

Green rust as a precursor for magnetite: an *in situ* synchrotron based study

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ABSTRACT

In this study, direct evidence for the formation of magnetite via a green rust intermediate is reported. The Fe(II) induced transformation of ferrihydrite, was quantified *in situ* and under O₂-free conditions using synchrotron-based time-resolved energy dispersive X-ray diffraction. At pH 9 and Fe(II)/Fe(III) ratios of 0.5 and 1, rapid growth (6 min) of sulphate green rust and its subsequent transformation to magnetite was observed. Electron microscopy confirmed these results, showing the initial rapid formation of hexagonal sulphate green rust particles, followed by the corrosion of the green rust as magnetite growth occurred, indicating that the reaction proceeds via a dissolution-reprecipitation mechanism. At pH 7 and Fe(II)/Fe(III) ratio of 0.5, sulphate green rust was the stable phase, with no transformation to magnetite.

KEYWORDS: magnetite, green rust, nanoparticulate, synchrotron, diffraction.

Introduction

NANOPARTICULATE magnetite (MGT) is a major end product of the dissimilatory reduction of ferric oxyhydr(oxides) in nonsulphidogenic anaerobic environments (Lovley, 1991), and its formation is often driven by the reaction of microbially generated aqueous Fe(II) with ferrihydrite (FHY) and may proceed via intermediate phases such as lepidocrocite (LP), goethite (GT) and sulphate green rust (GR) (Hansel *et al.*, 2003). The secondary mineralization of MGT via the 'Fe(II) pathway' is a process important to the biogeochemical cycle of iron in both ancient and modern sedimentary environments (Weber *et al.*, 2006). On the early Earth, this reaction is thought to have contributed to the deposition of MGT within banded iron formations. In modern anoxic soils and aquifers, this process can dictate the mobility and fate of both naturally occurring and anthropogenic pollutants (e.g. Cr, Pb, Zn) and thus impacts water quality. Therefore, the formation of highly reactive transient phases

along the FHY-Fe(II) to MGT pathway may be a key factor controlling the mobility and fate of these contaminants. Yet, the geochemical controls on the formation and subsequent conversion of intermediate phases on the pathway to MGT formation are poorly understood. One of these precursors is GR, a Fe(II)-Fe(III) layered double hydroxysalt, consisting of positively-charged Fe(II)–Fe(III) hydroxide sheets that are intercalated with layers of water molecules and anions, such as SO₄²⁻, CO₃²⁻ and Cl⁻ (Bernal *et al.*, 1959). Similar to MGT, GR is a nanoparticulate and redox-active mineral, and can be metastable with respect to MGT in alkaline and reducing conditions (Satapanajaru *et al.*, 2003). Numerous studies have shown that GR determines the fate of several redox-active metals and anionic contaminants (Hansel *et al.*, 2003). Despite the potential environmental significance of this reaction, the kinetics and mechanisms of MGT formation via GR are poorly constrained, largely due to lack of *in situ* data. The aim of this study was therefore to quantify the transformation pathway of FHY to MGT via GR using synchrotron-based *in situ* time-resolved energy dispersive X-ray diffraction (ED-XRD). The effect of varying Fe(II)/Fe(III) ratios and pH was investigated.

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Materials and methods

The 2-line FHY was prepared following the method of Cornell and Schwertmann (2003). The FHY slurry was purged with O₂-free N₂ under constant stirring to remove any O₂ dissolved in solution or sorbed to the mineral surface and immediately transferred into an anaerobic glove-box (95% N₂ + 5% H₂). All stock solutions (1 M NaOH, 0.5 M FeSO₄) were prepared using O₂-free water.

The transformation experiments were performed on station 16.4, Synchrotron Radiation Source (SRS), Daresbury Laboratory, UK and monitored using time-resolved ED-XRD (Clark, 1996). The reactions were carried out in a sealed polyetheretherketones (PEEK) reaction cell. FHY and Fe(II)_(aq) were reacted at Fe(II)/Fe(III) ratios of 0.5 and 1 at pH 9 and a Fe(II)/Fe(III) of 0.5 at pH 7. The flow of N₂ gas, base addition and pH were controlled by a remotely operated chemostat (see Fig. 1). Diffraction patterns of the cell contents were recorded at 1 min intervals until there was no further change in GR or MGT peaks. The integrated areas for the peaks were determined and the degree of reaction parameter (α) obtained by normalizing peak areas according to the equation: $\alpha = I_t/I_{max}$, where I_t is the peak area at a given time and I_{max} is the maximum area of the peak. The evolution of the solid phases over time was also studied with high resolution field emission gun scanning electron microscopy (FEG-SEM) in equivalent experiments carried out in the anaerobic glove-box (Fe(II)/Fe(III) = 1, pH 9).

