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

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24

25 **Abstract**

26 The Mössbauer spectroscopy was used to monitor the mineralogical transformations of
27 ferrihydrite (F), lepidocrocite (L) and goethite (G) into magnetite as a function of aging time.
28 Ferric oxyhydroxides were reacted with soluble Fe^{II} and OH^- in stoichiometric amounts to
29 form magnetite at an initial pH of ~ 9.7 . Observed transformation extent into magnetite
30 followed the order: $F > L > G$ with almost 30 % of untransformed G after 1 month. The
31 departure from stoichiometry, δ , of magnetite ($\text{Fe}_{3-\delta}\text{O}_4$) generated from F ($\delta \sim 0.04$) and L (δ
32 ~ 0.05) was relatively low as compared to that in magnetite from G ($\delta \sim 0.08$). The analysis
33 by transmission electron microscopy and BET revealed that generated magnetite was also
34 different in terms of morphology, particle size and surface area depending on the nature of
35 initial ferric oxyhydroxide. This method of preparation is a possible way to form nano-sized
36 magnetite.

37

38 **Keywords:** Ferrihydrite; Lepidocrocite; Goethite; Magnetite; Mössbauer

39

40 1. INTRODUCTION

41 Iron oxyhydroxides are abundant in the environment and influence the biogeochemical
42 cycling and availability of elements. In soils and sediments, iron oxides and oxyhydroxides
43 are commonly found as ferric minerals like goethite, ferrihydrite, hematite and lepidocrocite
44 with different characteristics such as crystallinity, stability, specific surface area and reactivity
45 [1, 2]. Due to their high specific surface area, iron oxyhydroxides act as important sorbents for
46 dissolved species. They strongly influence the transport and availability of various nutrients
47 (e.g., C, N, and P) [1, 2] and the mobility of organic and inorganic contaminants [3, 4]. In
48 reduced soil zone, they exist as mixed Fe^{II}-Fe^{III} compounds such as fougérite, the mineral
49 counterpart of the Fe^{II}-Fe^{III} green rust or magnetite (Fe^{II}Fe^{III}₂O₄) [5, 6]. Due to the presence of
50 structural Fe^{II}, magnetite is considered as reactive and is involved in the reductive
51 transformations of inorganic [7] as well as organic pollutants [3, 8].

52 Magnetite can be synthesized in laboratory by various biotic and abiotic pathways. Formation
53 of biogenic magnetite was reported as a result of microbial reduction of iron oxyhydroxides
54 [9-12]. Abiotic procedures to form magnetite include partial oxidation of hydroxylated Fe^{II}
55 solution [13] or co-precipitation of Fe^{II} and Fe^{III} salts in aqueous solutions [14]. Magnetite can
56 also be formed by interactions of ferric minerals with aqueous Fe^{II} that induce their structural
57 modifications and bulk phase transformations. These solid state transformations are controlled
58 by various factors like molar ratio $x(\text{Fe}^{\text{II}}) = \text{Fe}^{\text{II}}/[\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}]$ [15-18], pH [18, 19], anionic
59 media [20], OH⁻/Fe ratio [17, 21] and structure of initial iron oxyhydroxide substrate [22].
60 The interaction of iron oxides with aqueous Fe^{II} may lead to their transformations into ferric
61 and/or mixed Fe^{II}-Fe^{III} phases. Due to its poor crystallinity, solid state transformations of
62 ferrihydrite are more widely reported. In the presence of low concentration of Fe^{II} species,
63 ferrihydrite was transformed either into goethite [14, 18-20, 23], lepidocrocite [18, 20, 22] or

64 hematite [18, 24]. At high Fe^{II} amount, mixed Fe^{II}- Fe^{III} minerals such as magnetite [15-18,
65 22, 25] or green rust [17, 26] were formed from ferrihydrite or lepidocrocite. But, formation
66 of magnetite from goethite by Fe^{II} induced transformations has not been reported yet probably
67 because of its higher thermodynamic stability. Also a comparative quantification of magnetite
68 formation by using stoichiometric conditions from various ferric oxyhydroxides versus time
69 has seldomly been performed. In this study, Mössbauer spectroscopy was used to determine
70 the transformation extent of ferric oxyhydroxides when reacted with hydroxylated Fe^{II} species
71 in stoichiometric quantities to form magnetite. Mössbauer spectroscopy is a potentially useful
72 tool for an accurate quantitative determination of the relative proportions of magnetite and
73 remaining ferric oxyhydroxides. A special attention was devoted to determine the evolution of
74 stoichiometry during transformation by determining Fe^{II} and Fe^{III} contents in magnetite
75 structure where nonstoichiometric compound can be written Fe_{3-δ} O₄ [7, 27]. Indeed, the
76 reactivity and stability of magnetite is dictated partly by its stoichiometry defined by $x =$
77 $\text{Fe}^{\text{III}}/(\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}})$ where $0.67 \leq x \leq 1$, with stoichiometric magnetite ($x = 0.67$ or $\delta = 0$) being
78 the most reactive composition [7]. It was shown that stoichiometric magnetite had a lower
79 reduction potential than that of non-stoichiometric magnetite, consistent with higher reactivity
80 toward pollutants such as nitrobenzene compounds [7].

81 Experiments were conducted on three different iron oxyhydroxides including ferrihydrite,
82 lepidocrocite and goethite. Their transformation extent into magnetite was quantified as a
83 function of aging time (1 hour, 1 day and 1 month). Morphological properties of initial and
84 final products were determined by transmission electron microscopy and multipoint N₂ BET
85 analyses.

