Annual Report
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| PROGRAM TITLE: | Spectromicroscopy research at the Advanced Light Source |
| PRINCIPAL INVESTIGATOR: | Brian P. Tonner |
| INSTITUTION | Physics Department, University of Central Florida |
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# 1 Progress Report

## STRUCTURE OF COMPLEX SURFACES

The emphasis of our work during the prior year has been to extend the tools of precision atomic structure determination of surfaces to highly complex materials. The systems we are investigating are both natural mineral surfaces, and certain large unit cell structures that are produced metallurgically, or epitaxially grown.

The motivation for this work is to provide an atomic scale picture of the process of adsorption and structural change at complex interfaces in the environment. These interfaces are chosen for their relevance to remediation of actinide contamination of materials and of soils at Department of Energy sites.

This project is providing the fundamental surface physics support as a complementary project to a project that examines the interaction between mineral surfaces and biological agents, primarily bacteria. The principal investigator of this program is a co-investigator on the mineral-microbe interface project, which is funded by DoE/NABIR.

The emphasis on complex surfaces and minerals represents a strategic decision to follow the most scientifically challenging directions of research with the greatest potential relevance to DoE programs. It has resulted in a decrease in emphasis on electronic materials and microelectronics.

The difficulties involved in this project are very stimulating scientifically. We are attempting to evolve the methods of traditional surface science, which have been developed over 30 years for pristine materials like Cu(100) and Si(100), and make them work with the same level of detail and precision on materials that are "harvested" directly from the environment.

During the past year, we have moved our base operation from UW-Milwaukee to UCF. A new laboratory is being completed this academic year, which will include an impressive array of surface structural equipment for student training. Indeed, the list of equipment available rivals that of the largest surface labs in the U.S.: Imaging XPS, Imaging SIMS, UHV STM/AFM, atomic resolution Z-contrast STEM, Rutherford backscattering (RBS), FIB, SAM, and so forth.

We are also installing advanced processing equipment in the lab, coupled to surface analytical tools by UHV transporters. This equipment includes such tools as ion implantation (20-400keV), sputter deposition, and MBE. We expect to embark on unique experiments combining mineral surfaces with tools previously only available in the microelectronics industry.

Brief summaries of the work last year on various systems appears below.

## *1.1 Pyrite*

We have completed a series of surface structural studies of pyrite (iron sulfide) using synchrotron radiation XPD (x-ray photoelectron diffraction) and x-ray absorption spectroscopy (XAS), as well as XPS microscopy. These are the first studies of a mineral surface ever using XPS microscopy.

Among the sulfur-bearing minerals pyrite and marcasite predominate in environmental systems. Both are of the same stoichiometric composition ($FeS_2$) but have a different crystallographic setup. Because of its greater stability pyrite is the most widespread of all sulfide minerals and, as a result of its greater abundance in the eastern United States, pyrite is recognized as the major source of acid mine drainage. Pyrite together with other iron sulfide minerals, when exposed to those metal carrying acidic water, has also been recognized as plausible sorbents and/or reactands for environmental contaminants such as uranyl (U(VI)), Cr(VI), or Cu(2+).

The purpose of this study is to use surface sensitive synchrotron techniques in order to identify sorption sites for uranyl and structures of adsorbed uranyl species on clean and chemically treated sulfide mineral surfaces. This is essential for quantitative prediction of uranyl immobilization by sorption and uranyl transformation by reduction with reactive surface sulfide and/or iron (II) sites. Reduction of U(VI) leads to precipitation of unsoluble U(IV)-oxide which is an even more effective way to minimize the risk of water contamination by U(VI)-compounds.

The study of pyrite has been mainly driven by its prominence in aqueous environmental systems and by its possible usefulness as a photovoltaic material. Pyrite is the most abundant sulfide mineral, and often coexists in ores of other desired minerals. Its presence in coal is the source of sulfur released in burning, which leads to acid rain. In mining operations, the flotation process is generally used for separation by taking advantage of the hydrophobic pyrite surface, resulting in the attachment of air bubbles to pyrite particles.

The mobilization of sulfur and iron resulting from dissolution of pyrite is a major environmental concern. However, pyrite may also be an important model system for remediation research, since the surface of pyrite collects actinides from solution.

Pyrite has recently been identified as a medium for the uptake and possible reduction of toxic uranyl U(VI) compounds.[1] In that study, it was proposed that the additional presence of reduced uranium U(IV) may be correlated with differences in oxidation of the pyrite surface.

