

Working Group on the Environmental and Earth Sciences

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1. Introduction and Overview

Synchrotron light sources, primarily in the hard x-ray energy region (4 keV to 30 keV), have had a major impact on research in the environmental, soil, and earth sciences over the past decade and will, in all likelihood, continue to grow in importance in these areas in the foreseeable future. The emergence of the multidisciplinary field now referred to as molecular environmental science (MES) is a direct offshoot of research on environmental-science problems conducted at US. Department of Energy (DOE) synchrotron light sources during the past 5 to 10 years [1]. In the U.S. and Canada, there is an established community of experienced users from MES and the earth sciences that currently numbers about 200. There is also a growing number of new and inexperienced users from a variety of fields who fall under the MES heading. This expanding synchrotron user base in MES and the earth sciences requires (1) x-ray energies ranging from the infrared to the hard x-ray, (2) higher flux and higher brightness beamlines, (3) beamline optics that produce microfocused beams for spectromicroscopy and imaging studies, (4) state-of-the-art x-ray detectors, (5) more beam time on a regular basis, and (6) strong user support at each of the DOE light sources.

MES synchrotron-based research is conducted in both basic and applied contexts. Some of the fundamental research areas that have emerged during the past decade include studies of chemical processes at environmental (mineral-aqueous solution) interfaces, usually involving simplified model systems, using x-ray absorption fine structure (XAFS) spectroscopy and photoemission and studies of the interaction of water and metal-ion adsorbates with mineral surfaces using vacuum-ultraviolet (VUV) L-edge spectroscopy. There have also been some important XAFS studies of reaction kinetics that involve direct monitoring of the transformation of contaminant species as a function of time and system conditions. Over the past five years, MES researchers have also begun to use XAFS and microXAFS spectroscopy and other synchrotron-based methods to study the speciation of contaminants in real environmental samples, which are characterized by compositional heterogeneities on spatial scales ranging from nanometers to centimeters. In addition, there have been XAFS and microXAFS studies of phytoremediation processes in hyperaccumulating plants and soft x-ray spectromicroscopy studies of the reduction of iron and manganese oxides by bacteria, of functional groups on humic and fulvic substances, and of the interaction of heavy metals with microorganisms. These more applied studies, which rely heavily on the results of model-system studies for interpretation, have shown that XAFS and microXAFS spectroscopy can provide quantitative information on the speciation of contaminants ranging from chromium to plutonium in contaminated soils, sediments, mine tailings, tank wastes, plants, and organisms that cannot be obtained directly by other means.

In order for the results of XAFS and microXAFS analysis of complex environmental samples to be of real use to the regulators and engineers responsible for environmental assessment, remediation, and management, it will be essential to conduct large numbers of routine XAFS, microXAFS, and soft x-ray spectromicroscopy measurements on environmental samples in the future. Furthermore, there is also much fundamental MES research to be done using these methods to provide the basis for understanding important environmental processes. Thus, there is a pressing need for a number of synchrotron beamlines that are dedicated to these methods and that are permanently staffed and easily accessible to environmental users. There are a number of hard x-ray (4 keV to 30 keV) XAFS stations, as well as several microXAFS and powder-diffraction stations available to this user base on a peer-reviewed-proposal basis at the Advanced Light Source (ALS), Advanced Photon Source (APS), National Synchrotron Light Source (NSLS), and Stanford Synchrotron Radiation Laboratory (SSRL) (about 5.5 full-time equivalent beam stations in 1998 [2]). Within the next year, there will also be

several new hard x-ray beamlines optimized for XAFS and microXAFS spectroscopy at the APS (GSECARS-CAT, PNC-CAT, BESSRC-CAT) and SSRL (Beamline XI-2), which will increase the total number of full-time equivalent hard x-ray beam stations available to MES researchers to about 8.0 in 1999 [2]. However, there is no soft x-ray/VUV beamline at any of the U.S. synchrotron sources that is optimized for and dedicated to MES-type research. One of the primary objectives of this working group was to assess MES research opportunities in soft x-ray/VUV science and the need for a beamline of this type at the ALS. Given the unique brightness of the ALS in this energy region, the ALS is particularly well suited for soft x-ray/VUV spectromicroscopy applications. Given the importance of this energy region in the environmental and earth sciences areas, there is a clear need for such a facility. One of the major recommendations of this working group is that a spectromicroscopy beamline dedicated to MES should be built at the ALS and operated in the energy range of from about 800 eV to 4,000 eV. Such a beamline would provide unique information on the elements with low atomic numbers (low-Z elements, such as sodium, magnesium, aluminum, silicon, phosphorus, sulfur, and chlorine) that dominate the materials comprising the bulk of the Earth's crust. There is also a very clear need for an MES-dedicated ALS spectromicroscopy beamline that can access the K edges of boron, carbon, nitrogen, oxygen, and fluorine, which are also of great importance in the environmental and biological sciences. This combination of beamlines would provide unparalleled opportunities for cutting-edge soft x-ray/VUV MES research at spatial scales and energy resolutions that cannot be achieved at other U.S. synchrotron-radiation sources.

Although this working group focused primarily on MES applications of the ALS, in large part because of the make-up of the working group, there are many interesting and important applications of synchrotron-radiation methods in the earth sciences, most of which utilize hard x-ray synchrotron beamlines. These include: (1) studies of dissolution and sorption reactions at mineral surfaces, especially in contact or after reaction with aqueous fluids, (2) studies of trace element distributions in earth and planetary materials, (3) *in-situ* determinations of the compositional variations and coordination chemistry of metal ions in hydrothermal solutions and in fluid inclusions in minerals at temperatures and pressures characteristic of the Earth's crust, (4) characterization of amorphous geological materials and their analogs, and (5) studies of mineral phases and phase transitions under conditions of very high pressures and temperatures. Some of the most important advances in these domains have only been possible because of the availability of synchrotron radiation. More details on these topics can be found on pages 62 to 65 of the November 1997 report on DOE synchrotron-radiation sources and science by the Basic Energy Sciences Advisory Committee Panel chaired by Robert J. Birgeneau [3].

Several research areas were chosen for special emphasis by the Working Group on the Environmental and Earth Sciences, and the report is organized around these topics. Although our focus is on the ALS and its unique capabilities for soft x-ray/VUV spectromicroscopy and photoemission studies of environmental materials and processes, many of the topics discussed in the subgroup reports require complementary studies using both hard x-ray synchrotron-radiation methods and non-synchrotron methods. The research areas selected were:

1. Environmental Science Applications of the Advanced Light Source

Participants: Sally Benson (Co-Chair), Sharon Borglin, Steve Colson (Co-Chair), Steve Wasserman

2. Speciation, Spatial Distribution, and Phase Association of Chemical Contaminants

Participants: Paul Bertsch (Co-Chair), Susan Carroll, Harvey Doner, Robert Marianelli, Satish Myneni, Hans Ruppert, Dale Sayers (Co-Chair), Don Sparks, Albert Thompson, Tetsu Tokunaga

3. Chemical Processes at Solid-Aqueous Solution Interfaces

Participants: John Bargar (Co-Chair), Gordon Brown, Scott Chambers, Daniel Grolimund, Tom Kendelewicz, George Redden, Paul Smith, Glenn Waychunas (Co-Chair)

4. Actinide Environmental Chemistry

Participants: Ilham Al Mahamid, David Clark (Co-Chair), Norman Edelstein (Co-Chair), Donald Reed, Roland Schulze, David Shuh, Lynda Soderholm, Jeff Terry

5. Microorganisms, Organic Contaminants, and Plant-Metal Interactions

Participants: Sing-Foong Cheah, George Cody, Roland Hirsch, Chris Jacobsen, Geraldine Lamble, Brian Tonner (Co-Chair), Sam Traina (Co-Chair)

2. Subgroup Reports

2.1 Environmental Science Applications of the Advanced Light Source

(Sally Benson and Steve Colson, Co-Chairs)

2.1.1 Introduction

The ALS has an important role to play in addressing a number of national environmental issues, including environmental remediation, hazardous-waste management, nuclear-waste management, global climate change, agricultural sustainability, trace-element cycling in ecosystems, and environmental risk assessment. These problems present major scientific challenges, in part because natural systems are extremely complex at a range of scales from the atomic to macroscopic and field scales. Moreover, the behavior of these systems is determined by a complex interplay of chemical, physical, and biological processes in spatially heterogeneous environments. Many fundamental questions remain about these systems, and our ability to predict their dynamic behavior has been severely limited in large part by the lack of fundamental understanding at the molecular, microscopic, and mesoscopic scales. Fundamental questions that remain include the composition and speciation of elements in environmental samples, the spatial distribution of reactants, the dominant chemical and biological processes, and how competing processes interact to control reaction dynamics. The ALS can contribute to the knowledge base needed to address a variety of environmental issues by providing insight into the mechanisms of chemical processes at microscopic scales (from grain to colloid size) and molecular scales. Specifically, it can support the following types of investigations:

- Analytical chemistry (e.g., direct speciation of constituents in complex and wet matrices).
- Quantification of spatial distributions in microscopically heterogeneous media.
- Process definition in complex systems (e.g., reactive chemical transport).
- Environmental dynamics (kinetics of reactions in natural systems).

2.1.2 Specific Environmental Problems That Could Benefit from Investigations at the ALS

2.1.2.1 Fate and Transport of Contaminants in the Subsurface Environment

Past practices have resulted in the discharge of chemical and radioactive materials into the environment at many sites, thereby giving rise to extensive contamination of soils and groundwater. The use of conventional technology for remediation of federal and industrial sites is often cost prohibitive, and new technologies are sought to reduce the expense and/or time of remediation or stabilization.

