Soft x-ray spectroscopy and imaging of interfacial chemistry in environmental specimens

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Abstract

Interfaces between minerals and water, and minerals and microbes, are chemically complex and have traditionally been considered beyond the capabilities of surface science techniques, except for model systems under controlled laboratory conditions. We report on some advances in soft x-ray spectroscopy and imaging that make it possible to extract meaningful chemical information about interfaces of specimens that have complex histories, involving environmental exposure. These measurements utilize x-ray absorption spectroscopy, in combination with spatial resolution, in a technique called x-ray spectro-microscopy. Examples are drawn from attempts at Mn and Fe speciation of biologically produced minerals, bio-corrosion deposits, and clays.

1. Introduction

Core level electron spectroscopy has become indispensable as a tool for understanding the chemistry of interfaces in fields ranging from catalysis to microelectronics. With the wide variety of surface sensitive probes available, it is often possible to determine the chemical structure of an interface in complete detail, with full information about the adsorbates, the bonding geometry, and chemical state of the atoms involved.

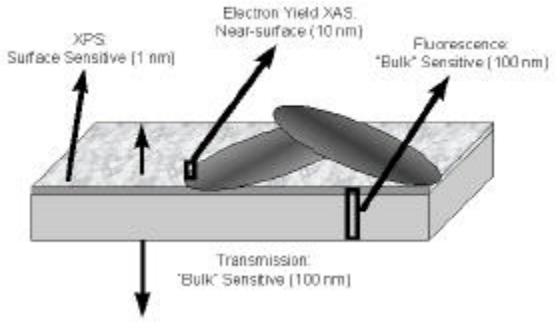

Fig. 1: An environmental interface with attached bacteria, a surface layer of mixed organic and inorganic components, shown with the effective sampling depths of a few types of probes.

This type of information is also needed in a wide ranging set of problems for samples that can be loosely termed 'environmental' interface specimens. An example is the study of the attachment to and modification of mineral surfaces by microorganisms (algae and bacteria). The study of environmental specimens presents difficult challenges for surface analytical techniques, which are often bound to use high or even ultra-high vacuum, and may be difficult to interpret when the specimen is composed of many mixed phases.

We can identify three particular areas in which some traditional surface science techniques may prove inadequate in the study of environmental interfaces. First is a need for spatial resolution, since many problems, even those that are considered to be composed of model systems, are by their nature inhomogeneous. The length scale needed can be approximated by consideration of the size of a typical bacterium, which may be about 1 micron long and 100 nm wide. A further com-

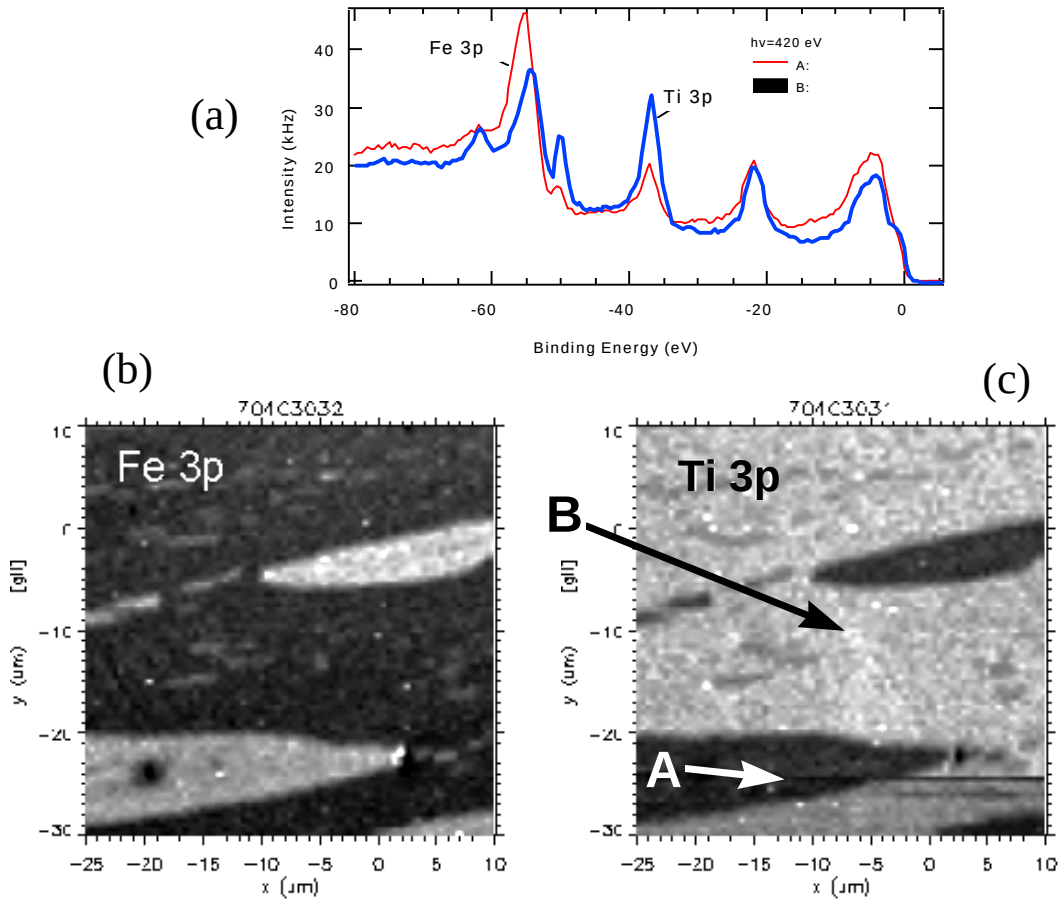

Fig. 2: Scanning XPS microscopy of a natural ilmenite sample showing, exsolution domain structure. (a) XPS spectrum from two regions of sample, identified in the Ti image. (b) Image acquired using Fe 3p photoelectrons. (c) Image acquired using Ti 3p photoelectrons.

plication is that in problems dealing with the interface between inanimate and living matter, the presence of water can be considered crucial in preserving the morphological and chemical integrity of the samples. Finally, there is the need for sufficient spectral resolution of core electron levels, to be useful in speciation of the interfacial compounds, where speciation typically involves both a determination of the atomic valence and the identification of the ligands.

