

## Studying ligands, metals and their complexes in aqueous systems using soft x-ray spectroscopy

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Soft X-ray spectroscopy and spectromicroscopy are emerging techniques that have unique applications in probing the electronic states of metals and their complexes in aqueous solutions. Using the soft X-rays, the  $1s$  electrons of light elements (e.g. C) and the  $2s$ ,  $2p$ , etc. electrons of transition metals and heavy elements (e.g. Se) in aqueous solutions and at mineral-water interfaces can be probed. Element-specificity and high-spectral resolution of soft X-ray methods also permit the examination of small changes in the electronic states of different elements in heterogeneous materials.

The availability of the third generation synchrotron X-ray sources and the development of high resolution zone plates has permitted the examination of wet mineral precipitates at a spatial resolution better than 20 nm recently. Such measurements are also possible for samples in wet state, and in complex heterogeneous matrices. The magnetic structures of nanoparticles and magnetic domains in micron sized minerals can also be studied in wet state using the plane and elliptically polarized soft X-ray beams.

A majority of soft X-ray spectroscopy techniques, and the required facilities to conduct studies on samples of geochemical interest are in the developmental stages. *Ab initio* calculations are also being conducted for different aqueous metal-ligand systems to correlate their spectral variations with the electronic structure.

An introduction to different soft X-ray spectroscopy and spectromicroscopy techniques, available research facilities at the synchrotron light sources, and examples of studies conducted using these methods in model and complex systems will be discussed.

## Quantification of Mn valence in minerals at the nanoscale using electron energy-loss spectroscopy

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### Introduction

Mn oxides are environmentally significant due to their efficiency in sequestering metals and their REDOX-active nature. These minerals are commonly very fine grained and intermixed so measurements of mineral properties such as valence should be conducted at an appropriate scale. With Electron Energy-Loss Spectroscopy (EELS) in the Scanning Transmission Electron Microscope (STEM), it is possible to measure the Mn valence in oxide minerals at the nanometre scale because the Mn  $L_{2,3}$  Energy-Loss Near-Edge Structure (ELNES) varies systematically with valence.

### Experimental Methods

In this study, synthetic Mn oxides of known valence were analyzed using EELS, and the  $L_{2,3}$  peak intensity ratios and peak separations were determined for the three common valences, MnII, MnIII and MnIV, and for mixed-valence oxides. A ternary calibration relating Mn valence to the  $L_{2,3}$  peak intensity ratios and peak separations was developed to quantitatively determine the Mn valence in natural minerals.

### Results

With increasing valence from MnII to MnIV, the  $L_{2,3}$  peak separations decreased from 11.6 – 10.3 eV and the total peak intensity ratios decreased from 4.0 – 2.1. The valence ratios measured for several natural mineral samples suggest that pyrolusite is dominantly MnIV but contains approximately 25% MnII. Similarly, manganite is dominantly MnIV with approximately 40% MnII. A romanechite sample approached 75% MnIV with 25% MnIII.

### Conclusions

A method for quantitative determination of Mn valence in oxide minerals was developed which utilizes the  $L_{2,3}$  intensity ratio and peak separation in EELS. The valence of Mn in natural minerals did not conform to the stoichiometry described by the mineral formulae.

## Soft X-ray spectromicroscopy study of chemical heterogeneities in iron precipitates formed at or near bacterial cells

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Iron oxides formed in neutral-pH aqueous environments are frequently associated with bacteria, indicating the importance of microorganisms in geochemical cycling of iron species (Fortin and Beveridge, 2000). In this study, soft x-ray spectromicroscopy was used to investigate chemical heterogeneities of iron-containing precipitates formed at or near *Shewanella putrefaciens* (CN32) cell surfaces. Spectromicroscopic measurements at the iron L<sub>3</sub>- and carbon K- edges with 30 nm spatial resolution provide direct evidence for chemical heterogeneities in biologically induced iron oxide precipitates both temporally and spatially. For example, adsorption or nucleation of Fe(III)- containing nanoparticles (e.g., ferrihydrite) was dominantly observed on *S. putrefaciens* cell surfaces at early stages (day 4) of batch culture experiments, whereas extensive coverage of the *S. putrefaciens* cells by Fe(II)- containing minerals (e.g., siderite (FeCO<sub>3</sub>)) becomes more dominant in later culture stages (day 8, see Fig. 1). These direct observations of temporal and spatial heterogeneities of iron oxide precipitates in bacterial cell surfaces strongly support previous suggestion by Zachara et al.(2002) on the importance of local micro-environments in determining the fate of secondary iron minerals.

