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SYNCHROTRON µ-X-RAY ABSORPTION SPECTROSCOPY IN THE EARTH SCIENCES

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Introduction - Basic theory

X-ray absorption spectroscopy (XAS) is a powerful tool for exploring local electronic structure that can be particularly useful in the absence of long range order (eg amorphous materials) where other methods like X-ray diffraction cannot be as informative. The measurement is element specific and the signal is a result of the rearrangement of electrons after excitation by X-ray photons based on quantum-mechanical selection rules for electronic transitions. The photon absorption probability, which gives rise to oscillations in the absorption coefficient, depends not only on the atom's electronic structure but also on the multiple scattering incidents in the local environment around the central atom, events which ultimately result in the modulations observed in the absorption spectra.

The sudden rise in absorption at the edge, at an energy characteristic of the element and the electronic shell, occurs when an incident X-ray has just sufficient energy to cause transition of an electron from a low bound state to an unfilled state. Further vacancies and subsequent rearrangement of electrons modulate the observed signal. Depending on the range of the energy region scanned XAS is commonly divided into X-ray absorption near edge structure (XANES), which goes typically up to ~50 eV above the absorption edge, and extended X-ray absorption fine structure (EXAFS) which extends to hundreds of eVs above the edge. The XANES region reflects electronic transitions to unfilled bound states, nearly-bound states, or continuum states of the appropriate symmetry while the EXAFS region reflects transitions to continuum states only.

The basic EXAFS equation is numerically solved with good quantitative accuracy for EXAFS data and from fitting the acquired spectra one can extract the type and number of neighbouring atoms and the corresponding bond lengths. The equation breaks down in the XANES region so the majority of such data are analysed with qualitative approaches often based on measurement of model compounds.

The key parameters that influence the shape and energy position of features in the XANES region are orbital occupancy, charge state, bond lengths, and local symmetry. Oxidation state is usually acquired from the position of the absorption edge while coordination geometry is often based on the analysis of the pre-edge (see Fig 1a). That said, the pre-edge is also influenced by oxidation state while the energy of absorption edge can vary with ligand symmetry which means that qualitative analysis is often not trivial and a large range of suitable reference materials may need to be measured.

Ab-initio simulation of XANES spectra is implemented in a number of software packages however this route of analysis is not very widespread despite recent advances on code sophistication and computational power. The fitting of EXAFS data is much more routine and again several packages exist for this. Various software tools have been developed for data reduction, processing and visualisation of XANES data. An overview of software packages for XAS can be found at the

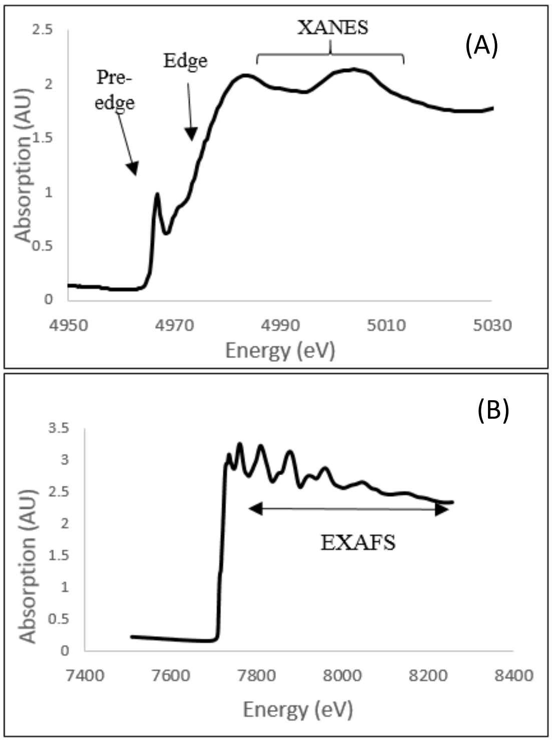

Figure 1. XAS scans demonstrating the different energy regions used for analysis. A) XANES start a few eV before and extend a few eV after the absorption edge, while B) EXAFS can potentially be acquired for several hundred eVs after the edge.

