Fe and S K-edge XAS determination of iron-sulfur species present in a range of Acid Sulfate Soils: effects of particle size and concentration on quantitative XANES determinations.

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Abstract. Acid sulfate soils (ASS) are soils and soft sediments in which sulfuric acid may be produced from iron sulfides or have been produced leaving iron oxyhydroxysulfates in amounts that have a long lasting effect on soil characteristics. If soil material is exposed to rotting vegetation or other reducing material, the Fe-oxyhydroxysulfates can be bacterially reduced to sulfides including disulfides (pyrite and marcasite), and Monosulfidic Black Ooze (MBO) a poorly characterised material known to be a mixture of iron sulfides (especially mackinawite) and organic matter. The chemistry of these environments is strongly affected by Fe and S cycling processes and herein we have sought to identify key differences in environments that occur as a function of Fe and S concentration. In addition to our chemical results, we have found that the effects of particle size on self absorption in natural sediments play an important role in the spectroscopic identification of the relative proportions of different species present.

1. Introduction

Substantial parts of Australia’s coastline contain sulfidic sediments that produce, or have the potential to produce sulfuric acid upon exposure to air. If sulfuric acid is released, it can dissolve minerals present in the sediment and release potentially toxic metals to the environment [1]. The release of sulfuric acid is mediated by the redox equilibrium between reduced and oxidized iron and sulfur species. The factors controlling this equilibrium are poorly understood, and a detailed understanding of the mechanistic chemistry of the systems may lead to better management protocols. The analytical characterization of sediments and soils is difficult because classical analytical approaches require sediments to be refined or dried before analysis. For example, Scanning Electron Microscopy (SEM) analysis commonly employed to study soils require samples to be dried which can oxidize reactive species [2]. Wet chemical techniques designed to study reduced S species such as Cr reducible S
(CRS) only measure one part of the reduced system and often aggregate several functionally distinct S species. This means that related but non-identical species cannot be identified [3]. One way to characterize a sample without oxidizing it or changing it chemically is to use X-ray Absorption Spectroscopy (XAS). As ASS environments are dominated by the redox chemistry of both Fe and S, additional information can be gained by coupling together information obtained at both S and Fe K-edges. We have complemented our analysis of these natural systems by a study which evaluates the effects of particle size and concentration of Fe and S components on XANES peak intensities.

2. Experimental

2.1. Determination of iron/sulfur redox species present in the ASS environmental samples.
Sediment samples were collected from three different environments around Australia (Tilley Swamp, SA; Loveday basin, SA and Shark Creek, Northern NSW) using standard techniques for the collection of air-sensitive samples [4]. The Fe K-edge data were collected on beam-line 20B at the Australian National Beamline Facility (ANBF) at the Photon Factory Tsukuba, Japan. The Sulfur K-edge XANES data were taken on beam-line 16A at the NSRRC in Taiwan [5]. In both cases the reduced “natural” samples were thawed under a nitrogen atmosphere and mounted into sample holders between two pieces of Kapton tape (for Fe) or between Kapton and polyimide film (for S). Care was taken to ensure samples remained cold and in an environment free from oxygen. This methodology allowed analysis to take place in a chemical environment as close as possible to that found in the natural system. To induce oxidation of the sediment samples hydrogen peroxide was added to the natural samples and they were mounted as described above.

2.2 Investigation of the effects of particle size and concentration on XANES peak intensity
The effects of particle size and concentration were investigated for both pyrite (FeS₂) and elemental sulfur (S₈). Pyrite samples were obtained from the collection at the Adelaide museum and purity was confirmed by analysis with X-ray powder diffraction. Elemental sulfur was obtained as AR grade from Sigma Aldrich, from which three particle size ranges were prepared. The smallest particle size was obtained using ultra fine slurry milling [6]. This technique employed 0.7mm partially stabilized Zirconia ceramic (PSZ) beads ground with elemental sulphur for 3 days. Mid range particle sizes were obtained by grinding the sample with a motor and pestle. The largest particle size was the unground powder. The effects of sample concentration were studied for each of the particle sizes to give an indication of the two factors mediating self absorption: dilution and particle size. Pyrite and elemental sulfur were diluted 3 fold, 9 fold and 27 fold by weight with boron nitride. S K-edge XANES data was taken by mounting samples in a thin film on Kapton tape.