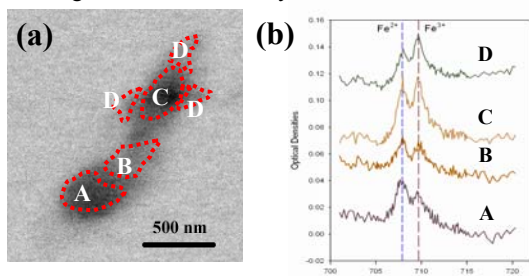


Fig. 1. (a) STXM images of single *S. putrefaciens* cell after 8 days in the presence of ferrihydrite coated quartz. (b) Fe L<sub>3</sub>-edge NEXAFS spectra collected from different areas of bacterial cell shown in (a)

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## Quantitative mapping of the ferrous to ferric ratio on a sub-micron scale using synchrotron spectromicroscopy

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Fundamental geological variables, including temperature, pressure and oxygen fugacity, may be estimated using the valence ratio of heterovalent transition metals, obtained via electron microprobe analysis or Mössbauer spectroscopy. In many rocks, meteorites and soils, however, the mineral inhomogeneities are too small to be analyzed with these traditional techniques. Recent transmission electron microscopes equipped with electron energy loss spectrometry (TEM-EELS) can determine the valence ratio in areas as small as 20 nm, and, separately, produce non-quantitative valence distribution maps. However, fully quantitative valence mapping on a sub-micron scale is not yet possible with TEM.

We developed a new method that couples x-ray absorption near edge structure (XANES) spectroscopy with high-resolution x-ray photoelectron emission microscopy (X-PEEM) [1]. Using previously established calculation methods [2,3], we produced high resolution chemical and elemental distribution maps and fully quantitative maps of the Fe(III)/ΣFe ratio from ilmenite containing hematite exsolution lamellae. This new modality is not limited to iron, and can also be applied to a variety of transition metal systems. X-PEEM analysis induces limited or no radiation damage to minerals, and does not require invasive or destructive sample preparations. This approach, therefore, is well suited for valuable and/or unique samples.

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## Prospects for actinide STXM

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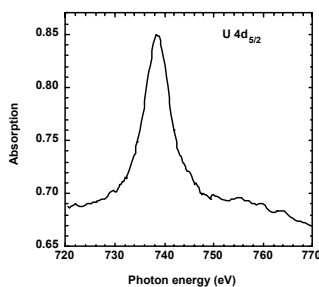
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In assessing the migration behavior of actinides and other radionuclides in the environment it is of great importance to have detailed knowledge of the chemical interactions between the migrating actinide species with surrounding minerals, as well as with particulates present in transporting groundwater. There are several methods used to experimentally gain such information such as laboratory sorption experiments and hard x-ray x-ray absorption fine structure (XAFS). Recently, scanning transmission x-ray microscopy (STXM) has been utilized with actinides and shows the ability to give spatially-resolved chemical information from high-resolution near-edge XAFS (NEXAFS) on the 25 nm length scale.

The results from the initial studies of the common uranium, neptunium, and plutonium oxides will be presented, demonstrating the capabilities and limitations of soft x-ray STXM spectromicroscopy for the investigations of actinide systems. The actinide 4d edges are employed for both imaging and for oxidation state determination. Additional information can be obtained from light element edges, such as the oxygen K-edge. The results from the initial investigation of actinide colloids and actinide sorption on mineral particles will be shown. Actinide sample preparation methods, as well as sample radiation damage considerations, will be described and discussed. The prospects for future actinide investigations by STXM will be critically evaluated.



