

Redox processes at the nanoscale: A TEM perspective of iron sulphide – iron (oxyhydr)oxide reactions

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Redox reactions between iron sulfide and ferric iron (hydr)oxides are of fundamental importance for the elemental cycles of both sulfur and iron. The oxidation of iron sulfides due to mining activities and natural events leads to the production of acidity and harmful concentrations of metals in ground and surface waters. The reverse reaction, the (biotic and abiotic) reduction of sulfate and ferric iron to form sedimentary sulfides, plays a key role in both marine and freshwater sediments as well as for remediation strategies. Although the overall chemical pathway of the reactions and their kinetics are reasonably understood, there is less knowledge on the transient stages and the electron transfer processes which involve the formation of amorphous or disordered as well as nucleation of (metastable) crystalline phases at the reacting interface as a function of time.

Here we report TEM observations on 1. experimentally formed iron sulfides as reaction products of dissolved sulfide and lepidocrocite under anoxic conditions and 2. the weathering of a natural pyrrhotite (Fe_{1-x}S , Dalnegorsk). Notwithstanding the obvious difference of each approach (experiment vs. nature; anoxic vs. oxic; sulfide formation vs. sulfide alteration) we highlight the common observation of nanocrystalline magnetite at the reacting interfaces which possibly act as electron link for both types of reaction.

For the experimental study, lepidocrocite has been reacted with a sulfide solution at pH 7. After a few hours the suspensions turns black and TEM reveal 10-20 nm thick sulfur-rich rims around all lepidocrocite crystals in which nucleation of crystalline mackinawite can be observed. Between these rims and the lepidocrocite a continuous, 4 nm thick layer of magnetite crystals has been formed.

TEM and Raman analyses of a weathering sequence of natural pyrrhotite display nanocrystalline magnetite at the reacting sulfide interface, followed by lepidocrocite and sulfur which finally converts to goethite and secondary pyrite.

Both studies indicate an alternative electron transfer mechanism via magnetite for reactions involving ferric iron (oxyhydr)oxides and sulfides and thus question the exclusive role of surface complexes utilized in most kinetic models.

Sorption and fractionation of hydrophobic fractions of dissolved organic matter (DOM) on Fe^{3+} - and Cu^{2+} -montmorillonite

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We studied sorption and fractionation of hydrophobic acid (HoA) and hydrophobic neutral (HoN) fraction of DOM on Cu^{2+} - and Fe^{3+} -montmorillonite.

Sorption of HoN was greater than that of HoA due to higher hydrophobicity and larger molecular size of HoN. Sorption of both samples was higher on Fe^{3+} -montmorillonite than on Cu^{2+} -clay. A pH increase of about one unit was recorded followed by HoA sorption on Fe^{3+} -clay, which suggested exchange of negatively-charged groups of HoA on hydroxyl groups of Fe^{3+} -montmorillonite surfaces.

The ratio of absorbance 250 to 365 nm (E_2/E_3) decreased followed by sorption of HoA and HoN on both clays, which indicated preferential sorption of larger-size fractions. This effect was much more distinct for Fe^{3+} -montmorillonite.

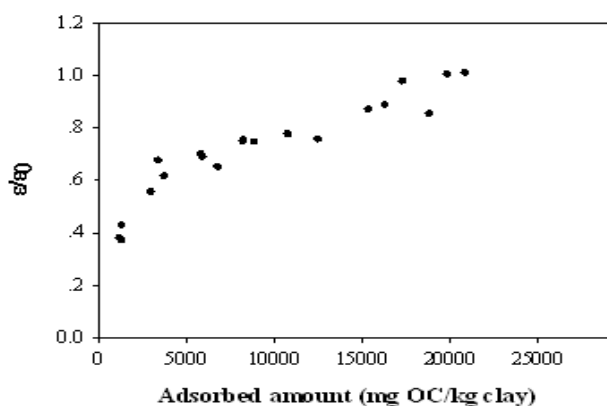


Figure 1: Changes in HoA molar absorptivity followed by HoA sorption on Fe^{3+} -montmorillonite.

Preferential sorption of HoA aromatic components (measured by UV absorbance at 280 nm) was clearly demonstrated only for Fe^{3+} -montmorillonite (Fig. 1). Similar results were obtained for interactions of fulvic acid with Fe^{3+} -montmorillonite. FTIR measurements confirmed preferential sorption of HoA aromatic moieties by Fe^{3+} -clay.

Hence montmorillonite enriched with Fe^{3+} enhanced sorption and fractionation of hydrophobic fractions of DOM.