of APS

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Abstract

The construction and commissioning of a new, dedicated, Transmission X-ray Microscope (TXM) at Sector 32 of the Advanced Photon Source at Argonne National Laboratory has been completed, and general-user operations began in spring 2014.

The highest resolution X-ray imaging system of Argonne aims to take up challenges of nanomaterial science in the field of energy storage, microelectronics, nanoporous materials functions as well as Earth and environmental science. The TXM, that is illuminated via an undulator in a low-β straight section and equipped with a fixed exit double crystal monochromator (Si 111), operates from 7 to 12 keV. The available set of optics offers fields of view ranging from 100 to 20 µm for spatial resolution of 60 and 20 nm. Techniques available include absorption, phase contrast and XANES tomography. 60 and 20 nm outermost zone width ($\Delta r_n$) zone plates offers working distances from 20 to 70 mm, allowing the TXM to accommodate various sample environments. Electrical and fluid feed-through to the sample environment were designed in such a way that no torque is applied on the high accuracy air bearing rotary stage during tomographic acquisitions.

The TXM activities are supported by several key programs. The fabrication of the TXM zone plate optics occurs in-house. A more complete set of zone plates that will provide a broader range of spatial resolution, as well as the fabrication of a 16 nm $\Delta r_n$ zone plate is expected for the next year.

The TXM is also the cornerstone of a Laboratory Directed Research and Development (LDRD) grant that focuses on scientific software development of methods for merging multi-length scale and multi-modality data. The outcome of this activity is the software framework called tomoPy, http://www.aps.anl.gov/tomopy/, an open source Python based toolbox for the analysis of synchrotron tomographic data that has the goal to unify the effort of different facilities and beamlines performing similar tasks.

A detailed description of the status of the TXM, the pathway to achieve high stability measurements as well as first scientific results will be presented here.

Figure 1: picture of the new TXM at 32-ID-C, APS.

Figure 2: Nanoscale 3D elemental mapping and analysis of a solid oxide fuel cell anode. 2 tomographic dataset acquired above and below Ni absorption edge [1].

References

We have used synchrotron radiation to obtain XANES spectra of calcium carbonate (CaCO$_3$) minerals and biominerals at the oxygen K-edge using PEEM at the ALS. The spectra are distinct for different CaCO$_3$ minerals; hence, O spectroscopy enables chemical analysis of biominerals composed of an unknown CaCO$_3$ polymorph. In addition, the O spectra for the crystalline forms of CaCO$_3$ exhibit strong polarization dependences due to x-ray linear dichroism. This effect forms the basis of the imaging technique Polarization-dependent Imaging Contrast (PIC)-mapping. PIC-mapping at the oxygen K-edge provides high-contrast, high-resolution measurement of the orientations of nano-crystals, and enabled unprecedented discoveries, including the largest single crystals of vaterite, in the tunicate *Herdmania momus*, and some of the smallest reported calcite prisms, in *Mytilus californianus*. Because PIC-mapping and PEEM spectromicroscopy are done on the same beamline and the same sample region, they provide simultaneous chemical and orientational information. Oxygen PIC-mapping can be extended beyond CaCO$_3$ to a wide variety of minerals and biominerals that exhibit x-ray linear dichroism, as well as polycrystalline metals and semiconductors or their oxides.


**Figure.** Calcite crystals in the prismatic layer of *Mytilus californianus*. In this PIC-map different colors quantitatively mean crystal orientation, as shown in the color bar.
Sulfur-mediated electron shuttling during bacterial iron reduction

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Understanding the flow of electrons through various types of microbial metabolisms is essential to predicting the fate and transport of contaminants as well as the speciation and distribution of carbon in the subsurface. Fe(III) minerals are critical electron acceptors in many aquifers, but the extent to which they provide energy for the growth of microorganisms depends greatly on the thermodynamic energy that is available to them from their environment. In alkaline, oligotrophic aquifers, for example, the amount of energy available to dissimilatory metal-reducing bacteria (DMRB) via the reduction of Fe(III) minerals decreases dramatically with increasing pH. Many DMRB, however, can also respire by reducing elemental sulfur [S(0)] to sulfide, a process which provides more energy under alkaline conditions than acidic ones. In a series of bioreactor experiments, we have shown that at pH 9, the DMRB \textit{Shewanella oneidensis} MR-1 can respire S(0) but not goethite. The sulfide produced subsequently reduced goethite abiotically. In experiments conducted with a mutant strain of \textit{S. oneidensis} (PSRA1), which is able to reduce Fe(III) but not S(0), no ferrous iron was produced. The reduction of S(0) to sulfide and the formation of mackinawite (FeS) was confirmed by sulfur K-edge x-ray absorption near-edge spectroscopy (XANES). Because the abiotic reaction of sulfide with Fe(III) produces S(0), in the absence of geologic deposits of S(0), DMRB in alkaline aquifers may require active respiration by sulfate-reducing bacteria (SRB) in order to respire. Under these conditions, Fe(III) reduction will proceed via S(0)-mediated electron shuttling pathways that requires a mutualistic partnership between DMRB and SRB rather than direct enzymatic reduction of Fe(III) minerals by DMRB alone.
Reactivity of Tc at the Groundwater-Surface Water Interface

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Technetium-99 (t^{1/2} =211,000y) is mobile in the environment as the pertechnetate oxyanion \([^{99}\text{Tc(VII)O}_4]^{-}\). Tc(VII) may react to less soluble Tc(IV) at intermediate redox potentials (E^o = -0.36 V) through heterogeneous reduction. \(^{99}\text{Tc}\) is forecast to migrate through groundwater to the Columbia River at the U.S. DOE Hanford site in Washington State. Discharge to surface water will occur through a groundwater-surface water interaction zone with complex hydrogeology and biogeochemistry. The reactivity of pertechnetate in reduced sediments from this zone was investigated to determine effects of ferrous-Fe and sulfide-S on Tc(VII) reduction rate, and the resulting speciation and mineral association.

We have investigated Tc(VII) reduction reactions in Hanford subsurface sediments and in well-defined model systems that include metal-reducing microorganisms and Fe-bearing minerals to explore speciation effects on reaction rates and Tc endproducts. In Hanford sediments collected from anoxic regions of the subsurface or oxic sediments subjected to microbial reduction, \(2 \times 10^{-5} \text{ M (20 } \mu\text{M)}\) aqueous Tc(VII) was reduced to below the detection limit (3.98 \times 10^{-9} \text{ M}) over times ranging from days to months. The rate and extent of reduction was dependent on sediment source, Fe(II) speciation, and sulfide concentration. X-ray microprobe analyses, including fluorescence mapping, elemental multichannel analysis, and micro-diffraction, were used to deduce Tc speciation and mineralogic association in the various sediments. In bioreduced Hanford formation sediments Tc(IV) was associated with phyllosilicates (mica), as indicated by associated Fe and Rb (analogous to K) signals. X-ray absorption spectroscopy (XAS) revealed the presence of Tc(IV)O_2 and Fe(III)-associated Tc(IV). Tc(VII) was also reduced by sediment-associated biogenic sulfide; Tc-S bonding at the nearest coordination environment around absorber Tc atom was revealed by XAS. These results indicate that Fe(II) associated with Hanford subsurface sediments can be a facile reductant of Tc(VII)O_4- and that the rate of reduction and nature of Tc end product is a function of Fe(II) speciation. These results have implications for far-field \(^{99}\text{Tc}\) migration at Hanford where groundwater flow paths traverse Fe(II)-bearing sediments that can reduce Tc(VII) to relatively insoluble Tc(IV) phases.
Manganese deposition in Drinking Water Distribution Systems.

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This is the first work to demonstrate the interrelationships between Mn (manganese) deposition and toxic metal adsorption in drinking water distribution systems (DWDS). Traditional physiochemical characterization techniques, synchrotron-based \textit{in-situ} micro X-ray adsorption near edge spectroscopy and X-ray fluorescence mapping were used to document Mn deposition on lead and brass piping from two fully operational DWDS. One system had been maintained with chlorine; the other with secondary chloramine disinfection. In both systems deposits of Mn oxides were composed of three phases; birnessite (Mn$^{3+}$ and Mn$^{4+}$), braunite (Mn$^{2+}$ and Mn$^{4+}$) and hollandite (Mn$^{2+}$ and Mn$^{4+}$) in varying concentrations. Chromium and strontium, in addition to the alloying elements lead and copper, were co-located with the Mn deposits. Because an increasing number of studies indicate that ingestion of Mn (manganese) from drinking water causes specific neurological disorders the US EPA established a lifetime health advisory value of 300 µg L$^{-1}$. Cobalt (Co), Cr (chromium), and Pb (lead) are either regulated or are currently monitored by the US EPA. Mn oxides can adsorb and oxidize these metals increasing their oxidation states and toxicity, a fact not previously considered. Ingestion of Mn particulates with adsorbed ions of Co, Cr, or Pb from drinking water therefore may increase the threat to human health. Little is known about the formation and composition of Mn oxides in DWDS or the environmental influences, e.g., disinfectant type and pipe material, that potentially impact their formation and composition.
Pyrite, FeS₂, is a widespread and important sulfide mineral. Pyrite is thermodynamically stable under reducing conditions and in saturated sediments provides surfaces for the adsorption of aqueous species. When exposed to oxidizing environments, for example through mining activities, pyrite oxidation leads to the generation of low pH solutions termed acid mine drainage. Detailed understanding of the reactivity of pyrite surfaces requires knowledge of their atomic structure under relevant conditions. Many groups have studied the surface chemistry of pristine and oxidized pyrite surfaces but the structure of a hydrated surface has never been experimentally determined. We have employed the crystal truncation rod (CTR) method and complementary surface-sensitive techniques in order to determine the structure of the water—pyrite (001) interface and to establish how adsorbates interact with this surface.

We developed an anaerobic chemical–mecanical polishing method that creates low-roughness pyrite (001) surfaces shown by atomic force microscopy (AFM) to be dominated by irregularly shaped (001) terraces. We studied the structure of the hydrated pyrite (001) surface using the CTR method, obtaining reproducible results from three crystals. Optimal fitting of the CTR data requires the incorporation of two structurally distinct termination surfaces that differ in the coverage, and likely the chemical speciation, of surface sulfur atoms. In each case, surface iron atoms and disulfur groups are significantly displaced from bulk positions. The adsorption of aqueous metal ions provides a complementary approach for assessing the chemical speciation of sites on the (001) surface. We observed modulation in the CTR scattering patterns following exposure to Fe³⁺ and Pb²⁺ ions, confirming that the termination surface is accessible and chemically reactive. Grazing incidence extended X-ray absorption fine structure (EXAFS) studies of surface-adsorbed Pb²⁺ revealed at least two near-neighbor distances consistent with a fraction of lead atoms adsorbing via inner-shell interactions with surface sulfur sites. The data suggest a model in which a high density of sulfur vacancies provides preferential binding sites for the Pb²⁺ cation.
The physical structure of mollusk shell nacre changes from species to species (1-3). We first set out to identify which environmental parameters correlate with which physical parameters in nacre (2). We then focused on a single species, the blue mussel *Mytilus edulis*, and analyzed its microstructure as a function of position in the shell, which corresponds to time of deposition, and therefore seasons of the year and water temperature. Preliminary data (4) indicate that it may indeed be possible to use nacre as a temperature proxy. If confirmed, this is an amazing result, as nacre was first formed 450 million years ago, and would therefore provide the oldest T proxy ever established.

Current Capabilities of the 20-ID Micro-spectroscopy Station

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Abstract

The micro-spectroscopy station on the insertion device beamline 20-ID, complemented by macroscopic capabilities on the bending magnet beamline 20-BM, is used extensively by researchers in environmental and related fields. During the past few years, the capabilities of the micro-spectroscopy station have been continually improved. This poster summarizes the current capabilities and shows some example data. The station is a KB mirror based microprobe providing a focus in the range of 2 – 8 microns with flux approaching 5x10¹² for the larger spot sizes. The available energy range is 4.4 to >35 keV. Some recent improvements include quick (fly) scanning in both ROI and full spectrum mode, confocal capabilities (25, 5 and 2 micron depth resolutions) using polycapillary or microchannel optics, and x-ray excited optical luminescence. A wide range of high resolution detection options is available, including a variety of miniXES spectrometers, microspec based WDX, bent Laue analyzers, and a polycapillary based flat crystal spectrometer. We continue to support standard detectors such as four and single element vortex and 13 element Ge solid state detectors. A Pilatus 100K is available for microdiffraction and miniXES, and MAR165 area detectors can be requested for more-detailed micro-XRD studies. Low temperature (80K) capabilities are available for radiation sensitive samples, in addition to sample mounts for anaerobic or radioactive samples. This combination of capabilities results in a versatile station that can be used for XRF mapping, valence sensitive mapping, micro-XANES and EXAFS, and resonant and non-resonant emission spectroscopy on a wide variety of samples.
Magmatic hotspots drive up P amount in Sahara dust and nourish the Atlantic and the Amazon

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Millions of tons of dust particles are eroded every year from the Sahara desert soils and are blown over the Atlantic Ocean and as far as the Amazon basin¹,². This dust flux provides an input of phosphorus (P) to the oligotrophic waters of the ocean³,⁴ and the P-depleted rain forests of the Americas²,⁵,⁶. Unlike nitrogen, P cannot be fixed from the atmosphere. Thus, dust is an important P source to these ecosystems, which are responsible for a considerable fraction of the global net primary productivity and CO₂ sequestration²,⁵. However, remarkably little data exist on the active sources and P quantities of Saharan dust over the Atlantic. This lack of data means that the sensitivity of these P-limited ecosystems to Saharan dust-P deposition is not well established. Here we performed the first identification of the P sources in dust arriving from the Sahara and investigated the relations between the dust-P origin and the bioavailable-P amounts. From analysis of phosphate oxygen isotopes signatures⁷ of all the major Saharan dust events of 2011 over the North-Eastern Atlantic, supported by remote-sensing imagery, we infer that a series of magmatic-P hotspots scattered in specific locations across the desert enrich the dust with bioavailable-P and elevates its concentrations (900 µg soluble-P g-dust⁻¹ on average) up to 20 times higher than previously assumed²,³,⁸. We estimate that a single dust event greatly increase the bioavailable-P levels of the Atlantic and also
increase by ~8% the typical Amazon forest soil stock of immediately-available-P. We also found that phosphate from the Bodélé depression, considered to be the largest source of Saharan dust, has a unique isotopic signature which is not evident in Cape-Verde but can be used in the future to identify this source. Our results provide new information on bioavailable-P for experimental and modeling studies of global biogeochemical cycles.
Professor Gordon Brown of Stanford University is one of the most important Earth scientists in the last half century. As a master thinker and writer, his papers are read and cited by mineralogists, crystallographers, geochemists (aqueous and non-aqueous), biogeochemists, environmental scientists, surface and interface scientists, materials scientists (crystalline and amorphous), and materials chemists and physicists (theoretical and applied). With hundreds of papers spread among dozens of geoscience, materials science, chemistry and physics journals, his citation count will soon surpass 20,000, with seven papers commanding well in excess of 300 citations each, and with his most cited work published by the American Chemical Society having well over 700 citations. A personal h-index of 70 puts an exclamation mark on his publishing career, which is far from over.