XAFS.ORG portal (http://www.ixasportal.net/wiki/Software). There is also a wealth of resources on XAS theory, see for example the extensive paper from Newville [1]. A number of tutorials covering theory, experimental and analysis methods have been written by Bunker and can be found at his website (http://gbxafs.iit.edu/training/tutorials.html).

2. *TECHNICAL - EXPERIMENTAL CONSIDERATIONS*

Absorption spectra are acquired when the energy of the X-ray beam delivered to the sample is finely incremented. The tuning of the beam energy is achieved with rotating crystal monochromators of various degrees of sophistication depending on the beamline specialisation. The monochromator crystals are usually, but not exclusively, made of silicon and the choice of crystal lattice planes determines the energy resolution of the XAS scan. The accuracy of the energy positions of features of XAS scans is ensured by scanning reference materials, usually metals foils, to calibrate the monochromator. Modern instruments are very stable so energy drifts are not as much of an issue as in the past.

The type of information acquired by XAS is common to bulk and microprobe synchrotron beamlines. When spatial resolution is required microprobes can be used in the first instance to select a specific area for analysis guided by an on-line optical microscope. When the exact location is not optically obvious, for instance if the element of interest is a constituent of a number of different minerals, micro-X-ray fluorescence (μ-XRF) elemental distributions of the target element but also of others present in the sample can be produced to facilitate the selection of specific points for XAS analysis. In some μ-XAS beamlines there is also the ability to acquire μ-XRD patterns at the same points as μ-XAS to facilitate phase discrimination.

One of the most appealing aspects of XAS is the ability to measure any form of material often with no or minimal sample preparation. That said, there are a number of parameters that need to be considered before planning an experiment so basic pre-characterisation of the samples is essential before planning a XAS experiment. The concentration of the element of interest will determine if the measurements need to be done in fluorescence or transmission mode; the boundary is not clear-cut as it depends on a number of parameters, but fluorescence is usually advised for up to the low % w/w levels. Concentrated samples measured in fluorescence suffer from self-absorption producing potentially misleading results; the effect is more pronounced in low atomic number atoms. Transmission imposes restrictions to the sample thickness which will depend on atomic number of the element of interest but also on the sample matrix. Samples with high concentrations of the atom of interest that cannot be made thin enough for transmission require techniques similar to those for surface sensitive XAS, such as ReflEXAFS (grazing incidence) or electron yield. For samples that are in the optimum concentration range for fluorescence often the only preparation needed is polishing in order to produced flat surfaces (only necessary for μ-XAS).

An important factor to keep in mind is that XAS is not a surface sensitive technique; using a beam with lateral resolution in the μm range does not preclude getting signal averaged from potentially hundreds of μm along the direction of the beam. In heterogeneous samples this can lead to the issue of signal emerging from a mixture of different particles/phases. If it is essential to acquire signal only from the surface then variants of the technique, like ReflEXAFS, are advised. Such modes are often incompatible with high lateral resolution analysis so are mostly used in bulk measurements. To reduce the information depth in μ-fluorescence measurements a "pseudo" grazing angle setup is sometimes implemented by reducing the angle of the detector in relation to the sample.

In terms of sensitivity XANES can measure concentrations as low as a few ppm (the precise limit depends on Z, thickness, matrix and line measured) while for EXAFS several hundreds of ppm are required. Powders and liquids can be measured but these are more suitable for a bulk rather than a μ-XAS beamline. Powders are relevant to μ-XAS as they are regularly used as model compounds and if not prepared and measured correctly can lead to misleading results. Weights and dilution ratios need to be calculated before making the pellets and particle size can be important for low Z elements.

Another problem can be radiation induced change of oxidation state. Certain elements in certain matrices (organic, hydrated) are susceptible to rapid photo-reduction or photo-oxidation. There are three general paths experimenters take to address this. Heavy filtering of the beam to reduce absorbed dose is the easiest method but is often impractical if the element of interest is very dilute. Cryostats that keep the samples at nitrogen or helium temperature are essential for such samples. There are several types of cryostats in regular use however the requirements for microprobes are very stringent as any degree of vibration transferred to the sample can have severe impact on the data acquired. A third route is fast scanning of the monochromator, a development which is becoming available in most beamlines as technical advances take place. This can dramatically reduce the duration of a XANES scan but again whether this type of measurement is viable depends on sample concentration. Another way that radiation sensitive samples can potentially be measured with microprobes, if they are not suitable for mounting in a cryostat as this can restrict sample size and mounting, is to extract an effective energy spectrum not by scanning the monochromator but by rapid mapping of a small sample area for a range of energies. XANES mapping can result in the integrated dose on each pixel being much lower than in a conventional XANES scan but again this approach is concentration limited as it is a fast counting technique. It also presents the additional technical requirement for precisely reproducible stage positions.

