

# **X-ray Absorption Spectroscopy in Mineralogy and in the Earth and Environmental Sciences**

*Jesús Chaboy Nalda*

Instituto de Ciencia de Materiales de Aragón (ICMA) and Departamento de Física de la Materia Condensada, CSIC-Universidad de Zaragoza, 50009 Zaragoza (Spain)

## **Introduction**

X-ray absorption spectroscopy (XAS) has proven to be an outstanding structural tool by allowing the determination of the local environment around a selected atomic species in a great variety of systems. An important advantage of this technique is its utility for heterogeneous samples in such a way that a wide variety of solid and liquids, including whole soils and liquids, can all be examined directly and non-destructively. Additionally, since the local structure does not depend on long-range crystalline order, the structure of amorphous phases (and that of dissolved species) is easily achieved.

XAS is useful for concentrations from about 10 ppm to major elements. As such, it is useful to speciate trace elements such as contaminants adsorbed to pure minerals, soils and sediments, and is also a valuable tool for studying the mineralogical composition of the soil or sediment (especially when used in conjunction with other techniques such as X-ray diffraction).

Our purpose here is to present a brief review of the principles underlying x-ray absorption spectroscopy. The main strengths of this technique mainly focused on Mineralogy and in the Earth and Environmental Sciences are highlighted and illustrated by showing different selected examples.

## **X-ray Absorption Spectroscopy (XAS): basic principles**

The basic process of X-ray absorption is the excitation of electrons from deep core levels of a selected atom by the absorption of a photon. When X-rays pass through any sort of material, a proportion of them will be absorbed. The absorption of x-rays by atoms is smoothly varying with photon energy except at some discrete energies where

abrupt increases occur, called absorption edges. These edges correspond to the x-ray photon attaining enough energy to free or excite a bound electron in the atom.

The absorption of x-rays on the high energy of the absorption edges does not vary monotonically in condensed matter but has a complicated behavior which extends past the edge by an amount typically of the order of 1 keV. The small oscillations can superimposed on the edge step gradually die away as the X-ray energy increases. The oscillations are known as EXAFS (Extended X-ray Absorption Fine Structure) are due to the interaction of the photoelectron with the surrounding atoms.

Usually the x-ray absorption spectrum is divided in several regions depending on the energy of incoming photons:

- \* the pre-edge, edge and the near-edge (XANES) regions, which extend about 20 eV below the edge to 30-100 eV beyond the edge.
- \* the EXAFS region which extends from 30-100 eV to 600-1000 eV beyond the edge.

The physical origin of the absorption features in the pre-edge and edge regions depend on the material, i.e. Rydberg states in free atoms, bound valence states or bound multiple scattering resonances in molecules, unoccupied local electronic states in metals and insulators. Thus, analysis of these near-edge features in the spectrum of a particular sample can provide information about vacant orbitals, electronic configuration and the site symmetry of the absorbing atom.

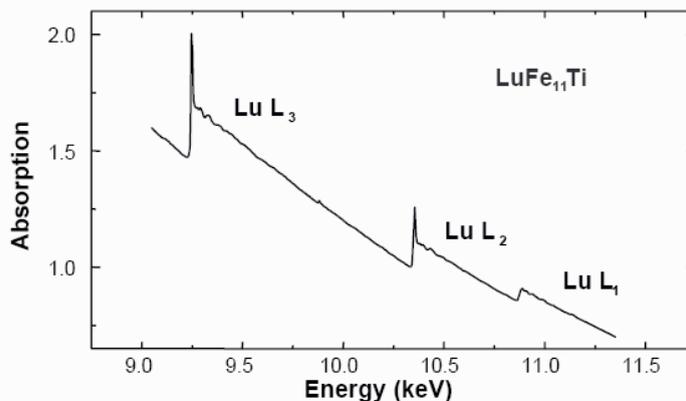


FIGURE 1. X-ray absorption spectra of  $\text{LuFe}_{11}\text{Ti}$  at the Lu L-edges, involving different final state symmetry:  $L_3$  ( $2p_{3/2} \rightarrow \epsilon\{d_{3/2}, d_{5/2}\}$ ),  $L_2$  ( $2p_{1/2} \rightarrow \epsilon d_{3/2}$ ),  $L_1$  ( $2s_{1/2} \rightarrow \epsilon\{p_{1/2}, p_{3/2}\}$ ).