Thus, the oxidation of pyrite is of particular practical interest, and is considered to be central to such diverse processes as acid mine drainage and uptake of actinide compounds. Numerous studies have investigated the oxidation process in aqueous, vacuum, and ambient environments, yet surprisingly little can be said about the fundamental aspects. In vacuum, chemisorption studies are difficult because the pyrite surface is inert.

There are several approaches to preparing the clean (100) surface of pyrite in a manner suitable for electron spectroscopic techniques. Most previous studies have cleaved natural or synthetic pyrite specimens, due to the ease with which it can be done in vacuum to expose a "pristine" surface. For our study, cleaving presents several problems. First, pyrite naturally fractures chirally, leaving a surface with significant topography which is problematic in angle-resolved techniques, and faces which are not (100). Second, natural samples may tend to cleave where impurity concentrations are greatest or along structural defects, resulting in undesired contributions. Finally, there has been concern that cleaved surfaces have sulphur-deficiencies in the (100) surface layer, resulting in monosulphide sites which do not represent the natural surface, although it should be noted that at least one study found no evidence for vacancies on a cleaved synthetic sample.[2] Recently, a sputter/anneal procedure was applied to the naturally grown (100) pyrite surface, resulting in a clean and ordered surface.[3] In that paper, it was argued that this may result in a better representation of the natural surface in general. In the present study, we adopted the sputter/anneal procedure as described later.

While certain aspects of the $FeS_2(100)$ surface have been studied in great detail, a comprehensive characterization of the clean surface including electronic and atomic structure has been lacking. Through various synchrotron x-ray techniques listed below, we have attempted to assemble a complete picture of the electronic structure of this material.

Techniques applied in the last year:
1. High resolution XPS to chemically resolve surface levels from bulk.
2. Variable photon energy XPS to identify surface and sub-surface atoms.
3. Angle-dependence of photoemission for band-structure mapping.
4. XPS microscopy to characterize impurities and prepare clean surfaces.
5. XAS determine chemical speciation of adsorbates, inclusions, and defect sites.

These XPS measurements were taken at ALS- BL 7.0 along with XPD, XANES and RESPES measurements. Most of the work focussed on the S-2p core level, which yields the most chemical state information about the pyrite surface, and exhibits at least two distinct surface core level shifts (SCLS). These data form the basis for the XPD measurements, where we attempt to chemically resolve the local atomic structure for the S atoms. Fe core level measurements were included well, but did not offer as much information. The XPS portion of the experiment also served to document the initial cleaning, and subsequent "maintenance" cleaning cycles, by monitoring O and C levels.

## Experimental Procedures

A high-purity single-crystal cubic pyrite specimen from Navajun, Spain with large (~2.5cm) natural (100) faces was obtained. A slab measuring ~6x6x1 mm was cut, presenting a naturally grown surface. The surface was not polished, and was cleaned ultrasonically in methanol and rinsed in ethanol before insertion into the ultra-high vacuum (UHV) chamber. The natural oxidation layer was removed in UHV by sputtering with 240eV Ne+ (6µA sputter current) for 10 minutes. The sample was then annealed radiatively to ~ 350°C to restore surface order. This procedure was repeated about 10 times initially to remove the natural oxidation layer. Only one cycle was necessary every 12-24 hrs. to maintain a clean surface, since $FeS_2(100)$ is relatively inert to typical UHV residual gases. XPS surveys indicated a small amount of oxygen on the prepared surface as the only detectable contaminant. However, we attribute this to the presence of mineral inclusions on surface which cannot be removed, based on SPEM data we obtained on the same surface, as detailed in the next section of this paper. Our method is similar to the method of Chaturvedi, et al. which they employed to preserve surface order and stoichiometry.[1] In that study, the authors found the low sputter energy and light ions to be necessary to prevent excessive damage of the natural surface. Our method differed slightly in that we substituted Ne+ for He+, which permitted slightly faster removal of the oxide layer without noticeably compromising surface order.