Results and discussion

Under all reaction conditions (Fe(II)/Fe(III) = 0.5, 1, pH 9 and Fe(II)/Fe(III) = 0.5, pH 7), the ED-

XRD data showed the initial rapid development of the GR (001) diffraction peak (Fig. 2). At pH 9, the complete transformation of FHY to MGT via GR was observed at Fe(II)/Fe(III) = 0.5 and 1. The intermediate GR reached maximum intensity after 6 min (Fig. 2a,b). The onset of MGT growth coincided with the start of the decline in GR, indicating that MGT growth occurred at the expense of GR. The complete conversion of GR to MGT was slower at larger Fe(II)/Fe(III) ratios (420 min at Fe(II)/Fe(III) = 1 and 100 min at Fe(II)/Fe(III) = 0.5; Fig. 2a,b). The FEG-SEM images of the transformation reaction at Fe(II)/Fe(III) = 1 and pH 9 confirmed the results of the ED-XRD study and showed that MGT formed at the expense of GR. The transformation proceeded via a dissolution-reprecipitation mechanism as evidenced by the corrosion features observed on the GR particles (Fig. 3b,c). At pH 7 and Fe(II)/Fe(III) = 0.5, the *in situ* data revealed the rapid formation and stabilization of GR and the absence of MGT peaks (Fig. 2c). A similar observation was made for GR formed from FHY at pH 7 and Fe(II)/Fe(III) = 1, where GR remained stable in the glove box for several days (data not shown).

The occurrence of GR as a transitory phase following bacterial reduction of ferric oxyhydr(oxides) has been previously reported, but until now, the parameters controlling the conversion of GR into MGT were unclear (Hansel *et al.*, 2003; Zegeye *et al.*, 2007). We have shown that in a purely abiotic FHY-Fe(II) system, both the nature of the end product and the kinetics of conversion are determined by the Fe(II)/Fe(III) ratio and pH.

The GR has an ideal formula of Fe₄(II)Fe₂(III)(OH)₁₂SO₄·8H₂O (Simon *et al.*, 2003) such that the Fe(II)/Fe(III) ratio is 2, while the ideal Fe(II)/Fe(III) ratio for MGT is 0.5. Evidence from electron microscopy and the ED-XRD studies suggest that both GR and MGT

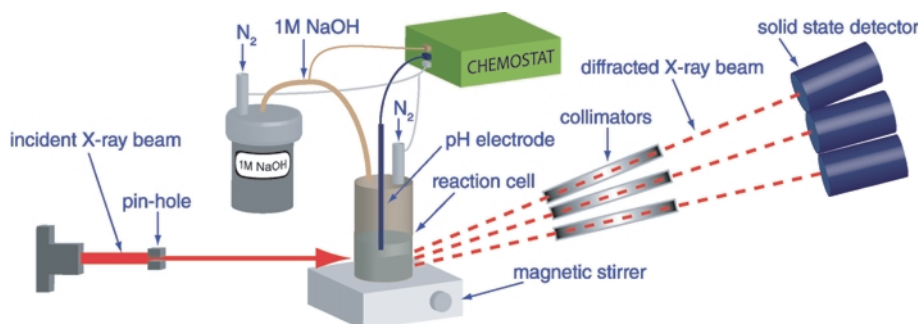


FIG. 1. Experimental set-up at the ED-XRD beamline 16.4, SRS Daresbury, UK.

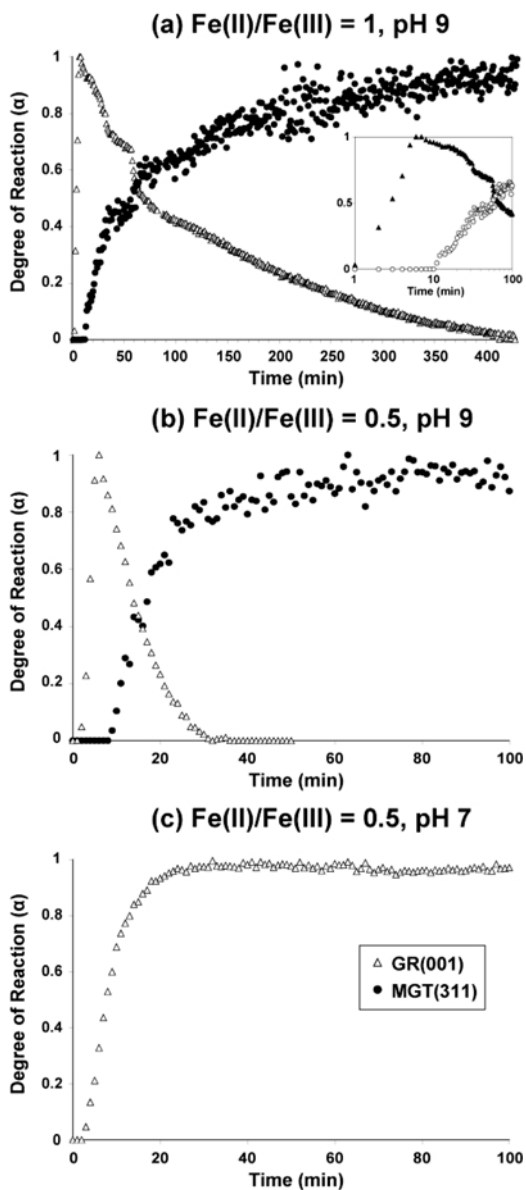


FIG. 2. Reaction progress for the GR (001) and MT (311) XRD peaks for varying Fe(II)/Fe(III) and pH values.