The underlying physics of the processes that occur to produce the XANES and EXAFS structures in the x-ray absorption spectra is easy to understand. The photon is completely absorbed and kicks out a core photoelectron from the absorbing atom leaving behind a core hole. This photoelectron will be ejected with an energy equal to energy of the incoming photon less its binding energy, when in the core. This photoelectron will interact with the surrounding atoms. Considering the wave nature of the ejected photoelectron and regarding the atoms as point scatterers a simple picture can be seen in which the backscattered waves interfere with the forward wave to produce either peaks or troughs. This is an interference effect on the final state. Since the transition probability is given by a matrix element between the final and initial states and the absorption coefficient is related to the transition probability, this interference affects the absorption coefficient which is the value that is measured in an XAS experiment.

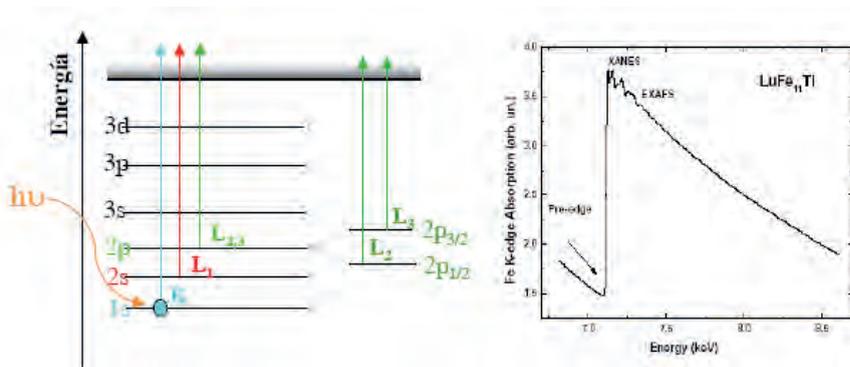


FIGURE 2. Schematic of the excitation of an electron by the absorption of an x-ray photon.

The wavelength of the photoelectron is dependent on its energy and thus the phase of the back-scattered wave at the central atom will change with the energy of the incoming photon. This leads to the oscillatory nature of the interference effect. Since backscattering amplitude and phase are dependent on the type of atom doing the backscattering and the distance it is from the central atom, information regarding the coordination environment of the absorbing atom can be obtained by analyzing the XANES and EXAFS.