Pyrite can be thought of as NaCl cubic, with a $S_2$ dimer at each “Cl” site. In the [100] plane, the dimers alternate between two orientations [111] and $[\underline{1}11]$, resulting in a sublattice structure. After each anneal, a fairly good unreconstructed LEED pattern could be obtained, including the half-order spots associated with the S-dimer sublattice, indicating reasonable long-range surface order. Our pattern is comparable to previous results on $FeS_2(100)$ [4] and the similarly structured $RuS_2(100)$.[5]

All data were collected on BL 7.0.1 at the Advanced Light Source, Lawrence Berkeley Laboratory. XPS, XPD, and partial-yield XANES were obtained using a Phi electron analyzer, usually with a pass energy of 2.95 eV. Overall instrumental resolution was about 100 meV. The angle between the incident synchrotron beam and the analyzer was fixed at 60°, and the angular resolution was better than 0.5°.

The SPEM chamber employs a zone-plate scheme which focuses the synchrotron beam to ~150 nm. The sample is stationary during imaging and the zone plate is rastered in the illumination field to carry the focused spot across the sample surface. An order sorting aperture (OSA) is positioned within 0.5 mm of the sample surface, and the zone plate assembly is cut back on one side to allow a line of sight for the spectrometer. The zone plate used for this study was optimized for $h\nu=620$ eV, the energy used in our experiments.[6]

## Results

### SPEM

The interpretation of surface core level shifts depends heavily upon the cleanliness of the prepared pyrite surface. To establish the distribution of the oxygen observed in XPS, a scanning photoemission microscope was employed.

The SPEM image (Fig. 1) shown in the adjacent represents the contrast between the signal at the O 1s core level (527 eV BE) and the adjacent background (520eV BE). This subtraction method successfully removes the topographical features typically present in raw SPEM images of pyrite, so the prominent feature in the lower left of the image is due to a substantial presence of oxygen. The spectra obtained for regions on and away from this feature, show a remarkable difference in composition. A conventional XPS survey of the same surface is shown for comparison.

The image feature shows strong Ca, C and O signals, and a reduced signal from Fe and S, suggesting a mineral inclusion such as $CaCO_3$. In contrast, the spectrum from a featureless region of the image actually shows essentially only Fe and S signals. All of the C and most of the O signal in the featureless spectrum can be attributed to artifacts of the zone plate system, as determined by biasing the sample to isolate the zone plate contribution.

Based on the SPEM data, we conclude the pyrite surface as prepared with our method is predominantly characterized by contamination-free sites; an essentially clean surface. The small oxygen signal observed in conventional XPS results from sparse local regions containing mineral inclusions, which do not appreciably contribute to the S and Fe signals relevant to our study.

It is important to note, however, that the presence of inclusions must be considered in measurements of sorbed species such as oxygen. The reactivity of defect sites could be enormously greater than for the pure $FeS_2$ surface, and it would be difficult to isolate their contribution to "oxidation". Indeed, several studies have reported very little chemical change in Fe and S core levels, while observing the adsorption of $H_2O$, OH, and related species.[7] Such inclusions are likely a general feature of natural pyrite surfaces, however they may easily go undetected with less surface-sensitive x-ray lamp XPS.

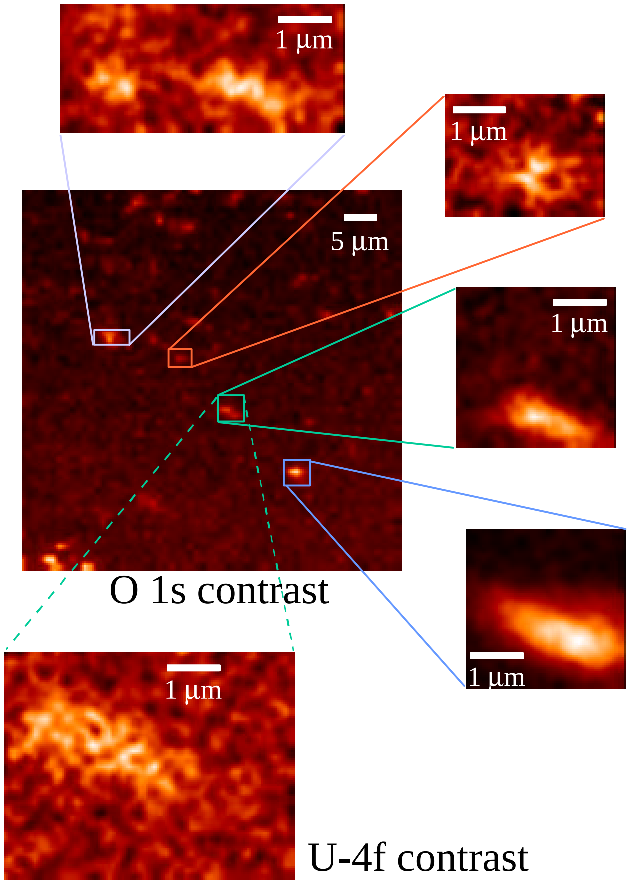

**Fig. 1 : X-ray Photoemission Microscopy of pyrite mineral surface, showing evidence of inclusions, including a U particle.**

