PROGRESS REPORT FOR ALNGRA10102

PROGRESS REPORT and RESEARCH OUTCOMES

Jarositic pedofeatures were sampled from a tidally inundated acid sulfate soil (ASS) wetland at East Trinity near Cairns in northeastern Australia. The study site previously contained large areas of tidal estuarine wetlands, including mangrove and saltmarsh communities, prior to extensive drainage and clearing of vegetation. The site has undergone remediation from 2002, consisting of the reintroduction of regular tidal inundation to the previously drained acid sulfate soils. For this study, a transect was established in the upper reaches of Firewood Creek sub-catchment across a toposequence to span the supratidal to intertidal zone (0.6-0.0 m AHD). Bulk soil samples were collected from the jarositic (or sulfuric) horizon (0.20-0.50 m depth) at selected distances along the toposequence. The field work component for this study was undertaken during May 2009. These jarositic pedofeatures were subjected to a laboratory-based batch experiment whereby extracted mineral samples were incubated over time in seawater solutions with additions of organic matter to facilitate reductive processes, and subsampled periodically. The laboratory work component for this study was undertaken from May to November 2010. Suitable jarositic materials were prepared for a total of 4 samples from these experiments as provided by this Award. Analysis was undertaken on the JEOL 2010F transmission electron microscope in May and October 2010. This encompassed imaging of crystal morphologies, selected area diffraction patterns (SADP) for crystal structure and chemical composition from EDX spectrums. Images, diffraction patterns and spectrums were collected and received from ANSTO at the time of analysis. These SADP are currently being used to identify crystal structures and measure lattice parameters.

The aim of this study was to contribute to the present knowledge of jarosite behaviour by examining for the first time the mineralogical variability with tidal inundation in an ASS environment. This is significant for determining implications for environmental rehabilitation and management of ASS. Direct evidence from SEM, TEM and XRD identified jarosite in the former sulfuric horizon of tidally inundated ASS. Under reducing soil conditions, natural jarosite from the intertidal zone exhibited features consistent with reductive dissolution. The combined use of TEM, SEM and XRD analysis as applied in this study has enabled a detailed characterisation of jarosite structure and composition following reductive dissolution in the estuarine sediments of a tidally inundated acid sulfate soil wetland.
DATA

Prior to re-establishing tidal inundation, soils along the toposequence had distinct sulfuric horizons in the upper 1 m with pedofeatures typical of ASS, including jarosite and Fe(III) oxides mottles (Figure 1). Following regular tidal inundation (~5 years), the abundance, size and prominence of jarosite mottles were observably lower in the intertidal ASS at lower elevation compared with the supratidal ASS at higher elevation. Under increasing pH and decreasing Eh conditions typical of tidally inundated ASS, jarosite is increasingly unstable.

Figure 1: Toposequence soil profiles with a distinct sulfuric horizon and pedofeatures typical of ASS, including jarosite and Fe(III) oxides mottles.

The natural yellow precipitates from the former sulfuric horizon were identified as jarosite from X-ray diffractometry (XRD) (Figure 2a). Crystal morphologies evident from scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were consistent with jarosite, and exhibited a classic euhedral ortho-rhomboidal form (Figure 2b; 3a). Jarosite from the supratidal zone (i.e. at 20 m upslope on the toposequence) was generally inter-grown euhedral crystals >1 µm with clearly defined edges and planar surface features (Figure 2b). In contrast, jarosite from the intertidal zone (i.e. at 100 m downslope on the toposequence) exhibited features consistent with dissolution, including smaller, sub-rounded crystals with clearly visible etch pits (Figure 2c; 3b).
Figure 2: Representative X-ray diffractograms of jarositic pedofeatures (a), and scanning electron photomicrographs of natural jarosite from 20 m (supratidal zone) (b) and 100 m (intertidal zone) (c) on the toposequence.

Figure 3: Transmission electron microscopy images of natural jarosite prior to tidal inundation (a) and at 100 m in the supratidal zone (b) on the toposequence.

Direct evidence from SEM, TEM and XRD identified jarosite in the former sulfuric horizon of tidally inundated ASS. Under reducing soil conditions, natural jarosite from the intertidal zone exhibited features consistent with reductive dissolution. Jarosite crystal morphology has become increasingly disordered, etched and fractured with reductive dissolution over time. The characterisation of natural jarositic weathering has identified some unusual crystal morphological features previously unreported. This includes the “hollowing” of jarosite crystals with reductive dissolution under both field (Figure 4a) and laboratory (Figure 4b) conditions.
TEM SADP were also analysed to identify changes to the crystal structure of jarosite and any newly formed minerals (Figure 5). Preliminary results from these diffraction patterns indicate that natural jarosite has undergone a structural shift to a more polycrystalline form. The unaltered natural sample displays a diffraction pattern with distinct spots for strong crystallinity (Figure 5a). This differs from the diffraction patterns of natural jarosite treated with seawater and organic matter following 6 months of reducing conditions (Figure 5b). The crystal structure in this sample displays polycrystalline features with a diffuse concentric ring pattern. This indicates a very small particle size, and is typical of low temperature, heterogeneous, natural soil samples.
The data presented in this report was collected in May 2010. Additional data will be collected on the instrument in October 2010. Combined, these data will contribute to two publications which will be undertaken following the interpretation of these and other analytical results. There are currently one paper in preparation for journal publication, and four presentations accepted and given at international conferences.


**PhD STUDENTS**

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Anticipated date of submission: Thesis currently on hold.