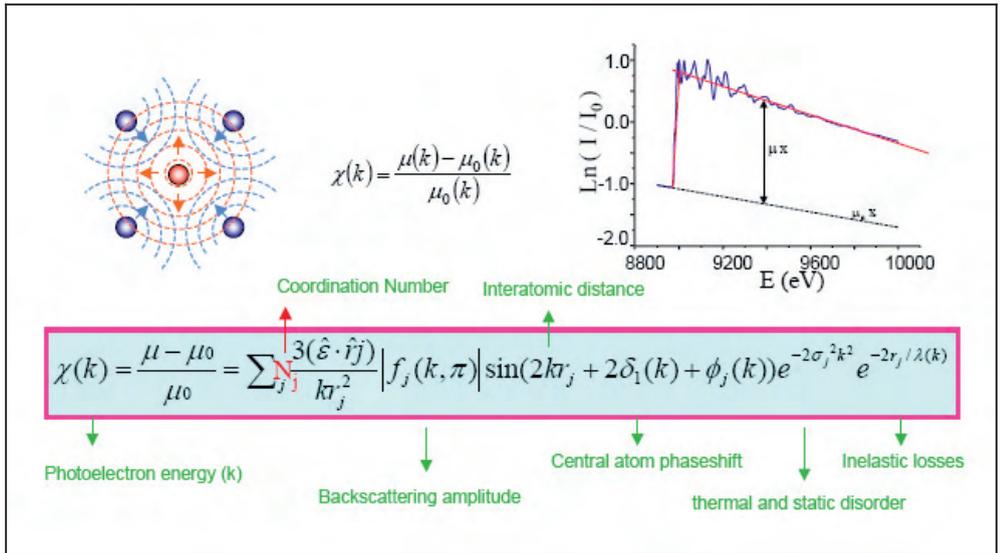


FIGURE 3. Schematic illustration of the interference phenomena giving rise to the modulations (EXAFS) in the x-ray absorption cross-section.

The only distinction between XANES and EXAFS regions is the relative weight of the multiple scattering processes of the excited photoelectron. Usually it is considered that in the EXAFS region only single-scattering processes are important contrary to the XANES region in which due to the low kinetic energy of the ejected photoelectron multiple scattering processes are dominant. Consequently, through careful analysis of the oscillating part of the spectrum after the edge, information relating to the coordination environment of a central excited atom can be obtained.

As outlined above, the near-edge and XANES parts of the x-ray absorption spectrum are sensitive to bonding environment as well as oxidation state. The position of the edge and the assignment of peaks near or on the edge give information about oxidation state, covalency (increasing ligand character of metal d orbitals), molecular symmetry of the site, and thereby coordination number. XANES spectra are commonly compared to standards to determine which species are present in an unknown sample. Once species are identified, their relative abundance is quantified using linear-combination fitting (or other curve-fitting algorithms) using XANES standards to reconstruct the experimental data.

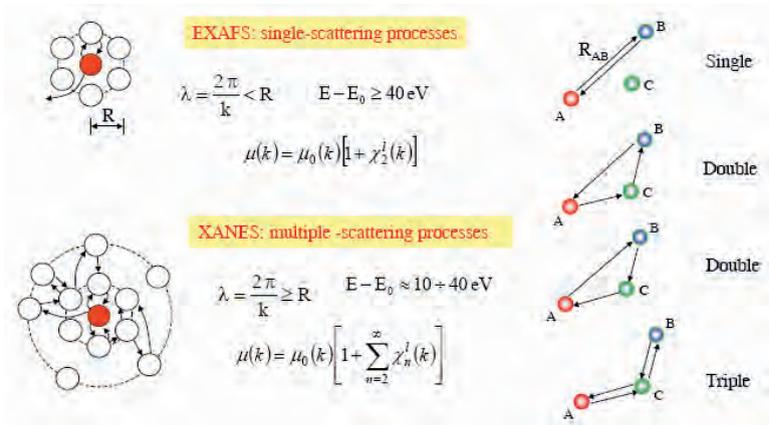


FIGURE 4. Single and multiple-scattering processes in x-ray absorption.

Often these features are diagnostic of coordination and are of use for geochemistry. For example, the toxic chromate anion is tetrahedral and as a result has a large absorption feature just below the absorption edge (the so-called pre-edge) that is not present in the more benign Cr(III). As a result, the presence of this feature is diagnostic for the more toxic form of chromium.

It is important to note that XANES is sensitive not only to the oxidation state, but also to the bonding geometry. The symmetry of the absorbing site strongly affects the pre-edge transition and, thus, XANES is capable of discriminating species of similar formal oxidation state but different coordination.