I have known Gordon well for 39 years, first as my graduate student advisor for five years, and thereafter as a remarkable colleague and dear friend. I have personally witnessed his deep commitment and never-ending passion for minerals, interfaces, instrumentation, Earth, and life. Going back in time, his formative years were spent in Jackson, Mississippi and later Millsaps College in the same city. This was followed by graduate work first at Penn State and then at Virginia Tech (the latter for both his Masters and Ph.D. degrees, but for both institutions Gordon studied under the legendary G.V. Gibbs who is still publishing remarkable papers himself at age 87), as well as a one year post-doc at Stony Brook, all important in Gordon’s career launching pad. This led to a faculty position at Princeton in 1971, and finally a move just two years later to Stanford which he has chosen to call home ever since. It has been a remarkable and amazing ride since graduate school days, with countless appointments (from society presidencies to high level boards), fellowships, grants, honors, major (and many) medals and awards, an intellectually rich and long line of highly talented graduate students, post-docs, and colleagues, and most importantly to Gordon, a forever marriage to Nancy, and two beautiful children and their wonderful families.

It is more than appropriate to honor Gordon by starting the tradition of an annual special lecture bearing his name at the Synchrotron Environmental Science Conferences. It has been nearly 30 years since Gordon come into my office during my Stanford days, simply beaming and exceptionally excited about his first successful synchrotron X-ray absorption spectra collected in situ from a sorbing species at a mineral-water interface. This truly pioneering genius resulted in Hayes et al. that appeared in Science in 1987 and has become the gold standard, and the original, synchrotron-based work in environmental geochemistry. That paper has more than 400 citations now, but much more importantly, there are a few thousand publications that have followed in its footsteps in this field of science. For this alone, for breaking the ice and showing the way, the Brown Lecture at SES conferences will be a special highlight for decades to come.
Nanoscale Mercury-Sulfide-Organic Matter Interactions: Implications for Bioavailability and Methylation Potential

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Mercury contamination in sediments and other benthic environments poses a health risk due to in-situ microbial production of monomethylmercury (MeHg), a highly bioaccumulative neurotoxin. The overall objectives of this research were to determine the forms of inorganic mercury that are bioavailable to methylating bacteria and to use this information to predict biomethylation potential in contaminated settings. We performed experiments with pure bacteria cultures and anaerobic sediment slurry microcosms to determine how mercury methylation rates changed as a function of the type of mercury sulfide added (dissolved, nanoparticulate, or bulk particulate) and microbial growth conditions (i.e. salinity, organic carbon). The structure and crystallinity of the nanoparticulate mercury was assessed by synchrotron small angle X-ray scattering and X-ray absorption spectroscopy.

The results generally indicated that production of MeHg was greatest in cultures receiving dissolved Hg. Cultures receiving nanoparticulate HgS (nano-HgS) generated less MeHg than the dissolved treatments, but much greater than the cultures receiving bulk scale metacinnabar HgS. The differences in MeHg production between dissolved and nano-HgS treatments also varied, depending on whether the productivity of methylating microbes (e.g. sulfate reducers) was a limiting factor. No clear correlation was observed between the net productions of MeHg and the concentrations of dissolved Hg(II) in the cultures, suggesting that the decrease in the methylation potential of aged nano-HgS was not simply because of the slower supply of dissolved Hg(II) by nano-HgS. The production of MeHg in the nanoparticle treatments also depended on the age of the nanoparticle stock solutions. Over the course of the aging process, nano-HgS agglomerated to form mass-fractal aggregates, although the size of each primary particle within the aggregates remained unchanged. Furthermore, the crystallinity of nano-HgS increased as the particles aged. While the link between the aging of nano-HgS and decrease of methylation potential is not fully understood, the results of our study indicate that freshly formed HgS particles in DOM-rich water will include a variety of nanoscale structures that have a wide range of methylation potentials. This knowledge provides a basis for improved predictions of mercury bioavailability and MeHg production in contaminated environments.
Interactions among aqueous ions, quartz, and Fe (hydr)oxide polymers during heterogeneous Fe hydroxide nucleation and growth

Yandi Hu, Chong Dai

Fe hydroxide nanoparticles, which can coprecipitate with aqueous metal cations through both surface adsorption and structural incorporation, are an essential carrier for heavy metals in many natural and engineered aqueous environments. Especially, heterogeneous iron hydroxide precipitation on mineral surfaces can immobilize aqueous heavy metals. In this study, the initial nucleation and growth of iron hydroxide on quartz were quantified in $10^{-4}$ M Fe$^{3+}$ solution in the presence of Na$^+$, $10^{-3}$ M Cu$^{2+}$, Pb$^{2+}$, $5 \times 10^{-4}$ Al$^{3+}$, or $3 \times 10^{-4}$ M Cr$^{3+}$ at pH = 3.8 ± 0.1, using synchrotron-based grazing-incidence small angle X-ray scattering technique (GISAXS). In 30 min, the average radius of gyration ($R_g$) of particles on quartz grew from around 2 to 6 nm in the presence of Na and Cu. While interestingly, the particle sizes remained to be $3.3 \pm 0.3$ nm in the presence of Pb, the particles sizes grew slowly from ~2 to $3.7 \pm 0.3$ nm in the presence of Al, and no particles were formed in the presence of Cr. To study the interactions among aqueous ions and quartz, the metal hydrolysis products were calculated using Geochemists’ Workbench (GWB), the metal ion adsorption onto quartz surface was studied with quartz crystal microbalance dissipation (QCM-D), and the surface charges of quartz in the presence of metal ions were also measured. Strongest hydrolysis reaction occurred for Cr$^{3+}$, followed by Al$^{3+}$; almost no hydrolysis of Cu$^{2+}$ and Pb$^{2+}$ occurred. Hydrolyzed Cr(OH)$_3$ and Al(OH)$_3$ adsorption onto quartz surface was observed by QCMD, such adsorption changed the surface charge of quartz from negative to positive, therefore inhibited heterogeneous precipitation of positively charged aqueous iron hydroxide polymers onto quartz. Especially, the strong hydrolysis of Cr
lower the pH of the solution and totally inhibited Fe hydroxide precipitation. For Cu$^{2+}$ and Pb$^{2+}$, no adsorption onto quartz occurred based on QCMD measurement, so the surface charge of quartz remained negative. The total masses of precipitates on quartz were also quantified using QCM-D. By utilizing multidisciplinary techniques, this study provides new insights on the interactions among aqueous ions, quartz, and iron hydroxide polymers during heterogeneous iron hydroxide coprecipitation with aqueous cations. Such information can be helpful for not only environmental remediation and wastewater treatment, but also for the doping design of iron oxide catalysts.
Environmental Application in the Medium Energy using SXRMB Beamline At CLS

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The Soft X-ray Micro-characterization Beamlne (SXRMB) is a medium energy, bending magnet-based double crystal monochromator (DCM) beamline at the Canadian Light Source. The main focus of SXRMB is research in the ‘intermediate energy range’ (between 1700 and ~6000 eV), which covers the K-, L-, and M-edges of many main group and transition metal elements. This energy range provides access to environmentally important elements such as the K-edge of Si, S, P, and Cl, together with 3d metals, such as Fe, Ca, Ti, V and Cr. Since 2009, it has been used in wide applications in materials, mineralogy, soil science, biogeochemistry, biology and environmental science.

The SXRMB beamline have four distinct capabilities. The standard, under vacuum, X-ray absorption fine-structure (XAFS) endstation is operational and is capable of measurements in total electron yield, X-ray fluorescence yield, X-ray Excited Optical Luminescence (XEOL) and transmission. The ambient table is a versatile XAFS endstation. Especially, the in-situ measurement can be carried out for a stirring liquid sample and heating and cooling for solid samples at ambient condition. The newly commissioned microprobe endstation will provide a focused X-ray beam (10 μm x 10 μm) that will enable micro-XAFS and micro-X-ray fluorescence (XRF) spectroscopy measurements on a small spot size in order to reduce the heterogeneity often present in natural samples. Another new feature at the SXRMB, ready for user experiments, is hard X-ray photoelectron spectroscopy (XPS). High energy XPS (up to 8 keV) allows for deeper penetration into a material, probing chemical information of the bulk and reducing the problem of surface contamination. In this presentation we will present several research highlights to demonstrate the capabilities of the SXRMB beamline in environmental research.
Tomography of Wood: Infrared Complements X-Ray

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Abstract

Tomographic images help clarify understanding of wood architecture, strength properties, durability, and wood cell wall deconstruction for conversion of lignocellulose to biofuels, nanocellulose and other value added chemicals in forest biorefineries. We describe here an infrared method for nondestructive chemical imaging of wood and wood-based materials that complements previous x-ray tomography taken on the X27 beamline at NSLS. Chemical detection, mapping and digital image constructions were obtained with a high resolution FTIR microspectroscopy facility at the University of Wisconsin Synchrotron Radiation Center, Madison, Wisconsin. This pioneering Infrared Environmental Imaging (IRENI) facility, equipped with a unique design for illuminating and analyzing samples, enabled rapid FTIR data collection of 2D images with high spatial resolution (pixel size of 0.54×0.54 µm$^2$), and 3D images of lignin, hemicellulose and cellulose in wood cell wall layers of commercially important Populus deltoides Bartr and Pinus taeda L.
ROLE OF DIATOMS IN THE REMOVAL OF IRON FROM ANTARCTIC SEAS

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Iron plays a key role controlling biological production in the Southern Ocean, yet the mechanisms regulating iron availability in this and other ocean regions are not completely understood. Based on analysis of phytoplankton from coastal Antarctic seas, we present a new pathway for iron removal from marine systems involving structural incorporation of iron into biogenic silica. Several lines of evidence generated from synchrotron based X-ray fluorescence microscopy and X-ray absorption near edge structure spectroscopy, demonstrate that iron incorporated into biogenic silica is reduced and associated with organic molecules. Export of iron incorporated into biogenic silica represents a substantial iron loss from the Southern Ocean. For example, in the Antarctic Ross Sea, burial of iron incorporated into biogenic silica is conservatively estimated as 11 micromoles per square meter per year, which is in the same range as the major bioavailable iron inputs to this region. As a major removal mechanism of bioavailable iron, incorporation of iron into biogenic silica may shift microbial population structure towards taxa with relatively lower iron requirements and reduce ecosystem productivity and associated carbon sequestration.
Approximately 400 million acres of public and private forest land in the United States need restoration. Typically, restoration means removing excess forest biomass. The estimated cost for one round of forest restoration is $69 billion, which is overwhelming compared to the $0.3 billion the U.S. Forest Service is funded annually for restoration efforts. However, inaction is not an option. The accumulation of excess forest biomass fuels catastrophic wildfires. In addition to the devastating loss in lives and property, the U.S. Forest Service typically spends over $3 billion annually fighting wildfires and costs continue to rise. Faced with this staggering challenge, the U.S. Forest Service is pursuing advanced materials research in an effort to find market-based outlets for the excess forest biomass removed during restoration. The aim is to recoup some or all of the restoration costs and accelerate forest restoration without having to rely upon additional federal funding.

One avenue to increase the use of forest biomass is to improve the durability of forest products. Durability issues include fungal decay, fastener corrosion, and dimensional instability. A commonality between these durability issues is moisture. Decay and corrosion only occur in moist environments, and moisture-induced swelling and shrinking cause dimensional instability. U.S. Forest Service researchers have recently begun to utilize the APS to help address these challenging durability issues. X-ray fluorescence microscopy (XFM) at beamline 2-ID-E is a new tool for forest products research. XFM has the sensitivity and spatial resolution to map out adhesive infiltration into wood cell walls. Using a custom-built humidity chamber, XFM was also used to identify moisture thresholds for chemical transport through wood cell walls, and to quantify diffusion coefficients of chemicals transporting through different wood cell wall layers. Chemical transport through wood cell walls is believed to be the onset mechanism for decay and fastener corrosion, and if the mechanism can be better elucidated improved protective treatments could be more effectively developed. Diffusion coefficients are also needed to optimize biorefinery processes for the production of fuels, chemicals, and nanomaterials. XFM is used to study fungal decay processes as well. X-ray computed tomography (XCT) at beamline 2-BM-B has also been used to investigate the effect of adhesive molecular weight distribution on the flow of adhesive into wood cellular structure. The moisture-induced swelling of wood’s nanostructure is also studied using small angle x-ray scattering and a custom-built humidity chamber at beamline 18-ID-BioCAT.
Examination of Cr(VI) treatment by zero-valent iron using in situ, real-time X-ray absorption spectroscopy and Cr isotope measurements


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Abstract

Hexavalent chromium (Cr(VI)) is a pervasive and highly mobile groundwater contaminant, frequently derived from industrial activities such as tanning and electroplating. Remediation methods typically focus on the reduction of the more toxic Cr(VI) to Cr(III), which is less toxic and exhibits limited solubility in groundwater. Stable Cr isotope analyses have shown that reduction processes produce significant isotope fractionation, suggesting that this may be a powerful tool for monitoring the performance of remediation processes. A series of replicate flow-through cell experiments was conducted to characterize Cr isotope fractionation during Cr(VI) treatment by granular zero-valent iron (ZVI). Synthetic groundwater containing 50 mg L\(^{-1}\) Cr(VI) was pumped upward through a custom-made cell packed with ZVI under anaerobic conditions. Real-time, in situ monitoring of the reaction products using X-ray absorption near edge structure (XANES) spectroscopy was achieved via a Kapton® window in the cell. The geochemical evolution of the system was monitored using pH and redox measurements, while aqueous effluent samples were retained for cation and Cr isotope analysis. Reduced Cr(III) was observed to accumulate on the ZVI throughout the experiment. Increases in \(\delta^{53}\)Cr values corresponding to decreases in Cr(VI) concentration suggested the occurrence of redox processes, which correlated well with the spectroscopic results. However, the complex isotope trend suggested a two-stage treatment system exhibiting multiple Cr(VI) removal rates and isotope fractionation values (\(\varepsilon\)). Reactive transport modeling was used to quantify these distinct rate and \(\varepsilon\) values, where rapid Cr removal was associated with very little fractionation (\(\varepsilon = -0.2 \%\)), and slower removal was associated with a greater degree of fractionation (\(\varepsilon = -1.2\) to \(-1.5 \%\)).