The development of improved technologies for mitigating subsurface contamination requires an understanding of the factors that control how fast the contaminants move (mass transport) and the fate of the contaminants (degradation or reaction). At the macroscopic level, hydrologic processes (e.g., fluid flow through porous media) and geologic processes (e.g., sorption on soil particles) play important roles. At this scale, soil composition and heterogeneity have a profound influence on contaminant fate and transport. At the microscopic level, it is important to know the speciation of contaminants, that is, the chemical form of the contaminant (e.g., the oxidation state of a metal, whether the metal is complexed, or whether a contaminant is adsorbed to a surface), the mechanisms of species transformations (e.g., adsorption/desorption, redox reactions, etc.), and the influence of colloidal particles on transport and transformation. Speciation affects not only the transport properties of a contaminant but its bioavailability as well. Some chemical species of a contaminant, zero-valent selenium for example, are not readily assimilated by an organism and consequently have low bioavailability. This is an important factor in setting standards for “safe” concentration of environmental contaminants. Molecular-level studies can provide fundamental understanding and critical information about microscopic mechanisms and macroscopic processes important to the success of remediation approaches. For example, molecular approaches can provide equilibrium constants, reaction-rate coefficients, and transport coefficients that determine the partitioning of contaminants between different phases, their speciation, and the microscopic rates at which equilibrium is attained.

2.1.2.2 Storage of Nuclear-Waste Materials

Fifty years of production of defense-related nuclear materials have generated large volumes (hundreds of millions of gallons) of complex mixed wastes that contain large amounts of radioactive materials, as well as hazardous chemical wastes. The long-term storage of much of these wastes will require converting them into durable solid forms. Most disposal options for the tank wastes use glass as the final waste form. There are still unanswered questions about the best formulation of the glass to meet disposal requirements. While hard x-rays have provided important information about the speciation of the waste elements, little synchrotron-based work has focused on the glass matrix, which is made up of low-Z elements, including silicon, boron, and oxygen, all of which are readily accessible for study at the ALS under a range of conditions. The high variability of the composition of high-level tank wastes provides a major challenge, since one waste-form formulation may not work for all waste streams, although that is the current baseline assumption. Fundamental understanding of the mechanisms of glass formation and of glass dissolution can provide the basis for design of new glass formulations with desired properties. Molecular-level knowledge of the binding of contaminant species in glass and the polymerization and depolymerization reactions important in glass and melts, as well as in the dissolution mechanism of glasses, can provide insight into the chemistry of these systems that improves our understanding of the microscopic mechanisms responsible for phenomena, such as phase separation, enhanced dissolution with ionic aqueous solutions, etc.

Storage of spent nuclear fuel from civilian nuclear-power plants is also a major challenge facing our nation. Geologic disposal is the preferred option at this time, and investigations are under way to evaluate whether Yucca Mountain, Nevada, is a suitable site for long-term disposal. It is a daunting scientific challenge to predict the behavior of the waste package, the dissolution of the fuel rods, and how radioactive materials will be transported to the accessible environment over a period of 10,000 years. Molecular-level understanding of all the important chemical processes would greatly contribute to our confidence in recommending a site for long-term storage.

2.1.2.3 Sustainable Agriculture

The growing global population creates ever increasing demand for more food. Enhancing the productivity of agricultural lands to meet these needs and mitigating consequent environmental impacts will require better understanding of soil/water/plant systems. Molecular-level investigations can be used to improve our fundamental understanding of nutrient uptake by plants, carbon and nitrogen cycling in soils, formation and stabilization of soil aggregates, environmental behavior of pesticides and herbicides, mobilization of trace pollutants in soil systems, and disposal of agricultural waste water and products. Improved understanding of these processes will lead to more efficient use of our soil and water resources, while at the same time minimizing the environmental impacts of agriculture.

2.1.2.4 Global Climate Change

Understanding the terrestrial and ocean carbon cycles is a critical link in predicting the long-term effects of CO₂ emissions into the atmosphere. Most of the carbon in the terrestrial biosphere currently resides in these two pools. Molecular-level understanding of the biogeochemical processes that contribute to the existence and enhancement of these pools will increase our confidence in climate change predictions, as well as help guide policy makers toward effective strategies for mitigating the effects of CO₂ emissions.

2.1.2.5 Trace-Element Cycling in Ecosystems

Past industrial processes and mining activities have led to surface-water discharges of large quantities of hazardous metallic and organic compounds. Stream flows and rivers have transported these pollutants over large parts of our estuaries, coast lines, and stream beds. While these constituents are usually present at relatively low concentrations, it is recognized that many processes can lead to accumulation of hazardous levels in some ecosystems. Processes such as accumulation in sediments, microalgae, and plant litter provide the opportunity for higher organisms to be exposed to unsafe levels of these pollutants. Bioconcentration and biomagnification of hazardous substances is also possible in the food web, leading to high exposure for aquatic birds and small mammals that feed at the top of the food web. Understanding of the processes that lead to accumulation and the bioavailability of accumulated species is a critical issue that will benefit from molecular-level studies of these processes.

2.1.2.6 Air Quality

Understanding tropospheric chemistry is key to any response to national concerns about the effects of energy production and use on air quality. Among the number of important issues, aerosols and their interaction with other components of the atmosphere, such as particulates and oxidants, remain poorly understood. The development of emissions standards and rational control strategies requires a detailed knowledge of the physical and chemical processes at work in the atmosphere. The Earth's atmosphere is complex, consisting of a multiphase mixture of gases, liquid clouds and precipitation droplets, solid ice crystals, and liquid and solid aerosols. The role of heterogeneous atmospheric processes are even more poorly understood; for example, heterogeneous processes are now known to play an important role in acid-rain formation and Antarctic-ozone depletion, but they are not understood quantitatively, and the role of heterogeneous processes on oxidant and aerosol formation in the troposphere is even less well understood. The lack of a fundamental molecular-level understanding of important atmospheric processes greatly limits our ability to model the impacts of emissions on atmospheric chemistry and air pollution and to design effective control strategies that have minimal impact on human activities.

2.1.2.7 Ecological and Human-Health Risk Assessment

Development of science-based guidelines for human and ecological health requires a comprehensive understanding of the response of living organisms to insults from radioactive and toxic chemicals. There is thus a critical need for fundamental data on health effects, data that will be an integral component of managing cleanup activities. In the past, animal and tissue studies furnished the primary basis for understanding the adverse health effects of toxic materials and for establishing regulatory guidelines. A new generation of risk assessment will require a fundamental understanding at the molecular and cellular levels of crucial cellular mechanisms and processes to provide a more accurate evaluation of risk and the establishment of genuinely protective statutes and standards. This mechanistic extension is required for both accurate extrapolations at high dose levels in animal studies and the low exposure/dose levels needed to set regulatory guidelines for humans. The one important element in this effort is to provide the structural basis at the molecular and cellular level for the mechanisms, including research in cellular processes involved in genomic protection, cellular response to chemical insults, and the mechanistic basis of bioremediation.

2.1.3 Selection of High-Impact Research Topics

One of the key challenges facing the MES community is to identify experiments that are relevant to the complex systems described above and to develop strategies for applying molecular information to solving real environmental problems. One helpful approach is to examine the hierarchy of spatial scales of importance to these problems. Figure 1 below illustrates the spectrum of important spatial scales and how the experimental capabilities of the ALS can be applied to them. Feedback between investigators working at each of the scales can be used to enhance the relevance of molecular-, micro-, and meso-scale experiments. Likewise, results from such directed experiments will be quickly used to guide field-scale approaches for environmental-problem solving. Establishing collaborations with those working more directly on environmental problems is one of the best ways to select research projects with the greatest impacts.

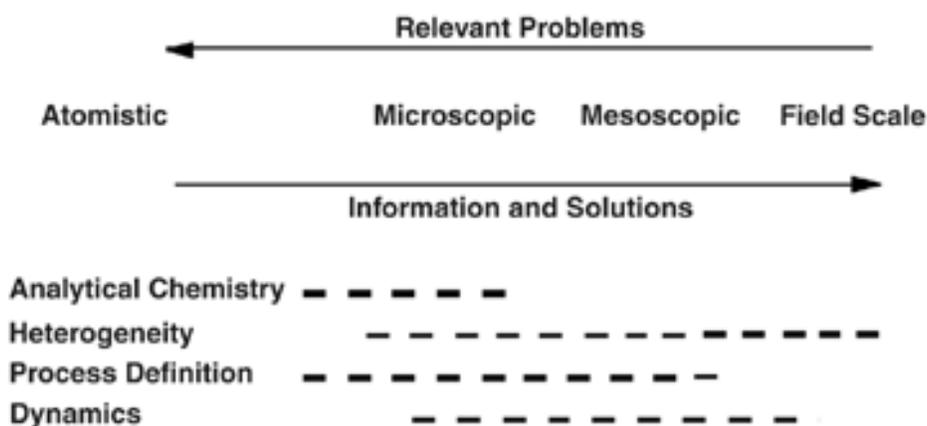


Figure 1. Hierarchy of spatial scales relevant to environmental problem solving.

In selecting high-impact problems, it is important to consider the unique features of the ALS that can contribute to addressing these problems, including the following:

- High flux and brightness in the energy range applicable to the low-Z elements (B, C, N, O, F, Na, Mg, Al, Si, P, S), which include the most abundant elements in earth materials and some of the most important elements in environmental samples.
- Ability to observe natural samples under conditions identical or nearly identical to their original state.
- Ability to examine spatial heterogeneity in natural materials at scales of tens of nanometers to millimeters.
- High spectral resolution for examining the near-edge and extended x-ray absorption fine structure (NEXAFS and EXAFS) spectra of molecules of environmental importance.
- Ability to perform time-resolved spectroscopy on time scales relevant to important environmental processes.
- Ability to perform multiple spectroscopies at different spatial scales and energy ranges on the same sample.