The nature of some of these problems is illustrated in

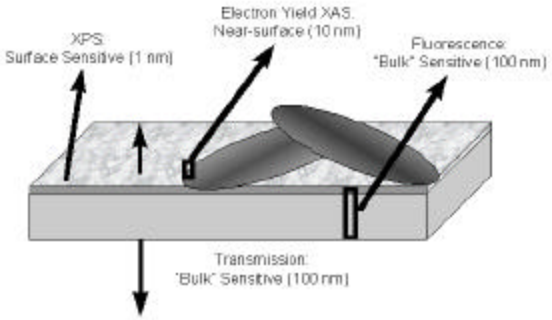

Fig. 1, which shows a fictitious environmental interface between microorganisms and a mineral surface. Many bacteria attach to surfaces by extruding an extracellular polysaccharide ‘glue’, which forms a coating over the bacteria and the mineral substrate[1]. Specimens retrieved from real

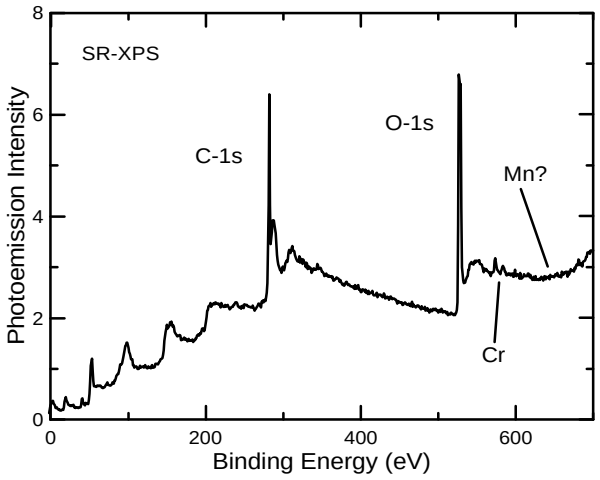

Fig. 3: High resolution XPS spectrum of vacuum-dried manganite mineral particles, taken with monochromatic synchrotron radiation at 700 eV. The Mn signal is not visible through the contamination layer, which contains large amounts of C and O.

'environmental' conditions, such as biologically produced mineral deposits, biofilms, or biocorrosion specimens, are likely to have coatings which are thick compared to the sampling depth of some surface science probes. Photoemission spectroscopy (XPS) is one of the more surface sensitive techniques, shown in the figure as detecting about 1 nm of the outer layers of the sample. Many proteins are 10 nm or more in size, so that XPS cannot 'see' through layers composed of these materials. Another core-level technique, X-ray absorption fine-structure spectroscopy (XAFS), can, however be used in these circumstances[2,3]. Electron yield detection can be used for specimens in vacuum, giving a sampling depth of about 10 nm, which is sufficient to penetrate layers of 'contamination' that may be present in the environmental sample. More material can be sampled in XAFS using fluorescence detection. In the soft x-ray region, roughly from 100 eV to a few thousand eV photon energy, this sampling depth is about 100 nm. We also can use specially prepared thin samples, whose thickness is about 100 nm, and then transmission XAFS can be used. Both fluorescence and transmission XAFS have the

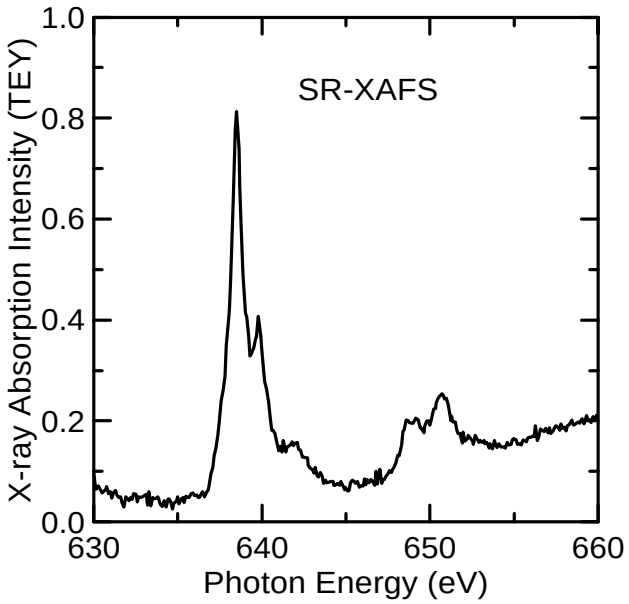

Fig. 4: Soft x-ray absorption spectrum of the Mn 2p edge region, of the same manganite sample as in the previous figure, taken under the same conditions as the XPS spectrum.

advantage of being compatible with samples coated by a few micron thick layer of water.

In this paper we describe some applications of soft X-ray spectro-microscopy, using XPS and XAFS spectroscopy with spatial resolution to investigate mineral-microbe interfaces, and some other problems of environmental relevance. X-ray spectro-microscopy can simultaneously provide sub-micron spatial resolution, high spectral resolution, while studying samples in the presence of water. Not all problems require full hydration, however, so that we also describe various studies in which electron yield detection has been found to be useful.