Other experimental issues to be addressed include cases where the element of interest is at trace levels in the presence of major elements with fluorescence lines in the vicinity of those from the atom of interest. On occasion suitable filters are used to remove unwanted signal but there are instances where conventional XAS is not adequate for addressing such problems, for example when there is overlap between the K-edge of a transition metal and the L-edge of a rare earth element. Cases like this and others that require higher spectral resolution can be addressed by using high-resolution X-ray emission and high-resolution X-ray absorption spectroscopy [2].

The aim of this short summary was to cover the most common approaches to XAS experiments. Detailed examples of a variety of applications and element specific considerations are presented in the comprehensive review of XANES applications to the geosciences by Henderson *et al.* [3].

3. MAIN THEMES – CASE STUDIES

Applications strongly or loosely connected to geosciences make up a significant percentage of the experiments taking place at a μ-XAS beamline. Minerals, melts, glasses, rocks, comet particles and meteoritic samples are brought to our hutches by mineralogists, volcanologists, petrologists, geochemists, palaeontologists and environmental scientists.

Types of analysis of XAS data include measurement of oxidation state based on the position of absorption edge or pre-edge, finger-printing of pre-edge or post-edge XANES features for chemical speciation, linear combination fitting, principal component analysis and the direct determination of structural parameters by numerical fitting of XAFS. Published work of XAS applications in the Earth Sciences is a vast field making the selection of a few case studies hard. The examples summarised in the following sections are from the collection of experiments that have taken place at the Microfocus Spectroscopy beamline I18 [4] at Diamond Light Source. They have not been chosen on the basis of scientific themes but with the aim of demonstrating some of the most common approaches in XAS measurement and analysis. Because of the numerous implications of iron oxidation state in many geo-significant materials, Fe oxidation state analysis based on the fitting of the pre-edge is a sub-group of its own. A detailed example of this is presented in a contributed paper in this issue.

3.1. Titanium in hibonite : XANES pre-edge analysis

The dramatic changes of pre-edge features based on local coordination environment are demonstrated for the case of titanium. Berry *et al.* [5] studied the case of hibonite, which is the second mineral after corundum to condense from a gas of solar composition; specifically the authors were exploring the earlier described hypothesis that $Ti^{3+}/\Sigma Ti$ may record oxygen fugacity (fO_2) at the time of crystallisation/condensation from the solar nebula. Hibonite incorporates both Ti^{3+} and Ti^{4+} at two possible sites so there are a number of possible combinations of Ti occupancy. The authors measured natural meteoritic hibonite with variable Ti content and two synthetic groups of hibonite, one from melt equilibration at different fO_2 and the other produced from oxides at high temperatures. They also compared measurements from natural and experimental samples to simulated XANES spectra, modelled with FDMNES [6], for various proportions of Ti^{3+} and Ti^{4+} at the different substitution sites.

The starting point is that $Ti^{3+}/\Sigma Ti$ influences the structure of the pre-edge, however this is also heavily dependent on symmetry. The pre-edge peak corresponds to the 1s →3d transition, which is forbidden in octahedral coordination, but gains intensity by orbital mixing in lower symmetry environments. A change in site symmetry from trigonal bipyramidal (5 coordinated) to octahedral (6 coordinated) is associated with a decrease in pre-edge intensity, as observed here in both measured (Fig. 2A) and modelled (Fig. 2B) spectra. Which substitution sites Ti occupies affects symmetry but site occupancy is in turn influenced by total Ti as when the element is more dilute it is more likely to be found as isolated cations.