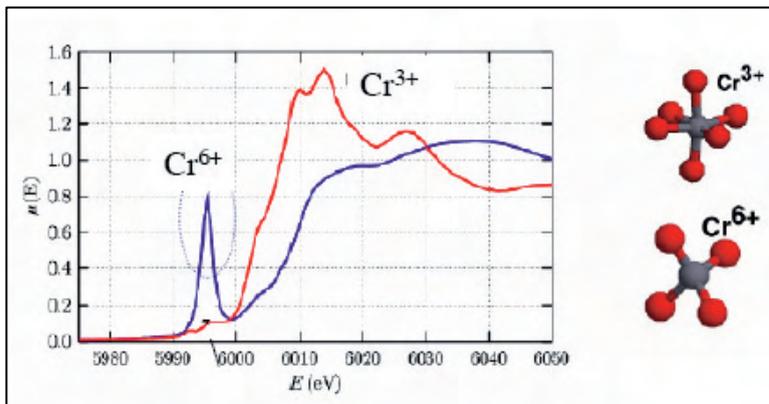


FIGURE 5. Cr K-edge XANES of  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  in octahedral and tetrahedral environments.

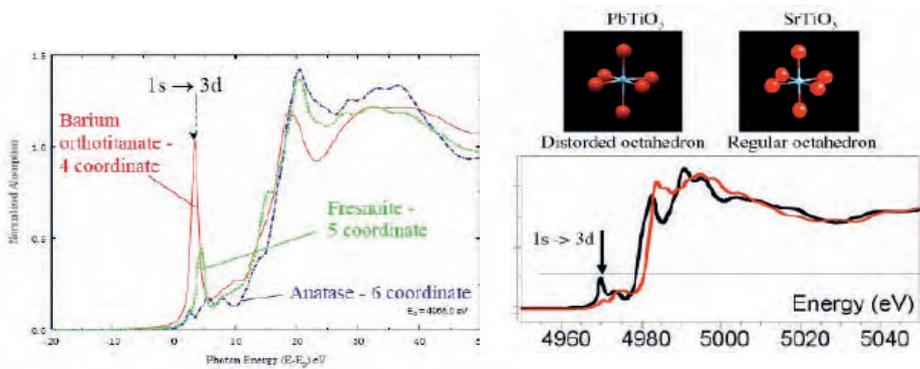


FIGURE 6. Ti K-edge XANES spectra of reference compounds in which Ti ion shows the same oxidation state but different coordination.

The more distant region of the X-ray absorption spectrum is termed the extended X-ray absorption fine structure (EXAFS) region. EXAFS spectra are best described as a series of periodic sine waves that decay in intensity as the incident energy increases from the absorption edge. These sine waves result from the interaction of the ejected photoelectron with the surrounding atomic environment. As such, their amplitude and phase depend on the local structure of excited atom and, consequently, the EXAFS provides direct, local structural information about the atomic neighborhood of the element being probed. The information content consists of the identity of neighbouring atoms, their distance from the excited atom, the number of atoms in the shell, and the degree of disorder in the particular atomic shell. These distances and coordination numbers are diagnostic of a specific mineral or adsorbate-mineral interaction; consequently, the data are useful to identify and quantify major mineral phases, adsorption complexes, and crystallinity.

Although the EXAFS formula (see Fig. 3) provides a complete description of the EXAFS oscillations, it is not a particularly convenient form for visualizing the information content of an EXAFS spectrum. Fourier transformation can be used to decompose a frequency-space signal into its different constituent frequencies. This is illustrated for crystalline and amorphous Germanium in Fig. 7. The Fourier transform

(FT) of an EXAFS spectrum gives a pseudo-radial distribution function. It is pseudo in that the FT amplitude cannot be related directly to electron density around the absorber due to the backscattering amplitude and the damping factors, and because the apparent distances in the FT are shifted by about 0.5 Å, due to the phase shifts. However, the FT is a useful way of judging qualitatively what shells may be present in a system and for comparing a fit to the data.