2. Soft X-ray spectroscopy and environmental applications

2.1 Advantages of spatial resolution

Natural surfaces of rocks are far from homogeneous, and even natural single crystals (minerals) can contain large inclusions or mixed phases. In any study of chemisorption on natural samples, this heterogeneity can

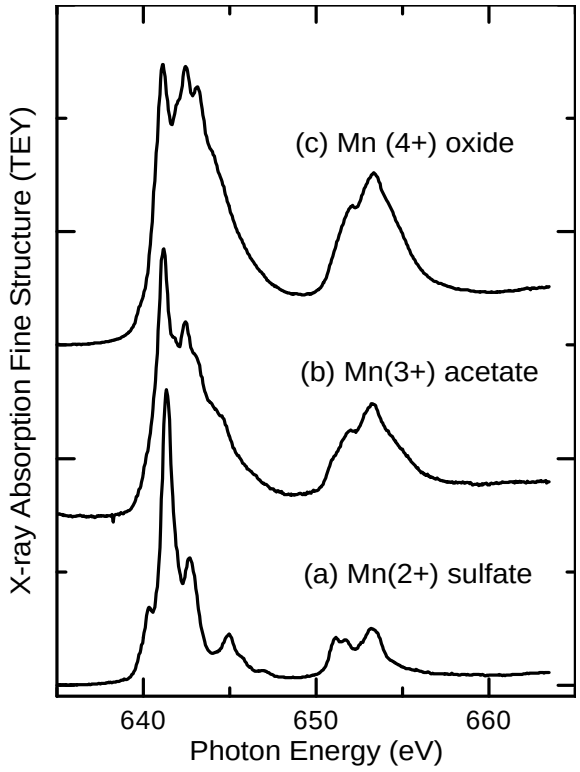

Fig. 5: Mn L-edge XAFS spectra of reference compounds, showing changes in both the intensity and energy positions of the multiplet splittings at the L_2 and L_3 edges as a function of metal atom valence.

make it very difficult to interpret surface sensitive spectra. As a result, the ability to couple a high degree of spatial resolution with excellent energy resolution is a distinct advantage.

As an example, we show in Fig. 2 a study of a mineral surface that naturally separates into two types of domains. The sample is a polished surface of the mineral ilmenite. Ilmenite, which has a nominal composition of $FeTiO_3$, is a constituent of black sands found in association with magnetite (Fe_3O_4), rutile (TiO_2), zircon and monazite. Ilmenite minerals form lamellar phases due to exsolution during cooling when the rock is formed, and these two phases consist of a Ti rich domain and a Ti depleted domain [4].

We are interested in studying the chemisorption of molecules on such natural surfaces, to see if there is differential adsorption and reactivity associated with the two types of domains. Since this requires good surface sensitivity and chemical selectivity, we would like to apply XPS as a probe[5]. In order for XPS to be useful in such an application, a high spatial resolution is required, to be able to map out the distribution of adsorbates in the different domains.

The spectra and images of Fig. 2 show how such a study can be done. The sample in this case was mechanically polished, and sputtered for a short time to remove the organic contamination layer, in preparation for further exposure to controlled atmospheres of adsorbates. The instrumentation used was a zone-plate based scanning XPS microscope, located at the Spectro-Microscopy Facility of the Advanced Light Source[6,7]. This instrument has a spatial resolution of better than 0.3 micron, using monochromatic synchrotron radiation with a band-pass of about 0.2 eV. Even at these stringent levels, the XPS count rates from shallow core levels is quite good, showing an intensity of 40 KHz in the example shown in Fig. 2 (a).

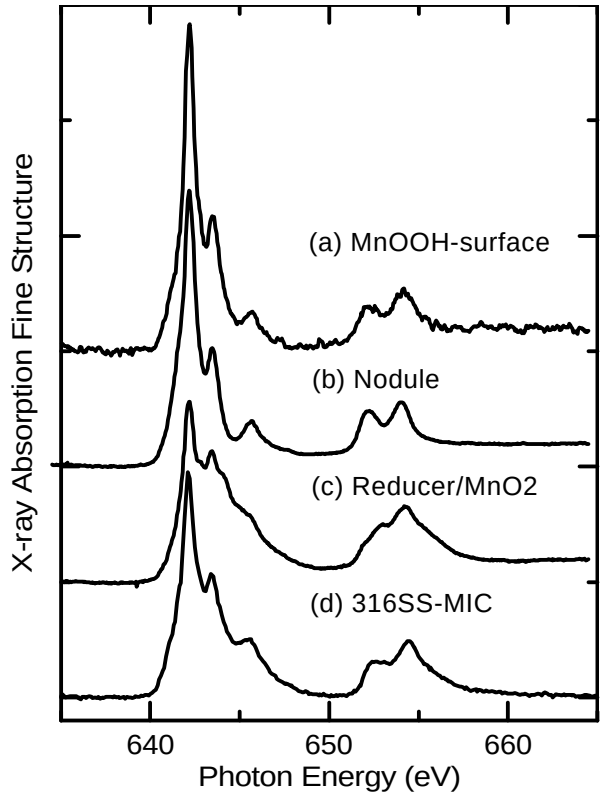

Fig. 7: L-edge Mn XAFS from environmental samples. (a) Manganite surfaces (b) Manganese nodule biomineral deposits (c) Surface of manganese oxide reduced by bacteria (d) Surface of 316-SS corroded with bacterial Mn deposit.