Different combinations of ΣTi and $Ti^{3+}/\Sigma Ti$ reflected in the XANES from natural and synthetic samples and from simulated spectra are displayed in Figs. 2A and 2B. Fig. 2A shows the pre-edge region from the XANES of two natural hibonite cases and six experimental ones, all but one are Ti^{4+} but varying in ΣTi. The pre-edge systematically decreases in maximum intensity and broadens (develops shoulders at lower and higher energies) with increasing ΣTi. These changes are mirrored in the modelled spectra of Fig. 2B (b-e) where a measured spectrum from natural hibonite (a) is also displayed for comparison. The pre-edge of the XANES measured from the natural sample (a) is essentially reflecting that of the simulated spectra (b) allowing for the loss of resolution due to experimental peak broadening in comparison to the ideal case calculated theoretically.

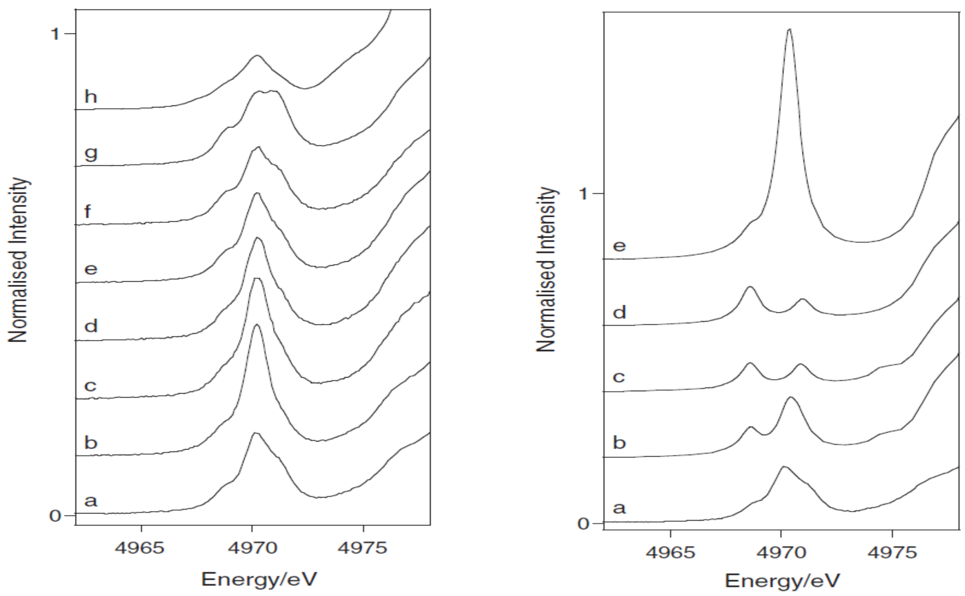

Figure 2. A) Pre-edge region of Ti XANES spectra from: (a)-(b): natural hibonite (predominately Ti^{4+}). (a) higher ΣTi than (b); (c)-(h): synthetic hibonite (all but (h) are Ti^{4+}) of increasing ΣTi. B) Ti pre-edge region of (a) natural hibonite of mixed Ti^{4+}-site occupancy; (b)-(e): simulated XANES for various Ti^{4+}-site occupancies. Reprinted with permission from Elsevier from "The limitations of hibonite as a single-mineral oxybarometer for early solar system processes", Berry *et al.* [5].

The XANES acquired from the experimental hibonites and the spectra simulated for various oxidation and occupancy combinations, suggest that changes in Ti^{4+} site occupancy resulting from variations in concentration, at constant fO_2, produce changes in the XANES spectra that could easily be misinterpreted as being due to differences in oxidation state. Therefore petrogenetic history and its effect on Ti site occupancy will be convolved with any differences in $Ti^{3+/}\Sigma Ti$ and as a result no simple relationship between Ti oxidation state and fO_2 should be expected.