Using synchrotron microanalysis to solve real-world environmental problems

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Fifteen years of using synchrotron microanalysis (notably micro-XRF, -XRD and -XANES) to characterize soils, sediments, mine tailings and dust has provided the opportunity to see research results translated to practical solutions for industry, government and communities. Identifying solid phases that host potentially hazardous elements improves risk assessment and remediation design, leading to more effective and affordable environmental management strategies for contaminated sites. Several examples will be presented that illustrate how analytical results, usually from M.Sc. or Ph.D. theses, have been communicated and applied to complex environmental problems:

(1) At the Giant Mine in Yellowknife, Northwest Territories, Canada, we were able to distinguish natural mineral hosts of As (arsenopyrite and its weathering products) from anthropogenic sources (As trioxide and maghemite from stack emissions) in soil samples near a former gold ore roaster. Micro-XRD and As micro-XANES were critical in discovering this contamination, which had been overlooked in the original remediation plan. Clean-up strategies for these soils are being reconsidered.

(2) Characterization of As-bearing minerals in samples of wetland sediments receiving drainage from an abandoned Ag mine demonstrated that the wetland was both a source and a sink for As in the overlying water. Seasonal changes in redox conditions result in As-hosting sulfide (realgar) being replaced by converting to As-bearing Fe oxide. The passive remediation design for this remote site has been revised to take into account our findings. New soil will be added to sequester As and the redox conditions in the constructed wetland will be controlled so that As sulfide is stabilized.

(3) Multi-element mapping and micro-XRD were applied to house dusts containing elevated concentrations of Pb, Zn, and Ba in bedroom dust, and Pb and As in living room dust, as well as garden soil. Paint pigments including white Pb (hydrocerussite) and lithopone (wurtzite and barite) are present in bedroom dust, probably related to renovation activity in the home at the time of sampling. The much lower Pb content in the living room dust shows a relationship to the exterior soil. The technique also confirmed the presence of chromated copper arsenate treated wood as a source of As in the living room dust.

(4) At historical gold districts in Nova Scotia, synchrotron microanalysis has been used to characterize the mineralogy of As-rich (mean = 12,000 mg/kg As) mine tailings that are located close to residential areas and occasionally used for racing off-road vehicles. Micro-XRF, -XRD and -XANES analyses show that As is hosted in arsenopyrite and a variety of weathering-related phases, including three forms of ferric arsenate (scorodite, amorphous Fe arsenate, kaňkite), two Ca-Fe arsenates (yukonite and an amorphous form), one arsenite phase (tooeleite), and As bound to Fe oxyhydroxides. These results have been used to interpret the results of bioaccessibility experiments on the tailings and are presently helping to guide long-term environmental management actions for these abandoned mines.

In our experience, micro-XRD is particularly powerful for unambiguous identification of metal-hosting compounds in complex mixtures, especially microcrystalline or nanocrystalline materials. Many metal-bearing anthropogenic compounds (pigments, alloys, ore processing waste) and natural weathering products (Fe and Mn oxyhydroxides) fall into this category. A specific advantage for geological materials such as soils, sediments and mine tailings, is that quartz, feldspar and other rock-forming silicates that would dominate a conventional XRD pattern are eliminated from the diffraction pattern (because they are too coarse-grained to diffract under most synchrotron microprobe experimental conditions), making it much easier to recognize the metal-bearing microcrystalline minerals.
Reduction of antimony(V) by iron(II) minerals

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Antimony (Sb) is a metalloid that is used in a variety of industrial manufacturing settings. While antimony has an assortment of useful applications, it has a similar toxicity to other Group 15 elements. As the mining and use of Sb continues to increase, environmental concerns involving the element grow. Sb(V) and (III) are the two most abundant oxidation states for the element however, their redox transformations in natural and engineered environments is poorly understood. Ferrous iron [Fe(II)] is one of the most abundant reductants typically present in aquatic and terrestrial environments under suboxic and anoxic conditions, often providing substantial redox buffering capacity to these systems, and common Fe(II)-bearing minerals such as magnetite, green rust, and various ferrous sulfide phases have been shown to effectively reduce a wide range of organic and inorganic contaminants. However, the redox behavior of Sb in the presence of Fe(II) minerals is poorly understood, as the few studies in this area have reported conflicting results. In this study we examined the behavior of Sb(V) in the presence of a suite of Fe(II) minerals including magnetite, green rust, and mackinawite (FeS) and in microcosms with Fe(III)- and sulfate-reducing conditions.

The interaction of Sb(V) with pure (synthetic) Fe(II) minerals was investigated in aqueous suspensions containing 2 mM K$_2$Sb(OH)$_6$ and 50 mM Fe(II) as either magnetite, green rust, or mackinawite. The behavior of Sb(V) under Fe(III)- and sulfate-reducing conditions was examined in aqueous suspensions containing 2 mM K$_2$Sb(OH)$_6$, 50 mM Fe(III) (as ferrihydrite), 10 mM sulfate, and 10 mM lactate, that were inoculated with sediment from a wetland on the campus of Argonne National Laboratory in Argonne, Illinois. Samples were collected over time to track changes in the concentrations of Sb, Fe(II), sulfate, and lactate. Samples were also collected for microbial community analysis. X-ray absorption fine-structure spectroscopy (EXAFS) was used to determine Sb valence state and chemical speciation.

We observed variable responses in the ability of specific Fe(II) minerals to reduce Sb(V) to Sb(III). No reduction was observed with either magnetite or green rust, however, in the presence of mackinawite, Sb(V) was reduced to Sb(III) in the form of an Sb-S complex. Likewise in the Fe(III)- and sulphate-reducing microcosms, Sb remained as Sb(V) under Fe(III)-reducing conditions, but was reduced to an Sb(III) sulfide phase under sulphate-reducing conditions. Our results suggest that reduction of Sb(V) is not likely in natural systems under Fe(III)-reducing conditions, but is expected in sulfidogenic environments.
Simultaneous Influences of Ionic Strength and pH during Early Stage of Manganese Oxide Nanoparticle Formation on Quartz

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Manganese (Mn) oxides play a crucial role for the fate and transport of heavy metals in environmental systems. Through redox reactions, Mn oxides can incorporate or release heavy metals in aqueous environments. Often these Mn oxides can be found in the form of coatings on rocks and they can immobilize contaminants. Therefore, the early formation of Mn oxide on a mineral surface is crucial in controlling the fate of heavy metals in environmental system. Using synchrotron-based grazing incidence small angle X-ray scattering (GISAXS) and small angle X-ray scattering (SAXS), the simultaneous effects of ionic strength (IS) and pH on the kinetics of the Mn oxide formation on quartz substrate were studied. Ionic strengths of 1, 10, and 100 mM and pH 9.5, 9.8, and 10.1 were reacted with aqueous $10^{-4}$ M Mn (II). Our analyses confirmed that the IS change significantly controlled the kinetics of Mn oxide formation on quartz. Among the varied pH and IS conditions, pH of 10.1 with 100 mM IS showed the highest number concentration of particles, and the largest particle growth on quartz. Our integrated analyses, using atomic force microscopy, aqueous Mn(II) concentration analyses, and classical nucleation theory, provided new information about how varied pH and IS changes supersaturation and affects the structural epitaxy between the formation of Mn oxides and quartz substrate. To the best of the authors’ knowledge, this is the first experimental work that shows ionic strength controls Mn(OH)$_2$ formation and this Mn(OH)$_2$ formation can affect the system saturation, and thus the heterogeneous nucleation kinetics of manganese oxide nanoparticles on quartz substrates. The unique information obtained in this work will help us understand manganese formation in natural as well as engineered aqueous environments (e.g., nuclear waste deposition and acid mine drainage remediation).
Imaging Dissolution Fronts at the Calcite-Water Interface in Intense Radiation Fields

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We present new results on the onset and evolution of dissolution fronts at the calcite-water interface that occur when imaging in situ with the X-ray Reflection Interface Microscopy (XRIM)¹. XRIM is a novel technique that captures the spatial variation of the X-ray reflectivity signal through the use of X-ray optics, providing real space images with sub-100 nm resolution over a large field of view (10 x 10 μm²). Due to the intrinsically low reflectivity signals of interfaces, the ability to image an interface requires that the sample be subjected to intense radiative flux (10¹⁰ photons/sec/μm²).

Our results show that the calcite surface undergoes significant morphological changes upon exposure to X-rays. Specifically, we observe two types of dissolution modes that propagate both laterally with an average velocity of 100 nm/sec, and into the calcite crystal with a velocity of ~ 5 nm/sec. The first type of dissolution front begins within seconds of radiating the surface and is initiated at the location of preexisting surface features, such as prevalent rhombohedral pits. The propagation direction of this dissolution front is anisotropic, following the rhombohedral symmetry of the calcite lattice. The second type of dissolution front is isotropic in shape and propagation, but is observed only at elevated flux densities. We propose that these observations are due to the production of radiolysis products (e.g., OH radicals, hydrated electrons) in aqueous solutions that can induce the dissolution of calcite. This is supported by the observation that the second dissolution mode is suppressed by dissolved radical scavengers (e.g. Br⁻). The first rhombohedral dissolution mode still occurs in the presence of Br⁻, but at an absorbed dose that is two orders of magnitude larger (i.e., in minutes). Ex situ atomic force microscopy of the reacted calcite surfaces confirms the topographic results obtained by X-ray interfacial microscopy.

Epitaxial growth of single-layer gibbsite on the muscovite (001) surface

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Synchrotron-based X-ray reflectivity (XR) has been used extensively to investigate the reactivity of mineral surfaces over the past decades. Its ability to “see” the atomic-scale structure, however, normally requires large (≥mm) high-quality (e.g., gem-quality) single crystals. To date, no XR study has been conducted on the surfaces of clay minerals, because they usually occur as sub-micron-sized crystallographically-disordered particles. Here, we present the first XR observation on the structure of single-layer gibbsite, a building block of many clay minerals, grown epitaxially on the basal surface of muscovite mica.

The growth of the Al-hydroxide mineral on the mica surface from aqueous AlCl₃ solutions (1µM-1mM) at acidic to near neutral pH (2-5.5) was observed using in-situ XR at the Advanced Photon Source, Argonne National Laboratory. In solutions slightly supersaturated with respect to gibbsite (i.e., saturation index, calculated using the ion activity product (IAP) and solubility product (K_{sp}) of gibbsite, log(IAP/K_{sp}) = ~1), sorbed Al formed a film whose thickness (2-3 Å) and vertical structure match those of a single Al dioctahedral sheet, i.e., a gibbsite, γ-Al(OH)₃, layer. A separate set of XR data was collected from a mica reacted in a solution containing a mixture of 90µM AlCl₃ and 10µM GaCl₃ at pH 4.3. The result showed that isomorphic substitution by Ga^{3+} occurred in the presumed Al site of the film, confirming the identity of the phase. Epitaxial films formed even from undersaturated solutions, but were structurally less ordered with smaller surface coverage. The stability of the film under changes in solution composition and saturation state was tested to demonstrate its potential application as a model system for probing clay mineral reactivity in-situ.
Chemical Speciation of Uranium in Savannah River Site Wetland Sediments

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Uranium mobility and biogeochemistry is expected to be profoundly different in wetland compared with upland sediments due to sharp geochemical gradients, elevated organic carbon concentrations and microbial activity, and the transient nature of hydraulic regimes. However, chemical speciation and biogeochemical behaviors of U in such systems are not well understood. We investigated chemical speciation and retention mechanisms of U in Savannah River Site (SRS) (South Carolina, USA) wetland sediments, using U L3-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), and X-ray fluorescence mapping. The SRS includes several former U processing facilities. Uranium contaminant has entered the surrounding environments through accidental and purposeful discharges and much of this U has concentrated in wetland areas. For example, approximate 70% of the 45,000 kg of depleted U released between 1958 and 1980 still remains in the Tims Branch and associated wetland sediments.

We studied the sorption of U onto the uncontaminated SRS wetland sediments, as well as the desorption of U from contaminated sediments from near Tims Branch. Uranium sorption and desorption profiles on the SRS wetland sediments, like other minerals, are that the sorption coefficient (K d) increased, then became a plateau and then decreased with pH increase. However, U sorption onto the SRS wetland sediment remained fairly strong (nearly 85% or K d values up to 700 mL/g) at pH < 4 and pH > 8, in contrast to previous studies which demonstrated that U has minimal sorption onto relevant mineral phases (e.g., goethite, kaolinite, and hydroxyl-interlayered vermiculite) at such pH ranges. In addition, we also investigated biogeochemistry of U in the SRS wetland using plant-containing microcosm experiment. Our findings include: (1) U is strongly bound to SRS wetland sediments primarily in the U(VI) form; (2) there were no U(VI)-bearing phases detected in the SRS wetland sediments; (3) there was evidence that U was bonding with C and/or Fe atoms at its second nearest neighbors; (4) the rhizosphere (the region influenced by root exudates) of wetland plants had extremely high U concentrations consisting of ~40% U(IV) and ~60% U(VI); five months later, all the U had transformed to U(VI). Mössbauer, HIM (He ion microscope), and HAADF-STEM (high angle annular dark field-STEM) revealed that the rhizosphere sediment was enriched with respect to the bulk sediments in nano-particles of ferrihydrite and NOM-Fe phases. Together, these findings indicated that the strong retention of U(VI) by SRS wetland sediments is likely attributed to binding with natural organic matters (NOM) and, to less extent, with goethite. In summary, wetlands, especially plant rhizospheres, can be well suited for immobilizing U(VI), even under oxidizing conditions, because of its strong binding to NOM and NOM-coated sediments.
Groundwater contamination, remediation, and management in mining environments

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Drainage emanating from mine waste deposits can have widespread negative impacts on water quality, ecosystem function and human health. Dissolved contaminants are derived from residual ore processing waters or released via in situ biogeochemical processes. Organic and inorganic compounds commonly occur at elevated concentrations in process waters used during ore extraction. Weathering of minerals within mine waste deposits may also contribute inorganic contaminants to pore water. The mobility and persistence of these contaminants largely dictates the long-term impacts of mine wastes on groundwater systems. Reclamation and management efforts aimed at reducing these impacts must therefore be based upon an integrated understanding of the chemical, biological, and physical processes that control dissolved contaminant concentrations. Combining synchrotron-based techniques with other geochemical and microbiological methods can offer valuable insight into controls on contaminant mobility. This information is critical to the development of new reclamation and management strategies aimed at promoting biogeochemical processes that limit contaminant mobility within mine waste deposits. This talk will examine biogeochemical processes related to groundwater contamination, remediation, and management within mine wastes generated at metal and oil sands mining operations.
The nucleation and overall precipitation of calcium carbonate (CaCO₃) are important in many fields, such as mineral trapping in geologic CO₂ sequestration, biomineralization, and pollutant adsorption. The aqueous environment where CaCO₃ nucleates varies largely in salinity. Here, by utilizing in situ grazing incidence small angle X-ray scattering, we studied heterogeneous nucleation of CaCO₃ on quartz substrates under different salinities. The salinities of aqueous solutions, represented by ionic strengths, were adjusted by NaCl to be 0.15, 0.5, and 0.85 M. At each salinity, the supersaturation indices (log(Q/K)) with respect to calcite were fixed at 1.40, 1.65, and 1.85. At each fixed supersaturation index, the nucleation rate was faster at a higher salinity, and presented a shorter induction time. By employing classical nucleation theory, the effective interfacial energy which governs the kinetics of nucleation was calculated for each fixed salinity. In general, the faster nucleation rates at higher salinities were related to smaller interfacial energies. The interfacial energies were 46, 40, and 35 mJ/m² for ionic strengths of 0.15, 0.5, and 0.85 M, respectively. In addition, at a fixed supersaturation index, particles’ growth was faster under higher salinities. This study provides important thermodynamic parameters (interfacial energies) for modeling CaCO₃ nucleation and overall precipitation on mineral substrates in seed-free systems. Findings of this study can help understand CaCO₃ nucleation at various salinities, such as in deep saline aquifers, brackish water, and reverse osmosis facilities, and can be transformative in understanding nucleation of other environmentally important minerals and in biomineralization.
Using Synchrotron Techniques to Analyze Iron and Phosphorus in Aerosols