In the last case, soft x-ray/VUV spectromicroscopy and photoemission measurements could be performed at the ALS, and hard x-ray spectroscopy measurements could be performed on the same samples at available hard x-ray beamlines at the ALS or on such beamlines at the APS, NSLS, or SSRL. A standardized sample holder, with easily identifiable fiducial marks, coupled with a standardized sample stage designed to accept the standardized sample holder at MES beamlines at the various light sources would greatly facilitate measurements on the same spot of a sample using different synchrotron-based methods at the four DOE synchrotron light sources. In addition, we foresee a class of user at the ALS who will wish to take advantage not only of soft x-ray microscopes but also of the infrared microscope and the microXAS capability that has recently been demonstrated in the 4-keV to 12-keV energy range.

It is also important to recognize that addressing environmental problems typically requires a multidisciplinary and multifaceted approach to developing solutions and that no single experimental method is likely to provide a unique solution. A variety of complementary analytical methods, including both synchrotron and non-synchrotron techniques, must be used in addressing environmental problems because of their complexity. Hard x-ray synchrotron light sources have proven to be uniquely suited for studying many classes of environmental problems at the molecular level. The challenge presented to this working group is to identify first-order, cutting-edge environmental problems that can be addressed in unique ways using the extremely high brightness soft x-ray/VUV light provide by the ALS.

Important scientific issues will expand across the realms of surface chemistry, analytical chemistry, microbiology, and other disciplines. Even more importantly, there are scientific needs common to all of the focus areas selected by this working group (in Section 1).

Figure 2 illustrates the cross-cutting nature of these focus areas with two of the important environmental problems facing us today. Sections 2.2 through 2.5 provide more information on the opportunities for scientific discovery in each of these cross-cutting scientific topics.

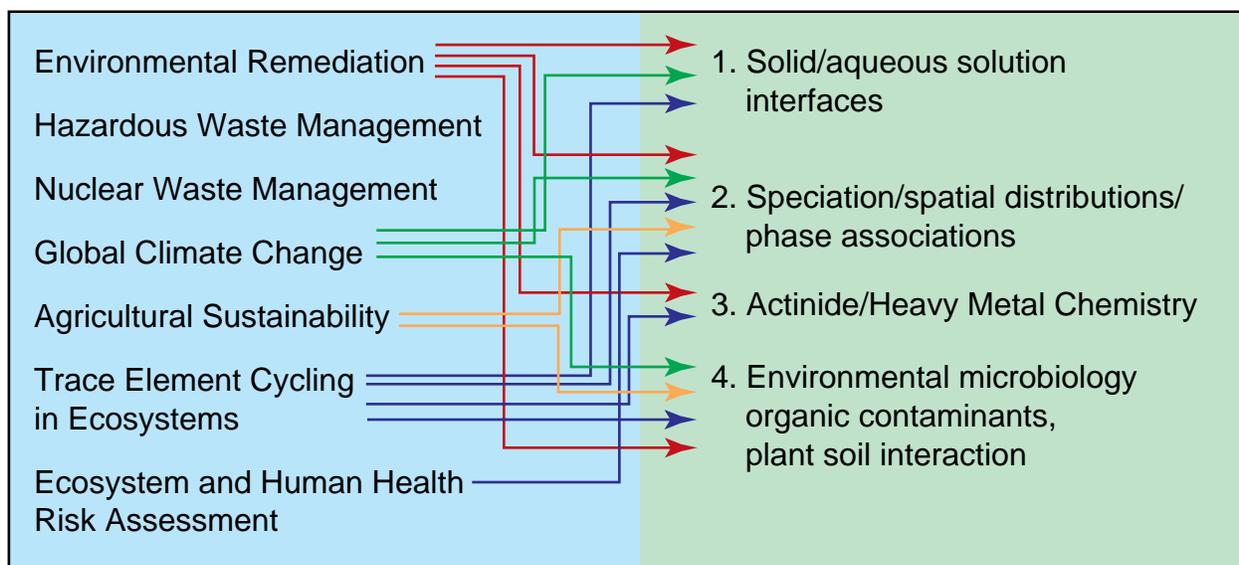


Figure 2. Cross-cutting nature of the scientific areas that form the basis for molecular environmental science.

2.1.4 Meeting the Needs of the Molecular Environmental Science User Community

Making the ALS accessible to the MES user community will require the following:

- High-quality user support.
- High capacity to meet the needs for dealing with the large number of samples commonly used to establish the representativeness of samples/processes and to provide adequate quality assurance.
- A wide range of natural and synthetic model systems representative of natural conditions.
- Rapid data collection and analysis.
- Theoretical support to interpret the spectra.
- Experimental infrastructure to support process-definition and environmental-dynamics experiments (e.g., multi-beamline access, flow-through experimental cells, etc.).

Availability of sufficient beam time is a key question facing the scientific community involved in real-world problem solving. This community must demonstrate that the samples they analyze are representative of the full spectrum of conditions at a field site, which may involve making hundreds to thousands of measurements. Moreover, new analytical tools such as those that could be provided by the ALS are not well known by local, state, and federal regulators. Consequently, they are often not accepted as suitable alternatives to conventional (but more ambiguous) analytical-chemistry techniques. Dealing with this issue will require a multifaceted approach. First, serious consideration should be given to developing dedicated beamlines at several of the DOE-supported synchrotron-radiation sources for high-throughput analysis to meet the needs of this community. Second, scientists who are developing and demonstrating new techniques must first educate the front-line engineers/scientists about the advantages of these techniques and then go with them to the regulators to explain the value in these improved methods. Finally, it must be recognized that we will never meet the needs of the entire environmental-science community for providing these kinds of sophisticated analytical services. Instead, we can work with them to enhance conventional methods of speciating environmental samples, such as sequential chemical-extraction techniques, by validating new techniques.

Another problem in the application of soft x-ray/VUV synchrotron radiation to environmental and geochemical problems is that of the non-expert who requires access to the results of such experiments. This issue relates to attracting new scientists and research problems to the ALS. A two-pronged solution is required. The first is providing easy access to information about a particular experimental station to those who have an interest in performing experiments at the ALS. These additions to the user base will often be seeking to learn whether the ALS can provide new insights into a problem, rather than acquiring immediate results. The infrastructure to support these people must be in place. This includes a designated point of contact for those who are in the exploratory phase of their investigation. The contact should be generally knowledgeable about all of the capabilities of the ALS, and should be able to direct potential “clients” to the appropriate beamline scientist who can provide a definitive answer. At this exploratory phase, a principal investigator working closely with the ALS staff should be able to perform preliminary experiments to demonstrate feasibility of the proposed work. Once the possibility of success has been demonstrated, responsibility for the experiments should shift to the principal investigator. The ALS should be committed, however, to providing adequate user support to ensure that these novice investigators are as successful as possible. It is also essential that the ALS management provide adequate beam time to this growing community of users. The current situation at the ALS results in grossly inadequate beam time allocations to most of the user communities, including the MES/earth-science community.

2.2 Speciation, Spatial Distribution, and Phase Association of Chemical Contaminants

(Paul Bertsch and Dale Sayers, Co-Chairs)

2.2.1 Introduction

It is now widely accepted and well documented with phenomenological observations that chemical speciation controls the mobility of contaminants in the environment, as well as their bioavailability and toxicity. Moreover, it is well established that important environmental interfaces and sorbate/sorbent interactions at these interfaces are among the primary controls on chemical speciation and chemical-species transformations. Over the past decade, there has been an effort to provide fundamental molecular-level information on the mechanisms controlling chemical speciation and chemical-species transformations at mineral surfaces. It has been generally assumed that molecular-scale information on sorbate-sorbent interactions can be used to constrain mechanistic fate and transport models. The utilization of this information to constrain such models at the field and landscape scales has been hampered in many instances by the inappropriate choice of mineral models or by the fact that well-defined monomineralic suspensions often are poor surrogates for natural, multiphase heterogeneous systems, such as soils and wastefoms. On the other hand, molecular-scale investigations of the interaction of chemical pollutants with simplified, well-defined, monomineralic suspensions are essential for unraveling the more complex natural systems, but this approach must be coupled with synchrotron-based studies of the same pollutant species in natural systems. It is only by this approach that information on speciation and chemical-speciation transformations in natural systems can be interpreted.

Over the past few years there has been a steady increase in the number of MES investigations that utilize elemental mapping and spectromicroscopy to interrogate domains within heterogeneous environmental samples via x-ray microprobes and other spectromicroscopic techniques. These studies have indicated that processes occurring at interfaces involving complex mineral assemblages, organic/mineral assemblages, and biological/mineral assemblages, as well as those occurring along pore faces

and fracture linings and in the rhizosphere, control chemical speciation and species transformations over wide ranges of spatial scales. The ability to probe molecular-level environmental processes at grain boundaries, in pores, and along micro- to meso-scale interfaces (e.g., the rhizosphere of plants, which are microbe-rich regions) at environmentally relevant concentrations and the ability to probe the nature of these complex mineral/organic-mineral assemblages are major scientific challenges. X-ray microscopy, micro-x-ray fluorescence, microtomography, and multielement spectromicroscopic techniques are among the most versatile for providing *in-situ* noninvasive elemental-mapping and detailed chemical-speciation information over the large spatial scale required and at environmentally relevant time scales over a wide range of environmental samples (e.g., contaminated soils and sediments, biological samples, wastefoms, etc.). For example, recent applications of synchrotron-based microscale elemental mapping and spectroscopy of zinc, cadmium, and lead in mine tailings from the Tri-State District have provided unique information on the association of these heavy metals with specific types of mineral phases and on the redistribution of zinc and cadmium from primary sulfide phases to secondary hydroxide phases. This type of information is critical for constraining chemical-speciation and contaminant-transport models used to predict the dispersion of heavy-metal contaminants in mine tailings and for realistic environmental risk assessment.