### ***XPS***

High-resolution XPS spectra of the S 2p core level have been completed (Fig. 2). Curve fitting was performed on each spectrum, fixing the branching ratio at 2:1, the spin-orbit splitting at 1.18 eV, and the Lorentzian-Gaussian ratio to 80:20. In general, at least three obvious doublets could be observed in each spectrum. The relatively bulk-sensitive top spectrum, taken at photon energy hν = 710 eV (KE ~ 550 eV), is dominated by a doublet with BE = 162.4 eV. (BE refers to the energy center of the $2p_{3/2}$ level). Additional structure on the lower BE side is evident including an obvious doublet with BE = 161.0 eV. The more surface-sensitive spectra at hν = 220 eV shown in the middle spectrum (normal emission) and the bottome spectrum (80° emission angle) display the same structures with different relative intensities. Namely, the doublets at BE = 161.0 eV and 161.7 eV are more pronounced. We therefore assign the doublet B (162.4 eV) to the bulk S 2p level, and the doublets S1 (161.0 eV) and

S2 (161.7 eV) to surface core level shifts.

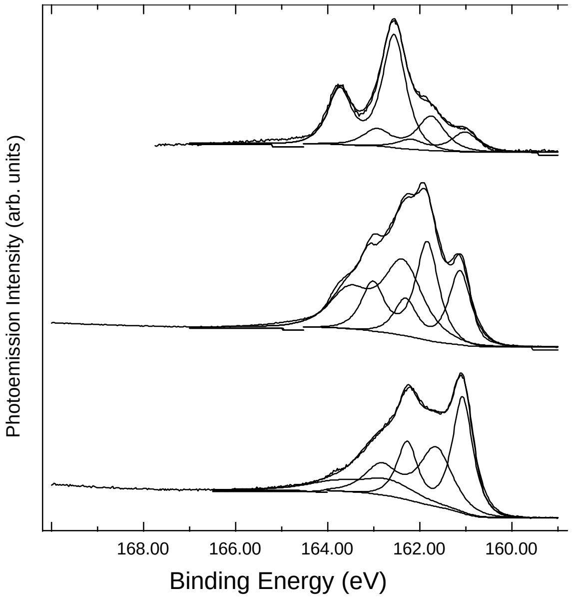

**Fig. 2: High resolution XPS of S 2p core level in pyrite.**

These results are in close agreement to results of Bronold et al., which were explained in terms of surface states derived from the Fe 3d valence bands.[8] These surface states had previously been explained in terms of missing-sulfur defect states arising in the semiconducting gap as a result of the reduced coordination of the S atoms.[9] The consequent rearrangement of charge results in a dipole field between the first and second planes, leading to a chemical shift in the S2p level. A subtle difference between our data and the work of Bronold et al. is a significantly narrower linewidth of S1 in our study. This may be due to the difference in preparation, since Bronold et al. used cleaved synthetic pyrite, which likely includes facets other than (100). Other studies of cleaved pyrite surfaces have attributed features in the vicinity of S1 and S2 to a “monosulfide” site, which presumably results from cleaving.[10,11] After prolonged exposure to water, the intensity of the “monosulfide” signal was observed to decrease. We suggest that this feature actually represents the same SCS’s that we have identified.

### *XANES*

Absorption spectra were obtained for both Fe and S $L_{II.III}$-edges. Spectra taken from reference compounds $Fe^{2+}$ ($FeCl_2$) and $Fe^{3+}$ (Goethite) compounds were used for comparison. The normal-emission PY spectrum, acquired by measuring the yield of 50 eV KE secondary photoelectrons, is identical to that of the TEY spectrum, although the PY data should be more surface sensitive. The $FeS_2$ spectra closely resemble the $Fe^{2+}$ reference spectrum, as expected from the stoichiometry of pyrite. The additional features in the pyrite spectrum several eV above each edge must result from additional transitions specific to the $FeS_2$ system. The grazing-emission PY spectrum shows a modified spectral shape. While we cannot rule out a small contribution from $Fe^{3+}$ sites on the pyrite surface, we believe the difference can be explained in terms of polarization effects.