3.2. Vanadium leaching during surface weathering of steel slug: XANES pre-edge and absorption edge analysis

Basic oxygen furnace (BOF) steel slag is enriched in potentially toxic vanadium which may be mobilised during weathering. As a significant proportion of slug waste is reprocessed and recycled, the fate of V during the mechanisms involved in weathering is a potential environmental concern. Hobson *et al.* [7] have used μ-XANES to investigate the oxidation state of V in the different phases found in laboratory weathered slug (aerated and air-excluded experiments). SEM/EDS measurements of the unweathered sample revealed four chemically discrete phases, two of those containing V (dicalcium silicate and dicalcium aluminoferite), while in the experimentally weathered blocks a compositionally distinct altered region was detected, marked by depletion of Si and Ca. This region, determined to be calcium silicate hydrate, contained V, Fe and P. On beamline I18, μ-XRF maps were collected from control and weathered blocks with a 2x2 μm^2

spatial resolution in order to resolve the different phases identified from their relative Ca and Fe composition. From selected points of interest (Fig. 3) vanadium µ-XANES spectra were subsequently acquired. XANES spectra were also collected from a range of laboratory chemicals and aqueous solutions to be used as reference materials.

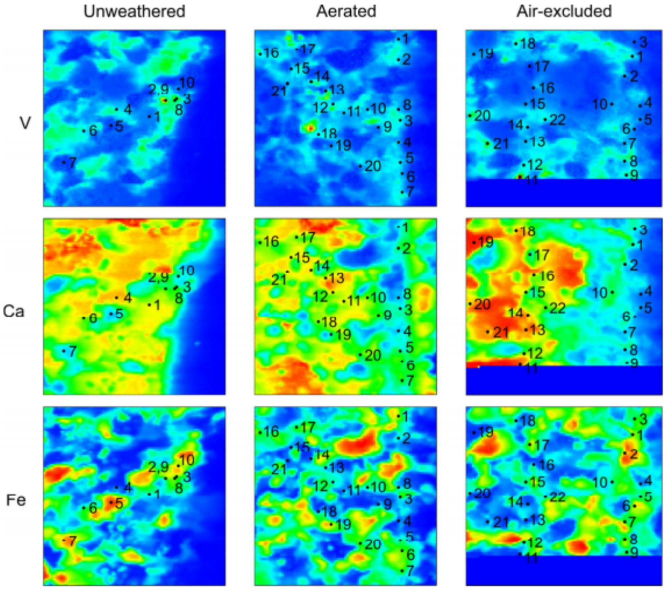

Figure 3. V, Ca and Fe µ-XRF maps collected from the slag blocks recovered from the aerated, air-excluded leaching experiments and from an unweathered sample; numbered points indicate locations where µ-XANES spectra were collected. Reprinted with permission from ACS Publications (open access article published under CC BY License). From "Mechanism of vanadium leaching during surface weathering of basic oxygen furnace steel slag blocks: A microfocus X-ray absorption spectroscopy and electron microscopy study"; Hobson *et al.* [7].

The oxidation state of V was obtained through the absorption edge position while symmetry information was extracted from the pre-edge peak height analysis (Figs 4A and 4B). In Ca_2SiO_4 vanadium found as V^{5+} and in tetrahedral coordination while in $Ca_2(Al,Fe)_2O_5$ both V^{4+} and V^{5+} (octahedral and tetrahedral) phases are present. In the altered region Ca-Si-H only the tetrahedral V^{5+} is evident. These findings suggest that essentially all of the vanadium released to solution must originate from the dicalcium silicate phase as V^{5+} which is predicted to be soluble as aqueous vanadate species at the measured solution pH.

3.3. Biogeochemical microenvironment of weathered shale cliffs : XANES linear combination fitting

Within the wider scope of studying the role of pyrite-containing shale cliffs in coastal erosion Cockell *et al.* [8] have investigated the hypothesis that biogeochemically active bacteria that inhabit