Major scientific issues identified by this subgroup include:

- Molecular-level characterization of important sorbent surfaces in complex multiphase systems, including mineral surfaces and the surfaces of humic and fulvic substances.
- Dynamics of these complex mineral/organic assemblages under varying geochemical conditions.
- Chemical speciation and chemical species transformations of contaminants and other environmentally important elements at environmental interfaces (e.g., mineral grain boundaries, plant root/soil interfaces) and at spatial scales ranging from nanometers to millimeters.

There is a clear need to probe these types of systems with a variety of spectroscopic and diffraction techniques at high spatial resolution (elemental mapping and spectromicroscopy) over a broad energy range (multielement capabilities) at high sensitivity (dilute “wet” systems) and on environmentally relevant time scales (microseconds to hours).

2.2.2 The Potential Role of the ALS in Addressing Problems Involving Contaminants

The ALS offers the environmental and earth-science communities exciting opportunities to begin addressing key scientific questions involving the speciation and transformation of contaminants. One of the greatest challenges in predicting element cycling in natural systems is understanding their chemical speciation and those processes controlling chemical-species transformations. The majority of the Earth’s crust is comprised of elements with K edges in the 1-keV to 4-keV range, and the ALS is potentially a world-class facility in this spectral range. Important environmental questions include both natural and anthropogenically accelerated weathering of soil minerals which can be examined by interrogating aluminum and silicon distributions and phase associations in micromorphological features within soil profiles. Other elements of interest to the MES community include boron, carbon, nitrogen, oxygen, fluorine, phosphorus, sulfur, and chlorine. Boron, for example, is a critical nutrient for animals and plants, but it is also a powerful toxicant at elevated concentrations, with a very narrow range between sufficiency and toxicity. In many regions of the world where irrigation is required for the production of food and fiber, boron is the major element limiting sustainable production. Macroscopic sorption experiments have suggested that aluminum- and iron- oxyhydroxide phases in soils are important in retaining boron, as well as in facilitating the nucleation of insoluble

calcium compounds. However, there is no compelling direct evidence to support these phenomenological observations. Elemental mapping at small spatial scales and spectromicroscopy and microdiffraction could be coupled to recent complementary Fourier-transform infrared (FTIR) and pressure-jump measurements to provide the information critical for understanding the behavior of boron over a wide range of geochemical conditions that can be used to develop strategies for reducing or managing hazards related to elevated concentrations. Similar studies with sulfur and phosphorus are required, as are complementary time-resolved x-ray absorption spectroscopy (XAS) sorption experiments on these important oxyanions with soil mineral phases. Other studies examining spatially resolved redox transformations of carbon, nitrogen, phosphorus, and sulfur across redox boundaries could provide insights into important abiotic and biotic processes.

Other important areas of research that can be addressed by the ALS include understanding the distribution and phase associations of elements such as carbon within soil aggregates, as well as the microstructure of the aggregates themselves as probed by x-ray tomography or x-ray microscopy. Humic substances are important yet poorly understood phases in soil that have a major role in controlling the surface chemistry of soil aggregates and the binding of cations. Most of the information on natural organic molecules indicates that they are a complex mixture of organic polymers having a variety of functional groups with a range of protonation constants. Preliminary studies have shown that NEXAFS spectra of the low-Z element (e.g., carbon, nitrogen, etc.) are useful for examining the functional-group chemistry and metal- and contaminant-complexation trends under a variety of solution conditions and on substrate surfaces. Since these organic molecules are ubiquitous in the Earth's near-surface environment where they often coat mineral surfaces, it is essential that we understand the chemistry and macromolecular structures of these compounds. These techniques can also be used to examine the chemical speciation and distributions of organic contaminants in soils.

The coordination chemistry of metal-ligand complexes has been traditionally examined using element-specific XAFS and other conventional laboratory spectroscopic techniques. However, the complexation constants for chemical states of different elements (including contaminants) are still in need of further development. This fundamental information is essential for understanding contaminant and nutrient dispersion patterns in the environment. For instance, the protonation constants of reactions at mineral surfaces, bacteria surfaces, and other biological material-water interfaces are not well understood. In this regard, exploration of low-Z ligands, such as oxygen and nitrogen, using soft x-ray/VUV XAFS methods could provide unique mechanistic information on the factors determining pKa values and metal-complexation constants. Also this information can complement spectroscopic information obtainable by other methods.

Other critical MES-research areas deal with the distribution and chemical speciation of metal and metalloid contaminants in soils, wastefoms, and biota and those processes leading to chemical-species transformations. Understanding these processes is critical for understanding the fate and transport of contaminants and for designing and evaluating strategies for chemical or biological remediation. Potential areas where the ALS could be used to make unique contributions include spatially resolved L- and M-edge spectroscopy of transition and heavier elements, which would provide detailed information on chemical speciation that would complement elemental-distribution information generated by x-ray fluorescence (XRF) spectroscopy and ongoing studies of K-absorption edge using hard x-ray synchrotron-radiation sources. Preliminary studies have shown that M, N, and (for the heaviest elements) O edges hold great promise in contaminant-speciation studies. These absorption edges can provide complete information on the electronic states of elements that can help in the evaluation of their affinities in complex reactions. Developments in theory should greatly enhance our ability to extract specific information in complex

multiphase systems. Primary examples include studies on oxidation/reduction reactions of selenium and chromium at critical interfaces associated with soil minerals and mineral assemblage. These reactions are important in the immobilization of these potentially toxic elements in soils and sediments, either through natural attenuation processes or as a result of manipulation for deployment of technology for chemical or biological remediation. Simultaneous spectromicroscopy studies of, for example, selenium (L edge), carbon (K edge), nitrogen (K edge), and iron (L edge) within heterogeneous multiphase systems are needed to understand the nature and controls on these oxidation-state transformations in both static and dynamic systems.

2.3 Chemical Processes at Solid-Aqueous Solution Interfaces

(John Bargar and Glenn Waychunas, Co-Chairs)

2.3.1 Introduction

It has long been recognized that adsorption of contaminants onto solid surfaces is a major control on their mobility in surface and ground waters. However, progress in identifying the contaminant-controlling adsorbents has been hampered by the chemical and structural complexity of natural materials and contaminant-adsorbent associations, the dilute concentrations of contaminants in natural environments, and a dearth of techniques capable of probing these systems *in-situ*, *i.e.*, in the presence of water and at ambient pressures and temperatures. Many important natural materials are microcrystalline or amorphous and compositionally variable. Often they occur as coatings on other materials and/or complex multiphase mixtures, with compositional homogeneity on the millimeter down to angstrom scale. To date, *in-situ* synchrotron x-ray fluorescence and spectroscopic measurements in the hard x-ray region have provided a wealth of information regarding the speciation and molecular structures of metal ions adsorbed at solid/aqueous-solution interfaces in model systems. However, x-ray absorption spectroscopy and microspectroscopy investigations on environmentally important elements having K edges in the soft x-ray region (B, C, N, O, Na, Mg, Al, Si, P, S, Cl) have been hampered by the scarcity of intense soft x-ray sources and the practical difficulties of preserving wet samples under high-vacuum conditions. In addition, very few x-ray spectroscopic investigations utilizing natural materials collected from the field have been performed, owing to a general lack of beamlines providing high-intensity focused flux in the soft x-ray region (1 keV to 4 keV). A corollary to this lack of capability is that little is known about the some of the components of soils, sediments, or aquifers that are most responsible for the sorption of pollutant and nutrient species. Currently, it often necessary to assume which matrix components are most reactive when designing model studies of reactive transport in such materials.

With these opportunities and needs in mind, the unique capabilities of the ALS can be appreciated. ALS beamlines provide high flux in the soft x-ray region, the capability to focus x-ray beams to sub-micron spot sizes, and instrumentation to study wet samples in vacuum or low-pressure conditions. For example, with ALS beamlines it should be possible to dynamically follow solid-solute reaction progress involving light elements *in situ* on microscale solid surfaces. We anticipate that this combination of experimental capabilities will drive major breakthroughs in our understanding of chemical speciation and reactions in natural earth materials.

This subgroup identified three overarching challenges in the area of chemical processes at solid/aqueous-solution interfaces that must be addressed in order to model the sources, sinks, and reactive transport of contaminants in the environment and to provide a scientific basis for the design of cost-effective and long-lived solutions to contaminant-remediation and disposal problems.

- What are the environmental solids, including components of multiphase solids, that exert the greatest control over the fate and transport of contaminants in natural waters? For example, what are those solids that have the highest surface areas or highest sorptive capacities for metal ions under common aquifer conditions?
- What are the chemical and physical aspects of the surfaces of these solids that control their interactions with the hydrosphere?
- What are the binding mechanisms and speciation of contaminants, including metal ions, organics, and metal-organic complexes, associated with these solids?

2.3.2 Major Issues Involving Earth Materials and Aqueous-Solid Interfaces

There are three major types of Earth materials with different reactivities that need to be considered and have broad implications for environmental science. Metal (e.g., aluminum, manganese, and iron) oxides and hydroxides, including silicates, are very common as grain-boundary phases and surface coatings on most other mineral grains and have high sorptive capacities for contaminants. Carbonate minerals have very reactive surfaces that can sorb and incorporate toxic contaminants and play a critical role in global carbon cycling. Sulfide materials are electrically conductive and thus can act as electron donors and acceptors in surface redox reactions. They can also be oxidized to release reactive agents, such as sulfuric acid, to groundwater, which often leads to the formation of low-pH groundwater plumes, with subsequent remobilization of sorbed contaminants. Metal oxides, sulfides, and carbonates have varying topological properties, compositional variations, surface defects (e.g., dislocations, stacking faults, growth steps, etc.), and morphologies depending on mode of formation and subsequent alterations. The manner in which these attributes affect reactivity at the mineral/water interface is not well understood, but it is expected to dominate surface reactions. Synchrotron-radiation-based studies alone will not provide the full range of information necessary for complete characterization of these structural, compositional, and morphological features that control chemical reactivity at surfaces, but they will provide essential parts of that information that cannot be obtained using other methods.

