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Fe^{II} induced mineralogical transformations of ferric oxyhydroxides into magnetite of variable stoichiometry and morphology

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ABSTRACT

The Mössbauer spectroscopy was used to monitor the mineralogical transformations of ferrihydrite (F), lepidocrocite (L) and goethite (G) into magnetite as a function of aging time. Ferric oxyhydroxides were reacted with soluble Fe^{II} and OH^- in stoichiometric amounts to form magnetite at an initial pH of ~9.7. Observed transformation extent into magnetite followed the order: $F > L > G$ with almost 30% of untransformed G after 1 month. The departure from stoichiometry, δ, of magnetite ($Fe_{3-\delta}O_4$) generated from F ($\delta \sim 0.04$) and L ($\delta \sim 0.05$) was relatively low as compared to that in magnetite from G ($\delta \sim 0.08$). The analysis by transmission electron microscopy and BET revealed that generated magnetite was also different in terms of morphology, particle size and surface area depending on the nature of initial ferric oxyhydroxide. This method of preparation is a possible way to form nano-sized magnetite.

1. Introduction

Iron oxyhydroxides are abundant in the environment and influence the biogeochemical cycling and availability of elements. In soils and sediments, iron oxides and oxyhydroxides are commonly found as ferric minerals like goethite, ferrihydrite, hematite and lepidocrocite with different characteristics such as crystallinity, stability, specific surface area and reactivity [1,2]. Due to their high specific surface area, iron oxyhydroxides act as important sorbents for dissolved species. They strongly influence the transport and availability of various nutrients (e.g., C, N, and P) [1,2] and the mobility of organic and inorganic contaminants [3,4]. In reduced soil zone, they exist as mixed Fe^{II}–Fe^{III} compounds such as fougerite, the mineral counterpart of the Fe^{II}–Fe^{III} green rust or magnetite ($Fe^{II}Fe_2^{III}O_4$) [5,6]. Due to the presence of structural Fe^{II}, magnetite is considered as reactive and is involved in the reductive transformations of inorganic [7] as well as organic pollutants [3,8].

Magnetite can be synthesized in laboratory by various biotic and abiotic pathways. Formation of biogenic magnetite was reported as a result of microbial reduction of iron oxyhydroxides [9–12]. Abiotic procedures to form magnetite include partial oxidation of hydroxylated Fe^{II} solution [13] or co-precipitation of Fe^{II} and Fe^{III} salts in aqueous solutions [14]. Magnetite can also be formed by interactions of ferric minerals with aqueous Fe^{II} that induce their structural modifications and bulk phase transformations. These solid state transformations are controlled by various factors like molar ratio $x(Fe^{II}) = Fe^{II}/[Fe^{II}+Fe^{III}]$ [15–18], pH [18,19], anionic media [20], OH^-/Fe ratio [17,21] and structure of initial iron oxyhydroxide substrate [22]. The interaction of iron oxides with aqueous Fe^{II} may lead to their transformations into ferric and/or mixed Fe^{II}–Fe^{III} phases. Due to its poor cristallinity, solid state transformations of ferrihydrite are more widely reported. In the presence of low concentration of Fe^{II} species, ferrihydrite was transformed either into goethite [14,18–20,23], lepidocrocite [18,20,22] or hematite [18,24]. At high Fe^{II} amount, mixed Fe^{II}–Fe^{III} minerals such as magnetite [15–18,22,25] or green rust [17,26] were formed from ferrihydrite or lepidocrocite. But, formation of magnetite from goethite by Fe^{II} induced transformations has not been reported yet probably because of its higher thermodynamic stability. Also a comparative quantification of magnetite formation by using stoichiometric conditions from various ferric oxyhydroxides versus time has seldomely been performed. In this study, Mössbauer spectroscopy was used to determine the transformation extent of ferric