### *ARPES (band structure measurements)*

The angle-dependence is rather weak, which may be the result of the large number of steps that appear in UHV cleaves. The symmetry of the $FeS_2$ lattice was observed in the ARPES measurements. There was no evidence of surface states.

***XPD (X-ray Photoelectron Diffraction)***

The intensity of the S 2p core level was measured for a range of solid angle encompassing polar angles from normal emission to 80°, and azimuthal angles over 180°. Several regions with a bandwidth of ~0.25 eV of the S 2p level were chosen to represent bulk and surface contributions. These data are displayed in Figure 3, symmetrized with single 180° rotation to represent a full 2π XPD pattern. A background pattern taken at an energy just below the BE of S 2p has been subtracted from each pattern, and each pattern is normalized to minimum and maximum intensity.

The S 2p signal is resolved into three components representing 3 different S atomic sites: a "bulk" site lying below the surface plane, and two different surface atoms.

The XPD patterns from all three are clearly distinct, as shown in Fig. 3. In addition, the patterns depend very sensitively on electron kinetic energy. This dependence will be used in our theoretical simulations to determine the precise bond geometry for all atoms.

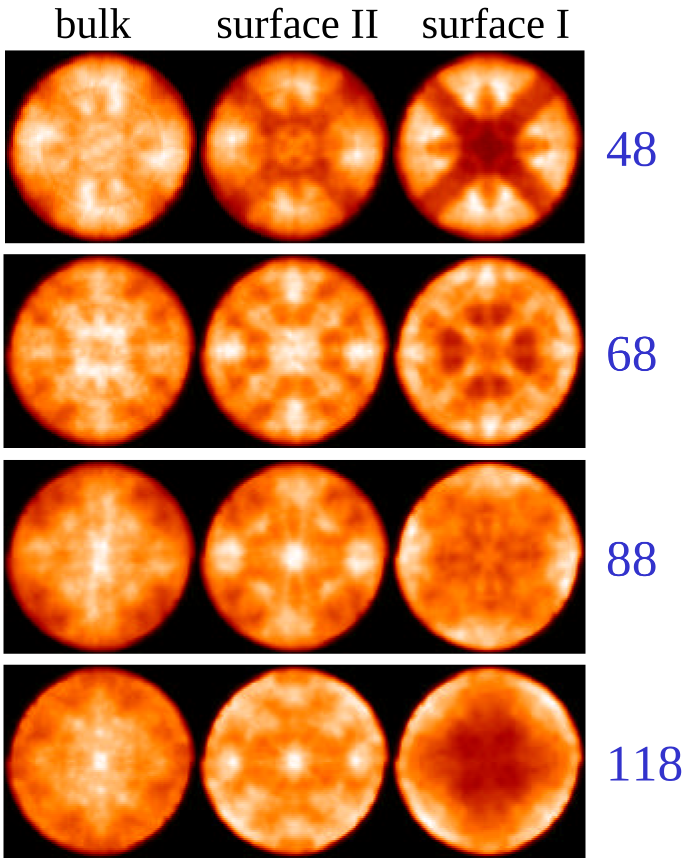

**Fig. 3: XPD patterns of the pyrite surface, resolving three distinct atomic species of sulfur, at a set of electron energies. The patterns are distinct for each species, and depend sensitively on kinetic energy.**

## *1.2 Chalcopyrite*

Chalcopyrite ($FeCuS_2$) was briefly investigated. The UHV cleave resulted in an angled smooth surface. The cleanest spot on the sample still showed C and Cl impurity. XPS was successful, XPD was not yet attempted.

## *1.3 Galena (PbS)*

We have initiated work on the clean surfaces of galena and pyrite. On galena, we have measured the electronic structure using ARP, and have conducted PED measurements of the $S_{2p}$ (Figure 3) and $Pb_{4f}$ core levels. We have begun XPS and PED measurements of water adsorption on a galena surface cooled well below room temperature (in vacuum, the surface of galena is inert to water). We have recently developed a recipe for preparing an ordered clean surface of pyrite in vacuo.

To our knowledge, this is the first photoelectron diffraction (PED) of galena.

### *1.4 Bixbyite*

This is an (Fe,Mn) oxide that has excellent crystallinity in natural form. It will be used as a model system for studies of actinide adsorption to oxide surfaces. The fact that there are equivalent Fe and Mn sites allows us to internally calibrate our XPD, XPS and XANES techniques, while looking at processes such as competitive adsorption. We have completed preliminary spectroscopic measurements (XPS and XANES) but have not yet succeeded in getting an XPD experiment to work.