It is vitally important to be able to characterize the surface and defect structures in these solid phases in order to (1) understand natural material systems more completely so that heterogeneity and complex structure can be accounted for in geochemical models and (2) develop better model systems incorporating defects and other surface aspects in a controlled manner. This latter consideration is necessary to provide greater control over critical experimental parameters, allow simplification of experimental assumptions, and permit efficient examination of parameter space, which is often necessary for testing hypotheses conclusively. The crucial issues here are identification of the types of defects, their concentration, reactions with water, and reactions with sorbed and other near-surface species. Further, the ability to theoretically model the surfaces and defects is a requirement for interpreting observations and developing a complete picture of the interfacial system.

Several types of surface reactions are important in the control of the fate and transport of toxic contaminants. These include adsorption, surface precipitation, surface-catalyzed redox, and surface-mitigated degradation. Important contaminants include organics, inorganics, and metal-organic ternary complexes, each of which requires specific strategies for detection and characterization. These complexes may be inner or outer sphere, or they may interact with other local species to form precipitates. Effective parameterization of geochemical models is not possible without a knowledge of the reactants, products, and stoichiometries of the reactions involved. Additional reactions include the nucleation and growth of new surface phases or the formation of passivating layers. The formation of passivating layers bears specific attention. Such coatings can restrict further reactions and thus

allow reactive species to be transported far beyond initial sequestration sites. An understanding of surface passivation, and its possible reversal, is needed if accurate models of toxic contaminant transport are to be developed.

Another question closely related to the nature of surface complexation is the nature of the aqueous solution at the mineral/water interface. We do not understand the density, precise composition, or structure of water in the near-interface region. This knowledge is important for accurate models of solvation of species near the interface, the bonding and cohesion of outer- and inner-sphere complexes, and the exchange rates of these species with the aqueous system as a whole.

Finally, much needs to be done to understand reaction rates in decreasing size regimes, including surface transformations, precipitation, and sorption at the nanometer scale, and reactive transport in heterogeneous systems in the grain-size regime (sub-micron to millimeter). Currently, the intermediate or meso-structural regime, comprised of mineral structures, interfacial regions, and co-existing biological entities in the sub-micron to 200-Å range, can only be investigated by transmission electron microscopy (TEM) and other electron-beam, in-vacuum methods that require drying or otherwise altering samples. Analysis of samples on these scales under wet conditions is required to determine chemical gradients, unravel complex heterogeneous mixtures of components, and estimate reaction rates in natural systems.

2.3.3 ALS Applications to Interfaces in Mineral/Aqueous Solutions

2.3.3.1 Characterization of Natural Materials

Most (about 94% by weight) of the surface of the Earth consists of elements whose K absorption edges are in the range from 1 keV to 4 keV. Most of these same species are the major players in natural waters of all types. Hence, investigation of these species in natural materials is fundamental to understanding their chemistry. The ALS bend-magnet source provides high brightness and high flux superior to that at other U.S. synchrotron sources in this energy range at the present time. But more importantly, an ALS undulator source could provide exceptional flux and brightness in this energy range, allowing classes of XAFS experiments not previously possible at these elemental edges. For natural materials, fundamental characterization at the finest possible spatial resolution is needed to understand all of the possible defect and growth structures. This requires both x-ray microscopic imaging and spectromicroscopy capabilities that in-turn require an extremely bright x-ray source. Further, in order to study elements in the range from 1 keV to 4 keV at near-natural compositional ranges, the greatest possible flux is needed. This follows not only from the low abundances of some of the important low-Z elements, but also from the attenuation effects of water and window materials separating specimen and detectors in this x-ray energy regime. An ALS undulator source would be an ideal match for these requirements.

2.3.3.2 Studies of Low-Z Elements

The ALS source provides great advantages for applications involving K edges of the very low-Z elements (boron, carbon, nitrogen, and oxygen). Both ALS bend magnets and larger gap undulator magnets would provide exceptional sources for spectromicroscopy and x-ray microscopy of organic, borate, and nitrate species on mineral surfaces, as well as the interfacial region between mineral grains. Emission spectroscopy can also be employed to aid in identification of particular molecules and characterization of surface geometry, orientation, chemical state, and bonding. These techniques represent tremendous opportunities for the study of biogeochemical processes at mineral interfaces, but they are limited by available technology for beam focusing (zone plates) and detection (scattering effects and very small geometry). Many challenges must be overcome to utilize this opportunity to maximum advantage, including the solution of many daunting experimental problems, the development of improved low-energy high-resolution detec-

tors, the development of new theory to model low-Z x-ray absorption (NEXAFS) and emission spectra, and the simulation of hydrophobic interactions of aqueous solutions and mineral surfaces with accurate electronic-structure theory and molecular-mechanics/dynamics models. This effort will require a broadly multidisciplinary input involving scientists from many institutions.

2.3.3.3 Characterization of Surfaces of Model Earth Materials

Model materials, some prepared with synthetic surface defects, allow a much greater degree of control over experimental parameters than do natural samples; hence models can be used to isolate particular types of interfacial processes. The synchrotron-based techniques currently being used to probe surfaces and interfaces include x-ray standing-wave-induced fluorescence, photoemission spectroscopy, surface and grazing-incidence XAFS, x-ray emission spectroscopy, and photoelectron diffraction. With present U.S. sources, these methods are compromised by low flux and especially by low brightness. However the brightness of ALS bend magnets and particularly of an ALS undulator source would dramatically improve sensitivity throughout this energy range. Even more significantly, methods such as photoelectron diffraction, high-resolution photoemission, photoemission microscopy, and x-ray emission spectroscopy could be applied to wet samples at low energies for the first time with such a source. These methods can provide important information about the electronic and chemical structure of mineral surfaces, but they are difficult to apply under wet conditions unless very high flux and brightness are available in this critical energy region that contains the K edges of the most abundant elements in the environment.

2.3.3.4 Characterization of Surface Complexes and Aqueous Solution Structure at the Mineral/Water Interface.

X-ray standing-wave (XSW) studies and grazing-incidence XAFS methods have not been employed extensively at lower energies, primarily because of flux and brightness limitations at existing synchrotron sources. However, both techniques can provide information about the structure and composition of the near-surface water layer on mineral surfaces, and they are especially important for the elements sodium, aluminum, silicon, chlorine, sulfur, and potassium in natural systems. Grazing-incidence XAFS may be particularly favored because there is much less Bragg scattering and diffuse scattering from substrates than occurs at higher x-ray energies. XSW methods will be able to use larger d-spacing Bragg reflections with larger structure factors at higher incidence angles, also a considerable advantage for probing the electrical double layer at solid-aqueous solution interfaces. Such studies in the energy range from several hundred eV to about 4 keV would be extremely well suited to an undulator source. At the ALS such sources might be used without mirrors, hence avoiding mirror absorption interferences from gold or platinum, which are commonly used coatings. Other complementary techniques that would be useful in determining water structure in this regime are x-ray photoelectron diffraction and holography techniques.

2.4 Actinide Environmental Chemistry

(David Clark and Norman Edelstein, Co-Chairs)

2.4.1 Introduction

The chemistry and physics of actinides are unique in many ways. For example, plutonium exhibits the most complex physico-chemical behavior of any of the known elements. Plutonium metal, for example, exhibits seven allotropic modifications. In some modifications, the 5f electrons are delocalized (itinerant) and bonding, and in other modifications, the 5f electrons are localized (magnetic).

The solution chemistry is equally as rich and complex. The redox potentials that couple the various oxidation states are all remarkably similar at approximately one volt. In addition to the similarity of redox potentials, the tendency of Pu(V) and Pu(VI) to disproportionate, and the slow rate of reactions involving the making and breaking of Pu=O bonds, it is possible for four oxidation states (III, IV, V, VI) to co-exist with one another in appreciable concentrations in the same solution. These factors make the study of fundamental actinide science both difficult and challenging.

The study of actinide chemical and materials properties has recently emerged as an important new area of clear national importance to the environment and to future energy and defense needs, and a relatively large scientific community is currently involved in basic and applied science centered on actinide materials. Many of these researchers are only now realizing the enormous potential of synchrotron-based techniques in solving fundamental and applied problems in actinide science. For example, tunable-energy photons available from modern synchrotron sources provide the capability for a variety of non-destructive experiments on non-crystalline and relatively small samples. The impact of synchrotron-based experiments is now beginning to be recognized within the actinide community, and it is expected to increase significantly over the next several years. Synchrotron-based research is anticipated to have an important impact in areas such as decontamination/ decommissioning, health/ecology/risk, waste forms, fissile materials and storage, spent nuclear fuel, subsurface characterization, waste characterization, waste treatment and destruction, plutonium stabilization, and cleanup.

The ALS will provide the actinide-science community with a unique and complementary x-ray energy range with which to expand fundamental studies of actinide environmental science. Examples of exciting new research opportunities include (1) actinide speciation through spectroscopic examination (absorption, photoemission, x-ray emission) of the actinides themselves and the low-Z elements associated with ligands and substrates (boron, carbon, nitrogen, oxygen, etc.), (2) probing actinide M, N, and O absorption edges where f-electron final states can be observed, (3) the development of new theoretical tools to advance our understanding of the role of f-electrons in actinide materials, (4) actinide surface-science studies to probe the interaction of water and other gaseous molecules with actinide metals and metal oxides, (5) the ability to probe small quantities of radioactive materials due to the high brightness and implementation of spectromicroscopic techniques, and (6) the capability to examine “wet” actinide interfaces in the VUV/soft x-ray spectral region.