86 **2.EXPERIMENTAL SECTION**

87 **2.1. Sample preparation**

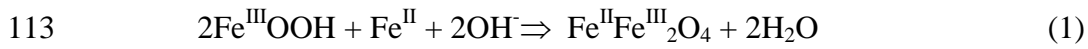
88 **2.1.1. Initial ferric oxyhydroxides substrates**

89 Experiments were conducted with three synthetic iron oxyhydroxides: 2-line ferrihydrite (F),
90 lepidocrocite (γ -FeOOH) (L) and goethite (α -FeOOH) (G). The 2-line ferrihydrite (F) was
91 synthesized according to the method of Schwertmann and Cornell [28]. It was prepared by
92 neutralizing a 0.2 M ferric chloride solution with 1 M NaOH to a pH of around 7.5. The
93 lepidocrocite sample (γ -FeOOH) was synthesized by vigorous air oxidation of the (0.228 M
94 $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ + 0.4 M NaOH) aqueous mixture under a constant neutral pH adjustment [28].
95 All the Fe^{III} precipitates were washed several times to remove electrolytes, centrifuged and
96 then dried. The goethite (G) sample was prepared by air oxidation of a hydrolyzed FeSO_4
97 solution following a procedure described by Olowe et al. [29].

98 **2.1.2. Transformation experiments**

99 The mineralogical transformations of synthetic ferric oxyhydroxides were examined in batch
100 experiments at room temperature (20 ± 1 °C). To ensure the exclusion of O_2 , experiments
101 were conducted in glove box, an anoxic chamber ($\text{N}_2:\text{H}_2 = 98:2$). Stoichiometric magnetite
102 ($\text{Fe}^{\text{II}} \text{Fe}^{\text{III}}_2 \text{O}_4$) contains the $\text{Fe}^{\text{II}}:\text{Fe}^{\text{III}}$ ratio of 1:2, so the quantities of ferric oxyhydroxide
103 (Fe^{III}) and Fe^{II} were chosen accordingly. Firstly, a suspension of Fe^{III} oxyhydroxide was
104 prepared (100 mM as Fe^{III} molar concentration) and purged for 1 hour with filter-sterilized N_2
105 (99.99%) in order to ensure the evacuation of dissolved oxygen which is known to rapidly
106 oxidize Fe^{II} in the presence of oxides at circumneutral pH [30]. The reaction was started by
107 adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with Fe^{II} molar concentration corresponding to 50 mM. An appropriate
108 amount of NaOH (1 M) was then added to the mixture ($\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ -oxyhydroxide) to provide the
109 ratio $n(\text{OH}^-) / n(\text{Fe}^{\text{III}}) = 1$ where n represents the number of moles. Such a quantity of NaOH
110 was required to form stoichiometric magnetite (Reaction 1), thus the starting pH was very

111 high (~ 9.7). The expected transformation of L and G into magnetite can be achieved through
112 the following reaction:



114 The suspensions were vigorously stirred for 1 hour, and then aged without stirring at room
115 temperature for 1 hour, 1 day and 1 month.

116 At specified aging time, the corresponding batch was withdrawn from the series, centrifuged
117 and the solid was dried in glove box for further analysis. To measure the aqueous
118 concentration of Fe^{II} at each time point, aliquots were sampled from the batches, filtered
119 through 0.22 μm filters and added to a tube that contained 2 N HCl. The Fe^{II} concentration in
120 a given solution was determined colorimetrically by the ferrozine assay as previously reported
121 [31]. Total Fe^{II} concentration was measured by performing the ferrozine assay after a full
122 dissolution of the suspension in a concentrated HCl acidic solution. The pH of the
123 suspensions was also measured at each time point.

124 **2.2. Sample characterization**

125 Solid samples were analyzed by Mössbauer spectroscopy. Backscattering Mössbauer
126 spectroscopy using the miniaturized Mössbauer spectrometer MIMOS II [32] was employed to
127 determine the oxidation state of iron and the iron mineralogy of the samples. The filtered
128 samples were inserted into a $\sim 3 \text{ cm}^2$ holder specially designed to perform backscatter
129 Mössbauer analyses at room temperature. Reemitted backscattered γ -rays (14.4 keV) were
130 selected by four Si-PIN-diodes detectors. Centre shifts CS were reported with respect to that
131 of α -Fe at room temperature. Mössbauer spectra were computer-fitted with either a sum of
132 Lorentzian shape lines or a Voigt profile analyses [33].

133 Transmission electron microscopy (TEM) observations were carried out with a Philips CM20
134 TEM (200 kV) coupled with an EDX energy dispersive X-ray spectrometer. The solid powder
135 was re-suspended in 2 mL ethanol under ultrasonication, and a drop of suspension was
136 evaporated on a carbon-coated copper grid which was placed on filter paper.

137 The specific surface area of synthesized solids was determined by multipoint N₂-BET analysis
138 using a Coulter (SA 3100) surface area analyzer and was found to be 190, 59 and 38 m² g⁻¹
139 for F, L and G respectively.

140

141 **3. RESULTS AND DISCUSSION**

142 **3.1. Initial ferric oxyhydroxides**

143 The Mössbauer spectroscopy was used to characterize ferric oxyhydroxides (F, L and G).
144 Hyperfine parameters corresponding to their spectra recorded at room temperature (Fig. 1) are
145 reported in Table 1. The F and L displayed typical Fe^{III} paramagnetic doublet and G spectrum
146 consisted of a sextet with asymmetrically broadened lines corresponding to a magnetically
147 ordered goethite.

148 Morphology of initial ferric oxyhydroxides is displayed by TEM images (Fig. S1) where F
149 particles are very small and heavily aggregated. The L crystals are lath-like and elongated
150 with gradually tapering ends like spindles. The length of the crystals is almost homogeneous
151 and varies between 200-300 nm. Crystal needle shapes were identified for G. These crystals
152 vary between 300 and 400 nm in length.