The two different types of domains are apparent in the scanning XPS images, taken with the electron analyzer tuned to the Fe 3p edge, Fig. 2 (b), and alternately to the Ti 3p edge, Fig. 2 (c). Spectra taken from two points (each about 0.3 micron in diameter) indicated in the Ti image show several differences between the two domains. The relative intensity of the Fe and Ti core-levels is different, of course, which gives rise to the contrast reversal in the two images that are shown. In addition, there are noticeable differences in the in the shape of the Fe 3p edges between the two domains, indicating a difference in oxidation state. These differences can now be studied as a function of exposure to various controlled atmospheres.

2.2 Near-surface spectroscopy by soft x-ray XAFS

To see how it is that soft X-ray absorption spectroscopy can be informative in environmental applications, it is useful to look at a specific example. We have investigated the interaction of bacteria with the surfaces of mineral particles, and specifically have been studying goethite and manganite transition

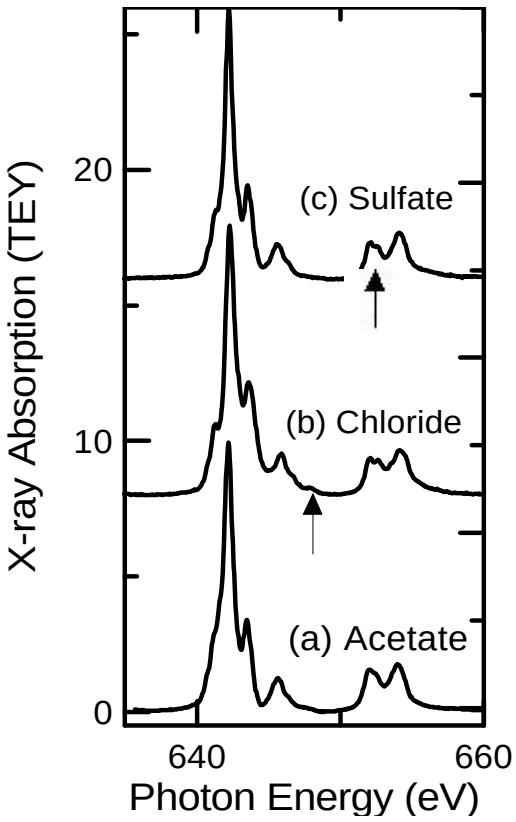

Fig. 6: Mn L-edge XAFS spectra of three different Mn(II) compounds, showing the effects of varying the types of ligands. The differences are small, some of which are indicated by the positions of the arrows.

metal hydroxides, in the form of needle-like crystals with a width of a few 100 nanometers, and lengths on the order of a micron. As a baseline for studying the changes in surface chemistry of these particles, we look at samples of manganite using XPS (Fig. 3) and electron yield XAFS (Fig. 4).

The samples were originally in aqueous suspensions, subsequently centrifuged, placed on a stainless steel sample holder and quickly

introduced into a vacuum chamber for vacuum drying. The XPS spectrum was taken with monochromatic synchrotron radiation at 700 eV. The spectrum shows strong peaks from a contamination layer containing large amounts of carbon and oxygen, and a signal from Si 2p (near 104 eV binding energy) which is presumed to be from silicate particles included with the manganite material. There is no detectable signal from the Mn 2p core level in this XPS spectrum at all, although there is a small signal from the stainless steel sample holder (Cr signal). This is attributed to the small sampling depth of the XPS technique, and the fact that the manganite particles are left wrapped' in a naturally occurring layer of organic material after the drying process. As a result, XPS is not useful in this attempt to determine the composition of the surface layers of the manganite particles, unless some further treatment of the samples is done to attempt to remove the contamination layer.

The situation is completely different for x-ray absorption spectroscopy, which shows a strong signal from the Mn L_3 and L_2 edge (2p core level) near 640 eV (Fig. 4). XAFS is a complementary technique to XPS, in that it measures the transition probability from occupied core-levels into un-occupied valence orbitals. With electron yield detection, the presence of the contamination layer is not a significant problem, since the low energy secondary electrons that are detected easily penetrate 10 nm or more of molecular compounds or insulators[8].

The L-edge spectra of the first row transition elements are characterized by very sharp multiplet features, limited by the core-level broadening of below 0.2 eV. The multiplet structure is sensitive to the crystal field parameters and local symmetry, and the L-edge spectra are very characteristic of the metal atom formal charge, as is shown in Fig. 5. It

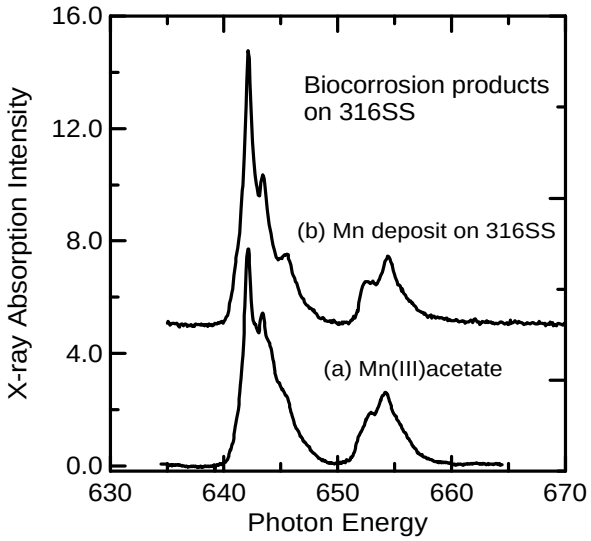

Fig. 8: Comparison of the spectrum of a bio-corrosion sample containing Mn deposits due to microbial growth, and a reference Mn(III) sample.

is generally possible to accurately model mixed-valence materials using reference compounds, and in many cases (such as the Mn(II) compounds) it is possible to get extremely good agreement between an atomic multiplet theory and experimental data[9].

