

Solid state transformation of green rust in response to oxidation

S.H.J. Eiby¹, D.J. Tobler¹, L. Voigt¹, Z. Yin², C.M. van Genuchten^{1,3}, K.M.Ø. Jensen¹, T. Stawski⁴, R. Wirth⁴, L.G. Benning^{4,5}, H.C.B. Hansen², S.L.S. Stipp¹ and K. Dideriksen^{1*}

¹Nano-Science Center, Dept. of Chemistry, University of Copenhagen, Denmark (*knud@nano.ku.dk)

²Dept. of Plant and Environmental Sciences, University of Copenhagen, Denmark

³Dept. of Earth Sciences, Utrecht University, The Netherlands

⁴German Research Center for Geosciences GFZ, Germany

⁵Dept Earth Sci, Free Univ. Berlin, Berlin Germany

Green rust (GR) consists of Fe(II)-Fe(III) hydroxide layers of edge sharing octahedra separated by interlayers of water, anions and occasionally cations. GR is able to reduce a range of contaminants and its Fe electrons are predicted to be mobile through small polaron hopping, meaning they could migrate within GR crystals to sites of contaminant reduction. During reduction, GR oxidation results in Fe (oxyhydr)oxides such as magnetite, goethite and ferrihydrite. Here we present data on the structural changes occurring during GR oxidation.

Pair distribution function (PDF) analysis shows that individual GR hydroxide sheets, isolated from each other by intercalated dodecanoate, restructure upon oxidation by O₂ to yield a majority of corner sharing Fe polyhedra, similar to goethite and ferrihydrite. This indicates that oxidation results in dislocation of part of the Fe(III) from the brucite-type hydroxide sheet in oxidized GR into the interlayer space. Modelling of the PDF data, with Fe in three parallel layers, results in reasonable agreement.

Interaction between chromate and GR with interlayer sulfate and sodium results in rapid redox reaction. High resolution transmission electron microscopy reveals that oxidation products largely inherit particle shape and crystal orientation from the original GR crystal. PDF results show that structure is variable, with the patterns from some samples being practically identical to those of the oxidised dodecanoate-GR sheets, and others, to patterns for goethite, spinel and ferrihydrite.

Thus, GR seemingly responds to oxidation by dislocation of Fe(III) into the interlayer region. If dislocations are ordered, interlayer collapse can result in structures identical to ferrihydrite or goethite. Such a transformation mechanism could account, for example, for the 1-2 nm particles observed at the edges of transforming GR [1].

[1] Dey, Lenders & Sommerdijk (2015) Faraday Discuss. 179, 215-225.