

Transient oxidant production during the oxidation of iron(II) monosulfides at pH 8

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Iron(II) monosulfides are widely distributed in a range of environments. Upon exposure to oxic conditions they are readily oxidized and transform to a range of minerals as well as dissolved products. Over sufficient timescales this leads to the oxidation of both the iron and sulfur content. It has been shown that oxidation of such sulfidic material is likely to occur in natural environments such as sediments exposed to tidal cycling, and that hydrogen peroxide (H_2O_2) is evolved during this process[1]. The co-occurrence of H_2O_2 and Fe(II) presents the possibility of Fenton-type reactions occurring, leading to the production of oxidizing species such as the hydroxyl radical (HO^\bullet); with the related mineral pyrite previously demonstrated to undergo chemistry of this nature [2].

We have investigated the nature of this oxidation process at a pH controlled to be near 8.0. The nature of the changes in the Fe minerals present was determined using Fe K-edge X-ray Absorption Spectroscopy (XAS) and the terminal sulfur products using ion chromatography, demonstrating the eventual formation of Fe(III) oxides and SO_4^{2-} , with substantial intermediary $S_2O_3^{2-}$. The ability of the Fe(II)- H_2O_2 system, as well as other potential oxidant generating pathways, to oxidize organic material during this process has also been examined by monitoring the oxidation of formic acid, confirming the formation of highly oxidizing species during the oxidation of Fe(II) monosulfides under circumneutral conditions.

[1] Murphy *et al.* (2014) *Environ. Sci. Technol.* **48**, 3815-3821. [2] Choi *et al.* (2014) *J Hazard. Mater.* **280**, 31-37.