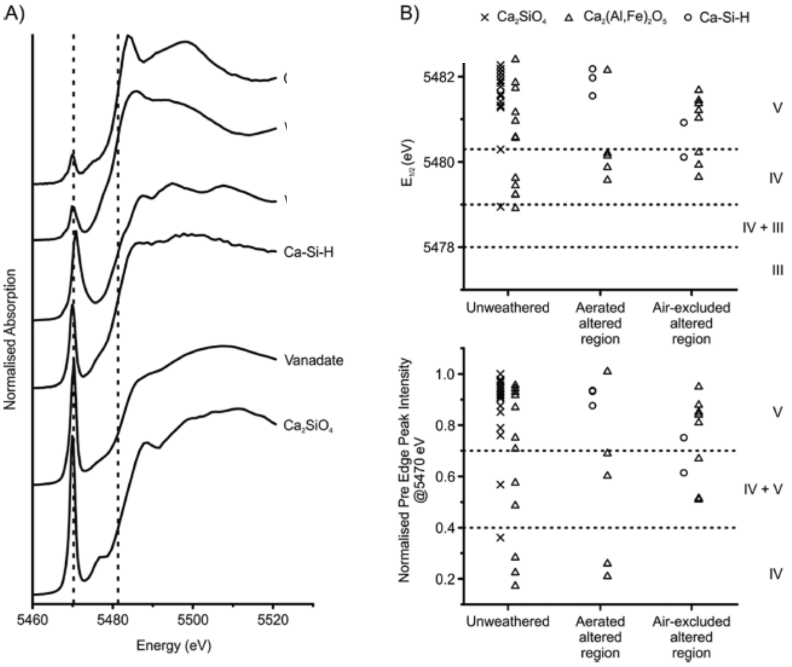

Figure 4. A) Representative V µ-XANES spectra collected from V-containing slag phases and standards; B) E1/2 position and normalised pre-edge peak height intensity determined from all data collected from slag blocks. Reprinted with permission from ACS Publications as in Fig. 3.

rock surfaces may contribute to coastal degradation. Certain microorganisms are known to catalyse pyrite oxidation and one hypothesis is that such microscale events may contribute to rock weakening.

The surface of the weathered shales is characterised by a thin layer of iron oxyhydroxides and XRD analysis suggested that that there are no well-defined crystalline phases within these layers. To gain more information on these disordered phases µ-XANES analysis was employed to investigate the oxidation states of iron within the surface layer of the shale.

As the iron distribution is heterogeneous a beam of approximately 6x6 µm^2 was used to first map the localisation of iron and to then obtain spectra from different regions (Fig. 5). XANES were also collected from a number of iron containing compounds which were then used to evaluate their contribution to the iron signal from the shale surface layers.

The oxidation state of iron was extracted from the position of the pre-edge (predominately Fe^{3+}) while differences in XANES features were attributed to varying contributions of different minerals. The spectra acquired from the shales broadly fell into three categories and linear combination fitting (LCF) of those, using the traces from the model compounds, revealed that the iron is predominately contained in ferrihydrite with varying contributions of goethite, magnetite and hematite. This, along with supporting evidence from other methods, lead to the hypothesis that the predominately Fe^{3+} nature of iron in the weathered surface is a product of oxidation of the iron