153 **3.2. Transformation products**

154 **3.2.1. Mössbauer spectroscopy**

155 *Quantification of formed magnetite*

156 The Mössbauer spectra of resulting products obtained by abiotic transformations of initial
157 ferric oxyhydroxides are shown (Fig. 2) along with hyperfine parameters (Table 1). Magnetite
158 formation was quantified after specified aging times of 1 hour, 1 day and 1 month.
159 Stoichiometric magnetite ($\text{Fe}^{\text{II}} \text{Fe}^{\text{III}}_2 \text{O}_4$) at room temperature (RT) has a spinel structure
160 whose Mössbauer spectrum at RT is constituted by a superposition of two subspectra
161 associated with the distribution of the iron in the octahedral (B) and tetrahedral (A) sites
162 represented by S_B and S_A respectively. The two valence states on octahedral sites are not
163 distinguishable above the Verwey transition (125 K) due to a fast electron hopping between
164 Fe^{II} and Fe^{III} in octahedral sites [34, 35]. The different Mössbauer spectra (Fig. 2) are
165 presented here to show the transformation of ferric oxyhydroxides into magnetite at each time
166 point. It was easy to distinguish the appearance of magnetite sextets (S) produced from F and
167 L substrates as both are characterized by doublets (D) in Mössbauer spectra at RT. In contrast,
168 G at the same temperature is characterized by magnetically ordered component that consist of
169 a sextet with lines that are asymmetrically broadened. The value of G magnetic hyperfine
170 field at room temperature (~ 378 kOe) [34] is much lower than the one obtained for sextets S_A
171 and S_B of magnetite (~ 490 and 460 kOe respectively; see Table 1).

172 The Mössbauer spectra of the F-M transformations are shown in Fig. 2a. After 1 hour of
173 reaction, a doublet is present in the center of spectrum which reveals the presence of
174 untransformed F, along with magnetic sextets corresponding to a spinel (magnetite). The
175 relative abundance of doublet decreases with the increase in time (Fig. 2a). The magnetic
176 components are very broad and the spectrum is fitted with a distribution of sextets. The
177 broadening of sextets probably corresponds to the crystal growth of a poorly crystallized
178 magnetite. These sextets become more resolved and narrow as the time proceeds from 1 hour

179 to 1 month that could be linked to the increase in the crystallinity of magnetite. Therefore,
180 only two sextets S_A and S_B are used to fit the spectrum after 1 month. Same trend is observed
181 in case of L (Fig. 2b), except that the transformation extent is lower. The sextets
182 corresponding to magnetite are also more resolved and narrow as compared to magnetite
183 formed from F. No other intermediate minerals are observed during magnetite formation.

184 The Mössbauer spectra of the G-M transformation exhibit a different trend, in particular in the
185 initial step of the reaction (Fig 2c, G-1 hour). The spectrum is constituted by the sextet S_G of
186 untransformed goethite and two additional components: (i) sextet S_A ($H = 491$ KOe) and (ii) a
187 Fe^{III} paramagnetic doublet ($\Delta = 0.71$ mms⁻¹). These two last components are attributed to the
188 initial growth of nanocrystalline magnetite, which could be described as the early stages of
189 spinel phase formation on the goethite surface. Indeed, traces of magnetite was also observed
190 by XRD analyses (Fig S2). Small crystal size of magnetite may induce drastic changes in the
191 Mössbauer spectrum (Fig 2c, G-1 hour) which reveals distinct components when compared to
192 the spectrum of the initial goethite (Fig 1). We observe the appearance of a paramagnetic
193 doublet D in the center and a sextet S_A which is superimposed upon those of S_G but with a
194 magnetic hyperfine field much larger than the one obtained for goethite. The doublet D
195 resembles that of many other paramagnetic Fe^{III} bearing species and is therefore generally not
196 applicable for identification of a spinel phase. However, the concomitant presence of doublet
197 D and sextet S_A similar to that obtained for iron in the tetrahedral site of the spinel inverse
198 structure indicate the presence of nanocrystalline magnetite should not be excluded. This
199 observation could explain consequently the spectral behavior which reveals the collapse of
200 magnetic ordering in octahedral sites governed by a superparamagnetic relaxation [36]. These
201 results could be interpreted by adsorbed Fe^{II} species transforming themselves into growing
202 epitaxial nano-magnetite layer with magnetically short-range ordering. Doublet D could be
203 attributed to Fe^{III} species formed by an electron transfer between adsorbed Fe^{II} species and

204 Fe^{III} species present on the goethite surface. Such Fe^{II}-Fe^{III} exchange was clearly
205 demonstrated by Williams et al. [37], by using the isotope specificity of ⁵⁷Fe Mössbauer
206 spectroscopy. Increasing the aging time (1 day to 1 month) enhances the spinel ordering as
207 confirmed by the vanishing of doublet D and the appearance of the classical magnetic
208 components (S_A and S_B). Sextets of magnetite are now clearly resolved and the partial
209 conversion of goethite proceeds by solid-state reaction [17].

210 All these results consistently show that the F was more reactive to transform into magnetite.
211 Almost 90% of F was transformed into magnetite after aging time of 1h, as compared to 75%
212 of L and 11% of G. After 1 month, almost whole of F and L was transformed (Table 2). Large
213 amount (~ 70%) of G was transformed into magnetite after 1 month, although, goethite is one
214 of the highly stable oxides. The order of reactivity can be classified as F > L > G, which is
215 consistent with previous findings [22]. Pedersen *et al.* reported that the transformation extent
216 decreases by approximately one order of magnitude going from ferrihydrite to lepidocrocite to
217 goethite and the main control on the transformation yield appears to be affiliated with the
218 properties and crystallinity of the iron oxide mineral. This order of reactivity found in present
219 work (F > L > G) is in accordance with surface area, solubility, thermodynamic stability and
220 dissolution data previously reported in literature [22, 23, 38-40]. Size and order of crystal are
221 important determinative factors, affecting dissolution rate of iron oxides as ferrihydrite, an
222 unstable Fe oxide with a large specific surface is more soluble, whereas crystallized iron
223 oxides such as goethite are thermodynamically stable with a relatively low dissolution rate
224 [22, 23, 40].