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Biological productivity in many oligotrophic ocean regions is controlled by the availability of the nutrients iron and phosphorus. In these oligotrophic regions, atmospheric aerosol deposition is a key source of these nutrients. Understanding composition of phosphorus and iron in aerosols is critical for determining the key factors controlling their solubility and ultimately their potential bioavailability to marine organisms. Aerosol composition was investigated using Near Edge X-ray Fluorescence Spectroscopy (P-NEXFS), X-ray fluorescence mapping, as well as measurement of total and soluble iron and phosphorus in samples collected in Bermuda and Crete. Iron(II) is generally considered to be the more soluble than iron(III); however, in these samples, iron oxidation state did not correlate with increased iron solubility. Aerosol phosphorus solubility was closely linked with aerosol composition, which was in turn linked to aerosol source regions. European and North African air masses are the main source of aerosol deposition to the oligotrophic Mediterranean Sea. European aerosols deliver on average 3.5 times more soluble phosphorus than North African aerosols and are dominated by organic phosphorus compounds relative to North African sources. The ultimate source of organic phosphorus does not stem from common primary emission sources. Rather, phosphorus associated with bacteria best explains the presence of organic phosphorus in European aerosols. Overall, our findings demonstrate the effectiveness of synchrotron-based approaches for understanding aerosol chemistry.
Current and future applications of Canadian Light Source beamlines to biogeochemical and geomicrobiological research

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In this poster I will present an overview of Canadian Light Source (CLS) beamlines that can be used for environmental research, including beamlines that are currently in development. I will provide examples of the use of synchrotron tools in geomicrobiological and biogeochemical projects, as well as examples of where CLS scientists have worked with mining companies to use these tools to address challenges in the mining industry. An overview of the CLS Green Mining Program will also be provided; our research group is conducting biogeochemical research that contributes to developing sustainable mining practices.
Impact of oxidation mechanism on the evolution of Fe (hydr)oxide mineralogy during biogeochemical redox cycling

Iron (hydr)oxides are commonly found in soils and sediments in a wide variety of forms ranging from poorly- (e.g., ferrihydrite) to highly-ordered (e.g., goethite, magnetite) oxides. The structure, composition and degree of crystallinity of these minerals vary greatly depending on the physical and chemical conditions of their surroundings. The transformation of Fe (hydr)oxides under microbial Fe(III)-reducing or abiotic Fe(II)-oxidizing conditions is well characterized. However, Fe(II) oxidation in anaerobic environments by bacteria that couple Fe(II) oxidation with nitrate (NO₃⁻) reduction remains poorly understood. Reactors containing synthetic Fe (hydr)oxides (goethite, ferrihydrite or lepidocrocite) and a natural inoculum, were subjected to four complete redox cycles by addition of either nitrate or oxygen to induce oxidation and glucose to induce reduction half-cycles. Here we demonstrate that aqueous Fe(II) concentrations appear independent of Fe (hydr)oxide when reduction is followed by biological oxidation (linked to nitrate reduction). However, when biological reduction is followed by oxidation via exposure to air, dissolved Fe(II) concentrations vary depending on initial Fe (hydr)oxide mineralogy. Additionally, characterization with XRD and XAS reveals that in addition to forming more thermodynamically stable Fe (hydr)oxides during redox cycling (e.g. magnetite and goethite), formation of less stable oxides (e.g. ferrihydrite) may occur under some conditions. Our results reveal that variations in initial mineralogy and oxidation mechanism may control the mineralogical evolution of Fe (hydr)oxides in natural environments. Examination of Fe (hydr)oxide development as a result of both biotic and abiotic redox processes is crucial for linking biological and geochemical processes occurring in soils and sediments.
Why should we study carbon chemistry using X-ray Raman?

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Increase in atmospheric emission of CO2 with the attendant global warming and environmental degradation are driven by global energy demand. Studies of carbon and nitrogen dynamics in ecosystems are leading to an understanding of the factors and mechanisms that affect the inputs to and outputs from soils and how these might be manipulated to enhance C sequestration. However, not all carbon in soil is created equal.

Plant litter is considered the primary resource for the organic matter content in soil. The amount of plant litter, its composition and speciation are the controlling factors for the formation of soil organic matter (SOM). Soil microbial activity, which in turn is related to the nature and characteristics of SOM in a given soil type, is the key biological process governing soil organic C (SOC) dynamics. C sequestration and storage in soil is a result of complex underlying biotic and abiotic interactions. The decomposition processes and turnover rates are highly influenced by the speciation of SOM. For modeling C sequestration and C transformations in soils, it is important to know the composition of the SOM. Current understanding of the relationships between different components of soil organic matter is far from complete. One of the primary reasons for this knowledge gap is the lack of adequate techniques for in-situ characterization of the chemical composition and speciation of bulk soil systems.

Among other popular techniques, 13C NMR suffers from low sensitivity for C in soil often necessitating acid extraction of the carbon pool from mineral rich sample matrices, and FTIR is a surface limited technique. C K edge NEXAFS (and STXM), which is otherwise a promising technique for obtaining spatially resolved chemical information about carbon, is both surface limited and prone to self-absorption effects – often precluding thicker and/or hydrated samples. However, X-ray Raman could be used for understanding the chemistry of carbon encapsulated inside soil aggregates in their native state. Hence X-ray Raman, which suffers from lower energy resolution than C K edge NEXAFS, could potentially emerge as a powerful technique for C speciation in bulk soil. Although energy resolution is usually the main concern in using X-ray Raman for low Z elements like C, we have achieved an energy resolution of 0.55 eV at sector 20-ID using Si 311 crystal analyzers. This energy resolution has allowed us to distinguish important C moieties like phenol-C, aromatic-C, aliphatic-C, carboxyl-C, and carbonyl-C. Our studies show that Carbon speciation using X-ray Raman compares well with NMR and C K edge NEXAFS. Comparison of standards and samples from a permafrost region in Alaska, the SPRUCE site in Minnesota, and tropical climates will be discussed.
Soil and sediment organic matter accumulates nearly all elements, and the stability of organic matter dictates the cycling of many associated elements. However, the interactions between organic matter and many of these elements are poorly understood, and traditional laboratory spectroscopy and microscopy techniques are insufficient to explore these interactions in detail. Recent developments at the soft X-ray synchrotron beamlines, and studies on model organic ligand-metal systems suggest that information on the speciation of many elements associated with organic matter can be obtained in detail at the nanometer scale. Our X-ray absorption spectroscopy and spectromicroscopy studies on the abundance and speciation of biologically important elements, such as N, P, S and halides, in organic matter in soil systems suggest that the speciation of these elements is highly dynamic and varies with the weathering of organic matter, climatic conditions, and the type of associated soils. Our results suggest that the speciation variations of these elements play an important role in their cycling in soil systems. A detailed discussion of applications of soft-XAS to the studies in organic matter-light element interactions, and how the XAS information can be used in exploring the speciation of light elements and elemental cycling will be discussed.
Uptake, transformation and fate of arsenic compounds in mushrooms

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Over 50 arsenic compounds exist in the environment and the toxicity of arsenic is greatly dependent on its chemical form. The only arsenic compound that is considered to be non-toxic is arsenobetaine (AB). The fruiting bodies, or mushrooms, of terrestrial fungi have been found to contain a variety of organoarsenic compounds, and compared with many other terrestrial organisms, a higher proportion of AB. The life stage at which the fungus produces AB is still unknown, as is whether the fungus, alternatively, accumulates AB from the surrounding environment. That is, the surrounding microbial community in the soil may produce AB or its precursors. The role of AB in mushrooms is also unknown. AB is found to make up the majority of arsenic in many marine organisms and its structural similarity to the osmolyte, betaine, has led to the hypothesis that AB can act as an osmolyte in these marine organisms. In order to elucidate the potential role or formation of AB in mushrooms arsenic speciation was determined in 16 species from an arsenic contaminated location to provide an accurate survey of arsenic metabolites produced in these fungal systems using HPLC-ICP-MS and complementary X-ray Absorption Spectroscopy (XAS). Different sections of a mature mushroom collected from this location and a laboratory grown primordium (an early life stage of mushroom development) from arsenic treated material were also selected for XAS imaging to investigate arsenic uptake and transformation in mushrooms that contain a high proportion of AB.

X-ray absorption near-edge structure (XANES) spectra were collected at the Pacific Northwest Consortium/X-ray Science Division (PNC/XSD) facilities, Sector 20 at the Advanced Photon Source (APS), Argonne National Laboratory. The XANES fitting results confirmed the major arsenic compounds determined during the HPLC-ICP-MS analysis. An arsenic sulfur compound was also identified, for the first time, in mushrooms that was not identified during the HPLC-ICP-MS analysis. As(III)-sulfur compounds are thought to be formed to initiate toxicity mechanisms or provide a mechanism to cope with high levels of arsenic exposure. Two dimensional XAS imaging of the mature mushroom sections and primordium was carried out on the insertion device (ID) line, Sector 20, using fluorescence data. Micro-XANES spectra were also collected at various points of interest to examine changes in arsenic speciation throughout the mushroom. Mapping of the cap, gills and stalk of the mushroom revealed that AB is sequestered in the cap and gills indicating that AB may act as an osmolyte to help maintain an elevated and rigid cap for maximum dispersal of spores from the gills. An As(III)-sulfur compound was also found throughout the gills and stalk. Mapping the primordium revealed that AB is the major arsenic compound at the earliest stages of fruiting body development. Presence of the compost material (growth substrate) within the primordium tissue contained inorganic and methylated arsenic compounds. This indicates that the microbial community in this material is capable of methylating the inorganic arsenic that was used to treat the compost material suggesting it is possible the microbial community associated with the mushroom may produce the precursors for AB that can then be selectively accumulated by the fungus.
Arsenate and Phosphate Oxyanion Incorporation Affects the Growth, Crystallinity, and Water Content of Newly-Formed Iron(III) (Hydr)oxides on Quartz

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Iron(III) (hydr)oxides play an vital role in the geochemical cycling of contaminants in natural and engineered aquatic systems. The ability of iron(III) (hydr)oxides to immobilize contaminants can be related to whether the precipitates form heterogeneously (e.g., form at mineral surfaces) or homogeneously (e.g., in solution). Water chemistry can influence the location, size, and abundance of iron(III) (hydr)oxides formation in the environment. In this work, we investigated the effects of aqueous arsenate and phosphate oxyanions on this process. Arsenate is a carcinogenic compound that can occur naturally in groundwater. On the other hand, phosphate has a similar structure and can compete with arsenate for binding sites on iron(III) (hydr)oxides and is abundant in fertilizer and waste sewage.

Utilizing a grazing incidence small angle X-ray scattering (GISAXS) technique, we studied heterogeneous iron(III) (hydr)oxide nucleation and growth on quartz substrates for systems containing arsenate and phosphate anions. We found that for the iron(III) only system, the radius of gyration ($R_g$) of heterogeneously formed precipitates grew from 1.5 to 2.5 (± 1.0) nm within 1 hour. For the system containing $10^{-5}$ M arsenate, $R_g$ grew from 3.6 to 6.1 (± 0.5) nm and for the system containing $10^{-5}$ M phosphate, $R_g$ grew from 2.0 to 4.0 (± 0.2) nm. While the systems containing these oxyanions had more growth, the system containing only iron(III) had the most nucleation events on substrates. Ex situ analyses of homogeneously and heterogeneously formed precipitates indicated that precipitates in the arsenate system had the highest water content and that oxyanions may bridge iron(III) hydroxide polymeric embryos to form a structure similar to ferric arsenate or ferric phosphate. These new findings are important because differences in nucleation and growth rates and particle sizes will impact the number of available reactive sites and the reactivity of newly-formed particles toward aqueous contaminants.
Probing the Effects of Temperature on the Spatial and Chemical Localization of Soil Organic Matter on Hematite using Scanning Transmission X-ray Microscopy

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Soil and sediments are the largest global reservoir of actively-cycling carbon. Soil organic matter (SOM) can be protected from decomposition and stored through the formation of organo-mineral complexes. Climate changes such as warming may have a large impact on such complexes, thus potentially altering the global biogeochemical cycling of soil carbon and the subsequent quality and fertility of soil. However, the effects of warming on SOM and organo-mineral complexes are currently debated partly due to the physiochemical complexity of SOM. As such, our research project focuses on the effects of warming on the flux of carbon from organo-mineral complexes to further understand the potential outcomes of climate change. The objectives of our research are to 1) quantify adsorption extent at different temperatures and 2) determine the spatial and chemical localization of SOM on mineral substrates at different temperatures.

Batch sorption experiments were conducted to determine the extent of adsorption at different temperatures. Hematite and goethite were used as representative mineral substrates and soil humic and fulvic acids as representative SOM. Preliminary batch sorption experiments were conducted at 25°C, 30°C, and 35°C. Figure 1 shows the results of total carbon analysis for the preliminary experiments and suggests the extent of adsorption of humic acids onto hematite is only significantly different (p<0.05) between 25°C and 35°C at lower SOM concentrations (30 ppm). Since it is unlikely for the number of available sites to change between 25°C and 35°C, it is possible that preferential adsorption of specific SOM components may be occurring at the different temperatures.

Scanning transmission X-ray microscopy (STXM) was used to determine the spatial and chemical localization of SOM on the hematite at different temperatures. Figure 2 shows the statistical cluster maps by principal component analysis (PCA) for hematite and humic acids at 25°C and 35°C. Our preliminary STXM results appear to 1) agree with our hypothesis of preferential adsorption of specific SOM components and 2) suggest that organic matter on the surface exhibits a microscale pattern (i.e., layering) at elevated temperatures. The increased sorption capacity at elevated temperature might be due to the formation of zonal (multi-layer) organization of humic components on the surface of hematite. The compounds most closely associated with the Fe-oxide surface could be N- and S-containing structures such as those in amino acid-like and peptide-like compounds.