Note that the line widths in these 2p edge XAFS experiments are much narrower than is found in the corresponding XPS spectra (compare Fig. 3 and Fig. 4, for example). This can be understood from the different lifetimes involved. In the case of photoemission, the lifetime of the core-hole and the high energy photoelectron are both included in determining the linewidth. In XAFS, it is the lifetime of the core-hole (relatively narrow) and a low energy electron promoted to an unoccupied valence resonance orbital that are involved[10].

Although the L-edge spectra are narrow and reflect the cation valence, these spectra are less directly useful in determining the precise type of ligands. This is illustrated for the case of Mn^{2+} in Fig. 6. All of the Mn(II) spectra are very similar, with only small differences evident in line intensities and positions, as

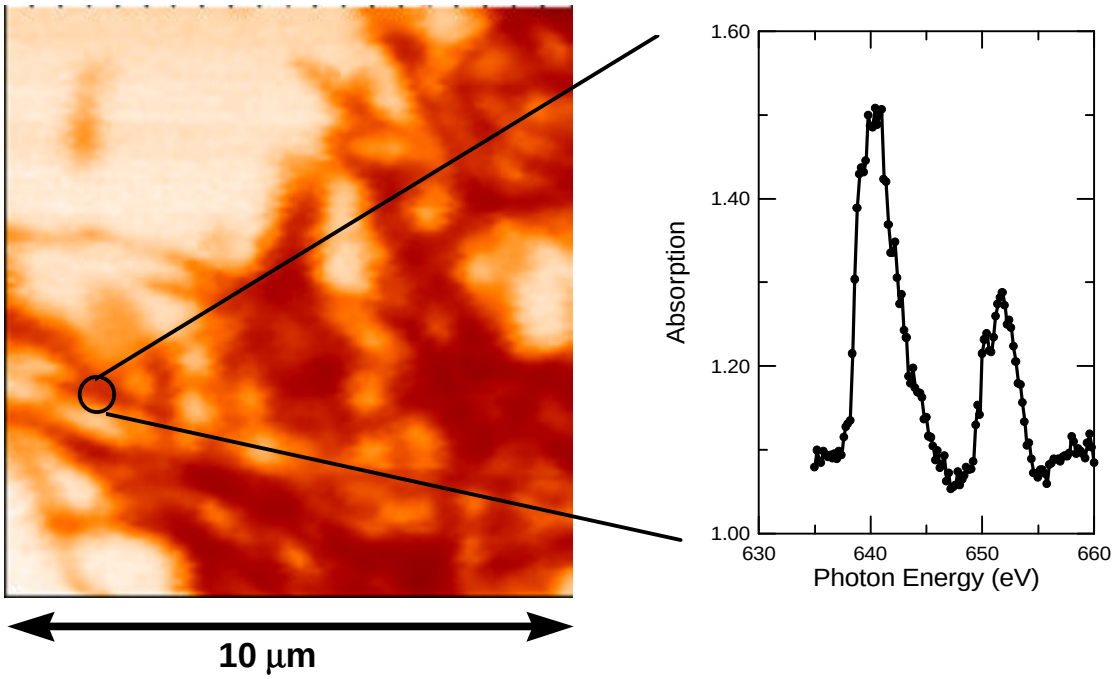

Fig. 9: A STXM experiment studying needle-shaped mineral crystals of manganite in a water suspension; (left) image of cluster of crystals, (right) spectrum of Mn(III) from the indicated region of the image.

indicated by the arrows in the figure. With very good spectra (high signal-noise and signal-background) it is possible to determine the crystal field 10Dq value to within a few tenths of an electron-volt, and local symmetry has been accurately modelled theoretically for several metal-organic complexes[11]. Of course, in model systems where the range of ligand types is restricted, it is possible to get considerably more information on the ligands from the absorption edges of the ligand atoms themselves.

The L-edge XAFS from environmental samples is generally very good, particularly as compared to the XPS spectra from the same materials. Examples of several specimens from a variety of investigations is shown in Fig. 7. These spectra cover a range of interesting environmental studies. The spectrum in Fig. 7(a) is of vacuum dried manganite mineral needles, similar to that described above but with higher resolution and better statistics. The spectrum shows predominantly Mn(II) character, which indicates that the surface layers have reduced from the bulk value of Mn(III)OOH. A very similar spectrum, characteristic of Mn(II), is found for a biomineral deposit shown in Fig. 7(b). This sample is from a large “nodule” recovered from Lake Oneida, which is the result of microbial activity removing Mn from solution and creating insoluble precipitates (see below). From a study of the interaction of Mn metabolizing bacteria, we select spectrum Fig. 7(c), which shows the reduction of MnO_2 particles to Mn(III) in the surface region. Finally, spectrum Fig. 7(d) is of a bacterially produced deposit of Mn on a 316-stainless-steel surface.

The two spectra, Fig. 7(c) and Fig. 7(d), both have a Mn^{3+} character. A direct comparison of the bio-corrosion sample, Fig. 7(d), with a reference compound Mn(III)-acetate, is shown in Fig. 8.