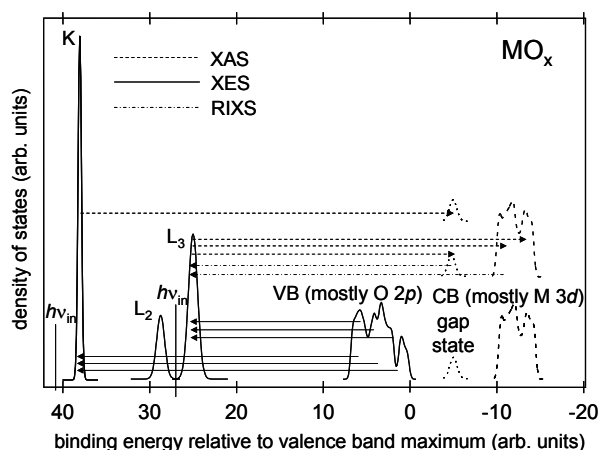
NEXAFS spectrum collected at the U 4d<sub>5/2</sub> edge from a 35 nm edge region of a UO<sub>2</sub> particle.

## Soft X-ray absorption and emission spectroscopies as probes of metal dopants and clusters

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Characterization of isolated transition metal (TM) dopants and TM clusters in both organic and inorganic media is a formidable challenge with significant implications for the chemical, electronic, magnetic and optical properties of the material as a whole. In this talk, I discuss the physical underpinnings of x-ray absorption and emission spectroscopies with spatial resolution, and illustrate what can be learned using a variety of material systems of interest to solid-state physicists, mineralogists, environmental scientists and physicians. Specific examples include ferromagnetically doped TM oxides in which the dopant is dispersed or clustered, elemental speciation in minerals such as ilmenite and zircon, Fe speciation in Fe-oxidizing bacteria, and Gd neutron capture therapy for treatment of brain tumors.



Schematic representation of x-ray absorption (XAS) and emission (XES) processes in a metal oxide. In XAS, electrons are excited from core states to low-lying unoccupied states. XES results from the decay of electrons in occupied states to the core holes created in XAS. XES can be obscured by the direct decay channel accompanying XAS, and the resonant inelastic x-ray scattering (RIXS) of these x-rays. RIXS can be distinguished from XES by varying the incident x-ray energy ( $h\nu_{in}$ ); RIXS disperses with  $h\nu_{in}$  whereas XES does not.

### Acknowledgement

Work supported by the U.S. DOE Office of Science, Divisions of Materials and Chemical Sciences.

## Spectroscopic characterization of nano-magnetite: Facts and mystery about an illusive mineral phase

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The non-destructive spectroscopic characterization of structural and electronic properties of nano-forms (< 50 nm crystallite size) of Magnetite (Fe<sub>3</sub>O<sub>4</sub>) and related iron-based phases has become of utmost importance, because of their great potential for new applications in a variety of different fields. Biosensors, magnetic storage devices and environmental remediation are just a few examples of promising applications and new markets for such materials.

We've used a suite of surface and bulk sensitive microscopic and spectroscopic techniques (TEM, HREELS, XPS, XRD and synchrotron L-edge STXM) to study nano-magnetite particles coming from different sources (bio-synthesis, wet chemical synthesis routes (Gee et al.)). We have found that the application of non-microscopic techniques, such as XPS or conventional powder XRD can yield incomplete information because of particle size dependant variations in structural and electronic composition and because of effects of aggregation. The soft X-ray absorption signature of L-edge spectra taken from individual particles or sub-micron clusters of crystallites indicates a size dependant variation in oxidation states of iron. As confirmed by TEM-HREELS, spectra of the smallest particles (<5 nm) show a higher content of reduced iron, whereas those averaged over single larger crystallites (>7 nm) resemble spectra of partially or fully oxidized isomorphs (e.g.  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). Also, the outer surface layers (<1 nm) of the bigger particles appear more reduced than the corresponding core volumes indicating surface stabilized forms of reduced iron in nano-magnetite. Our results are discussed in the context of recent results by Park et al., possible quantum confinement effects, probe damage and charge localization in nano-magnetite as compared to more extended crystals or thin films.