Fig. 1. Batch sorption results showing that the extent of adsorption is only significantly different between 25°C and 35°C. Experiments were conducted in 10 mM NaCl at pH 6.

Fig. 2. STXM results showing the scan at 735 eV showing iron-rich regions and corresponding PCA cluster analysis of similar areas for (a) 25°C and (b) 35°C. At 25°C, the hematite particles were surrounded by carbon exhibiting complex NEXAFS spectra (red area) similar to the overall humic acids spectra. At 35°C, the hematite particles were surrounded with a thin layer of complex humic acids-like spectra which was then covered by an amine-rich area (yellow). Experiments were conducted in 10 mM NaCl at pH 6.
A novel nanoparticle approach for imaging soil bacteria

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The metabolic activities of soil microbes are the primary drivers of biogeochemical processes controlling the terrestrial carbon cycle, nutrient availability to plants, contaminant remediation, water quality, and other ecosystem services. However, we have a limited understanding of microbial metabolic processes such as nutrient uptake rates, substrate preferences, or how microbes and microbial metabolism are distributed throughout the three-dimensional complex of the soil. Here we use a novel imaging technique with quantum dots (QDs, engineered semiconductor nanoparticles that produce size or composition-dependent fluorescence) to measure bacterial uptake of substrates of varying complexity. Cultures of two organisms differing in cell wall structure -- Bacillus subtilis (a member of the Firmicutes) and Pseudomonas fluorescens (a member of the Proteobacteria) -- were grown in biofilms in one of four ecologically relevant experimental conditions: nitrogen limitation, phosphorus limitation, nitrogen and phosphorus limitation, or no nutrient limitation. The biofilms were then exposed to QDs with and without organic nutrients attached.

We found that uptake of QDs conjugated to organic substrates varied depending on growth conditions and substrate, suggesting that they are a useful indicator of bacterial ecology. Cellular uptake was similar for the two bacterial species (2222 ± 273 nanoparticles per cm³ of cell volume for B. subtilis and 1826 ± 278 for P. fluorescens). Uptake of QDs not conjugated to an organic molecule was negligible, indicating that bacteria actively consume the QD-labeled nutrient rather than QDs passively entering cells. On average, QD assimilation was six times greater when nitrogen or phosphorus was limiting (i.e., the substrate conjugated to the QD-provided nitrogen and/or phosphorus that was experimentally limited in the growth medium). Overall, cells took up about twice as much phosphoserine compared to other substrates, likely because it was the only compound providing both nitrogen and phosphorus. These results showed that regardless of their cell wall structure, bacteria can selectively take up quantifiable levels of QDs based on substrate and environmental conditions. X-ray fluorescence imaging experiments were performed at 2ID-D at the Advanced Photon Source to determine the elemental distributions within planktonic and surface-adhered (i.e, biofilms) P. fluorescens and B. subtilis bacterial cells. The APS images are consistent with those produced with the confocal and optical microscopes, indicating that the XRF approach can indeed detect bacterial uptake of CdSe-core QDs. These findings offer a new way to experimentally investigate basic bacterial ecology such as metabolic activity and biofilm development and function.
Acid extraction overestimates the total Fe(II) in the presence of Fe(III) oxide and Fe(II) sulfide minerals

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Aquatic and terrestrial environments are dynamic systems where coupled microbiological, geochemical, and hydrological processes define the complex interactions that drive the biogeochemical cycling of the major and minor elements. Fe(III) is ubiquitous in these environments and is typically present as various minerals, including Fe(III) oxides such as ferrihydrite, lepidocrocite (γ-FeOOH), goethite (α-FeOOH), and hematite (α-Fe₂O₃). Ferrous [Fe(II)] sulfide minerals [e.g., mackinawite (FeS), greigite (Fe₃S₄), pyrrhotite (FeS₁ₓ), and pyrite (FeS₂)] are also common in soils and sediments, particularly under anoxic conditions. Accurate determination of Fe(II) concentrations and distribution is key to understanding iron redox processes involved in the biogeochemical cycling of Fe in environmental and engineered systems and acid extraction followed by a colorimetric assay is a widely used approach for determination of Fe(II) in soil and sediment samples. Under sulfidogenic conditions, these samples can contain both metal sulfides and Fe(III) oxides. We compared the Fe(II) concentrations determined with acid extraction followed by colorimetric analysis to those determined by extended X-ray absorption fine structure (EXAFS) spectroscopy for samples containing Fe(III) oxide (as ferrihydrite, lepidocrocite, or goethite) and mackinawite (FeS). Our measurements of Fe(II) concentrations in these systems showed that concentrations determined by acid extraction were 1.5 to 3 times higher than those determined by EXAFS analysis depending on the Fe(III) oxide due to reduction of Fe(III) to Fe(II) by sulfide following acidification (which causes dissolution of FeS and release of sulfide into solution) of the samples. These results illustrate the need for caution when using acid extraction with colorimetric analysis to determine Fe(II) concentrations in samples containing Fe(III) oxides and ferrous sulfide minerals.
Synchrotron X-ray Fluorescence Microanalysis of Biological Tissue: From Plants to Placentas

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Abstract
The presence of an element – be it a nutrient or a contaminant – in discrete cellular and subcellular locations within biological organisms is usually the end result of a series of tightly regulated trans-membrane transport events, rather than passive diffusion. These events are controlled by an interaction between the genes encoding the membrane transporters and the environment, both of which can either be manipulated in a laboratory setting via the use of model organisms and growth conditions, or directly measured in vivo. Elemental maps can therefore provide a great deal of information about elemental homeostasis, and this knowledge has numerous and varied applications in the life sciences. I will present my past and present experimental work using elemental imaging, in particular SXRF as a technique of choice, on membrane transport of essential and non-essential contaminant elements. This will include examples from a broad range of life science applications, including analysis of mutants of the model plant Arabidopsis for biofortification of limiting micronutrients such as iron and zinc, determining the transport pathways for the metalloid contaminant arsenic in the staple food rice, and I will introduce new work on elemental imaging of the human placenta, one of the most critical and yet understudied organs, in a large pregnancy cohort exposed to arsenic via drinking water.
Structural study of Sb(V) adsorption on the hematite(1-102) surface

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The adsorption mechanism of Sb(V) on a single crystal hematite (1-102) surface was studied by using crystal truncation rod X-ray diffraction technique. The hematite samples were prepared following a chemical mechanical polishing protocol, which would favor a stoichiometric surface termination but with a vacancy of near surface Fe sites (usually named as the half layer termination). The lattice symmetry on a half layer termination hematite surface determines a topographic pattern with a feature of the site degeneracy, i.e. a symmetry related site could be defined for each single site. Such site degeneracy was explicitly accounted for by including each degenerated site pair during the model fitting. The best fit model results indicated that Sb(V) adsorbed on the hematite surface with a octahedral local structure via inner-sphere binding to three surface functional groups (two singly coordinated oxygen (I\text{I}O) and one doubly coordinated oxygen (II\text{I}O)), which forms a tridentate binding configuration through an edge-sharing and a corner-sharing binding structures. The Sb octahedral local structure is distorted with Sb-O bond lengths ranging from 1.95 to 2.31 Å. The Sb-O bond length associated with one of the I\text{I}O group (2.31 Å) is significantly longer than the other Sb-O bond lengths (~2.0 Å), which could be interpreted as a protocol to maintain a larger Sb-Fe separation. The chemical plausibility of the proposed surface adsorption structural model was verified based on the bond valence analysis, which gave rise to a bond valence saturation state for each interfacial atom within 0.1 v.u. after accounting for the possible valence contribution from a proton or a hydrogen bond. The protonation schemes of surface functional groups suggested a deprotonation for each binding surface oxygen. Protons were not involved in the surface complexation, which implied that the Sb(V) adsorption on hematite surface should be relatively pH independent.

The site coverage (71%) achieved from our best fit model is significantly lower than the value for the theoretical monolayer saturation (200% considering the site degeneracy). A computer simulation test of site assignment on a random basis was undertaken to reveal the possible relationship between the site coverage and the adsorbate-adsorbate distance. Unlike the solute in a fluid system, where the position of a solute is undefined due to its mobility, a sorbate, however, will be registered at specific surface binding sites on a crystal and thus form a characteristic occupation pattern as a function of the site type, the sorbate type and the solution chemistry. Such an occupation pattern of surface sites would determine that the adsorbate-adsorbate distances on a crystal surface are a series of discrete values rather than mathematically continued numbers. Results of a series of simulation tests gave rise to a Sb-Sb distance of ~5.0 Å for our system, whereas a monolayer saturation site occupation would require a Sb-Sb distance as short as <3.6 Å. The site occupation simulation could provide an important implication for the possible relationship between the adsorbate-adsorbate distance and the site coverage, although a fundamental understanding of such a relationship will rely on a higher level simulation test based on the molecular dynamics theory (like DFT).
Halogen cycling in Arctic-Boreal Soils – a biochemical, metagenomic and XANES study

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The complexity of biogeochemical Chlorine cycling in the biosphere is just beginning to be fully appreciated. Chloride (Cl\textsuperscript{-}) was once considered biologically inert, entering terrestrial ecosystems through rainfall and exiting in runoff, barely interacting with biological systems (Öberg 2002). Microbes capable of transforming chlorinated compounds mainly receive scrutiny in the context of bioremediation of chlorinated solvents or pesticides. Yet we know now that even in non-contaminated soils, there are potentially thousands of naturally occurring organohalogens (Gribble 2003), with Cl participating in a wide variety of biotic and abiotic transformations, cycling between organic and inorganic forms. However, Cl-cycling rates in most natural ecosystems are still poorly constrained (Öberg & Bastviken, 2012). Organic Cl (Cl-org) can be formed through a variety of pathways, including both abiotic and enzymatically driven processes (Bastviken et al. 2009). A wide variety of organisms, including plants, insects, fungi, bacteria and marine invertebrates produce haloperoxidase or perhydrolase enzymes converting hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and halides to hypohalous acids (e.g. hypochlorous acid, HOCl), which react spontaneously and nonspecifically with organic compounds. Low molecular weight humic substances (HS) such as fulvic acids appear to be likely targets for chlorination in soils. Alternatively, reactive Cl compounds may arise through reactions of dissolved organic carbon (DOC) and Cl\textsuperscript{-} with iron (Fe) and/or light (Page et al. 2013, Rao et al. 2012), leading to abiotic generation of Cl-org (Fahimi et al. 2003, Keppler et al. 2000). Sequencing our Arctic soil samples has uncovered multiple genera of microorganisms capable of participating in many Cl-cycling processes including organohalide respiration, chlorinated hydrocarbon degradation, and perchlorate reduction. Metagenomic analysis of these soils has revealed genes for key enzymes of Cl-related metabolic processes such as dehalogenases and haloperoxidases, and close matches to genomes of known organohalide respiring microorganisms from the Dehalococcoides, Dechloromonas, Carboxythermus, and Anaeromyxobacter genera. A TOX-100 Chlorine pyrohydrolysis unit was used to quantify total Cl in arctic soils, and these data were examined further to separate levels of inorganic-Cl compounds and Cl-org.

K-edge X-ray absorption near-edge spectroscopy (XANES) of Cl is performed on soils and purified fractions at energies of 2800-2860 eV at BL 9-BM-C of the APS. This technique complements our other analyses in that it provides information on all Cl compounds in soils, without respect to choice of extraction or analytical technique. XANES for Cl is performed at energies of 2800-2860 eV. Spectra collected to date show that it is straightforward to distinguish Cl-in from Cl-org (Leri et al. 2006, 2007; Leri & Myneni, 2010), with the XANES peaks occurring at lower energies for org-Cl than inorganic salts. The symmetry of some chloride salts is evident in distinct pre-edge features. These are believed to arise from dipole-forbidden transitions, and the position of
the pre-edge peak can be related to the degree of covalency in a metal-Cl bond. XANES spectra are extremely sensitive to the immediate neighborhood of Cl in natural systems: (1) oxidation state (based on the peak of the ‘white line’ energy peak), (2) local symmetry of the absorber (based on pre-edge, and to post-edge features), (3) bond lengths (pre-edge intensities) \((\text{Leri et al. 2006, 2007})\). This bulk spectroscopic technique is a powerful tool to determine the speciation and the environment of elements, and the analysis is non-destructive, element-specific and sensitive. We have collected Cl-XANES spectra for samples down to 100 ppm \([\text{Cl}]_{\text{tot}}\) in short integrations. XANES spectra will be collected on Beamline 9-BM-C at the Advanced Photon Source near Argonne, Illinois. The experimental arrangement is essentially as described in \textbf{Bolin (2010)} and consists of a Si(111)-monochromator, with focusing achieved using a Rh-coated toroidal mirror. Harmonics are rejected through a flat, Rh-coated mirror; providing an energy resolution of 0.1-0.2 eV at 2.8 keV. Quantification of organic chlorine is achieved by linear comibining fitting of normalized spectra to a standard library collected under identical beamline conditions as soil/humic substance spectra. To date we have used standards containing aliphatic-Cl (monochlorodimedone), pyranosal-Cl (‘sucralose’), aromatic-Cl (2-methyl-4-chlorophenoxyacetic acid, MCPA), humic acid-Cl, fulvic acid-Cl, amino acid-Cl, and a variety of chloride salts (NaCl, KCl, and SnCl\(_2\)). Salts dispersed in BN\(_3\) (to minimize Cl self-absorption) serve as Cl-peak energy standards by which we compare whole soils, humic fractions, or representative organics. Finally, we have initiated a forward-modeling exercise using the ADF (Amsterdam Density Functional) to better understand the multi-scattering features of XANES’ spectra.

