Using X-ray Absorption Spectroscopy to Unravel Iron Biomineralisation Pathways in Re-flooded Acid-sulfate Soils

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Acid-sulfate soils (ASS) form via the drainage-induced oxidation of iron-sulfide minerals, such as pyrite (FeS_2). These soils adversely affect over 80 million hectares of valuable coastal floodplains and wetlands around the world (Andriesse and van Mensvoort, 2005). The widespread extent of environmental degradation associated with ASS makes their remediation an issue of considerable importance.

One approach to remediating these soils involves the re-flooding previously drained areas. This approach has the benefit of encouraging the onset of anoxia in the re-flooded soils, and the associated generation of alkalinity by bacterial Fe(III)- and SO_4-reduction.

Our previous research has demonstrated that ASS re-flooding drives important changes in arsenic availability. These changes are coupled with reductive biomineralisation of iron minerals, such as schwertmannite ($Fe_8O_8(OH)_6SO_4$). Recent studies have shown that interactions between schwertmannite and Fe^{2+} can cause relatively fast recrystallization of schwertmannite to goethite. This important biomineralisation pathway is initiated in re-flooded soils when Fe(III)-reducing bacteria utilise schwertmannite-bound Fe(III) as a terminal electron acceptor, thereby liberating Fe^{2+}, which then interacts with the remaining schwertmannite.

We hypothesized that the Fe^{2+}-catalysed transformation of schwertmannite to goethite may significant affect arsenic mobility in re-flooded acid-sulfate soils. In order to test this, we conducted a series of examining schwertmannite-arsenic interactions in anoxic, Fe^{2+}-bearing solutions (Fig. 1).

Fig. 1: Photograph showing the set-up of the anoxic transformation experiments used to evaluate arsenic effects and behaviour during the Fe^{2+}-catalysed transformation of schwertmannite to goethite.

All experimental runs involved 5 g of schwertmannite suspended in 1 L of 0.1 M NaCl, buffered at pH 6.5. Depending on the experimental treatment, a buffered 0.1 M NaCl background solution contained either no arsenic (Runs 1 and 2), 1 mM As(III) (Runs 3 and 4) or 1 mM As(V) (Runs 5 and 6). In addition, Runs 2, 4 and 6 contained 10 mM Fe^{2+}, whereas Runs 1, 3 and 5 contained no Fe^{2+}.

The change in solid-phase Fe speciation over a 9-day reaction period was quantified by Fe k-edge EXAFS spectroscopy (Fig. 2). Linear combination fitting of the EXAFS spectra revealed very little (Run 1) or zero (Runs 3 and 5) transformation of schwertmannite in experimental systems which did not contained Fe^{2+}. In the presence of 10 mM Fe^{2+}, but in the absence of As, there was 97% transformation of schwertmannite to goethite. The presence of 1 mM As retarded this transformation over the 9-day reaction period, with 72% schwertmannite transformation in Run 4 and only 6% transformation in Run 6.

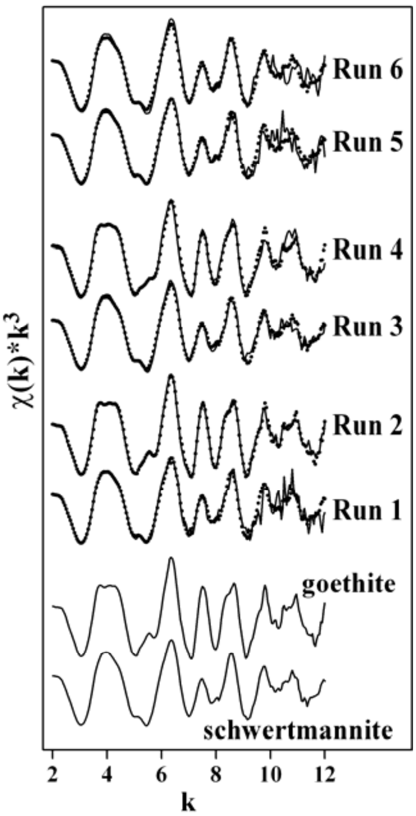

Fig. 2: k^3-weighted Fe EXAFS spectra for schwertmannite, goethite and experimental samples collected from Runs 1 – 6. The solid-line denotes data, whilst the dotted line for Runs 1 - 6 shows the linear combination fit.