2.4.2 Scientific Challenges

2.4.2.1 Surface Chemistry of Actinides

The state of the art in understanding the chemical and structural properties of the surfaces of actinide materials is lagging substantially behind that of other materials systems. Because of radiological safety concerns, the actinide surface-science community has never been able to take advantage of the synchrotron-radiation methodologies in the VUV and soft x-ray regions that revolutionized the approach to surface chemistry and physics over a decade ago. These concerns arise from the difficulty of safely handling, preparing, and performing measurements on actinide surfaces and materials at a soft x-ray/VUV synchrotron-radiation user facility. There have been more than three workshops within the last decade that have specifically addressed the need of the actinide-science community to utilize spectroscopic techniques unique to the soft x-ray/VUV region. Traditional ultrahigh-vacuum (UHV) synchrotron-radiation surface-science experiments need to be performed to understand the surface structures of nominally clean actinide surfaces and to characterize the chemical interactions of small molecules with the surfaces of actinide materials. This knowledge is important to a variety of

actinide-science areas, since advancing the basic understanding of actinide-interface reactions in well-controlled systems directly benefits efforts by those studying processes at complex actinide environmental interfaces. These types of studies span the areas of actinide aging and corrosion, fundamental gas-solid interactions, and fundamental liquid-solid interactions. Specific surfaces of interest include various forms of uranium and plutonium metal allotropes and their corresponding oxide surfaces. Surface chemical reactions of interest include oxygen, water, hydrogen, nitrogen, carbon monoxide, and other small-molecule interactions.

The brightness and flux of the ALS permit the use of actinide microsamples, thereby lessening the radiological risk of handling these materials to an acceptable level. Furthermore, the spectral attributes of the ALS coupled with existing end-station capabilities yield results such as those shown in Figure 3 for actinide microsamples. Specific techniques unique to the soft x-ray/VUV photon-energy region that would be used to investigate actinide surface science will include valence-band and shallow-core-level photoemission, photoelectron diffraction, NEXAFS, soft x-ray emission, and x-ray fluorescence holography. Of particular interest is utilization of soft x-ray emission techniques that are amenable to studies of wet, buried, and poorly prepared actinide materials. Sample requirements include the capabilities to handle larger amounts of actinides to facilitate the preparation of clean, well-characterized surfaces in a UHV environment. In the case of metal or metal-oxide samples, this may require handling up to one gram of non-dispersible material.

Scientific opportunities at the ALS would significantly advance or revolutionize the fundamental knowledge of actinide surface chemistry. Furthermore, these actinide surface-science efforts will also support science-driven programmatic efforts within DOE, including non-proliferation, long- and short-term storage and disposition of nuclear materials, and science-based stockpile stewardship.

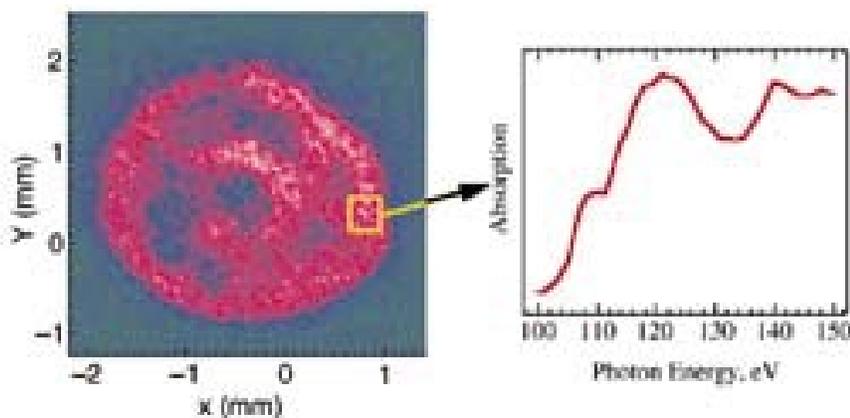


Figure 3. Plutonium (magenta) surface-elemental-concentration map of about 1 microgram of PuO_2 on a platinum (green) substrate obtained from photoemission of plutonium 4f electrons is shown on the left. The right panel is the plutonium near-edge spectrum obtained from the region of the PuO_2 indicated by the box. [Results from ALS Beamline 7.0.1 courtesy of J. J. Bucher, N. M. Edelstein, D. K. Shuh, and E. Rotenberg, LBNL; J. D. Denlinger, University of Michigan; S. D. Kevan, University of Oregon; and B. P. Tonner, University of Wisconsin-Milwaukee.]

2.4.2.2 Transport and Sorption of Actinides

The migration of actinide contaminants in the subsurface will be partially determined by surface interactions between actinide species and the mineral, bacterial, and natural organic surfaces present in the environment. Additionally, anthropogenic complexation may facilitate enhanced transport and affect key surface interactions. A molecular-level understanding of these processes is needed both to predict/model subsurface transport and to design remediation/ immobilization strategies. The ALS can make significant and unique scientific contributions to these molecular-level studies.

There are a wide variety of subsurface environments throughout the complex of sites managed by the DOE where contaminant plumes exist. These include vadose zones in highly silicic iron-rich volcanic ash, groundwater-saturated basaltic rock, deep-subsurface high-salinity groundwaters, and organic-rich near-surface aquifers. Despite this variety, a common theme in the sorption of actinides is the importance and role of metal-oxide minerals. The chemical behavior of actinide/heavy-metal contaminant species in the environment is frequently driven by surface-mediated processes, and it is largely driven by adsorption processes on two types of materials: mineral surfaces, which contain a variety of metal oxides and hydroxides, and colloidal organic matter (COM), which consists of natural humic and fulvic acids and associated compounds.

The ultimate goal here is to understand the fate of the actinides in the environment and the potential risk for contaminant transport from a source term to the far field. This goal is accomplished by understanding the chemical behavior of the solution-borne actinides at the solid-liquid interface. This work also ties in very closely with speciation studies (see Section 2.2) that would in part provide a database of spectral measurements (i.e., core-level binding-energy shifts and valence-molecular-orbital energies) of compounds with actinides in different oxidation states.

There is growing recognition that microbiological interactions play a very important role in defining actinide speciation and mobility in the subsurface. Important interactions include bio-reduction of the multivalent actinides, biosorption, and bio-uptake. Surface complexation of actinide species by microbes, although well established, has not been investigated in detail. This is likely due to the carboxylato, phosphato, sulfato, and nitrogen-based functional groups present on the surface of the microbes in specific geometries. Surface complexation processes may include redox phenomena as well. Soil microbes are typically in the 0.5- μm to 2- μm size range. The key elements for mapping molecular interactions in microbiological systems are ideally situated within the soft x-ray energy range of the ALS. The brightness and flux of the ALS are prerequisites for the spatial resolution needed to distinguish between extracellular and intracellular processes. NEXAFS can be used to provide information on the identity of the actinide element, its oxidation state, and the local coordination sphere about the actinide metal center to identify key details of actinide speciation.

Historically, information about the electronic structure of solid-liquid interfaces has been difficult to obtain. Electron-detection techniques could not be used because of the short attenuation lengths in solution. The capability of performing x-ray emission measurements and XAFS in the total-yield fluorescence mode will allow the study of the electronic structure of these interfaces. By utilizing this technique in the soft x-ray region, both the oxidation state of the actinide and the oxidation states of the light elements in the ligands can be determined. This information cannot be directly observed in the hard x-ray regime.

Experimentally these measurements would be made initially by studying sorption of actinide ions and compounds onto homogeneous, well-understood, and well-characterized planar surfaces of metal oxides and oxyhydroxides of mineralogical interest. These include silicon, aluminum, and

iron-oxide and iron-oxyhydroxide materials. Sorption involves a variety of actinide oxidation states and chemical compounds of interest (carbonates, nitrates, etc.). Chemical interactions of actinides with COM is relevant because of the potential for strong complexation by various functional groups on these materials and their presence in environmental ground water. These experiments may be performed as an actinide/COM binary system or as an actinide/COM/mineral-surface ternary system. Finally, adsorption experiments onto real, heterogeneous, mineral surfaces are required to tie the fundamental investigations to the appropriate environmental situation.

Key advantages and features of the ALS in this general research area include:

- Spectral resolution for speciation studies.
- High spatial resolution for imaging/microscopy of real heterogeneous mineral surfaces.
- Focused beam to investigate small samples (radiological materials).
- Low-energy photons for valence-band and shallow-core-level photoemission.

2.4.2.3 Speciation of Actinides/Heavy Metals

Speciation was identified in the Airlie Workshop Report [1] as one of the most important factors influencing the behavior of contaminants in complex environmental systems. Depending on the system of interest, there are various degrees of detail to which the system has to be defined. Elements of speciation include (1) the identity of the element, (2) the physical state, (3) the oxidation state, (4) the empirical formula, and (5) the detailed molecular structure.

A wide variety of techniques were listed in the Airlie Workshop Report along with the approximate sensitivity limits. Synchrotron techniques were discussed, and it was pointed out that XAFS spectroscopy and variable-wavelength x-ray diffraction techniques provide unique information not available from the usual laboratory-based methods. The ALS provides unique capabilities for studying actinide materials in the soft x-ray/VUV energy region because the small beam size and high brightness allow the use of radioactive microsamples and make it possible to measure directly both the metal ion (M, N, and O edges) and the ligands (K edges), including ligands containing low-Z elements, such as carbon, nitrogen, oxygen, fluorine, and sulfur. An important need is the development of experimental end stations so that radioactive and “wet” samples can be measured with photons in the energy range from 50 eV to 1500 eV to obtain detailed information on “real” samples.