225

226

227 *Stoichiometry of final magnetite*

228 The degree of stoichiometry (δ) of magnetite $\text{Fe}_{3-\delta}\text{O}_4$ was quantitatively determined by using
229 the Mössbauer data obtained during transformations (Table 1). The stoichiometry is defined
230 by $x = \text{Fe}^{\text{III}}/(\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}})$ where $0.67 \leq x \leq 1$ with stoichiometric magnetite corresponding to
231 $x = 0.67$ and $\delta = 0$. Stoichiometry of magnetite was calculated as a function of aging time
232 from experimental values of relative areal (RA) of both sextets, S_A and S_B , as explained by
233 Zegeye *et al.*[9]. Because Mössbauer spectroscopy was not always able to detect
234 unambiguously the presence of low amount of hematite (< 10 wt%) in the presence of
235 magnetite [41], XRD was used to confirm the absence of $\alpha\text{Fe}_2\text{O}_3$ in the final products (Figure
236 S2). A slight departure from stoichiometry was observed for final magnetite obtained from F
237 ($\delta \sim 0.04$) and L ($\delta \sim 0.05$) after 1 month. Magnetite formed from G was the least
238 stoichiometric as the transformation was not fully accomplished. A higher departure ($\delta \sim 0.2$)
239 was observed for G product after 1 day that evolved towards lower value ($\delta \sim 0.08$) in 1
240 month. On the contrary to magnetite formed from G, slight increase in departure from
241 stoichiometry of magnetite ($\delta = 0.005$ - 0.05) in L product was observed with an increase in
242 aging time. Stoichiometric magnetite ($\delta = 0$) was not obtained in any of the final product
243 regardless of initial ferric oxyhydroxide, although, the stoichiometric conditions were
244 imposed in the initial suspension. It suggests that small part of the initial soluble Fe^{II} did not
245 incorporate in the final solid product leading to a non-stoichiometric magnetite. Similarly it
246 was reported elsewhere that excessive washing of stoichiometric magnetite caused the
247 magnetite to become oxidized due to Fe^{II} dissolution [7, 8]. On the other hand, biogenic
248 magnetite was stoichiometric with $\delta \sim 0$ when the mineralogical transformation of L was
249 investigated in a *Shewanella putrefaciens* culture under anaerobic conditions using
250 methanoate as the electron source for almost 1 month [9]. Thus, stoichiometry of final
251 magnetite could vary according to the nature of initial ferric oxyhydroxide, aging time and the
252 pathway of magnetite formation. Stoichiometric magnetite may form directly by

253 coprecipitation [14] or bioreduction of lepidocrocite [9], while topotactic formation from
254 ferric oxyhydroxide leads to non-stoichiometric phases. Stoichiometry of magnetite is an
255 important characteristic as it can influence its reactivity.

256

257 **3.2.2. Evolution of pH and concentration of soluble Fe^{II}**

258 Total and soluble Fe^{II} concentration, pH in the oxide suspensions at specified aging times
259 during transformation process are reported in Table 2. The pH at the start of reaction was
260 almost same for F, L and G (~ 9.7). This value is significantly higher than the pH of
261 precipitation (~ 7) of Fe(OH)₂ corresponding to the initial Fe^{II} concentration. As the reaction
262 proceeded, a decrease in pH was observed as the OH⁻ species were consumed to form
263 magnetite as shown in reaction (1). Decrease in pH could positively be correlated to the
264 dissolution of the initial Fe(OH)₂ precipitates into hydroxylated Fe^{II} species adsorbed on the
265 ferric oxyhydroxides. After 1 month, the pH observed for F and L suspension was ~ 5.5 while
266 pH was higher (~ 7.5) for partially transformed G. The total Fe^{II} concentration of the final
267 suspension (transformation product and solution) was measured during experiment and it was
268 almost the same as the initial concentration (50 mM) suggesting the absence of Fe^{II} oxidation
269 (Table 2). On the other hand, concentration of soluble iron was very low after 1 hour of aging
270 time. Almost 98% of the input Fe^{II} amount was rapidly removed from the aqueous solution
271 although the extent of transformation of F, L and G was different. It is probably due to
272 sorption of Fe^{II} species on iron oxide surface as reported elsewhere [25, 38]. In this case, Fe^{II}-
273 to-Fe^{III} electron transfer and precipitation processes are contributing to the observed sorption
274 phenomena. These observations are consistent with literature [40] stating that the Fe^{II}
275 adsorption edge was the same for the three oxyhydroxide phases: goethite, hematite and
276 ferrihydrite. At pH > 7.5, the adsorption of Fe^{II} onto iron oxyhydroxide phases reach 100 %

277 regardless of the tested oxide. Calculations using PHREEQC2 [42] of the pH dependence of
278 adsorption of Fe^{II} on F, L or G confirms that all Fe^{II} is adsorbed at a pH higher than 7. A
279 progressive release of Fe^{II} in solution ($\sim 5\text{-}8\text{ mM}$) was observed during the formation of
280 magnetite from F and L when the pH reached a value lower than 7 (Table 2). This
281 phenomenon could be attributed to a progressive desorption of previously sorbed Fe^{II} species.
282 After 1 month of aging time, the transformation extent of F and L was very close to 100%
283 (Table 1). The departure from stoichiometry of the obtained magnetite is $\delta \sim 0.04$, its chemical
284 composition is therefore $\text{Fe}^{\text{III}}_{2.08}\text{Fe}^{\text{II}}_{0.88}\text{O}_4$ ($\text{Fe}^{\text{II}} : \text{Fe}^{\text{III}}$ of 2.36 instead of 2 for $\delta \sim 0$). By
285 considering that all the initial Fe^{III} species (100 mM) were present inside the magnetite, 42.4
286 mM of Fe^{II} are taking part in the formation reaction. Therefore, a concentration of 7.6 mM of
287 unreacted Fe^{II} species is expected, which is in good agreement with that measured in solution
288 after 1 month of reaction for F and L (Table 2). On the other hand, pH was still higher than 7
289 after one month of G transformation therefore soluble Fe^{II} was almost negligible.