2.3 Samples requiring the presence of water

There are times when it is either necessary or very desirable to perform the spectral analysis on an environmental sample in the pres-

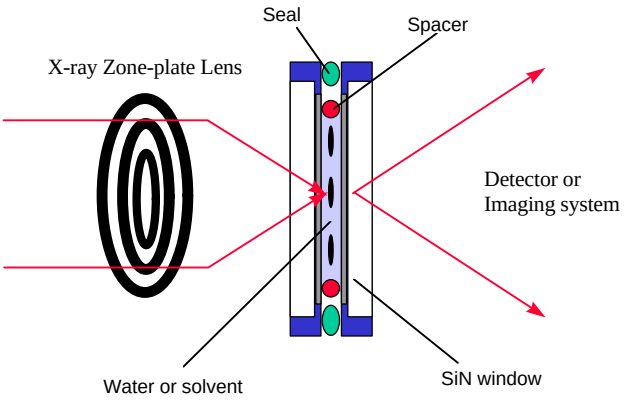

Fig. 10: Schematic diagram of a "wet cell", which is used for transmission XAFS spectroscopy in the presence of liquids.

ence of a thin layer of water, or at least under high humidity so that a few atomic layers of water remain on the sample surface. With soft x-ray spectromicroscopy, it is possible to retain a relatively thick layer of water, in certain circumstances. The absorption of water peaks at the oxygen K-edge near 530 eV, and drops off both below and above this value. At the photon energies needed for XAFS of Mn and Fe, it is possible to have a few microns thick layer of water and still achieve sufficient transmission to record undistorted XAFS spectra.

A special experimental arrangement is used for experiments in aqueous solution, which is also applicable to other liquid solvents. It is illustrated in Fig. 10, which shows a diagram of the "wet cell" that we use for both full-field imaging and scanning transmission x-ray microscopy. The cell consists of two silicon-nitride membranes, which are 140 nm thick. Although very fragile, these membranes trap the water-bearing sample and prevent it from drying out during the experiment. The membranes can be held at a specific thickness by plastic spheres, and can be sealed with glue. Surrounding the cell is an atmosphere of He, to prevent excessive absorption of the soft x-ray beam, and to eliminate structure from absorption edges of air.

An example of a wet-cell experiment is shown in Fig. 9, which is a scanning transmission x-ray microscopy (STXM) experiment on the needle-shaped mineral particles of manganite, MnOOH. These crystallites are only about 0.1 micron wide, and in this image the resolution is about 0.25 micron, so the crystallites appear somewhat blurred (the resolution of STXM has subsequently been improved[7]). The selected area absorption spectrum, also shown in this figure, reflects the composition of the interior of the manganite particles. The surface region, probed by electron yield spectroscopy in Fig. 7(a), gave a spectrum that was dominated by Mn(II), indicating a change in chemical state for Mn atoms at the surface of the mineral particles. The transmission data (Fig. 9), show a spectrum similar to Mn(III), which is the expected state for bulk MnOOH.

Another good example of specimens that need a layer of water present is that of clays, an example study of which is shown in Fig. 12. Clays are ubiquitous crystalline particles found in nature that are responsible for contributing to a wide range of chemical reactions in soils. The structure of these mineral particles changes when the particle is hydrated ("wet"), from that when it is dry. This makes a study of the microscopic distribution of chemical content of these microcrystals difficult using standard techniques that require vacuum. In addition to large structural changes, it is likely that chemical changes accompany the drying process. As a result, spectroscopic measurements on dried clay particles may not accurately reflect the actual composition of the material as found in the environment.

We are studying mineral particles of montmorillonite clay, which is an Fe bearing clay which can be prepared with a wide distribution of Fe concentrations, and with Fe occupying different substitutional sites. The reac-

tivity of these particles in the environment is related to the charge state of the active Fe sites, and to the distribution of these charge states in the particles themselves (basal surface, edges, or interior sites). In the example data shown in Fig. 12, the Fe L-edge spectrum taken at the center of the clay particle, from a region of about 0.25 micron in diameter, gives a very good spectrum which is that of Fe(III), the main valence of substitutional iron in this clay.

2.4 Biologically induced mineralization

X-ray spectromicroscopy is finding use in studies of the process by which microbial colonies produce mineral deposits, a process called biologically induced mineralization (BIM). The formation of minerals by microbial metabolism is a widespread phenomenon, occurring in many species of microorganisms under the right conditions[12]. The species *Shewanella putrefaciens*, which we are investigating, produces Mn rich mineral deposits under anerobic conditions[13]. These deposits range from microscopic in size to very large agglomerates, and can be found in both fresh water and marine environments. The transformation of soluble Mn(II) into a precipitate can take place by many chemical or biochemical routes, including indirect mechanisms like the complexation of Mn by ligands produced by the bacteria, or by a direct mechanism involving enzymes on or in the bacteria themselves. We believe x-ray spectromicroscopy can be useful in helping to understand such problems.

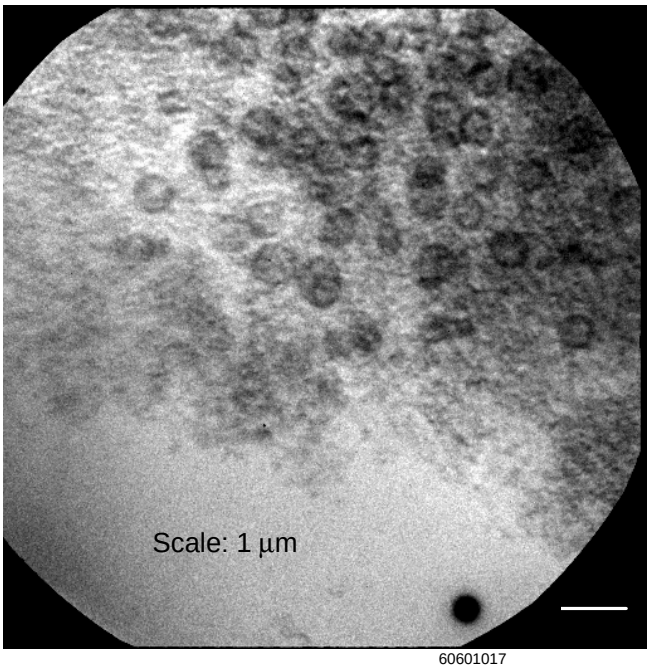

Fig. 11: X-ray transmission micrograph of bacteria inside a Mn precipitate that the microbes are producing. Image taken with XM-1 microscope, operated by CXRO at the ALS.