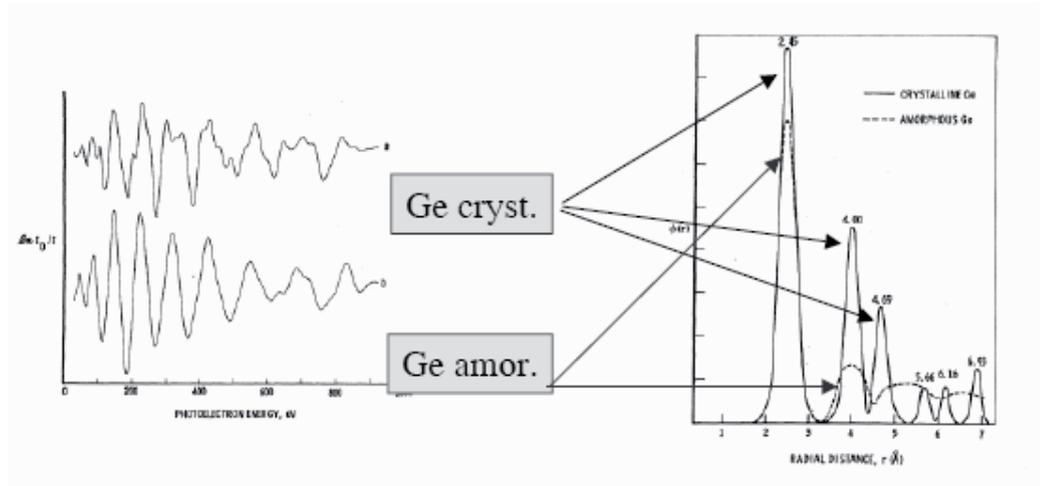


FIGURE 7. Ge K-edge EXAFS spectra and their Fourier transforms in the case of crystalline and amorphous Germanium.

### X-ray Absorption Spectroscopy in Mineralogy and in the Earth and Environmental Sciences.

X-ray absorption spectroscopy has become a common technique in mineral studies suited to extend structure determination down to an atom local environment, thus some three orders of magnitude less than the structure volume, best inspected by methods based on X-ray diffraction.

The unique capabilities offered by XAS are due to its main general features:

i) the absorption spectrum is element specific: the inner-shell absorption steps occur at x-ray energies characteristic of the absorbing element, so that individual element absorption spectra can be picked up out in samples containing a complex chemical mixture of different elements simply by changing the x-ray wavelength;

ii) by tuning the x-ray energy one can not only select specific elements in the sample but to select different absorption edges for the same atom, i.e. select the final-state symmetry.

iii) the principal advantage of XAS as a structural probe is that it is a local structure probe and the presence of long-range order is not required. This means that XAS can be used to study non-crystalline samples or to compare solution structure with solid state structure. In ideal circumstances EXAFS data can be analysed to determine the absorber–scatterer distance with an accuracy of 0.02 Å (and a precision that is substantially better, 0.004 Å, and perhaps even better under carefully controlled conditions). Coordination numbers can be determined with accuracy better than 20% and scatterer identity can typically be defined to the nearest row of the periodic table.

iv) Flexible detection mode. Different detection schemes are available for XAS measurements. The detection system depends on the concentration of the absorbing atom, on the photon flux of the beam line and on the energy of the absorption edge to be investigated. Transmission and fluorescence modes are typically used for XAS detection. For bulk experiments using hard X-rays on atoms with  $Z > 20$  present with concentrations greater than 0.1% in the sample (atomic ratio), standard X-ray transmission techniques are used, under gas (He, N) or in air. Indeed, the Transmission mode is the preferred one when there are no experimental constraints that suggest another. Limiting conditions are excessive thickness of the sample that forbids the beam to pass through, and diluteness of the absorber species ( $< 1$  wt.%), when the XAS features become comparable with the statistical noise. Transmission through the sample assures that the whole bulk content of absorber present in the sample is probed and it is relatively independent upon the matrix effect, although the signal to noise ratio (S/N) may be somewhat reduced in the case of matrices having an average  $Z$  close to that of the absorber. On the other hand, recording a spectrum in the fluorescence yield (FY) mode is a highly efficient experimental method for high- $Z$  atoms and highly diluted samples. Using appropriate filters, only the photons emitted by the excited absorbing atom are recorded. This detection mode crosscuts all problems of sample thickness that affect the transmission mode, thus even very thick samples ( $> 1$  mm) can be probed, and is particularly effective when the absorber is diluted, as it increases detection by at least