290

291 **3.2.3. Morphological properties of transformation products**

292 The morphology of the particles produced is available to clarify the transformation of ferric
293 oxyhydroxides into magnetite as shown by transformation products after 1 month (Fig. 3).
294 TEM findings were consistent with Mössbauer results. Variations in size and shape of
295 magnetite particles were observed among the products of tested ferric oxyhydroxides.
296 Magnetite particles resulting from F transformation (Fig. 3, F-1 month) were smaller with
297 non-uniform size or shape. The shape of magnetite particles was between hexagonal to
298 octahedral in the transformation products of both G and L substrates (Fig. 3, G-1month, L-
299 1month). TEM images showed that there was still large amount of G which was not
300 transformed into magnetite, while traces of L were also visible. A difference in morphology

301 and particle size of generated magnetite was observed dependent on the nature of initial
302 substrates. Indeed, the transformation of ferrihydrite produced small magnetite particles (< 50
303 nm) while those found in the transformation products of L or G have larger particles
304 (magnetite particles with 70-80 nm and 200-300 nm in L and G products respectively). It
305 seems that magnetite, formed by reaction with Fe^{II} , has morphology and particle size similar
306 to those of the initial oxyhydroxides which occurs in topotactic conversion of initial
307 compounds to magnetite [14, 43]. In addition, the Mössbauer spectra of magnetite formed
308 from ferrihydrite displays broad lines, often caused by a structural disorder. This observation
309 is also in favor of a topotactic formation of magnetite onto poorly crystallized ferrihydrite. In
310 contrast, well ordered magnetite with sharp Mössbauer lines was obtained from crystallized
311 iron oxides (i.e. L and G) (Fig. 2&3).

312 Since final product of G transformation is a mixture of goethite and magnetite, only magnetite
313 produced from F and L were characterized by N_2 adsorption isotherm. The specific surface
314 area (SSA) experimental value of magnetite, formed from F or L, determined by the BET
315 method was found to be 40 ± 2 and $20 \pm 2 \text{ m}^2 \text{ g}^{-1}$, respectively. The radius of the supposed
316 spherical particles (the density of magnetite, $\rho = 5.15 \times 10^6 \text{ g/m}^3$) can be related to the surface
317 area as $A = 6/(\rho.d)$. Thus, the calculated average diameter of a supposed spherical particle is
318 $\sim 30 \text{ nm}$ and $\sim 60 \text{ nm}$ for magnetite from F for L respectively, which is consistent with the
319 average size estimated by the TEM observations. The size of magnetite particles in F product
320 falls in the size range of nano-particles of magnetite observed for commercially available
321 nano-magnetite (i.e. $48 \text{ m}^2 \text{ g}^{-1}$, 30 nm) [44].

322

323 5. CONCLUSION

324 The transformation of ferric oxyhydroxides into magnetite was investigated in the present
325 work which contributes to our understanding of the magnetite formation in natural
326 environments. Order of reactivity to transform into magnetite was $F > L > G$. The evolution of
327 stoichiometry of final magnetite was also monitored. This study demonstrates that the
328 transformation of ferric oxyhydroxides in the presence of Fe^{II} can be affected by many factors
329 including mineralogy of initial oxyhydroxide, aging time and solution chemistry. Magnetite
330 was the product, with variable stoichiometry, particle size and surface area, obtained from
331 different ferric oxyhydroxides. Magnetite was non-stoichiometric regardless of the initial
332 ferric oxyhydroxide although stoichiometric conditions were imposed. In the case of goethite,
333 it is more striking as observed by Mössbauer spectroscopy over aging time. The results
334 suggest a solid-state transformation of goethite into magnetite with an electron transfer
335 driving the spinel ordering between adsorbed Fe^{II} and the ferric oxide. Moreover, reactivity of
336 the magnetite could be different depending on its source of ferric mineral which need to be
337 explored for remediation purposes. For example, magnetite produced from ferrihydrite was
338 more close to stoichiometry with smaller particles and higher surface area; all these factors
339 could possibly contribute towards its high reactivity. Fe^{II} -induced transformations of ferric
340 oxyhydroxides could be a novel way to synthesize nano-sized particles of magnetite. These
341 findings have important implications for remediation technologies using magnetite as catalyst,
342 and also for the natural attenuation of contaminants in soils and sediments.

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424 **Figure captions**

425

426 **Figure 1:** Mössbauer spectra of original ferric oxyhydroxides, ferrihydrite (F), goethite (G)
427 and lepidocrocite (L). Hyperfine parameters corresponding to these spectra are presented in
428 Table 1.

429 **Figure 2:** Mössbauer spectra of the transformation products of (a) F-ferrihydrite, (b) L-
430 lepidocrocite and (c) G-goethite, obtained after aging time of 1 hour, 1 day and 1 month.
431 Hyperfine parameters corresponding to these spectra are presented in Table 1. The percentage
432 corresponds to the relative emission of the most intense lines.

433 **Figure 3:** Bright field TEM images showing the transformations products after an aging time
434 of 1 month where M stands for magnetite, L for lepidocrocite and G for Goethite.

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Table 1: Mössbauer hyperfine parameters of the spectra presented in Figure 1 and Figure 3. *CS*: centre shift with respect to metallic α -Fe at room temperature; Δ : quadrupole splitting in the paramagnetic state or ε : quadrupole shift; *H*: Hyperfine magnetic field; *RA*: relative area and δ : departure from stoichiometry of non-stoichiometric magnetite ($\text{Fe}_{3-\delta}\text{O}_4$) determined by classical Mössbauer analysis ($\delta = 0$ for stoichiometric magnetite, Fe_3O_4).

* δ calculation is possible only when fitting of magnetite spectrum is done with two sextets; S_A and S_B .