2.4.2.4 Waste Forms

The long-term stability and durability of waste forms for radionuclide disposal are being addressed in repository and actinide-stabilization programs. The general types of waste-form matrices being considered are glasses, ceramics, cements, and the as-is storage of spent nuclear uranium-oxide fuel. Durability issues are centered on surface oxidation and corrosion, stress due to both lattice defects and radiation damage, and solubility of the various phases. Thus, the waste-form materials-science community is a natural candidate to utilize the spatial and spectral resolution of the ALS. This is especially true since many of the important interacting constituents of waste forms can be investigated by XAFS at the K edge (boron, oxygen, alkali metals, aluminum, and silicon) only in the energy regime for which the ALS is optimized. Currently, many of the structural issues in waste-form glasses with these low-Z elements are investigated by nuclear magnetic resonance (NMR) of surrogate materials. However, the capability of the ALS to study small samples will permit the investigation of “real” waste forms containing radioactive material.

In many respects, the scientific issues in this topical area are similar to those being addressed in the areas of speciation and surface chemistry. Molecular-level interactions centered on waste form constituents such as the actinides (M, N, and O thresholds), alkali metals, boron, oxygen, aluminum, and silicon can be studied in the energy range below 2 keV, which is a unique strength of the ALS. Interactions centered on wetted surfaces, near-surface alteration layers that define apparent solubility, and phase identification/characterization in encapsulated and incorporated actinide phases are key to predicting and understanding the long-term durability of waste forms.

2.4.2.5 Fundamental Electronic and Magnetic Structure of Actinides

The major question in actinide chemistry and physics is the nature of the 5f orbitals and their role in chemical bonding. For example, in the light actinide metals and metallic compounds, the 5f orbitals are extended, and 5f electrons display delocalized (band-like) properties. In the heavier actinide metals and metallic compounds, the 5f orbitals are contracted, and 5f electrons are localized into discrete bonds. Heavy-fermion materials are the most dramatic and exciting example of the variety of 5f-electron behavior. The f electrons in these materials are localized at room temperature but exhibit an enormous effective mass as they are cooled, and they can even become superconducting at low temperature. To date, this phenomenon has been mainly limited to cerium and uranium compounds, but it should exist in heavier actinides. Variable-energy resonant-photoemission studies of these materials should provide detailed information about their electronic structure. Theoretical efforts to describe the transition region between localized and itinerant configurations and the formation of quasiparticles responsible for heavy-fermion behavior are also needed. Other fundamental problems that can be examined both experimentally and theoretically in heavy-element research include quantification of material properties arising from the influence of relativistic effects, as well as unusual magnetism in systems exhibiting large orbital moments. Fundamental understanding in these areas will provide insight into the chemical behavior of a wide range of materials, not just the actinides.

(1) Soft x-ray/VUV absorption fine structure (XAFS)

The energy position and detailed features of the x-ray absorption edge contain electronic and structural information about the absorbing ion. Because of safety issues, sample size, and availability restrictions, synchrotron-based x-ray absorption methods often provide information not obtainable by other techniques. Information about the oxidation state, nature of the bonding, and local site symmetry are contained within the edge region. Until recently, this information has been largely qualitative. Recent theoretical efforts have begun to change this picture. Modeling approaches involving scattering to continuum final states are beginning to provide a more quantitative picture of near-edge structure. For example, energy positions of the actinide L edges (17 keV to 24 keV) are currently being used to estimate the oxidation state(s) of the actinide ion(s) in complex environments. The structure of the edge resonance can sometimes be used to infer the presence of a trans-dioxo ion. These data are often augmented by data in the extended (EXAFS) region of the absorption spectrum.

Whereas XAFS at the L edges has become a rather routine tool for probing actinide-ion speciation, the potential of the low-energy actinide edges remains relatively untapped, in part because of the lack of a high-intensity, bright, tunable source of photons in the region of interest (80 eV to 5000 eV). The ALS provides photons in exactly this energy region with extreme brightness, which permits the use of safe amounts of radionuclides, thereby allowing access to these transitions. Their importance is understandable when it is realized that the M, N and O_{4,5} edges involve transitions to the valence f

states. It should be possible to extract much more detailed information about the metal-ion environment, bonding, and electronic structure from these edges. Therefore, XAFS spectra at these edges may provide invaluable and unique information about the electronic structure and bonding of actinide ions. Unfortunately, this information cannot be extracted from higher energy edges using the same theoretical procedures that have proven successful for the K and L edges, because these final states are localized, and modeling approaches that are based only on scattering into continuum final states are expected to provide only part of the picture. However, by bringing to bear known electronic-structure information about actinide ions in well-defined environments, already quantified to some extent by the atomic-spectroscopy community, it will be possible to model the electronic contributions to these near-edge spectra. By combining the experimental and modeling expertise of the synchrotron community with the modeling procedures developed by the atomic-spectroscopy community, this problem could be overcome. Two major research groups will be affected by this effort. The first is the actinide- and environmental-science community, where more detailed information about structure and bonding would help to further understand complexation and reactivity of these environmentally important elements. Information of this type has already proven invaluable to transition metal and main group chemistry. The second is the XAFS community. The electronic contribution to near-edge spectra is not well understood currently. By taking advantage of the simplifications to this problem provided by the lower energy absorption-edge data, it should be possible to extend the information content of this emerging spectroscopy.

(2) Resonant magnetic diffraction

The cooperative magnetic behavior of actinide materials is difficult to quantify. Standard procedures, involving neutron diffraction, are vitiated by the small sample sizes available for experiments. Thompson scattering involves scattering of x rays from electron charges, and therefore is insensitive to magnetic moments. Recently, it has been discovered that when the x-ray energy is tuned near an absorption edge, the standard Thompson scattering is enhanced by second-order effects. Diffraction from magnetically ordered spins can be enhanced by as much as a factor of 10^7 for actinide samples when the x-ray energy is tuned to the M edges. Under favorable conditions, the magnetic-scattering contribution to the diffraction profile is comparable to the charge scattering. Although the details of resonant scattering are not yet fully understood, the potential of this technique for providing heretofore unavailable information about magnetic ordering in a variety of compounds germane to environmental stewardship issues is clear. The magnetic behavior of materials such as plutonium alloys are intimately tied in with the details of their electronic structure. The elucidation and prediction of electronic structure in these materials are necessary for predicting materials behavior over the longer term.

2.4.3 Actinide-Safety Considerations

Working with radioactive materials requires the development of sample-management procedures and safety protocols at the beamline facility where radioactive samples are being run. For many of the soft x-ray/VUV studies, this will require a specialized end station in addition to the one that is currently being constructed at the ALS for electron spectroscopy of the actinides. There will also be the need for radiological monitoring, emergency procedures, and special sample-transport and handling protocols. For example, actinide work might employ an air-exhaust system that has continuous air monitors (CAMS) that can be accessed remotely. The set-up, calibration, and maintenance of these monitors must be carried out by appropriately trained personnel. The protocols for performing experiments with radioactive materials require intensive participation from radiological-safety personnel.

2.5 Microorganisms, Organic Contaminants, and Plant-Metal Interactions

(Brian Tonner and Sam Traina, Co-Chairs)

Biological processes and transformations profoundly influence the fate and impact of inorganic and organic contaminants in the natural environment. These processes are inherently complex in that they involve multiple species and phases, as well as a wide range of spatial domains. Fundamental questions remain on the effects and mechanisms of microbial-mineral interactions, microbially mediated redox reactions, plant and microbial uptake of contaminant metals and trace elements, reactions of organic contaminants and natural biomolecules with mineral surfaces, and the role of mineral systems in the origin of life. All of these problems require spatially resolved information and chemical speciation across a range of spatial scales.

2.5.1 Microbial-Mineral Interactions

Many of the reactive surfaces in these environments are coated with microorganisms and/or biomolecules exuded by plants and microorganisms. These interactions can fundamentally influence the interactions of reactive surfaces with aqueous solutions and with polar and nonpolar solutes. Blocking of mineral surface sites by microorganisms or exuded biomolecules may decrease uptake of metals and oxoanions by metal oxides and clay minerals. Additionally, the biosurfaces represented by microorganisms, tissues, and extracellular biomolecules can provide sites that compete with inorganic sites for uptake of dissolved metal ions or participate in ternary complexes comprised of minerals, metals, and organic functional groups. Molecular-level information on these important systems is presently lacking. In particular, information is needed on the local speciation and surface-coordination environments of metals on microbial and plant surfaces, as well as within subcellular structures. Biogeochemically induced changes in metal oxidation states have been observed at the cellular and subcellular level of microorganisms and plants. However the current scale of spatial resolution available is inadequate to fully understand the local chemical environments within and on subcellular organelles that are responsible for observed macroscopic changes in metal concentrations and metal oxidation states. *In vivo* NEXAFS spectromicroscopy on the scale of 0.1 μm (K-, L- and M-edge spectra of metals and carbon, sulfur, nitrogen, and phosphorus K-edge spectra of metal binding sites) will facilitate a much greater understanding of the biogeochemical speciation of metals in natural environments.

Microorganisms also play an important role in the formation of many minerals. Many of the reactive minerals in soils and sediments are of biogenic origin, and microorganisms participate in the formation of precipitates of these solids (metal oxides, carbonates, phosphates, sulfides, etc.). These biogenic phases can significantly alter the solubility and transport of many contaminants in natural systems. For example, the formation of plutonium phosphates by soil microorganisms can potentially decrease the concentrations of dissolved plutonium in groundwater, thus diminishing plutonium transport. These are particularly challenging systems to investigate because the reaction products are often of nanoscale dimensions, with only short-range order and variable chemical composition. Our current state of knowledge is limited by *ex-situ* studies of these systems, which potentially introduce artifacts associated with sample preparation. Additionally, questions remain on the exact composition of these biogenic materials. Conventional microscopic methods can provide information on trace-metal composition, but data on the inclusion of biomolecules are lacking. Yet, it can be anticipated that close association of these solids with microorganisms may result in the incorporation of low-molecular-weight organic acids within the solid matrices. Such possibilities beg for spatially resolved,

spectral information on the contents and speciation of both organic and inorganic components within these materials. With such information, it will be difficult, but possible, to predict their thermodynamic solubilities and long-term stabilities. Lacking this information, such predictions are not possible.