two orders of magnitude. Consequently, S/N is enhanced and XANES spectra on even very diluted heavy atoms can be measured proficiently.

v) Finally, it should be noted that XAS experiments can be performed on a highly flexible sample environment. In this way, XAS experiments can be performed under extreme conditions of temperature, different gas atmospheres, and even under high-applied pressure on solid, liquid and gaseous samples.

These characteristics make XAS an incomparable tool to face different problems in Mineralogy and in the Earth and Environmental Sciences. Indeed, the flexible sample environment allows approach the temperature and pressure conditions of the Earth's interior where phase transitions in minerals under high pressure are known to govern some of the major geophysical properties. In a similar way, XAS provides an unique insight into the accurate knowledge of trace-element behaviour in rock-forming and accessory minerals that results fundamental to understand and model petrologic and geochemical processes. These rock-forming minerals are always complex solid solutions and, therefore, the only approach capable of characterising the local coordination of the individual substituents is the use of element-selective spectroscopic methods like XAS.

This is for example the case of the characterization of trace Nd and Ce site preference and coordination in natural melanites. The identification of the crystal-chemical parameters controlling trace-element partitioning between minerals and silicate melts is a topic of considerable interest. Garnets represent an important group of rock-forming minerals in this regard, since they are stable over a wide range of physico-chemical conditions and are able to incorporate several trace elements commonly used in geochemical modeling. For these reasons, aluminosilicate garnets ( $X_3Al_2Si_3O_{12}$ ,  $X = Fe^{2+}$ ,  $Mn^{2+}$ , Mg, Ca) have received much attention, regarding their complex crystal chemistry, their thermodynamic properties or trace-element behaviour. Despite the importance of the geochemical behavior of REE in garnets, little work has been done to decipher their site preference and local coordination in trace or minor amounts. Indeed, there are no examples in the literature of direct structural investigations on the site location and geometry of REE in natural garnets, possibly due to their low concentrations. A recent work by Quartieri et al. has reported the XAS study of the site location and geometry of trace amounts of neodymium (from 176 to 1074 ppm) and

cerium (791 ppm) in natural garnets. The comparison of the experimental spectra recorded at high energy (Nd K-edge, 43569 eV; Ce K-edge 40443 eV) with theoretical ab-initio computations demonstrate that, in all the samples, the trace elements are located in the dodecahedral X site and not in extended structural defects or interstitial sites. The local geometry around the two rare-earth elements is compatible with their ionic radius and is compared with that of Ca, the major element at the X site, as determined by single-crystal X-ray diffraction data. This work represents the first example of direct investigation of trace-level REE coordination in natural garnets, and confirms the great relevance for the Earth Sciences of the use of fluorescence XAS at high energy.