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oxyhydroxides when reacted with hydroxylated Fe^{II} species in stoichiometric quantities to form magnetite. Mössbauer spectroscopy is a potentially useful tool for an accurate quantitative determination of the relative proportions of magnetite and remaining ferric oxyhydroxides. A special attention was devoted to determine the evolution of stoichiometry during transformation by determining Fe^{II} and Fe^{III} contents in magnetite structure where nonstochiometric compound can be written $Fe_{3-\delta}O_4$ [7,27]. Indeed, the reactivity and stability of magnetite is dictated partly by its stoichiometry defined by $x = Fe^{III}/(Fe^{II}+Fe^{III})$ where $0.67 \leq x \leq 1$, with stoichiometric magnetite ($x=0.67$ or $\delta=0$) being the most reactive composition [7]. It was shown that stoichiometric magnetite had a lower reduction potential than that of non-stoichiometric magnetite, consistent with higher reactivity toward pollutants such as nitrobenzene compounds [7].

Experiments were conducted on three different iron oxyhydroxides including ferrihydrite, lepidocrocite and goethite. Their transformation extent into magnetite was quantified as a function of aging time (1 h, 1 day and 1 month). Morphological properties of initial and final products were determined by transmission electron microscopy and multipoint N_2 BET analyses.

2. Experimental section

2.1. Sample preparation

2.1.1. Initial ferric oxyhydroxides substrates

Experiments were conducted with three synthetic iron oxyhydroxides: 2-line ferrihydrite (F), lepidocrocite (γ-FeOOH) (L) and goethite (α-FeOOH) (G). The 2-line ferrihydrite (F) was synthesized according to the method of Schwertmann and Cornell [28]. It was prepared by neutralizing a 0.2 M ferric chloride solution with 1 M NaOH to a pH of around 7.5. The lepidocrocite sample (γ-FeOOH) was synthesized by vigorous air oxidation of the (0.228 M $FeCl_2 \cdot 4H_2O + 0.4$ M NaOH) aqueous mixture under a constant neutral pH adjustment [28]. All the Fe^{III} precipitates were washed several times to remove electrolytes, centrifuged and then dried. The goethite (G) sample was prepared by air oxidation of a hydrolyzed $FeSO_4$ solution following a procedure described by Olowe et al. [29].

2.1.2. Transformation experiments

The mineralogical transformations of synthetic ferric oxyhydroxides were examined in batch experiments at room temperature (20 ± 1 °C). To ensure the exclusion of O_2, experiments were conducted in glove box, an anoxic chamber (N_2:H_2=98:2). Stoichiometric magnetite ($Fe^{II}Fe_2^{III}O_4$) contains the Fe^{II}:Fe^{III} ratio of 1:2, so the quantities of ferric oxyhydroxide (Fe^{III}) and Fe^{II} were chosen accordingly. First, a suspension of Fe^{III} oxyhydroxide was prepared (100 mM as Fe^{III} molar concentration) and purged for 1 h with filter-sterilized N_2 (99.99%) in order to ensure the evacuation of dissolved oxygen which is known to rapidly oxidize Fe^{II} in the presence of oxides at circumneutral pH [30]. The reaction was started by adding $FeSO_4 \cdot 7H_2O$ with Fe^{II} molar concentration corresponding to 50 mM. An appropriate amount of NaOH (1 M) was then added to the mixture (Fe^{II}/Fe^{III}-oxyhydroxide) to provide the ratio $n(OH^-)/n(Fe^{III})=1$ where n represents the number of moles. Such a quantity of NaOH was required to form stoichiometric magnetite (Reaction (1)), thus the starting pH was very high (~9.7). The expected transformation of L and G into magnetite can be achieved through the following reaction:

$$2Fe^{III}OOH + Fe^{II} + 2OH^- \Rightarrow Fe^{II}Fe_2^{III}O_4 + 2H_2O \qquad (1)$$

The suspensions were vigorously stirred for 1 h, and then aged without stirring at room temperature for 1 h, 1 day and 1 month. At specified aging time, the corresponding batch was withdrawn from the series, centrifuged and the solid was dried in glove box for further analysis. To measure the aqueous concentration of Fe^{II} at each time point, aliquots were sampled from the batches, filtered through 0.22 μm filters and added to a tube that contained 2 N HCl. The Fe^{II} concentration in a given solution was determined colorimetrically by the ferrozine assay as previously reported [31]. Total Fe^{II} concentration was measured by performing the ferrozine assay after a full dissolution of the suspension in a concentrated HCl acidic solution. The pH of the suspensions was also measured at each time point.

