



Mechanism of reductive dissolution of lepidocrocite by S(-II)

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Reduction of ferric oxides by dissolved sulfide species plays an important role in the redox dynamics of anaerobic subsurface environments. For example, S(-II) may be the dominant reductant for ferric oxides in sulfidic sediments and the reaction significantly contributes to the retention of reduced sulfur in these environments. The mechanism and rates of the reductive dissolution of ferric oxides by S(-II) have been frequently investigated and the reaction is generally considered to be a surface controlled process. The proposed mechanism includes the reduction of Fe(III) at the mineral surface upon S(-II) adsorption followed by the release of Fe(II) into solution, which is eventually followed by the precipitation of FeS at suitable conditions. However, several reported experimental observations, such as the remarkable high rate of lepidocrocite (g-FeOOH) reduction and the accumulation of surface bound Fe(II) (Poulton et al., 2004) are difficult to align with the proposed reaction mechanism. Here, we report experimental results which indicate that the prevailing idea about a surface controlled reaction between lepidocrocite and S(-II) has to be revised.

We have studied the reaction of lepidocrocite and S(-II) in batch reactors at constant pH 8.0 by adding Na₂S solution to the ferric oxide suspension. During the reaction, wide angle X-ray scattering (WAXS) and spectra from X-ray absorption (XANES and EXAFS) at the Fe K-edge (about 7.1 keV) were collected in situ by pumping suspension through a capillary, which was positioned inside the X-ray beam. These experiments were performed at the beamline BM26a (DUBBLE) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France (Nikitenko et al., 2008). Combining WAXS, XANES, and EXAFS allowed us to follow the change in the long-range periodic structure of the minerals simultaneously with changes in Fe redox state and local coordination environment.

At pH 8.0 the reaction between lepidocrocite and S(-II) was relatively fast and, in excess of S(-II), the characteristic lepidocrocite diffraction peaks completely disappeared about one hour after starting Na₂S addition. No secondary crystalline phases were detected in the WAXS diffractograms. The disappearance of lepidocrocite diffraction peaks was accompanied by reduction of Fe(III) to Fe(II), inferred from linear combination of XANES spectra. These observations are in agreement with the proposed transformation of lepidocrocite into amorphous FeS. Interestingly, EXAFS spectra reveal that the Fe coordination environment in the product is not the same as that of Fe in FeS formed by adding sodium sulfide solution to a solution containing dissolved Fe(II). The spectra indicate that part of the lepidocrocite short-range structure is preserved in the product of lepidocrocite reduction. This can be explained by the replacement of structural OH groups by SH groups leading to distortion and partial disintegration of the lepidocrocite structure. However, the arrangement of edge-sharing Fe octahedra might be partially maintained in the product.

The suggested new mechanism implies that not only surface hydroxyl groups but also structural OH groups are accessible for the reaction with S(-II) and that the reaction does not only proceed by progressive corrosion at the mineral faces. In the presentation the consequences of our findings regarding the reversibility of the process and the reactivity of the product will be discussed.

Literature

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