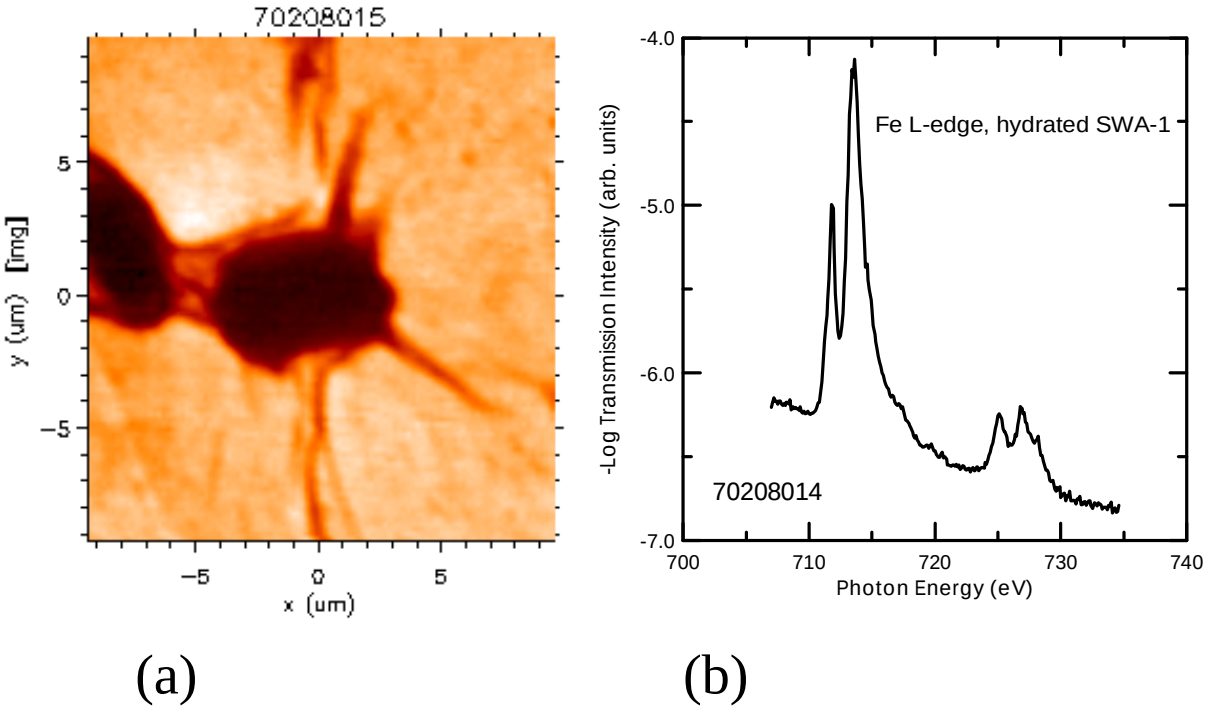

Fig. 12: A STXM experiment studying Montmorillonite clays. The image at left shows a clay particle, and the spectrum at the right shows the Fe L-edge spectrum from a point in the center of the particle.

An example of a high resolution x-ray micrograph of *S. Putrefaciens*, producing insoluble Mn deposits, is shown in Fig. 13. This micrograph is a 'wet cell' image of a living colony of bacteria, surrounded by the inorganic, insoluble Mn oxides that are produced by their anaerobic respiration. Although the x-ray exposure kills the cells, which are seen as the darker circular or ellipsoidal structures, the spatial relationship of the bacteria and the mineral deposit is preserved. This micrograph shows that the intial micro-nodules are produced as porous structures, that support a live colony of microorganisms on the interior. Growth of denser precipitates takes place, then, both on the interior and exterior of the growing nodule particles.

It is also important to know the chemical composition of these biologically induced minerals, or nodules. The biochemical pathways involved in transforming Mn(II) into an insoluble precipitate are expected to have Mn(III) as an intermediate. Although the formation of Mn(IV) oxide is the expected end product, there are also insoluble Mn(II) carbonates which could form as a result of other chemical processes taking place in the environment, reducing the total amount of Mn(IV). The *average* Mn valence in nodules can be determined by chemical techniques that determine the total Mn content and total oxygen content of the nodules. Such studies have been done both for large nodule deposits in sediments[14], and for the initial reaction products of the oxidation of Mn(II) in laboratory conditions[15]. However, until now, it has not been possible to directly map the *distribution* of Mn valence states, in a biologically produced mineral with water present.

This is the goal of our x-ray spectromicroscopy studies of minerals produced in association with bacterial colonies, an example of which is shown in Fig. 13 and Fig. 14. This is a sample of a micro-nodule containing large amounts of Mn, taken from Lake Michigan. The image shows an irregularly shaped, varying density particle, which is x-ray dense at the Mn L-edge, indicating large