![Normalized Cl_XANES spectra from APS BL 9-BM-C comparing two standards, NaCl and sucralose, vs. whole soils (from medium (Med) and ancient (Anc) Arctic drained](image)

Normalized Cl_XANES spectra from APS BL 9-BM-C comparing two standards, NaCl and sucralose, vs. whole soils (from medium (Med) and ancient (Anc) Arctic drained
thermokarst lake-basins, and purified humic acid from an ancient DTLB. (A: pre-edge region, B: Cl-edge, C: post-edge, > 50 eV)
Mineralogy and geochemistry of tetrahedrite-tennantite oxidation products from abandoned waste rock piles

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Synchrotron-based μ-XRD, μ-XRF, and μ-XANES combined with electron microprobe analyses have been used to determine the mineralogy, chemical composition, element distribution and Sb speciation in tetrahedrite-tennantite oxidation products in waste rock from abandoned Cu mines in Slovakia. Samples were collected from Špania Dolina and Libietová, one of the most important Cu deposits in Central Europe during the medieval period. The most intensive mining occurred during the 15th century with continuous mining and exploration activities until 1985. Cu ore is hosted in chalcopyrite (CuFeS₂) and sulphosalt solid solution tetrahedrite-tennantite (Cu₁₂Sb₄S₁₃ - Cu₁₂As₄S₁₃), which shows widespread oxidation. Nearby streams, groundwater and soil are contaminated by both As and Sb. Tetrahedrite and tennantite can be significant sources of As and Sb contamination, especially from hydrothermal deposits, but there is a lack of research on the oxidation products of these minerals, and the role they may play in the immobilization of As and Sb. Our results show that oxidation products contain significant amounts of hazardous elements, mostly Sb (with average content 40.55 wt%), together with Cu (average 22.09 wt%), As (average 9.79 wt%) and Bi (average 1.55 wt%), for samples where the primary mineral chemical composition is close to tetrahedrite end member. These phases were identified as a mixture of tripulyite FeSbO₄ and romeite group mineral with pyrochlore structure. Micro-XANES spectra indicate that the predominant Sb oxidation state is 5+. For samples where the primary sulphosalt is close to tennantite composition, the oxidation products contain Sb (average 3.23 wt%), As (average 28.34 wt%), Cu (average 26.22 wt%) and Fe (average 22.32 wt.%). Some of the secondary phases associated with tennantite are pharmacosiderite BaFe₄(AsO₄)₃(OH)₅·5H₂O and goethite FeO(OH). The toxicity and bioavailability of As and Sb depends on the speciation of both elements. This study shows that different Sb and As hosts with different stability may exist in the near-surface environment as oxidation products of tetrahedrite - tennantite.

This study was supported by the Slovak Research and Development Agency under the contract No. APVV-0663-10: “Contamination of mining country by toxic elements at selected Cu-deposits and possibilities of its remediation".
Nitrous acid (HONO) is an important OH radical source that is formed on both ground and aerosol surfaces in the well-mixed boundary layer. The release of gaseous HONO is largely dependent on the pH of the surface of origin as, at high pH, it can remain on the surface as nitrite (NO$_2^-$) or, at very low pH, the nitrous acidium ion (H$_2$ONO$^+$). Recent studies report the release of HONO from circumneutral soil suggesting that surfaces more basic than the pKa HONO have the potential to serve as atmospheric HONO sources. We report here the importance of surface acidity rather than bulk soil pH in determining the HONO uptake coefficients onto actual soil and other substrates under atmospheric conditions as well as the key role that amphoteric Al and Fe (hydrrous) oxides play in determining surface properties. Kinetics experiments were performed using a coated-wall flow tube coupled to a highly sensitive chemical ionization mass spectrometer (CIMS). Additional experiments measuring the evolution of HONO from NO$_2^-$ adsorbed to pH-adjusted surfaces and the determination of surface charge support these conclusions.
Iron hydroxide nanoparticles play an important role in aqueous systems by absorbing heavy metal contaminants. When formed on surfaces, iron oxides can effectively sequester contaminants; when formed in solution, can transport them downstream. Organic compounds are also ubiquitous in aquatic environments and may exist as surface coatings or as coagulants in water treatment systems. Therefore, in order to better understand iron hydroxide nanoparticle formation, it is crucial to include systems with organic surface coatings. To study this, we used a unique, simultaneous small-angle X-ray scattering (SAXS) and grazing incidence (GISAXS) technique to monitor nanoparticle nucleation in solution and at substrate surfaces. Quartz, and polyaspartate- and alginate-coated substrates were chosen as model substrates found in these systems. After 2 h of reaction, polyaspartate (the most negatively charged substrate) had 10 times less precipitation of positively-charged iron hydroxide nanoparticles than quartz (least negatively charged substrate) implying that electrostatics do not govern nucleation. Quantification of surface functional groups indicate that polyaspartate fewer surface functional groups than alginate; yet, more than two times as many surface functional groups than quartz; therefore, functional group density was also eliminated as a nucleation mechanism. Contact angle measurements indicated that hydrophilicity was the dominant mechanism as quartz is highly hydrophilic and polyaspartate the least hydrophilic. This work provides in situ quantitative information of hetero- and homogeneous nucleation to help predict the fate and transport of nanoparticles in the presence of organic matter in the environment.
Measurement of the C K-edge in environmentally relevant samples

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Determining the chemical speciation of carbon in soils and sediments is important for elucidating the role of organic matter in contamination mobility and carbon cycling. Despite these important applications, bulk soft x-ray absorption spectroscopy at the carbon K-edge has not been extensively applied to environmental samples until recently. The primary reasons for this gap are the lack of non-UHV beamline endstations that are suitable for soft x-ray measurements of so called ‘dirty samples’ and the technical challenges related to acquiring and normalizing spectra from dilute carbon containing samples.

On the Spherical Grating Monochromator beamline at the Canadian Light Source, the development of procedures and instrumentation for the collection of the C K-edge from dilute carbon containing environmental samples has been ongoing. Sample preparation procedures have been established that allow for consistent results and sample loading into the high vacuum endstation is routine. The use of a customized silicon drift detector array allows for the acquisition of partial fluorescence yields, removing complications that arise due to nonlinear backgrounds and second order effects. A monochromator slew scanning mode has been implemented to minimize the dose applied to the sample and prevent beam-induced oxidation of the organic matter. Lastly, accurate normalization at the C K-edge has been made possible by measuring the x-ray scattering from a carbon free substrate to determine the first order incident flux of the beamline. These technical developments have resulted in the ability to obtain C K-edge XANES from standard samples with as little as 0.2% carbon by weight.

As part of a major upgrade to the SGM beamline, an ambient pressure endstation is being installed in 2015. This endstation will feature an optical microscope, an 8 element silicon drift detector array, x-ray focusing to 10 x 10 microns as well as a hexapod sample positioning system. Studies of the spatial distribution of organic matter, coupled with light element microspectroscopy at the 10 micron scale will be possible under controlled atmospheres.
New Opportunities for Soil and Environmental Science Research using the Proposed Multi-bend Achromat Lattice Upgrade of the Advanced Photon Source


The Advanced Photon Source (APS) is planning a new storage ring magnet lattice design – the multi-bend achromat (MBA) – that promises a revolutionary increase in brightness two orders of magnitude beyond that of the current APS. The new MBA lattice technology will provide three key improvements over the current APS design: the ability to focus all of the X-rays from an undulator to sub-micron size, dramatic increases in coherent flux, and orders of magnitude increase in brightness per X-ray pulse for time-resolved experiments. These new capabilities will open up new scientific opportunities in soil and environmental science research.

Solving important soil and environmental science questions requires characterization of samples at all scales, from the molecular level through field scale. Enhanced characterization of highly heterogeneous natural materials, made possible by the new MBA capabilities will particularly advance the understanding of processes at the nano- and meso-scales. This presentation will outline some of the key technical aspects of the MBA upgrade and provide some examples of soil and environmental science applications where the advanced capabilities will extend knowledge of the properties of earth materials and related processes.

The essential feature of the MBA upgrade is the replacement of each of the large synchrotron bending magnets, devices in the accelerator used to curve the electron beam to produce a closed loop, with multiple, smaller bending magnets. The result is a dramatic reduction in the horizontal emittance of the electron beam which in turn greatly increases the brightness of the X-ray sources.

Soil and environmental science applications that will particularly benefit from these advances will be any that can take advantage of higher flux in smaller beams. Notable are scanning probe applications involving microbe-mineral interactions, such as those that control the speciation, migration and toxicity of contaminants, and those that are important in nutrient and metal cycling in the oceans. Higher flux in smaller spots also translates into more rapid chemical and mineralogical mapping of larger samples at higher spatial resolution. Greater analytical speed will also allow the characterization of more rapid geochemical reactions and better definition of intermediate states. The MBA upgrade will allow for increasing the intensity in the focal spot on the sample until radiation damage rather than beam flux is the limiting factor.

An exciting opportunity is the ability to obtain detailed chemical state information at the highest spatial resolutions (~ tens of nanometers) using resonant inelastic X-ray scattering (RIXS) measurements at fixed-incident-energy with crystal analyzers or high-resolution energy-dispersive detectors (currently under development) and zone plates or KB mirrors for focusing. Such analyses are currently limited by small-scale instabilities associated with energy-scanning methods.

The coherence of the X-ray beams is a property that the geoscience community has yet to exploit to any great extent but has enormous potential. One example is the application of coherent diffraction imaging which allows a detailed structural analysis of minute samples without the use of focusing optics which can degrade resolution. The MBA upgrade to the APS will increase the coherent flux by a factor of 100, and hence dramatically increase the capability of coherent X-ray imaging.
The accumulation of Ni in “garnierites” from Falcondo lateritic deposits (Republica Dominicana) elucidated by means of microXAS.

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ABSTRACT:

The Falcondo Ni-laterite deposit (Dominican Republic) contains a significant amount of “garnierites” (Ni-Mg bearing phyllosilicates). Despite its geological relevance and economical interest, no detailed studies exists with regards the crystallochemical characterization of Ni incorporated in (or attached to) the main Ni-containing minerals forming the lateritic profile from the Falcondo Ni-laterite deposit. The garnierites are found within the saprolite horizon as fracture filling and coating joints. In this study a set of samples corresponding to different stages of “garnierites” development have been selected and studied by means of powder X-ray diffraction (XRD), electron probe micro analysis (EPMA) and synchrotron radiation microfocus X-ray Fluorescence (XRF) and X-ray absorption spectroscopy (XAS) to gain structural and chemical information on Ni. The data obtained has revealed that the lateritic regolith decomposes to a mixture of phyllosilicates, maghemite with some fosterite relicts. The elemental mapping from the “garnierites” showed a migration from the original regolith towards the new precipitated phyllosilicates and demonstrates that Ni is preferably accumulated within the phyllosilicates structure. The local environment of Ni shows a Ni-Ni coordination at 3.07-3.08 Å that does confirm that Ni is accumulated forming clusters within the phyllosilicates in “garnierites”. These results are comparable to those obtained by the authors on falcondoite and kerolite standards from the same site. Thus, this study demonstrated that using XAS microfocussing techniques allowed to determine the decomposition of the regolith and showed the migration of Ni from the host mineral fosterite to the new precipitated phyllosilicate phases in “garnierites” across the Falcondo lateritic deposits.
Speciation of Nickel in Solidified/Stabilized Waste Form

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Treatment by solidification/stabilization (S/S) with cement-based binders is an option for wastes that cannot be prevented or reduced, such as metal treatment sludges from a variety of industries. The sludge is usually produced by treating the metal plating waste with alkaline solutions such as those of calcium or sodium hydroxide. It is expected that the metals will precipitate as hydroxides. Mixing of the sludge with cementitious binders usually leads to significantly less leaching. The exact process by which this occurs is still not clear. X-ray absorption spectroscopy, which studies the local structure, should be of great help in studying this problem. A similar process is also practiced by the nuclear waste industry but in that case the waste is usually directly mixed with the cementitious binder.

A metal treatment sludge from an industrial source containing tens of thousands of ppm of nickel, copper, nickel and zinc was solidified/stabilized (S/S) with different proportions of portland cement, ground granulated blastfurnace slag, calcium hydroxide (lime), and fly ash to produce solidified/stabilized waste forms.

The wasteforms were studied by X-ray diffractometry (XRD), thermogravimetric and derivative thermogravimetric analysis (TG/DTG), Fourier transform infrared (FTIR) and X-ray absorption (XAS) spectroscopy.

Very weak peaks of metastable α nickel hydroxide were identified in the sludge by XRD but could not be detected in the solidified/stabilized wasteforms at all. Principal component analysis of nickel K edge XANES showed that only one nickel species is present in the wasteforms and it is identical to the one in the sludge. Nickel K edge EXAFS indicated that nickel is present in the α hydroxide form which is metastable and unlike the stable β form. The alkaline environment of the binders did not induce its re-speciation and the solidified/stabilized process thus mechanically encapsulates the waste in the cementitious matrix.
Nanoparticles Down the Drain – Then What?

Kirk Scheckel
EPA

Nearly 7 million tons (dry weight) of biosolids (sewage sludge) are produced annually in the United States at roughly 16,500 wastewater treatment facilities (WWTF). Approximately 55% of biosolids are land applied; the remainder is incinerated for energy recovery, processed for compost or landfilled. Historically, biosolids were a source of metal contamination in the environment until regulations were developed to limit the amount of metals in land applied biosolids. Nanoparticles are commonly used in consumer products and are released to WWTF through bathing, flushing, and washing of clothes. Nanoparticles pose a potential risk if released to the environment through WWTF biosolids. While the concentration of nanoparticle-derived metals in biosolids has not exceeded regulatory limits in national surveys yet, the potential reactivity of nanoparticles in environmental systems is a cause for concern. The purpose of this research was to assess the chemical transformation of nanoparticles in aged, fresh, and incinerated biosolids from a pilot scale WWTF and composted municipal solid waste in order to provide information for nanoparticle life cycle analyses.

Typically, regulations on metals in the environment are based on total concentrations regardless of the speciation and solubility of the target element. While this provides a very conservative approach to risk, it may impair practical aspects of environmental, social, and economic variables necessary for a community to function. The application of synchrotron techniques in environmental science can demonstrate which forms of metals in environmental systems pose a real risk to humans and ecosystems, which goes far beyond determination of total concentrations.
Interfacial Reactivity of Pu and Th at the Muscovite (001) Basal Plane

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The geochemistry of the actinides is of utmost importance in understanding and predicting their behavior in contaminated legacy sites as well as nuclear waste storage facilities. The unique chemistry of this group of elements including strong hydrolysis, complex redox chemistry, and the potential for polymerization reactions in combination with the actinides’ inherent radioactivity and toxicity makes studies challenging. However, especially for artificial elements like Pu and other transuranics, no natural analogues are available and homologues frequently fall short in accurately reproducing the actinides’ behavior.

We will present and discuss recent results from in situ resonant anomalous x-ray reflectivity (RAXR) and crystal truncation rod (CTR) experiments, shedding light on the interaction of Th(IV)1 as well as Pu(III)2 and Pu(IV)3 with the negatively charged muscovite (001) basal plane. The example of Th(IV) demonstrates how the strong hydration of the highly charged cations prevents a close approach to the surface, instead favoring adsorption as a highly hydrated extended outer sphere complex. Subsequently, it will be shown how similar adsorption behavior in combination with the complex redox chemistry of plutonium, leads to a surface-enhanced formation of nanoparticles.

Results from surface x-ray scattering will be supplemented by ex situ alpha-spectrometry quantification and atomic force microscopy (AFM), to yield a more complete understanding of the interfacial structure.