Sample	Component	<i>CS</i> (mm s^{-1})	Δ or ε (mm s^{-1})	<i>H</i> (kOe)	<i>RA</i> (%)	Stoichiometry δ
<i>Ferrihydrite</i>	D	0.35	0.68	-	100	-
F-1 hour	D	0.38	0.71	-	9	
	S1	0.30	0.20	459	13	
	S2	0.42	-0.07	430	68	*
	S3	0.25	0.01	485	10	
F-1 day	D	0.34	0.61	-	4	
	S1	-0.01	0.005	476	12	*
	S2	0.346	0.02	407	59	
	S3	0.678	0.02	462	25	
F-1 month	D	0.30	0.77	-	2	
	S_A	0.27	0	479	40	$\delta = 0.04$
	S_B	0.64	0	444	58	
<i>Goethite</i>	S_G	0.38	-0.13	351	100	-
G-1 hour	D	0.39	0.72	-	7	
	S_G	0.37	-0.13	364	89	*
	S_A	0.37	0	491	4	
G-1 day	S_G	0.38	-0.13	378	68	
	S_B	0.64	-0.02	460	7	$\delta = 0.23$
	S_A	0.32	-0.004	491	25	
G-1 month	S_A	0.31	0.008	491	32	
	S_B	0.66	-0.003	458	35	$\delta = 0.08$
	S_G	0.38	-0.14	377	33	
<i>Lepidocrocite</i>	D	0.48	0.54	-	100	-
L-1 hour	D	0.39	0.56	-	26	
	S_A	0.32	0.01	484	25	$\delta = 0.005$
	S_B	0.61	-0.05	452	49	
L-1 day	D	0.39	0.56	-	2	
	S_A	0.33	0.006	488	47	$\delta = 0.045$
	S_B	0.63	0	453	51	
L-1 month	D	0.40	0.53	-	2	
	S_A	0.33	0.01	490	41	$\delta = 0.05$
	S_B	0.58	-0.02	456	57	

Table 2: Percentage of magnetite formation measured by Mössbauer spectroscopy and various concentrations measured in the supernatant.

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Sample	Magnetite formation (%)	pH	Total Fe ^{II} concentration [mM]	Soluble Fe ^{II} concentration [mM]
<i>Ferrihydrite</i>				
F- $t = 0^*$	-	9.7	-	
F-1 hour	91	6.9	49	Not detected
F-1 day	96	6	48	2
F-1 month	98	5.6	49	8
<i>Goethite</i>				
G- $t = 0^*$	-	9.8	-	
G-1 hour	11	8.4	47	Not detected
G-1 day	32	8.2	48	Not detected
G-1 month	67	7.5	49	Not detected
<i>Lepidocrocite</i>				
L- $t = 0^*$	-	9.6	-	
L-1 hour	74	7.8	49	Not detected
L-1 day	98	6.4	48	2
L-1 month	98	5.6	47	5.5

* The pH was measured just after the addition of NaOH into the Fe^{III}-Fe^{II} suspension