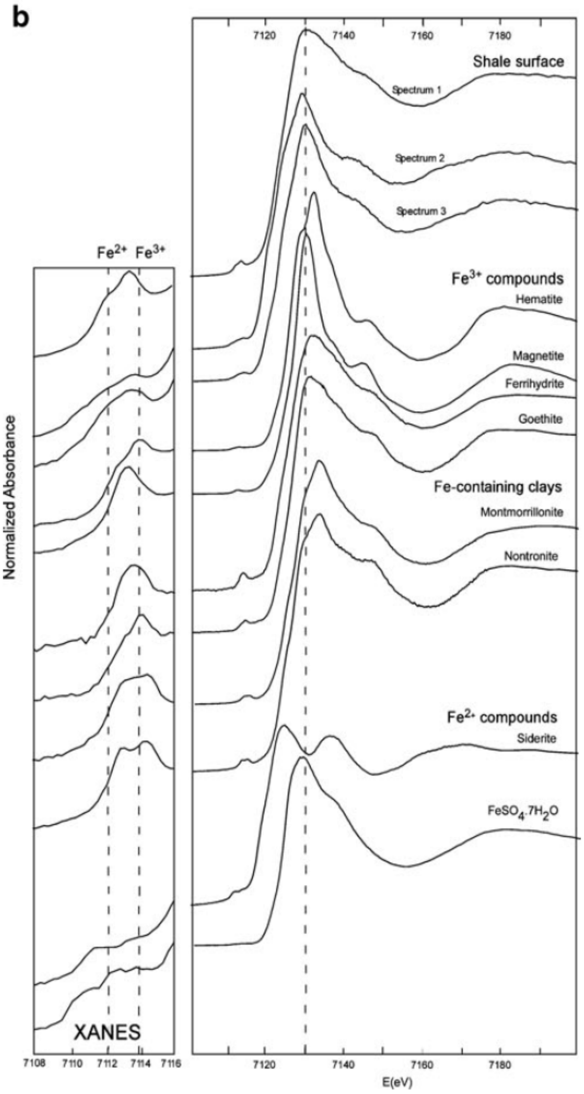

Figure 5. Fe XANES spectra of weathered surface shale iron oxides and control compounds. Expanded insert shows the pre-edge region with the two dotted lines marking the Fe^{2+} and Fe^{3+} peaks. Reprinted with permission from Springer Nature, from “Molecular characterization and geological microenvironment of a microbial community inhabiting weathered receding shale cliffs”; Cockell *et al.* [8].

leached from the shale pyrite as, amongst all Fe-bearing minerals in the shale, this is the most rapidly weathering. There are a number of routes via which pyrite oxidation can contribute to rock weakening, for example by-products of the process promote acidic microenvironments with further consequences. Microbial activity contributing to pyrite oxidation has been shown elsewhere however in this work biochemical characterisation of the particular strain of bacteria inhabiting this shale did not provide conclusive evidence for their role in the erosion of the pyritic component of the shale.

3.4. Arsenic in bauxite affected soils: XANES & EXAFS

Red mud (RM), the fine fraction bauxide residue remaining after aluminium extraction, carries a number of potentially toxic metals including arsenic. RM contamination gained widespread exposure after the 2010 dam breach incident in Hungary. Lockwood *et al.* [9] studied the potential for As mobilisation from RM, how this is affected by pH and redox conditions and the biogeochemical effects of adding RM into soil. Aerobic and anaerobic experiments were ran with different amounts of RM added to unaffected soil from the same geographical area and XAS was one of the techniques used to determine changes in solid or aqueous phase As speciation induced by long term incubation of the soil.

To determine the form arsenic takes in RM XANES data were collected (Fig. 6) and showed that As is predominately present as As^{5+}, however no coordination information was extractable (no pre-edge features). EXAFS (Fig. 7) data were therefore collected allowing the determination of the nearest neighbours as four oxygen atoms at tetrahedral coordination suggesting that the main species is arsenate. The fit of the data could not be improved by adding a second coordination shell therefore the exact nature of the phases present could not be resolved.

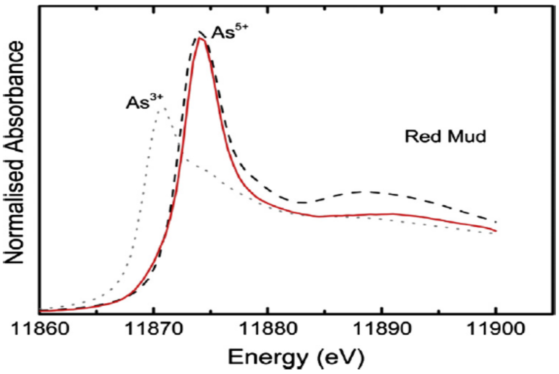

Figure 6. Arsenic XANES of RM and standards of arsenite and arsenate. Reprinted with permission from Elsevier (open access article under the CC BY license). From “Mobilisation of arsenic from bauxite residue (red mud) affected soils: Effect of pH and redox conditions”; Lockwood *et al.* [9].

One of the aims of the study was to determine the changes to As speciation in the unaffected soil (organic, wetland and sandy) after the addition of RM and anaerobic incubation. XANES absorption edge analysis showed that the As in all types of unamended soil is predominately arsenate while at the end of incubation some of the As had been reduced to As^{3+} in all three types of soil (Fig. 8). With the addition of RM some reduction still takes place in organic rich soil but in the other two types As remains mainly in the As^{5+} state. This suggests that the microbial reduction of As^{5+} to As^{3+} is inhibited by the addition of RD therefore affecting a change in this common biological process.