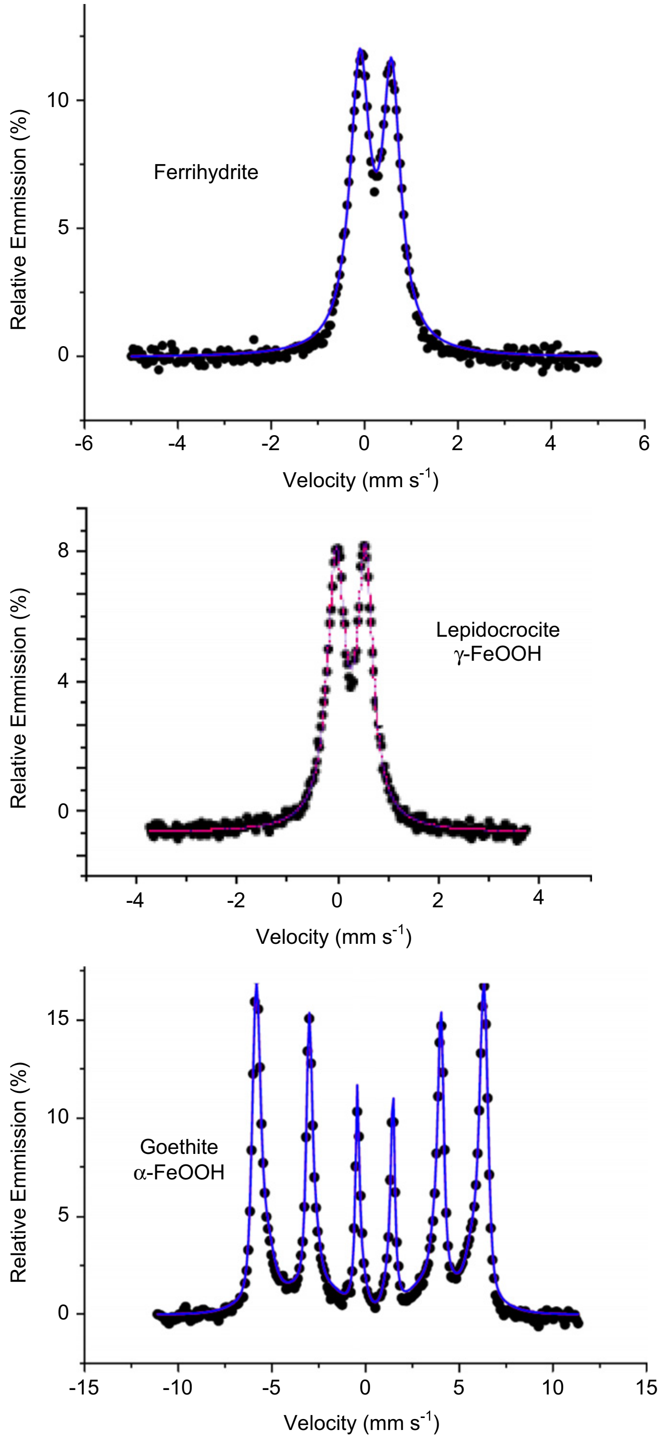

Fig. 1. Mössbauer spectra of original ferric oxyhydroxides, ferrihydrite (F), goethite (G) and lepidocrocite (L). Hyperfine parameters corresponding to these spectra are presented in Table 1.