Fe and S K-Edge XAS Study of the Reactivity of Monosulfidic Black Ooze and Related Compounds

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Acid sulfate soils (ASS) are soil materials in which sulfuric acid may be produced from iron sulfides or has been produced leaving iron oxyhydroxy sulfates in amounts that have a long lasting effect on soil characteristics. Under anaerobic or reducing conditions ASS contain mostly iron disulfides (e.g. pyrite FeS_2) and monosulfides (e.g. mackinawite - FeS); under aerobic or oxidising conditions mostly Fe oxyhyrdoxides (e.g. ferrihydrite) and Fe-oxyhydroxysulfate minerals (e.g. jarosites and schwertmannite). If sulfidic material is exposed to atmospheric oxygen/or oxygenated water the sulfides will be oxidised catalytically by bacteria producing sulfuric acid and Fe-oxyhydroxysulfates. If sulfates are exposed to rotting vegetation or other reducing material they can be bacterially reduced to sulfides including pyrite, mackinawite and Mono-Sulfidic Black Ooze (MBO).[1] Experiments have linked the oxidation of iron monosulfides in MBO to the rapid de-oxygenation of water-ways, which causes a range of environmental problems the most well known of which is fish kills.[2] Despite MBO being the cause of significant environmental problems, metal speciation and oxidation of elements (iron and sulfur) associated with its chemical reactivity are not well understood, nor are the differences between MBOs found from different environments.[2, 3]

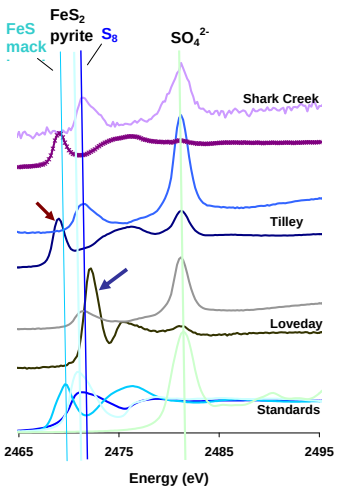

Figure 1. S K-edge data on a series of MBO sediments on both their native form (lower) and peroxide oxidized (upper).

In July and October 2007 we were allocated beam time on beam-line 16A. We used this time to both characterise a range of sediments from different environments and to examine the mechanistic S chemistry of the systems. Figure 1 shows the distinct finger-print of MBO's from different environments. Based on these data we are for the first time able to characterise MBO sediments from different environments, identifying key differences in the natural sediments that have important implications for managing the systems. Red arrow shows the most reduced mackinawite, blue arrow identifies and organo-S species, highlighting the differences in chemistry of these natural sediments.

A second study was carried out that examined the biotic and abiotic transformations of S in the natural environment. Figure 2a shows the initial sediment dominated by mackinawite FeS_M. Figure 2b shows the two step biotic oxidation of mackinawite to elemental sulphur (α-S_8) then to SO_4^{2-}. The second series shows that in the absence of bacteria the sediment does not become fully oxidized.

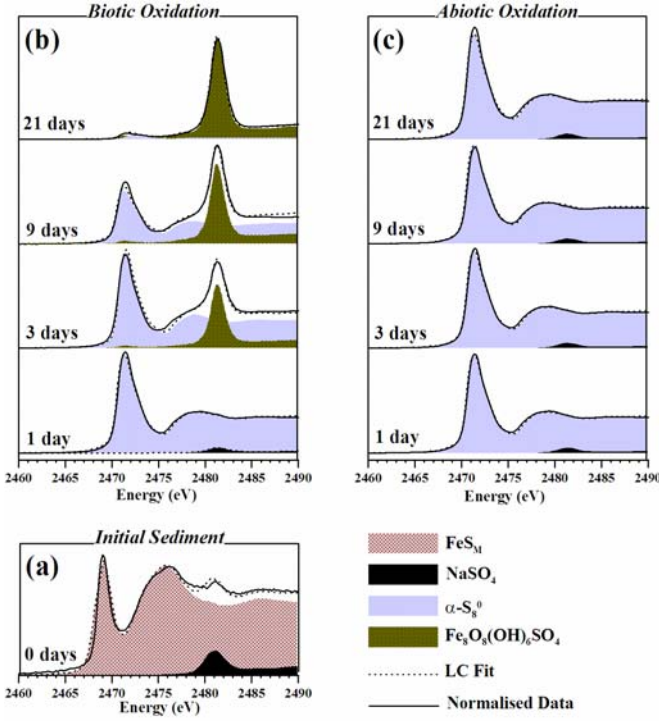

Figure 2. Sulfur K-edge XANES data for the initial MBO (a)initial (b) under biotic (c) and abiotic conditions at 1, 3, 9 and 21 days.

References. 1. Bush R. T.; Fyfe D.; Sullivan L. A., Aust. J. Soil. Res. **42(6)**, 609-616 (2004). 2.Bush R. T.; Sullivan L. A.; Fyfe D.; Johnston S., Aust. J. Soil. Res. **42 (6)**, 603-607 (2004). 3. Smith J., Aust. J. Soil. Res. **42**, 659-666 (2004). 4. George G. N.; Pickering I. J.; Yi E. Y.; Prince R. C., Microbiology **148**, 2267-2268 (2002).