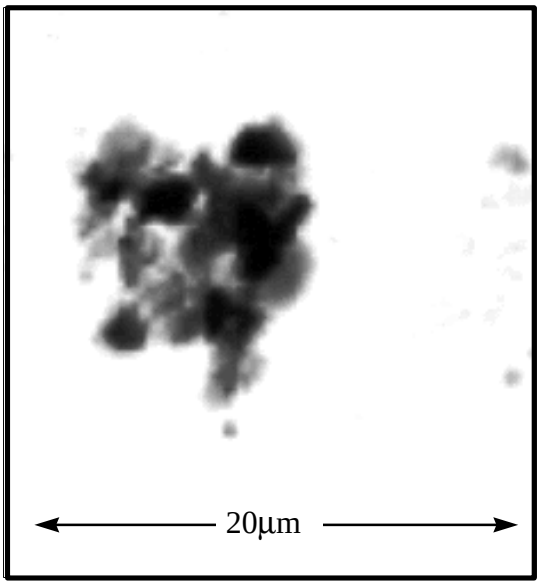

Fig. 13: X-ray spectromicroscopy study, using STXM, of a biologically produced mineral micro-nodule. Scanning x-ray micrograph, 20 micron image width.

concentrations of Mn in this particle. By taking images as a function of the incident photon energy, we have created oxidation state maps for the entire particle. Alternatively, we can extract XAFS spectra from each 'pixel' of the x-ray image, Fig. 13. Examples of these spectra are shown in (b) and (c) of Fig. 14. The spectra are particularly interesting, since they show how these particles vary in chemical composition on a microscopic scale. These experiments use transmission XAFS, so the sampling is over the entire 'bulk' of the particle. Two regions of the particle give spectra shown as Fig. 14 (b) and (c), and are compared to a reference spectrum of Mn(IV), Fig. 14 (d) and Mn(II), Fig. 14 (a). This qualitative study shows that the micro-nodules are primarily composed of Mn(II) and Mn(IV) in close proximity. The Mn(II) could be in the form of insoluble carbonates. This is a very different conclusion from that found by bulk chemical techniques on marine nodules, which were found to be entirely Mn(IV)[14].

3. Future directions

Most of the work presented here represents the beginnings of projects which have been shown to benefit from soft x-ray spectromicroscopy. Combinations of different types of x-ray microsope and detection are needed to form a complete picture of the interface chemistry in mineral-microbe interactions, so that the composition of the surfaces, interfaces, and interior can be separately identified. Special challenges face the experiments that require the presence of water, since these experiments must use photon detection. In transmission, we sample over the entire sample in the path of the photon beam, so that true interfaces can only be isolated as edges. This limitation can be removed using some form of fluorescence detection, which we plan to implement in the future.

Biological interactions with minerals produce complex substances, but the combination of high spatial resolution and multiple spectroscopic probes can help make new progress towards understanding the reactions that are taking place. One consideration in any work involving environmental or biological components is that conclusions must be drawn only after examining a sufficiently large number of specimens that generalizations can be made. This creates a demand for large amounts of time on the x-ray microscopes, as well as creating pressures to improve their ease-of-use.

Not all problems require the presence of water layers, but there is always a question in the vacuum experiments about whether the sample preparation techniques have altered the surface or interface chemistry. One of our immediate goals is to use comparative experiments in vacuum and with wet-cells, to try to establish reliable experimental techniques that can minimize the chemical changes taking place in a 'vacuum' experiment. The large sampling depth of XAFS spectroscopy in total electron yield gives an advantage in this case.

Acknowledgements

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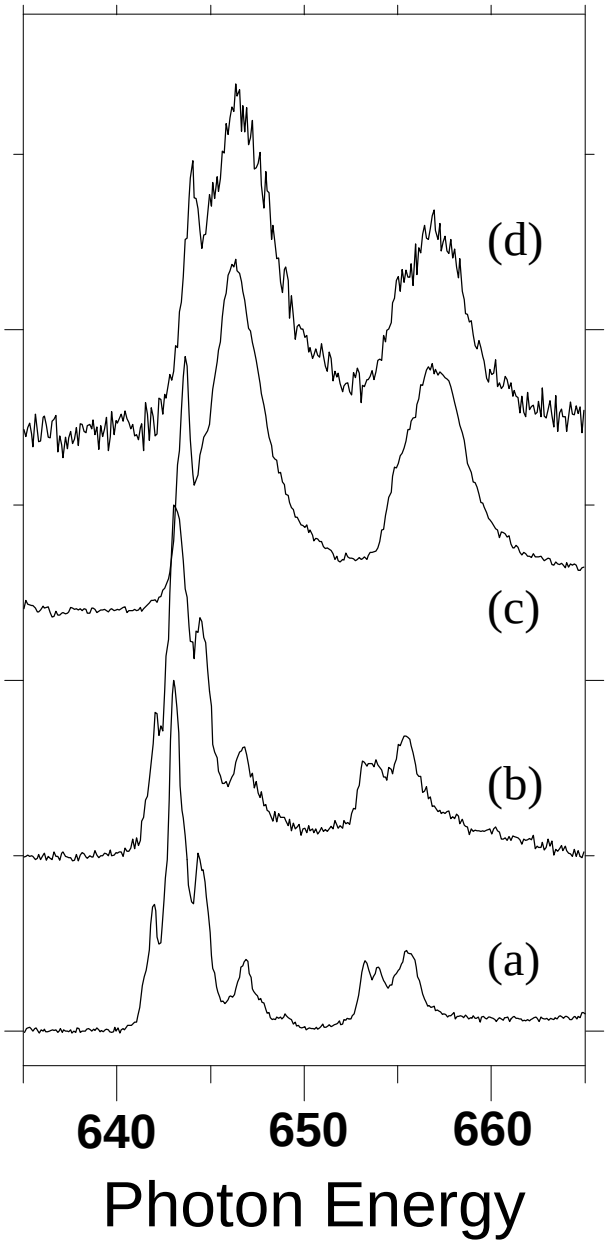

Fig. 14: Spectra from specific pixels in the previous x-ray image, (b) and (c), along with reference spectra for Mn(II) (a) and Mn(IV) (d).

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