2.5.2 Microbially Induced Redox Environments

The metabolic activities of microorganisms have been postulated to cause the formation of micro-redox environments with local oxidation-reduction potentials much different from that of the bulk solution or the surrounding porous media. The spatial scale of these effects is thought to range from nanometers to millimeters. The former should occur at the buried interfaces between microorganisms and mineral surfaces, while the latter may span from the interior to the exterior of a soil aggregate. These microscopic redox environments could cause important changes in the oxidation state and chemical mobility of important metals and anions that cannot be predicted from the macroscopic redox state of the bulk-soil or sedimentary environment. Unfortunately, direct information on these redox gradients is lacking. Spatially resolved spectromicroscopy would allow the determination of local oxidation states in the environments of interest. This has major implications in the distribution of trace elements, as well as larger scale issues, such as the potential for anaerobic microbial processes (e.g., denitrification and microbial methane production) in dominantly aerobic environments. Whereas trace-element distributions are important relative to local-scale problems of contamination, the production of N_2O and CH_4 by soil and sedimentary microorganisms has implications in green-house gas cycles and global change.

2.5.3 Corrosion and Biofilm Formation

Corrosion shortens the life of pipes, ships, and buildings. It is now recognized that many corrosion reactions are mediated by microbes. The onset of these corrosion reactions often involves attachment of microorganisms to the substrate and subsequent biofilm formation. Spectromicroscopy can potentially help us to answer the following questions: what induces the microbes to attach to the surface and are there particular geometries or conditions that the microbes prefer? A better understanding of microbial attachment and biofilm formation would help in the synthesis and design of corrosion-resistant materials and the preservation of archaeological sites. This could result in significant monetary savings for society.

2.5.4 Origin-of-Life Issues

Clay minerals have long been postulated to have served as a template for the origin of life. Organization and polymerization of base pairs on clay surfaces may well have led to the formation of the first oligonucleotides and proteins. Questions remain on the exact nature of the reactions at the clay-water interface. Spatial variability in layer charge and crystal chemistry of individual clay particles precludes a full understanding of these paleo-organic chemical reactions. Noninvasive *in-situ* studies are needed to examine these local-scale effects on interactions of protein precursors with the clay mineral surfaces.

The potential for life on other planets and/or extraterrestrial origins of life on Earth have recently received greater attention, owing to the reported discovery of extraterrestrial biomolecules in Martian meteorites. Admittedly, much controversy remains concerning the origin of these materials. Nevertheless, the possibility of extraterrestrial microscopic life remains an intriguing concept. A definitive assessment of this possibility is perhaps one of the most scientifically and philosophically challenging

issues for humankind today. Careful examination of extra-planetary materials requires highly resolved spectrochemical information on organic molecules and their surrounding mineral matrix to distinguish between substances produced by biotic and abiotic processes. Such information could be provided by x-ray spectromicroscopy, aiding us in our quest to understand the origin of life.

2.5.5 The Interactions of Plants with Heavy Metals and Trace Elements

The uptake and biochemical transformation of heavy metals and trace elements by plants has long been an area of study in the fields of plant physiology and agriculture. Much of this effort has been driven by the desire to increase production of food and fiber. Recently, considerable attention has focused on the use of plants as extraction systems for the removal of pollutants from soils and aquatic systems. When applied to soils, this process begins with growing plants that can hyperaccumulate toxic elements in their tissues and finishes with harvesting these plants to remove the toxins from the contaminated site. Some hyperaccumulating plants may also transform a toxic species into a less toxic form or produce a volatile species of the toxic element. This field, known as phytoremediation, faces several pressing scientific challenges. Perhaps the greatest of these is determination of the specific loci and chemical composition of metal binding sites within the plant materials. Higher plants are complex multi-cellular organisms with molecular structures that vary in composition at the single-cell and organ levels. Information is needed on the temporal and spatial variations, as well as compositional variations of metal-binding proteins within these organisms. Unfortunately, many of these are located in subsurface structures (roots). Thus, metal-accumulating plants grown in metal-contaminated soils often lead to the accumulation of metals in the roots and not in the above-ground biomass that can be more easily harvested and removed off site. Specific chemical information is needed on the nature of the metal-binding sites within hyperaccumulating plants. Namely, information on the local chemical speciation of the trace elements within the plants as well as the chemical structures of the metal binding proteins must be obtained to develop a comprehensive understanding of this phenomena. Coupling this information with plant-molecular biology methods may lead to better and more efficient metal accumulating plants, ultimately, facilitating timely treatment and cleanup of toxic environments.

3. General Conclusions and Recommendations

Several major conclusions and recommendation can be derived from the information provided above and from the results of two past workshops devoted to synchrotron-based molecular environmental science [1,2]:

3.1 Conclusions

1. Synchrotron-based methods, particularly XAFS, microXAFS, soft x-ray/VUV spectromicroscopy, and photoemission methods, are having a major impact on MES and the earth sciences by providing unparalleled information on molecular speciation of elements ranging from boron to plutonium at unprecedented spatial scales (nanometers to millimeters) in complex multiphase materials. Such methods are also providing unique molecular-scale information on important chemical processes relevant to these fields, including those occurring at environmental interfaces, in plants, and in microorganisms.
2. Although there will soon be an adequate number of hard x-ray beam stations devoted to or available for MES research (estimated to be about 8 full-time equivalent beam stations by 1999), which

should satisfy the needs of this community for the next three years, according to a national user survey [1,2], there is no soft x-ray/VUV beam station optimized for and dedicated to MES research at any of the DOE synchrotron light sources.

3. Technical support of MES and earth-science users at the ALS is currently inadequate, which means that only a few experienced users can effectively utilize the unique capabilities of the ALS in the soft x-ray/VUV energy region.

4. Because of the growing need for routine XAFS and microXAFS analyses of large numbers of environmental samples, it is important for the DOE to consider the development of several beam stations, including both hard x-ray and soft x-ray/VUV stations, at DOE synchrotron light sources that would be devoted to routine analytical work involving XAFS and micro-XAFS spectroscopy. Adequate staffing of these beam stations is an important issue that might be best handled by a small business that would provide an analytical service. Without these types of facilities, it is unlikely that synchrotron-based studies of environmental samples will have a major impact on environmental decision making. It is apparent to the members of this working group that information on chemical speciation in environmental samples could result in enormous cost savings to the U.S. government, as well as private citizens, through improved and more cost-efficient remediation technologies.

5. Based on joint discussions of the Working Groups on the Environmental and Earth Sciences and on New Directions in Surface Science at the ALS Workshop, there is significant scientific and intellectual overlap between these two groups, particularly in the area of surface and interfacial chemical processes, and a need for similar specialized experimental facilities at the ALS. Development of compatible facilities required by these two communities will also lead to desirable collaborations among scientists in these complementary disciplines.

3.2 Recommendations

1. This working group strongly recommends that a beamline be designed and built at the ALS that would operate in the 800 eV to 4,000 eV range and would be equipped with appropriate optics to provide spot sizes in the submicron range for microXAFS applications. The extreme brightness of the ALS in this energy region would result in unique microspectroscopy capabilities for many of the low-Z elements that comprise the bulk of the Earth's near-surface environment. This capability could also be extended to the L edges of the first-row transition metals and the M and N edges of the actinide elements, which are extremely important in an environmental context. Such a beamline would help satisfy one of the most important needs in MES research—quantitative information on the spatial distribution at the submicron scale of the different chemical forms of metal ions in complex environmental samples.

2. This working group also strongly recommends that a beamline designed for spectromicroscopy studies in the VUV energy region (50 eV to 800 eV) be developed at the ALS and optimized for MES applications, including the study of wet samples using differentially pumped sample cells. Innovative research in this area at the ALS is already providing some of the first molecular-scale, chemically specific information on functional groups on humic and fulvic substances, which are ubiquitous high-molecular-weight organic compounds in the environment and are responsible for the sequestering and transformation of many heavy metals. However, the current level of beam time for these types of projects at the ALS is so restricted that little work can be accomplished each year.

3. X-ray emission spectroscopy is a venerable technique that has been explored to new depths at the ALS and has great potential for providing unique information on the bonding of adsorbates at

environmental interfaces, including solid-water interfaces [4]. We strongly recommend that the ALS management devote adequate resources to rebuild the unique x-ray emission capability that was previously provided by the loan of equipment by the University of Uppsala and the expertise of Dr. Anders Nilsson.

4. A concerted effort should be made to increase the level of technical support provided by the ALS to the user community in general and the MES community in particular. This is especially important in the soft x-ray/VUV area where the technical difficulties associated with a UHV experiment are often greater than those in the hard x-ray region, which do not generally require UHV systems.

5. To help stimulate cooperation among the four DOE synchrotron-radiation laboratories in the area of MES research, as well as among individual researchers, this working group recommends that MES beam-station facilities at the various labs be standardized as much as possible so that samples can be transferred from one beam station to another among the facilities for spectroscopic, spectromicroscopic, and diffraction studies on the same portions of a sample using beamlines operating at different energies. A standardized sample stage, with appropriate fiducial marks, and standardized sample holder available at different MES facilities at the four labs would greatly facilitate such studies.

6. The MES effort in the U.S. involves a growing community of users working at all four DOE-supported synchrotron-radiation laboratories. It is essential that future developments of MES beamlines and beam-station experimental facilities supported by DOE funding be based on community needs and community input. In order to help stimulate cooperation among MES users at the ALS, APS, NSLS, and SSRL and to further develop the MES community nationally, an ENVIROSYNC organization should be formed. This organization should meet annually to assess the synchrotron needs of the MES community and to develop a roadmap for future facilities developments.

4. References

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