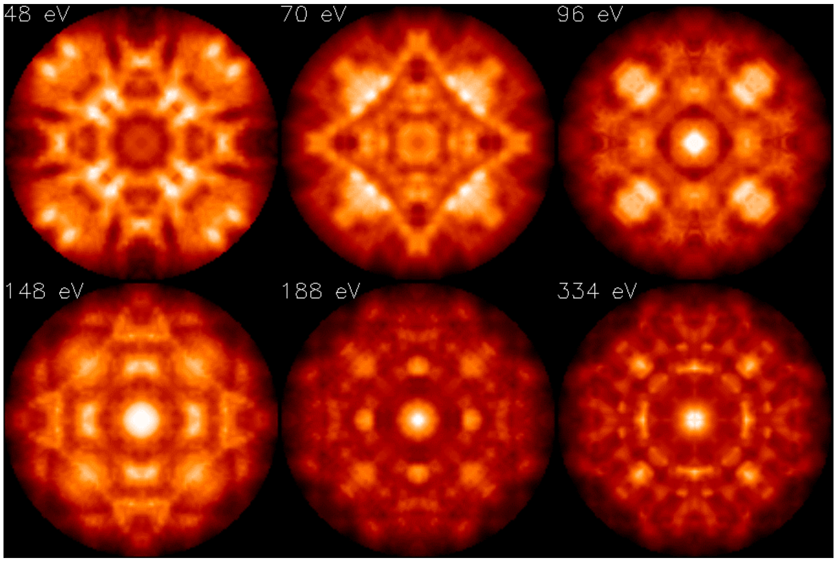

**Fig. 4:** XPD images of the S2p core level of clean PbS(001). Data are plotted such that the radius is linear in polar emission angle, with the [100] azimuth horizontal.

## 2 Summary of Future Research

We have completed the experimental portion of the surface structural studies of galena and pyrite. Theoretical analysis of these data is complex and will proceed through next year. We use full multiple scattering methods in collaboration with theory groups.

With this background in the pure mineral surface structure, we will study the uptake of uranyl compounds onto the clean and oxidized surfaces of galena (PbS) and pyrite ($FeS_2$). We will first study the adsorption of water on galena and pyrite as a basis for the uptake in aqueous solution experiments. Secondly, we will investigate the oxidation process of the sulfide surface, with particular attention to oxidation in aqueous solutions. Unoxidized as well as controlled oxidized sulfide minerals will be treated in solutions of U(VI) at different concentrations and pH-values. To avoid uncontrolled contamination by air oxidation, handling of samples will be done in an anoxic glove box. Additionally, we will establish a correlation between XPS core level energies and valence states for uranium using reference compounds. We anticipate that most of this preliminary work will be accomplished using spectroscopic techniques (e.g. XPS, XANES). In addition, XPD will be used to help establish details such as the atomic geometry of the oxidized layer. For the U uptake experiment, we will first identify the specific chemical states of $U_{4f}$, $S_{2p}$, $Fe_{2p,3p}$/$Pb_{4f}$, and $O_{1s}$ XPS levels pertaining to the principal surface species relevant to the uptake process. Once these levels are established, we can perform PED and EDPD measurements of each chemical state. An essential component of PED is comparison of data to calculated patterns of model structures; thus we will perform multiple-scattering calculations. In this way we plan to establish the surface atomic geometry of the U sorbed sulfide surfaces. It may be possible to easily resolve (in XPS) the U(IV) and U(VI) species with the high energy resolution available at ALS. This would enable us to directly resolve the adsorption geometry of each U species independently.

While advancing the research to the stage of the atomic structure of actinide adsorbates in the case of pyrite and galena, we will also continue to identify and characterize "clean" mineral surfaces. The work on bixbyite is not complete, since we do not yet know of a way to prepare the sample properly for XPD. Similarly, techniques need to be developed to handle samples like chalcopyrite.

One very promising area of research we are pursuing is the use of microelectronics tools to study mineral-actinide interfaces. We are exploring two things in particular. One is the use of focussed ion beam (FIB) tools to cut precise samples from bulk minerals. The other is to use implantation of oxygen or other species to form a buried layer for cleaving, similar to the SIMOX technique.

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