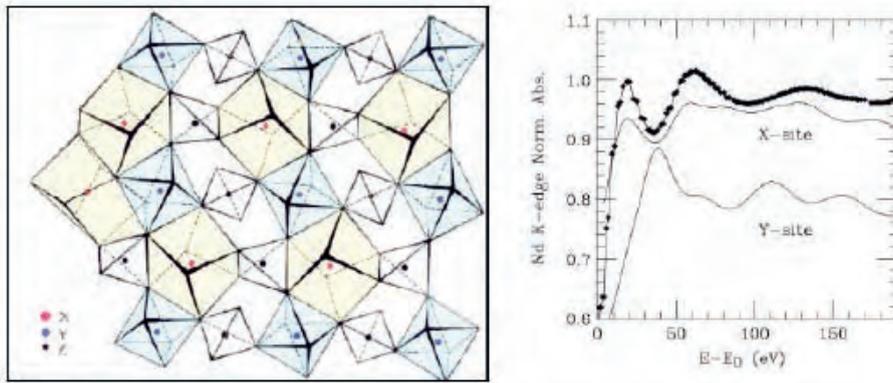


FIGURE 8. Schematic view of the crystal structure of  $X_3Y_2(ZO_4)_3$  garnets and the comparison between the experimental Nd K-edge XANES signal of a natural garnet (A204) and those calculated on the basis of the FMS theory assuming Nd in the dodecahedral (X) or in the octahedral (Y) site of garnet structure. This garnet contains traces of Nd (1125 ppm) and Ce (830 ppm) being its composition  $(Ca_{2.9}Mg_{0.06}Mn_{0.02}Nd_{0.02}) (Mg_{0.08}Ti_{0.89}Zr_{0.04}Al_{0.28}Fe^{3+}_{0.71}) (Si_{2.33}Fe^{3+}_{0.62})$ .

The capability of XAS to detect and characterize even trace amounts of atoms that are dispersed within minerals has been recently exploited also by Earth and Environmental scientists working on the understanding of the mineralogical and biogeochemical processes and interactions associated with environmental pollution. Within this scenario XAS is the main experimental weapon supplying information on the speciation of toxic materials. Understanding the transport and deposition of metals is crucial to both predicting toxic metal bioavailability and the accumulation of economic concentrations of metals to form mineral deposits. Toxic metals at the Earth's surface are

often present as non-crystalline forms either as sorbates on mineral species or fixed in amorphous phases. Therefore, XAS is the perfect probe for identifying those species, which are key components in the cycling of these metals.

Moreover, certain living organisms can concentrate and tolerate high amounts of heavy metals and determining the reasons for their adaptability provides strategies for remediation of contaminated land. Studies of metal take-up by biological samples have included investigation of the speciation of nickel, zinc and manganese in hyper-accumulator plants. The Ni hyper-accumulator plant *Berkheya coddii* has nickel complexed with histidine, while zinc in *Cardaminopsis halleri* and manganese in *Grevillea exul* are co-ordinated to oxygen probably as carboxylic acid anions. These relationships point to considerable selectivity in the metal-binding ligands in different classes of hyper-accumulator plants. Similarly, arsenic, lead and zinc have been found in earthworms and *Lumbricus rubellus* has adapted to living on arsenic contaminated soils with no observed deleterious effects. XAS shows that As(III)-S-thiol complexes are present in the intestines and body walls of this earthworm. As an example of the XAS capabilities in this field, we summary here the work on the changes of chemical states of toxic metals in aquatic sediments by bacteria reported by Fujiwara et al.

The implementation of Pollutant Release and Transfer Register (PRTR) obliged to report the total amount of chemical substances, such as toxic metals, released into the atmosphere, hydrosphere and soil. The total amount of these substances that have been released into the environment due to human activity is now becoming clear. However, the chemical state changes of toxic metals have not been clarified. Therefore, it is customary to clarify the behaviour of toxic metals in the environment to ensure safety against damage due to toxic metal contamination, because the toxicity of a metal depends on its valence or combined states. In many cases, microorganisms have assumed a vital role in the chemical state changes of metals.

The use of microorganisms is expected to lead to the development of environmental restoration technologies by revealing the biological reaction pathway of metals. Recently, a selenate reduction bacterium, *Sulfurospirillum barnesii*, was isolated from a freshwater sediment (R.S. Oremland *et al.*: Appl. Environ. Microbiol. **65** (1999) 4385). *S. barnesii* has the ability to reduce selenic acid [Se(VI)] under anaerobic conditions, using organic acid as an electron donor.