can be formed off stoichiometry, e.g. GR was formed at Fe(II)/Fe(III) = 0.5, 1 while MGT was the only end product when Fe(II)/Fe(III) = 1. Alternatively, during the reaction, poorly-ordered ferric or ferrous phases (e.g. Fe(OH)_2 or FHY) may also form, but these were neither detectable by ED-XRD nor was there any evidence of

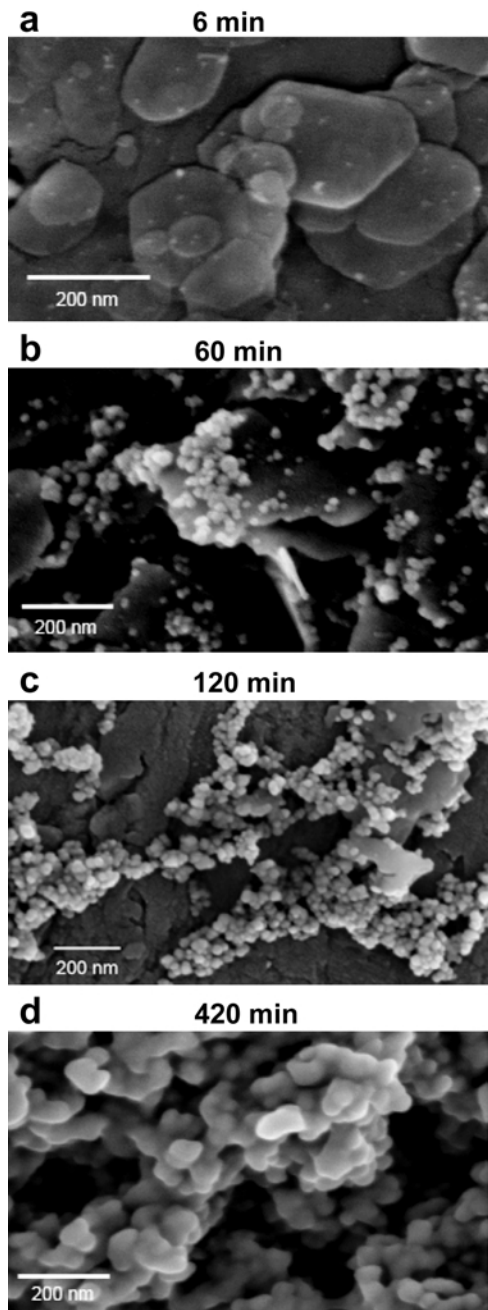


FIG. 3. FEG-SEM images of phases formed during the reaction of FHY + Fe(II) at a Fe(II)/Fe(III) ratio of 1 and pH 9; (a) hexagonal GR particles; (b) partially corroded GR particles + isometric MGT nanoparticles; (c) extensively corroded GR particles + isometric MGT; and (d) single phase MGT end product.

additional phases from the SEM images of the reaction products (Fig. 3). The formation of GR off stoichiometry has been reported in very few studies although Mazeina *et al.* (2008) have recently shown that GR can form over a range of Fe(II)/Fe(III) ratios (0.5 to 1.34) and that they display no thermodynamic preference for any particular ratio. Knowledge on the low-temperature formation of MGT with excess Fe(II) is limited. Such MGTs are termed cation-excess (CE) MGTs and are powerful reductants. Of the numerous studies of MGT formation via the dissimilatory reduction of ferric oxyhydr(oxides), few have focused on the properties of the MGT end product (e.g. stoichiometry). The only observation of the formation of CE MGT via the biotic Fe(II) pathway is by Kukkadapu *et al.* (2005) who reported Fe(II)/Fe(III) ratios in the range of 1 to 1.5. The formation of CE MGT may have a significant impact on the dynamics of nutrient and contaminant cycling.

Conclusion

In this study, synchrotron-based ED-XRD in combination with HR-imaging has been used to quantify the intermediate formation of GR during the Fe(II) induced transformation of FHY to MGT. The GR formed as an intermediate phase at non-stoichiometric Fe(II)/Fe(III) ratios and spontaneously converted to MGT under alkaline conditions (pH 9). At neutral pH however, GR was the stable phase even at MGT stoichiometry. The direct observation of GR as a transient precursor to MGT and its persistence at circumneutral pH has significant implications for the biogeochemistry of Fe in anoxic environments. Also, this novel pathway for GR and MT formation has to be taken into account when predicting the fate of contaminants in systems where dissimilatory Fe reduction is a predominant process.

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