Literature

An X-ray absorption spectroscopy study of Cd binding onto a halophilic archaeon

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This study uses bulk Cd adsorption isotherm experiments and X-ray absorption fine structure (XAFS) spectroscopy measurements to examine the binding environment of Cd adsorbed to the halophilic archaeon Halobacterium noricense. Halophilic archaea may influence the mobility of toxic metals such as Cd in underground high ionic strength aqueous systems by adsorption to the cell wall. The isotherm experiments indicate that adsorption is not strongly affected by pH within the tolerance range of the archaeal species (approximately 5.5-9.7). Kinetics experiments indicate that adsorption is slow, reaching maximum adsorption after about 8 hours of equilibration time. Preliminary study seems to suggest that Cd adsorption is irreversible. Isotherm experiments indicate a limited number of sites available for Cd adsorption, as the amount of adsorbed Cd plateaus and remains relatively constant once maximum adsorption is attained. XAFS results indicate that adsorption occurs mainly at sulfur sites, with careful comparison of the EXAFS region showing significant differences from the CdS powder standard. This suggests that the Cd attaches to the archaeal surface via sulfhydryl binding.
Environmental toxic metal contamination remediation and prevention is an ongoing issue. Graphene oxide is a promising material that adsorbs significant quantities of a wide variety of heavy metals under different pH and ionic strength conditions. We present X-ray absorption fine structure (XAFS) spectroscopy results investigating the binding environment of Pb(II), Cd(II), and U(VI) ions onto multi-layered graphene oxide (MLGO). Analysis indicates that the dominant sorption mechanism of Pb and U to MLGO changes as a function of pH. In contrast, the sorption mechanism of Cd to MLGO remains electrostatic across a wide range of pH values for a variety of pH values and ionic strength conditions. Determination of the sorption mechanism of various metals to MLGO will guide remediation strategies and prevention methods for toxic metal removal from aqueous environments.
Identification of Minerals Hosting Trace Elements in an Unusual Ore Deposit Using Synchrotron-based Microanalysis

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Prairie Creek is an unmined high grade Zn-Pb-Ag deposit in the southern Mackenzie Mountains of the Northwest Territories, Canada, confined within the boundaries of the Nahanni National Park. The upper portion of the primary quartz-carbonate-sulphide vein mineralization has undergone extensive oxidation, forming high grade zones rich in smithsonite (ZnCO₃) and cerussite (PbCO₃). This weathered zone is a significant economic resource and a potential component of mine waste material. This research is focused on the characterization of the geochemical and mineralogical controls on metal mobility at Prairie Creek, with particular attention to the metal carbonates as a host for trace elements. Analyses were conducted using a combination of scanning electron microscopy (SEM), electron microprobe analysis (EMPA), LA-ICP-MS (laser-ablation inductively-coupled plasma mass spectrometry), and synchrotron-based μXRD and μXRF techniques.

Results include the identification of previously unknown minor phases that host potentially hazardous elements (e.g. cinnabar HgS) and economically important metals (acanthite Ag₂S). Antimony is hosted in the Pb-Sb-oxide bindheimite. Arsenic is hosted in several arsenate phases including adamite, mimetite, duftite, bayldonite, arsentsumebite, segnitite and beaudantite. Synchrotron-based μXRF and μXRD proved to be very useful for mineral identification, element distribution, and correlation analyses. Targets of unknown phases or interesting elemental composition were pre-selected using SEM and EMPA. The majority of phases that were still unidentified after EMPA were successfully identified through μXRD and the HighScore™ peak matching software. Element maps and correlations from μXRF enabled the identification of trace elements distribution patterns and associations. Not all phases could be definitively identified, however, nor all μXRD peaks reliably matched with specific minerals, either due to poor diffraction, or complex mineral mixtures. Higher energy elements, like Sb, Cd, and Ag, could not be easily detected at trace concentrations at the beamline that was used for most of the synchrotron work. Time was also a limiting factor, and precluded analyses of all unknown phases, as well as allowing for only a few large scale maps to be created that could be used for representative correlation analyses.

Results from this research will be used to design the optimal processing and waste management plan for this ore deposit.
Oxidative corrosion of uraninite (UO$_2$) surfaces

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Uraninite (UO$_2$) is the most abundant uranium ore mineral, the product of proposed bioremediation strategies for uranium-contaminated soils and aquifers, and its synthetic analog is the primary constituent of most nuclear fuels. It incorporates interstitial oxygen up to a stoichiometry of UO$_{2.25}$ without disruption of the uranium lattice, but the structural details of the process are the subject of ongoing study and debate. Because the solubility and dissolution kinetics of uraninite depend heavily on the oxidation state of uranium, understanding the mechanisms of UO$_2$ surface oxidation and corrosion is essential to predicting its stability in the environment throughout the nuclear fuel cycle. To date, however, no study has addressed this process at the atomic scale at ambient pressure and temperature.

We present synchrotron-based crystal truncation rod (CTR) x-ray diffraction studies of pristine and oxidized UO$_2$ (111) and (100) surfaces. The clean (111) surface shows minimal contraction of the uppermost atomic layers and a layer of oxygen or hydroxyl group adatoms above the vacuum-terminated surface. Upon exposure to dry O$_2$ gas, an oxidation front proceeds into the crystal, interstitial oxygen atoms penetrate to depths of 30 Å or more, surface-normal layer distances contract (consistent with bulk uraninite oxidation), and an ordered superlattice with three-layer periodicity forms, laterally commensurate with the underlying bulk. Using first principles computational methods we show that this non-classical diffusion is driven by electron transfer from multiple uranium atoms to each interstitial oxygen. X-ray photoelectron spectroscopy indicates the presence of both U(V) and U(VI) in the oxidized layer, consistent with our computational results.

Oxidation under liquid water results in dissolution and roughening of the surface, which is enhanced in the presence of dissolved CO$_2$. Similar oxygen surface penetration and layer contraction are observed upon oxidation of the (100) surface. The structures determined here contrast with previously published structures for bulk UO$_{2+x}$ and U$_4$O$_9$, and highlight the importance of surface structures in controlling surface-mediated processes such as corrosion and dissolution.
Elucidating the Oxidation and Speciation of Uranium in Marcellus Shale Utilizing Synchrotron Microscopy and Spectroscopy

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The Marcellus Shale of the Appalachian Basin is a type of methane-rich black shale from which natural gas can be extracted using hydraulic fracturing (fracing). In addition to being rich in organic matter, the shale can also be abundant in trace metals, including but not limited to: uranium (U), barium, zinc, copper, chromium and nickel depending on locale and lithology. The goal of this study is to gain knowledge of the speciation and binding environment of U in the Marcellus Shale, which will assist in proper assessment of the geochemical risks related to fracing.

Twenty two samples, including 16 from 3 different cores, 2 outcrop and 4 drill cuttings, with bulk U concentrations between 9 and 86 ppm as measured by ICP-MS, originated from various locations in NY, PA, and WV. Uranium X-ray absorption near edge spectroscopy (XANES) spectra of all samples and extended X-ray absorption fine structure (EXAFS) spectra of selected samples were collected using a 100 element Ge detector on beamline 11-2 at the Stanford Synchrotron Radiation Light Source (SSRL). Absorption at the U LIII edge was identified in samples with uranium concentration greater than 20 ppm. The initial analyses of all spectra indicate that the majority of the uranium is present as U(IV), potentially as uraninite (UO\textsubscript{2}) (pending further LCF against standards). These data indicate that uranium is resistant to oxidation as no precautions were taken to limit exposure to atmospheric oxygen during the collection and processing of these samples (e.g., selected core samples were archived for 40 years). In addition, U(IV) was found to dominate in drill cutting samples (materials brought to the surface during drilling of the production well); which indicates that the particular drilling processes of these samples did not cause significant oxidation of the uranium. The dominance of U(IV) in Marcellus Shale is consistent with data from 1 M bicarbonate extractions on core and drill cutting samples which released <4% of the total uranium in each sample. This prevalence of U(IV) is also consistent with data from various geochemical leaching experiments that release < 2% uranium.

Thin sections made from one outcrop sample and two shale cores were studied via mesoprobe and microprobe combined with micro-XANES at beamlines 10-2 and 2-3 at SSRL. Spot sizes of 50 \textmu m and \sim 2 \textmu m for mesoprobe and microprobe were used. Uranium appears to be relatively evenly distributed in the fine-grained sample matrix with noticeable “hot spots” of higher concentration. Micro-XANES spectra were consistent with bulk analyses, implying the dominance of U(IV) in the more concentrated hot spots.

This work demonstrates the dominance of U(IV), the more insoluble form of uranium, in samples used in this study. However, further study will be required to investigate the impact of oxidation processes on uranium mobilization from Marcellus Shale samples.
Seeing the Forest through the Trees: Environmental Science with X-ray ‘macro’ probes

Ryan Tappero, Photon Sciences Directorate, Brookhaven National Laboratory

This talk will highlight several recent research projects that were well matched to the capabilities of the NSLS microprobes. It will premise with the fact that researchers want smaller beams for higher spatial resolution and brighter beams for better detection sensitivity, but still need chemical probes that can examine the centimeter and millimeter scales. The age-old analogy of “seeing the forest through the trees” captures the idea of multi-scale imaging and the complementary nature of sub-micron and super-micron X-ray probes.

In the first science example, the localization and speciation of calcium (a macro-nutrient) in whole leaves of wildtype and mutant cultivars of alfalfa were examined as part of a biofortification effort (Punshon et al.). Sample size was several centimeters and target element concentration was approaching weight percent. Wildtype and mutant cultivars had similar leaf morphology and bulk Ca concentration; however, calcium localization was altered at the whole leaf scale by the gene knockout, and Ca speciation was shifted toward a more bioavailable form.

In an enviro-toxicology study, researchers had a need for quantitative imaging of chromium (Cr) in tissue of the small intestine (duodenum) of mice following Cr(VI) ingestion (Seiter et al.). Recent studies reported that mice developed duodenal tumors upon chronic exposure (20 mg/L) of hexavalent chromium. Sample size was several millimeters and target element concentration was low parts-per-million. Exposure to Cr(VI) induced villus damage (e.g., blunting) and crypt hyperplasia; the crypt compartment is where stem cells reside. Chromium accumulation averaging 10 µg/g was observed in the duodenal villi, as trivalent Cr(III), but was absent from the duodenal crypts.

Chromium chemistry in forsterite (Mg$_2$SiO$_4$) within the MacAlpine Hills 88136 EL3 chondritic meteorite was studied (McKeown et al.). Understanding Cr valence states can shed light on the $f_{O_2}$ conditions of formation for these meteorites. Sample was a petrographic thin section with 50 – 200 micron size forsterite grains having ca. 0.13 wt% Cr. XANES findings indicate highly reduced Cr$^{2+}$ species, and EXAFS data indicate an average 2.02 Å Cr-O nearest neighbor distance and 2.69 Å Cr-Si second-nearest neighbor distance consistent with Cr$^{2+}$ substituting for Mg$^{2+}$ in the forsterite M(1) site. Forsterite in this condrite is an ideal crystalline Cr$^{2+}$-silicate standard.

In conclusion, a range of environmental systems can be studied with super-micron resolution and moderate photon flux. In some cases, lower flux density is beneficial due to reduced sample damage. Furthermore, samples that are centimeters or millimeters in size are measured efficiently with super-micron probes, and the importance of scaling-up results cannot be overemphasized. Lastly, the utility of super-micron probes extends to a more efficient and effective use of the sub-micron probes, allowing one to “see the forest” before looking at the trees.
Hg(II) bacterial biouptake: The role of organic ligands in solution and spectroscopic evidence of ligand exchange reactions at the cell surface

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Understanding how chemical speciation influences the biouptake of metals is crucial to predict their fate in aquatic environments and the effect they have on living organisms. We have used a whole cell biosensor to investigate how the chemical speciation of aqueous Hg(II) affects its biouptake. The reporter system consists of a model gram-negative bacterium (Escherichia coli) with a chromosomally inserted merR::luxCDABE fusion. Synthetic aminopolycarboxylate organic ligands (EDTA, DTPA, EDDS, and NTA) as well as naturally-occurring thiol-containing ligands (cysteine, penicillamine, and glutathione) were used to control Hg(II) speciation in solution. We observed that all aminopolycarboxylate ligands are able to promote the biouptake of Hg(II), following trends unexplained by Hg(II) speciation. Hg(II) biouptake was enhanced in the presence of micromolar concentrations of cysteine, whereas it was inhibited in the presence of penicillamine and glutathione. Bioreporter exposure to increasing concentrations of Hg(II) fully complexed with EDTA, DTPA, EDDS and cysteine showed that the extent of uptake is dose-dependent until a plateau is reached (Fig. 1A). Additionally, Hg L_{III}-edge XANES spectra of Hg(II) associated with the bioreporter membrane under the conditions used to perform the biouptake experiments suggest that a ligand exchange reaction occurs between the Hg(II)-EDTA complex and thiol moieties at the cell membrane (Fig. 1B). We conclude that ligand-exchange reactions at the cell surface explain the bioavailability of Hg(II) complexed with EDTA in solution and must play a critical role in the bacterial biouptake of Hg(II).

Figure 1: (A) The luminescence emitted by the Hg biosensor (E. coli) in response to increasing concentrations of Hg in the presence of 1 mM organic ligand, where Hg is fully complexed with the organic ligand. Luminescence intensity is indicative of the concentration of intracellular Hg(II). The dotted line represents luminescence emitted in the absence of added organic ligand. (B) Normalized Hg L_{III}-edge XANES spectra of Hg standards – Hg(cysteine)$_3$, Hg(cysteine)$_2$, Hg-EDTA, and Hg(acetate)$_2$ – and samples – Hg at the cell surface of the biosensor initially introduced as 50 µM and 500 nM Hg pre-equilibrated with 1 mM EDTA or in the absence of organic ligand. The cell concentration was $\sim 3 \times 10^8$ cells/mL.
Non-destructive technique analysis of environmental contaminants in museum eggs: Unlocking environmental secrets in old bird eggs.