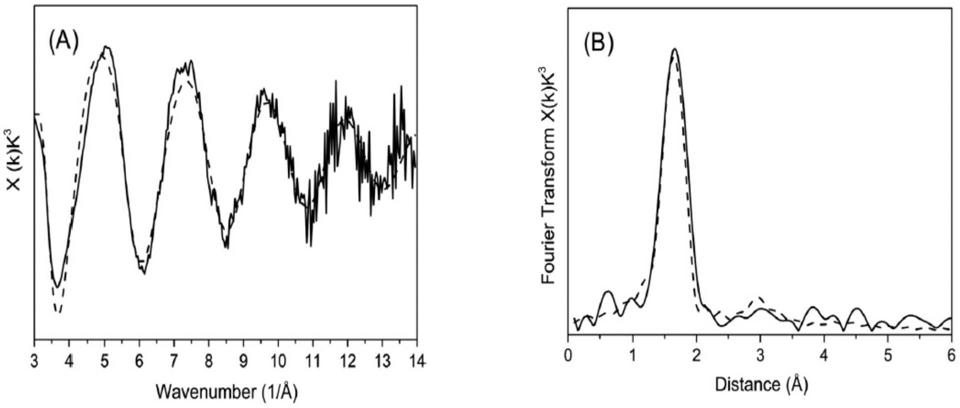

Figure 7. As RM EXAFS and Fourier Transform. Dashed lines are model fits (4 x As-O bonds). Reprinted with permission from Elsevier as in Fig. 6.

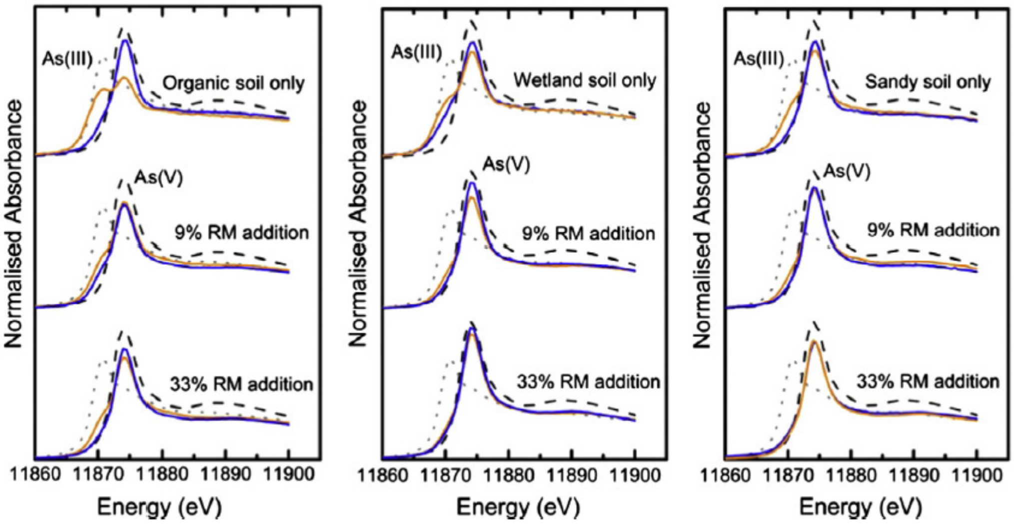

Figure 8. Arsenic K-edge XANES from standards, soil and recovered solids from anaerobic experiments and heat treated controls. The presence of a shoulder at the energy of As3+ edge allows the reduction of arsenate to be followed. Reprinted with permission from Elsevier as in Fig. 6.

4. REFERENCES

[1] Newville M 2014 *Rev. Mineral. Geochem.* **78** 33
[2] de Groot F 2001 *Chem. Rev.* **101** 1779
[3] Henderson G S, *et al.* 2014 *Rev. Mineral. Geochem.* **78** 75
[4] Mosselmans J F W, *et al.* 2009 *J. Synchrotron Radiat.* **16** 818
[5] Berry A J, *et al.* 2017 *Chem. Geol.* **466** 32
[6] Joly Y 2001 *Phys. Rev. B* **63** 125120
[7] Hobson A J , *et al.* 2017 *Environ. Sci. Technol.* **51** 7823
[8] Cockell C S, *et al.* 2011 *Microb. Ecol.* **61** 166
[9] Lockwood C L, *et al.* 2014 *Appl. Geochem.* **51** 258