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## Mapping of metal species in biofilms using scanning transmission X-ray microscopy

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Metals, even at low concentrations, can pose a hazard to ecosystems. Both quantity and the chemical form of the metal are critical determinants of risk. To understand metal dynamics in the environment we must define oxidation state, ligands and elemental quantitation. X-ray absorption spectroscopy at the metal 2p edges can provide this information. The ALS STXM11.02 provides both speciation and quantitation at 50 nm spatial resolution in microbial biofilms. We have combined results obtained with STXM on the ALS Molecular Environmental Sciences beamline 11.0 with those from STXM 532 to detect, speciate, and quantitatively map the oxidation state of metals in the context of microbial biofilm microstructure and chemistry. We have shown that Mn, Fe, and Ni 2p signals provide metal speciation and quantitative spatial distributions of the identified species, with a sensitivity equivalent to a monolayer of the metal species. Spectra from STXM 532 facilitate the mapping of biomolecular structure and allow correlation of metal species with protein, lipid, carbohydrate and nucleic acid components of the biofilm. The resultant observations are relevant to metal dynamics and biotechnological applications of biofilms for remediation of metal contaminated environments.

## Simulation and theoretical modeling of L-edge XANES of transition metals

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There has been dramatic progress in recent years both in calculations and in the interpretation of x-ray absorption spectra (XAS). Essential in such calculations is a "quasi-particle" treatment that takes into account inelastic losses and lifetime effects and includes a final state potential with a screened core-hole potential.

Moreover, for L-shell spectra "local fields effects," can also be important. Such local fields arise from the dynamic screening of both the external x-ray field and the coupling to the core-hole created in the absorption process. These effects require a theory that goes beyond the independent-particle approximation.

We have developed an efficient approach for treating such effects in solids and molecules based on a generalization of time-dependent density functional theory (TDDFT) together with a local approximation for core-hole screening. This approach has been added to our self-consistent, real-space Green's function code FEFF8. Results are presented for XAS at the  $L_{2,3}$  edges of 3d transition metals. This approach accounts for the deviations of the  $L_3/L_2$  intensity branching ratio from the 2:1 value of the independent electron approximation.

### Acknowledgements

Supported by DOE grant DE-FG03-98ER45623 and facilitated by the DOE CMSN.

## Rigorous theoretical determination of L-edge soft X-ray absorption spectra for transition metal complexes

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The structures of spectra generated by L-edge soft x-ray absorption spectroscopy contain a wealth of information on the chemical state of the element of interest. Coupling experiment with theory is a powerful approach to better interpret these spectral features. Most theoretical approaches that are used for this purpose are semi-empirical, e.g., de Groot (1994). There are of course both strengths and weaknesses in following the semi-empirical path. By increasing the number of adjustable parameters and scaling exchange integrals, one can usually get good agreement between experiment and theory. In some cases, a minimum number of adjustable parameters may suffice, which can lead to a better understanding of the physics and bonding environment. However, as recently shown by Bagus *et al.* (2004), there is the very real danger of not discovering the correct physics when taking semi-empirical short cuts. We believe that it is the discrepancies between experiment and theory that are most illuminating and have great scientific value because they may indicate that the theoretical model used is incorrect or incomplete. Consequently, we have been developing and applying rigorous *ab initio* models for the description of core-level excitation processes. In our work, we include the response of the orbitals, used to form the final state wavefunctions, to the presence of the core-hole; an effect neglected in semi-empirical treatments. This orbital relaxation may involve changes in the covalent character of oxide valence levels. We will report on our methodology and initial results for clusters that model bulk transition metal oxides, and compare these cluster results with those obtained for isolated atomic cations.

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