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Collecting eggshells was a popular hobby at the turn of the twentieth century, thus there are numerous egg collections from that time. When eggs are laid, pollutants or contaminants in the mother’s blood are deposited in the eggshell. Many of the private collections now reside in museums where they represent a potential window to the environment at that time. It is unthinkable to use destructive techniques on museum samples, so we have developed a non-destructive technique using a microcapillary optic on an energy resolving detector to collect fluorescence data from the inside of the eggshell matrix, the volume between the inner and outer surfaces. Because arsenic was heavily used in taxidermy prior to the 1970’s, it is important to rule out any incidental surface contamination of museum specimens. XANES from one eggshell clearly shows the arsenic to be As (V). We measured the depth-resolved fluorescence from osprey eggshells dating from 1891 to 1897 from 5 different locations across the US and found that the metal concentrations differed in eggs from different locations, although all eggs had arsenic contamination. Differences included the presence of titanium, copper, manganese, iron, zinc, and lead. Osprey eggs from 1918 and eagle eggs from 1913 taken from the same watershed had similar metal contaminants. An osprey egg fragment from 2014 from that same watershed showed an absence of arsenic and lead after the 100 year span while there was an increase in manganese which is currently used in smelting and as an additive in unleaded gasoline. This technique promises the potential to extract environmental toxicology information from museum egg collections while guarding against any incidental surface contamination.
Iron mineral phases are an important factor in determining the fate of both nutrients (e.g., C, N, P, S) and contaminants (e.g., As, Cr, U, Cd, Se) owing to their inclination toward both biological and chemical processes in the environment. For this reason, the transformations of iron (hydr)oxides under reducing conditions have been extensively investigated. However, several environmental systems such as riparian zones and rice paddies are subject to fluctuating redox conditions, which undoubtedly affect mineralogy and consequently the fates of nutrients and contaminants. This study examined the transformation of ferrihydrite (Fe(OH)_3) during anoxic (with Fe^{2+} acting as a reductant) and oxic periods in an effort to elucidate the mineralogy in redox dynamic environments. Fe-K edge EXAFS spectroscopy demonstrates that during anoxic periods goethite dominates the mineralogy at a low ratio of Fe(II)/g ferrihydrite, while a higher ratio promotes the formation of magnetite. Unlike previous investigations of iron minerals in redox dynamic systems, metastable phases such as ferrihydrite (low Fe^{2+}) and maghemite (high Fe^{2+}) form during oxic periods. Results from this study demonstrate redox dynamic conditions influence iron mineralogy differently than strictly reducing conditions. These variations in mineralogy have implications for the mobilization of contaminants and nutrient biogeochemical cycles in redox dynamic environments and merit further investigation.
Environmental fate of engineered nanomaterials determined by X-ray absorption spectroscopy

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The early 21st century is witnessing a transition of nanotechnology from discovery to commercialization. With the increasing use of engineered nanomaterials (ENMs), one needs to better characterize their environmental fate and potential impacts on ecosystems. Although numerous studies have evidenced the toxicity of ENMs to various organisms, a fundamental understanding of the transformations of ENMs in the environment is necessary to unveil the toxicity mechanisms and to reasonably assess the corresponding risks. Herein, we present X-ray absorption spectroscopy (XAS) studies of ENMs in aquatic environments. First, the transformation of nano-ZnO in multiple aqueous media used to perform toxicity tests was explored. Results show that nano-ZnO is converted to other Zn species in phosphorus buffer saline (PBS) and most cell culture media, indicating that toxic effects observed in those matrices are unlikely due to nano-ZnO per se. Further, we used XAS to probe Zn speciation in the particulate fraction of nano-ZnO/nano-TiO₂ mixtures dispersed in Lake Michigan water. Linear combination fits (LCF) of XANES and EXAFS spectra consistently quantify the partition of Zn(II) between nano-ZnO and Zn²⁺ adsorbed on nano-TiO₂. It explains the chemical interaction of nano-ZnO with nano-TiO₂, as described by a simple kinetic model. Second, Ti XAS spectra of environmental samples collected from a wastewater treatment plant (WWTP) and natural sediments were obtained and analyzed to characterize the speciation of TiO₂, which is closely linked to the photoactivity of phototoxicity of nano-TiO₂. We discover that WWTP samples exhibit distinct features compared to natural sediments, and the dynamics of TiO₂ phase composition in WWTP samples within a two-month duration was captured. These findings provide insights about the sources and toxicity potential of nano-TiO₂ in natural aquatic environments.
Nucleation of Uranyl Phosphates in the Presence of Mineral Surfaces

As the result of historic uranium mining and milling activity, 6.4 trillion liters of U contaminated groundwater has been reported in the United States alone. The most common strategy for remediation of contaminated groundwater is biostimulation resulting in the reduction of aqueous U(VI) to less soluble U(IV)O₂. Although UO₂ is stable under anoxic conditions, remobilization of U may occur at remediated sites with naturally oxic conditions. As an alternative to or to complement this remediation approach, the addition of phosphate has been used to cause the precipitation of sparingly soluble U(VI) phosphate minerals. The addition of phosphate has also been shown to reduce the mobility of U by enhancing U(VI) adsorption onto mineral surfaces. Although uranyl phosphates are known to be stable under environmental conditions, little is known about the reactions controlling their formation. The mechanisms controlling precipitation of uranyl phosphates must be understood in order to design an effective remediation approach for contaminated sites. The objective of our work is to examine U(VI) reactions with phosphate in the presence of mineral surfaces.

Experiments were conducted at pH 8 with montmorillonite or goethite, 100 µM phosphate, and with varying concentrations of U(VI). The pH was chosen to simulate the slightly alkaline conditions common to U contaminated sites. After 48 hours of reaction, both the aqueous phase and the mineral phase were collected for analysis. Results show that a nucleation barrier exists between uranyl adsorption and precipitation of uranyl phosphates. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy was performed on selected samples in the transition between U adsorption and precipitation in order to examine changes in local U structure. Differences between the nucleation barrier and the extent of adsorption and precipitation were observed between montmorillonite and goethite, indicating that uranyl phosphate nucleation behavior is dependent upon the type of mineral surface present.
What X-rays can tell us about the interfacial profile of water near hydrophobic surfaces

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The free surface of water and the interface between water and a hydrophobic surface both have positive interface energies. The water density near a free surface drops below the bulk density, and thus it is expected that water near a hydrophobic surface will also show density depletion. In addition to the fundamental condensed-matter interest in the nature of the interfacial fluid phase, hydrophobic surfaces are common in nature; therefore, the structure and properties of water near hydrophobic surfaces are important in a large variety of geobiological and geochemical contexts. Understanding the behavior of interfacial water is crucial, for example, to predicting the behavior of molecules such as proteins in aqueous environments and to modeling wet chemical reactions at interfaces.

Synchrotron X-ray scattering is the preeminent tool to study interfacial liquid/solid structure. However, efforts by multiple groups to detect and characterize the predicted gap at water-hydrophobic interfaces have produced contradictory results. We have studied the interface between water and fluoroalkylsilane self-assembled monolayers using specular X-ray reflectivity and analyzed the parameter-space landscapes of the merit functions being minimized by data fitting. This analysis yields a better understanding of confidence intervals than the customary process of reporting a unique best fit. We conclude that there are unambiguous gaps at water-hydrophobic interfaces when the hydrophobic monolayer is more densely packed.

References:

2- S. Chattopadhyay et.al., Physical Review Letters 107, 249802 (2011)
The Sulfate Coordination Environment in Schwertmannite

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Schwertmannite (Fe₈O₈(OH)₆₋ₓ(SO₄)ₓ·nH₂O) is an abundant mineral and plays an important geochemical role in acidic iron- and sulfate-rich environment. Presumably, schwertmannite is a tunneled structure resembling akaganeite but with sulfate ions existing in the tunnels. Thus, sulfate acts as a template ion and stabilizes the tunnel structure. Understanding the stabilization role of sulfate requires information on the sulfate coordination environment, which, however, is still being debated. Previous studies using infrared spectroscopy (IR) suggested that sulfate was Fe-bonded, H-bonded, or existing as free protonated sulfate species in the schwertmannite structure. In contrast, S K-edge XANES spectroscopic analyses indicated a negligible amount of Fe-bonded sulfate ion. The inconsistency is owing to that both IR and XANES analysis provide indirect structural information, preventing convincing characterization of the sulfate coordination environment. In the present study, we used recently available S K-edge EXAFS spectroscopy to directly determine the S local atomic environment in both wet and air dried synthetic schwertmannite samples. S EXAFS analysis clearly showed a S-Fe interatomic distance of 3.17 ± 0.05 Å with a coordination number of ~2 for the air dried sample, suggesting that sulfate ions were mainly Fe-bonded in the bidentate-binuclear mode. Surprisingly, no second coordination shells were observed for the wet sample, indicating sulfate was not Fe-bonded, probably H-bonded or existing as free sulfate ions under wet conditions. The results have important implication for understanding schwertmannite structure, formation mechanism, and crystal chemistry.

Figure 1. A comparison of the fitted data to the experimental for S K-edge EXAFS spectra and their Fourier transforms of the air-dried and wet schwertmannite samples, and a bidentate-binuclear structure of sulfate binding to schwertmannite.
Sorption mechanisms of Cd(II) ion to hematite ($\alpha$-Fe$_2$O$_3$) nano particles with varying size and pH environment.

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Naturally occurring mineral nanoparticles have gained attention due to their wide occurrence in soil and high sorption capacities for cationic and anionic contaminants due to their small size and different surface coordination environment compared to the bulk. Hematite ($\alpha$-Fe$_2$O$_3$) is a mineral whose particles are found in the nano-sized region. This study involves investigating the sorption mechanisms of the highly toxic heavy metal cadmium to hematite. The sorption mechanisms are investigated under different hematite particle sizes (8nm and 40nm surface area normalized (SAN)) and different pH environments (pH 7.5 and pH 9). The adsorption edge experimental results suggested particles sorbed more Cd(II) as the pH environment was increased and the particle size was decreased. X ray absorption near edge structure (XANES) results on the smaller nanoparticles and the 40 nm SAN at pH 7.5 indicated the presence of similar coordination environment around the absorbing Cd atom. However, the larger nano particles at higher pH value indicated the presence of more than 60% of cadmium carbonate precipitate. Extended X ray absorption fine structure (EXAFS) results reveal binding site details as a function of pH and particle size and will be presented.
Protactinium (Z=91) is a naturally occurring radioactive element in the actinide series. Its longest lived isotope, $^{231}$Pa, is formed as part of the $^{235}$U decay series. Because of its position in the actinide series between thorium and uranium, the electronic structure, and therefore the observed chemical properties of protactinium are hypothesized to be intermediate to that of the actinide f- and transition metal d-behavior. Industrially, Pa is a substantial component of thorium based nuclear fuel cycles, being the decay intermediate between fertile $^{232}$Th and fissile $^{233}$U, and is a ubiquitous component of all nuclear waste. Owing to its scarcity, most experiments with Pa have been conducted on the tracer scale with little if any direct structural information being obtained. Our recent experiments at the Advanced Photon Source using macroscopic quantities of protactinium have focused on its chemistry in fluoride containing solutions. EXAFS experiments, coupled with laboratory based Raman spectroscopy, inorganic synthesis of Pa complexes, and single crystal X-ray diffraction studies have allowed us to identify the stoichiometry and structures of aqueous protactinium fluoride complexes across a wide range of fluoride concentrations. In addition to EXAFS studies of Pa, we have also investigated the aqueous speciation of Ta and Nb fluoride complexes, the transition metal homologues of Pa, in order to make observations regarding the hypothesized intermediate behavior of protactinium as both an actinide and transition metal. This work was conducted at the Argonne National Laboratory and the Advanced Photon Source at Argonne National Laboratory, operated for the U.S. Department of Energy, Office of Science by UChicagoArgonne LLC under contract number DE-AC02-06CH11357, and the Office of Science Early Career Award Program.
Effects of resuspension on speciation and mobilization of zinc in sediments

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Abstract:
Metal contaminants deposited in sediments are not permanently sequestered, but instead slowly release to the water column, posing ongoing threats to aquatic ecosystems. The fate of metal contaminants is strongly regulated by the coupling of hydrodynamic transport and biogeochemistry in sediments and pore waters. While many of the relevant processes have been studied individually, it is extremely important to understand how they interact to control the mobility and bioavailability of metals in sediments. We conducted a series of laboratory experiments in Gust mesocosm chambers to study the effects of overlying flow and sediment resuspension on the redistribution of metals between sediments, pore water and the overlying water column, and associated changes in metals speciation. X-ray absorption spectroscopy (XAS) analysis revealed that oxidation of surficial sediment generated weakly-bound metal species, liberated aqueous metals to the pore water, and contributed a net flux of metals to the overlying water. In addition, episodic resuspension caused transient changes in metals concentration and speciation in both pore water and overlying water. XAS analysis indicated that dissolution of resuspended particles mobilized zinc during the resuspension event. The results obtained in the experiments clarified that oxidation and dissolution of zinc-sequestered species in surficial sediments control the mobilization of metals in the sediments, and episodic resuspension enhances sediment oxidation and efflux of metals from sediments. The results obtained here can also be used to improve assessments of the effects of hydrological variability on net, long-term efflux of metals from contaminated sites.
Precipitation Pathways for Ferrihydrite Formation in Acidic Solutions

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Ferric iron (Fe$^{3+}$) oxides and oxyhydroxides (abbreviated as Fe oxides unless otherwise stated) are among the most important environmental minerals, playing crucial roles in nutrient cycling and contaminant fate and transport. Fe$^{3+}$ hydrolysis and subsequent polymerization and precipitation is the major formation pathway for Fe oxides in many aqueous environments. Knowledge of the pathway at the molecular scale has important implications for understanding the environmental mineralogy and chemistry of Fe oxides. Identification of the intermediate metal polymeric species is a critical step in elucidating formation mechanisms, and hydrolysis products, particularly oligomers and polymers, and their role in the formation of nuclei and particles, have been extensively investigated. Much information has been gained on Cr$^{3+}$, Rh$^{3+}$ and Al$^{3+}$ hydrolysis and precipitation processes as these occur slowly due to slow ligand-exchange rates, allowing separation and detailed structural characterization of each intermediate formation product. However, Fe$^{3+}$ hydrolysis and precipitation occurs very rapidly, and any intermediate products larger than dimers have not been isolated and successfully characterized, greatly hindering revelation of the reaction mechanisms.

In this work, using combined quick-EXAFS, UV-vis, and Mössbauer spectroscopic approaches, we were able to identify and quantify the long-time sought ferric speciation over time during ferric oxyhydroxide formation in partially-neutralized ferric nitrate solutions ([Fe$^{3+}$] = 0.2 M, 1.8 < pH < 3). Results demonstrate that Fe exists mainly as Fe(H$_2$O)$_6^{3+}$, $\mu$-oxo aquo dimers and ferrihydrite, and that with time, the $\mu$-oxo dimer decreases while the other two species increase in their concentrations. No larger Fe oligomers were detected. Given that the structure of the $\mu$-oxo dimer is incompatible with those of all Fe oxides, our experimental results suggest that reconfiguration of the $\mu$-oxo dimer structure occurs prior to further condensation leading up to the nucleation of ferrihydrite. The structural reconfiguration is likely the rate-limiting step involved in the nucleation process. Further condensation reactions, into oligomers and eventually the ferrihydrite phase, must occur very quickly with low activation energy barriers, such that these species, including dihydroxo dimers are not present in detectable concentrations using available methodology. By providing novel kinetic data and Fe$^{3+}$ speciation analysis, this work is an important step towards a complete revelation of the complicated Fe$^{3+}$ hydrolysis and polymerization chemistry.