2.3 Data Analysis
Multiple scans were combined using the Average 2.0.6 program [7]. Data were baseline corrected using the PySpline program [8]. S K-edge spectra were calibrated to the maximum of the first feature of Na₂SO₄·5H₂O at 2472.02 eV, Fe K-edge spectra were calibrated by reference to the first inflection point of an Fe foil to 7111.2 eV. After the data was energy and baseline corrected, text files containing only the energy and intensity of the peak were created and standards were fitted to the sediment samples using Excel. These files were opened in Athena [9] and their intensity estimated using the ‘Linear Combination Fit’ option.
3. Results and Discussion

3.1 Particle size and concentration effects on S K-edge XAS peak intensity

Figure 1: The effects of particle size and particle concentration on the intensity of K-edge peaks

Figure 1 shows the S K-edge data collected on samples of different particle sizes and dilutions. The spectra on the left of Figure 1 were of samples run undiluted as thin films. Clear differences can be identified; the largest peak intensity is due to the smallest particles. These differences are further shown by dilution with boron nitride. From the data it is clear that particle size and dilution have a significant effect on peak intensity. This observation is important in the context of sediment analysis because a natural sample will usually contain a range of unknown particle sizes and dilutions both of which can effect quantitative XANES fitting. If carefully considered the S K-edge data may be used to give us an indication of S8 particle size in natural systems [4].

3.2 Sulfur K-edge Data

Figure 2: Sulfur K-edge data of reduced and oxidized sediment spectra from three acid sulfate soil environments, Loveday, Tilley Swamp and Shark Creek.

Figure 2 shows the S K-edge XANES data from three different environments in their native reduced form labelled “reduced” and in their peroxide oxidised form labelled “oxidised”. From Figure 1 key differences in the S distribution in the three different environments can be identified. The iron poor Loveday environment has a peak intensity (~2472.2 eV) consistent with it being rich in organo-sulfides. These organo-sulfides oxidize to two species consistent with the peak energy positions for either elemental sulfur and/or pyrite and sulfate. Pyrite and elemental sulfur have rising edges that are very close in energy (~2471.1 eV) which makes it difficult to differentiate between the two based on S K-edge data alone. From the data shown it is clear that the reduced S chemistry of the “Loveday” environment is dominated by organo-sulfide type materials in contrast to Tilley Swamp and Shark Creek which are dominated by Fe-S mineral phases. Interestingly the reduced S species of both Tilley Swamp and Shark Creek are slightly different, and neither fit perfectly with mackinawite or greigite. The sediment peak shape matches that of mackinawite, however, energy position is closer
to that of greigite indicating chemical differences between the sediment and the standards. All of the sediment samples contain sulfate, which could be free sulfate in solution or sulfate contained in an iron mineral phase, such as schwertmannite. Our data is not of sufficient resolution to speciate sulfate. While the fits to the sediment are good there are clear differences in peak intensities which could be related to particle size and concentration effects [10].

3.3 Fe K-edge data

Fe(III) +goethite Fe(III)) both fit the data well. (EXAFS fits of A were slightly better). The oxidized phase (far right) gave a better fit with the inclusion of ferrihydrite. While goethite has a similar rising edge position in the Fe XANES the peak shape was slightly different allowing us to differentiate between the two based on XANES. One interesting observation related to the results above is that the iron data suggests the presence of the reduced Fe-S mineral phase mackinawite, and the sulfur edge does not. This indicates that the S present as mackinawite (and other iron sulfides) represents only a small % of the total S. This is consistent with the fact that Loveday is an Fe poor environment.

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