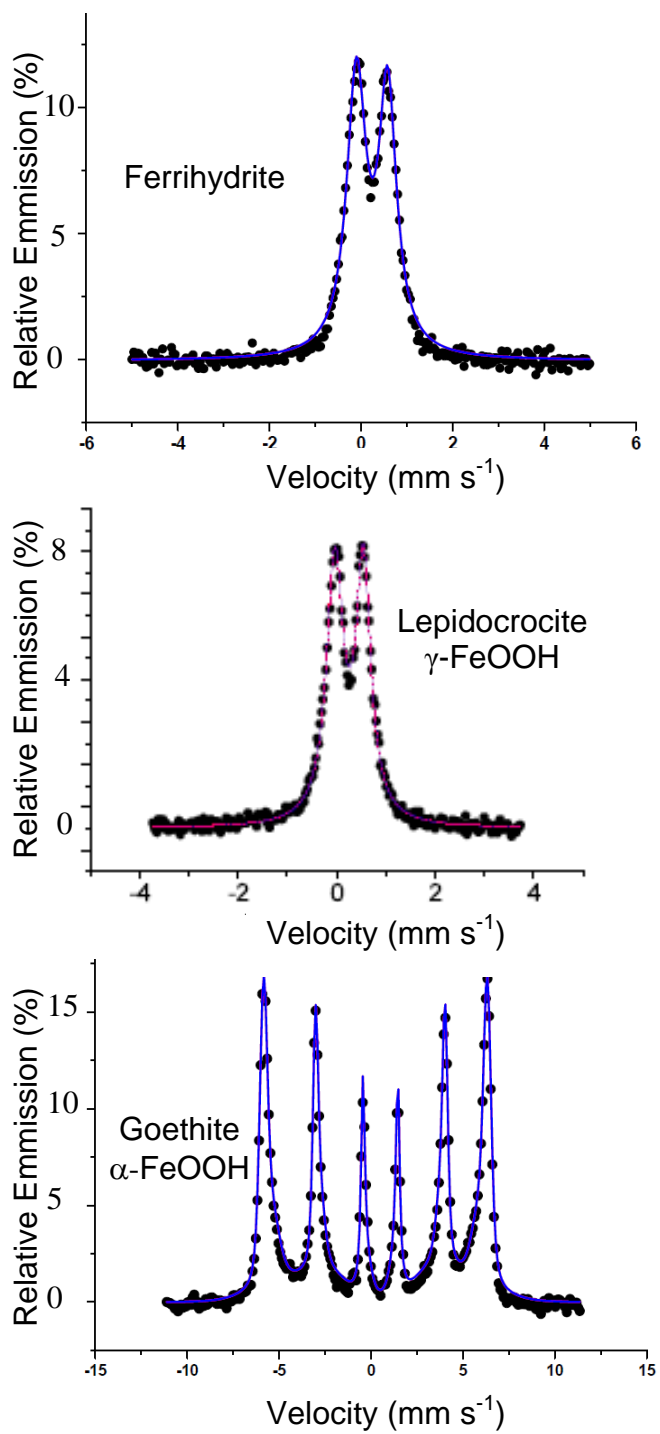
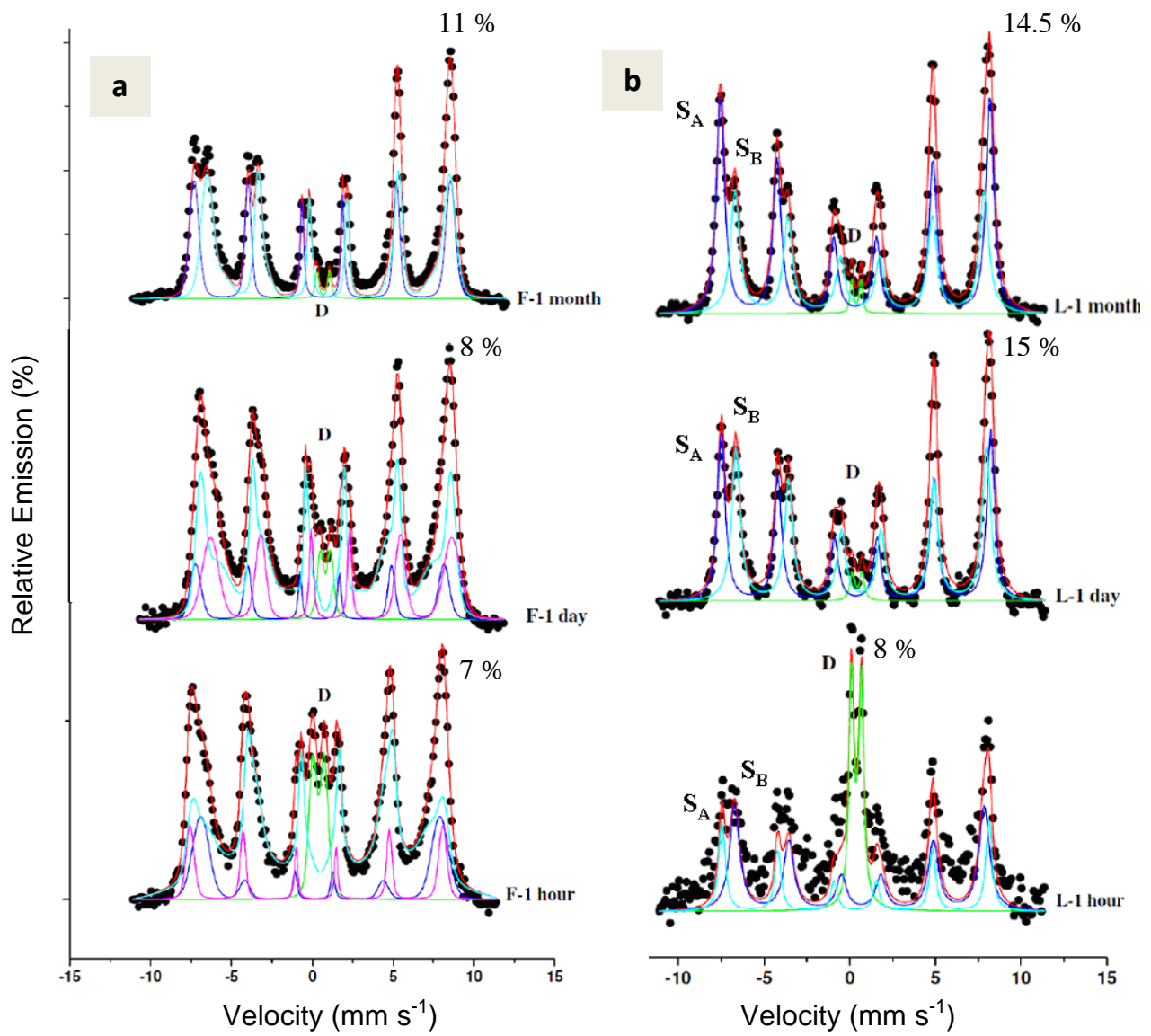


Figure 2:



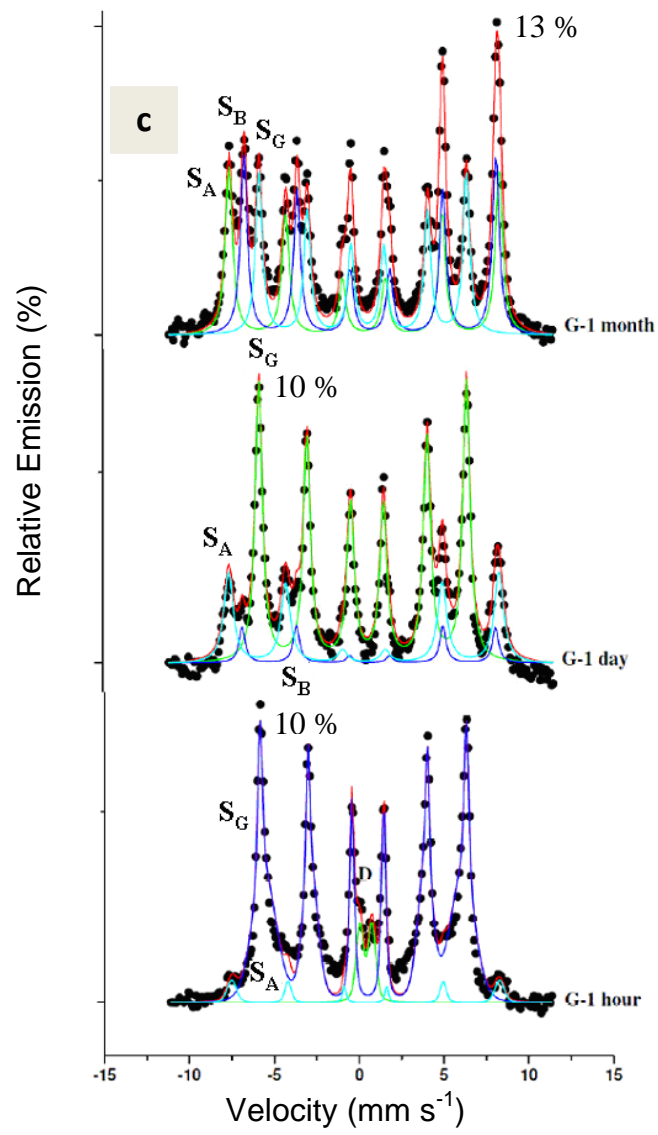
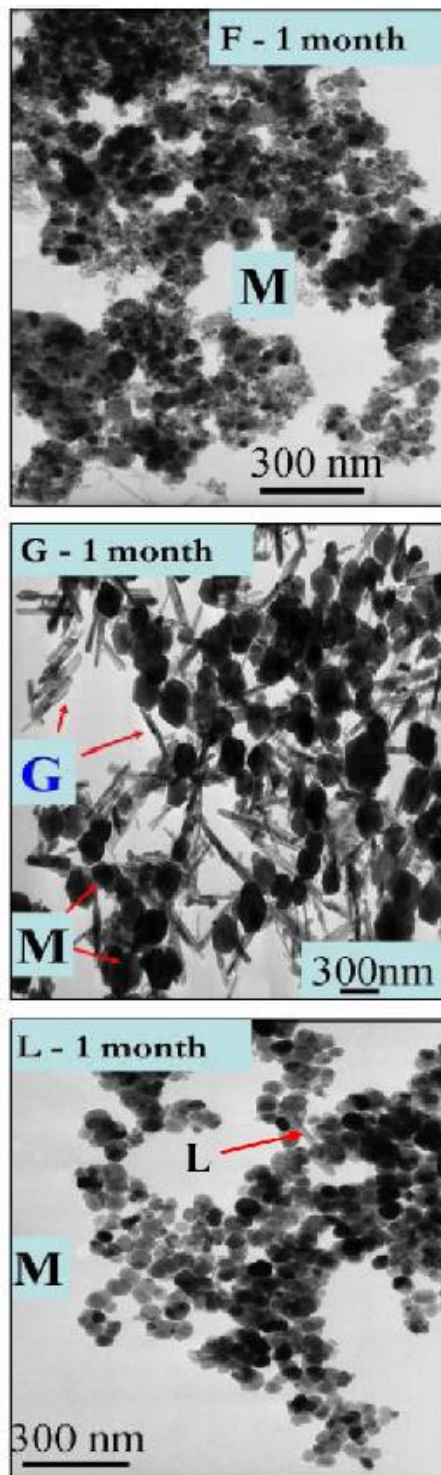


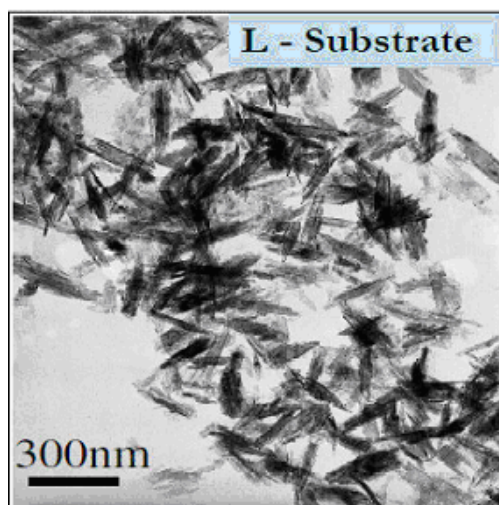
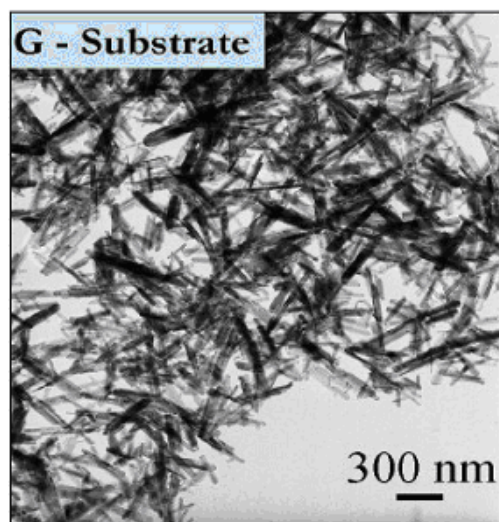
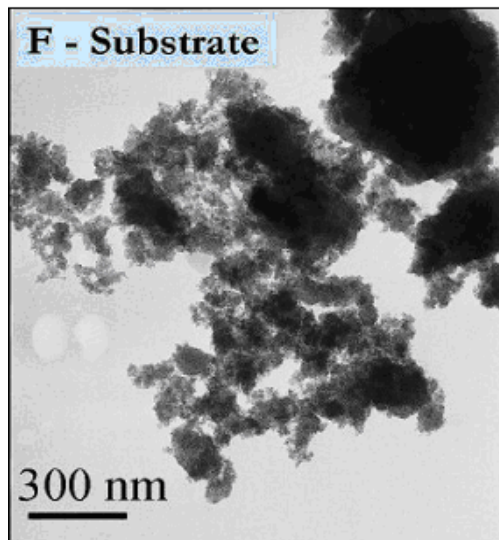
Figure 3:



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Figure S1: Bright field TEM images showing initial ferric oxyhydroxides (F-ferrihydrate, L-lepidocrocite and G-goethite).



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466 **Figure S2:** Evolution of the X-ray diffraction patterns of the various samples as a function of
 467 aging time. Initial substrate is Ferrihydrite F (a), Lépidocrocite L (b) and Goethite G (c). M
 468 stands for magnetite
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