X-ray absorption spectroscopy allows one to monitor the change of the chemical state observed for selenium in a biological reactive process in connection with the reduction ability of *S. barnesii*. Shigeki Fujiwara, Norizo Saito and Yasuhiro Konishi used a DSM 10660 strain for *S. barnesii*, cultivated in a 500 ml sealed bottle with *Sulfurospirillum* II medium containing 83 mg/l Se(VI). Cultivation was carried out at constant temperature (30 C) under anaerobic conditions with the injection of inert gases (N<sub>2</sub>/CO<sub>2</sub>). XAFS spectra of *S. barnesii* culture were collected in the fluorescence mode using a Ge 19-element solid-state detector.

Figure 9 shows Se *K*-edge XANES spectra of *S. barnesii* culture and reference materials. A peak due to metallic selenium [Se(0)] was clearly observed in the spectra after 28, 37, 43, 53 and 66 hours. Also, a peak due to tetravalent selenium [Se(IV)] was observed in the same spectra. This result shows that the reduction pathway from Se(VI) to Se(0) by *S. barnesii* goes through Se(IV). In addition, the chemical composition of selenium in each moment was estimated from the ratio of each chemical states calculated by the curve-fitting method using the spectra of the reference materials. The change of the chemical composition of selenium indicates that Se(VI) constantly decreases with increasing *S. barnesii* growth rate. In this case, although a rate-limiting step of the reduction pathway from Se(IV) to Se(0) occurred for 20 hours after seeding, the reduction of Se(VI) to Se(IV) proceeded constantly. Thus, from the above finding, it is assumed that the reduction of Se(VI) to Se(IV) by *S. barnesii* is faster than that of Se(IV) to Se(0) under such a high selenium concentration (83 mg/l selenium). The results also indicate that selenium released in to the hydrosphere is immobilized as metallic selenium by anaerobic bacteria, such as *S. barnesii*, which have the ability to reduce selenium. Figure 9 shows pattern diagrams of dynamics of selenium in aquatic sediments. If we can accelerate the growth of selenium reduction bacteria, and keep them in high density, we will be able to effectively render selenium harmless.

This work illustrates how researchers using synchrotron radiation are now able to establish the mobility and bioavailability of toxic metal in contaminated land and can play a crucial role in developing methods for environmental 'clean up'.

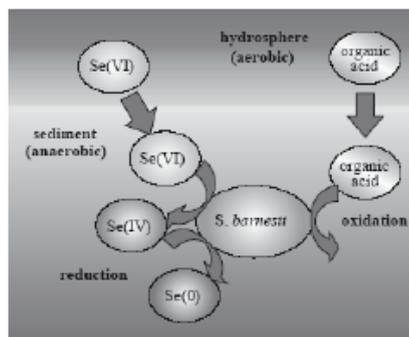
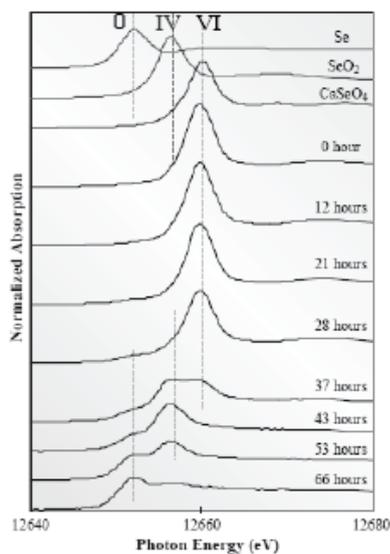


FIGURE 9. Left: Se K-edge spectra of culture after 0, 12, 21, 28, 37, 43, 53 and 66 hours from seeding *S. barnesii*, along with Se,  $\text{SeO}_2$  and  $\text{CaSeO}_4$  for reference. Right: Pattern diagrams of dynamics of selenium in aquatic sediments.

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