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Insight into the magnetic properties of Pb-doped iron oxide nanoparticles during Fe(III) bio-reduction by *Shewanella oneidensis* MR-1

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► To cite this version:

Fatima Meite, Thomas Hauet, Patrick Billard, Tom Ferté, Mustapha Abdelmoula, et al.. Insight into the magnetic properties of Pb-doped iron oxide nanoparticles during Fe(III) bio-reduction by *Shewanella oneidensis* MR-1. *Chemical Geology*, 2022, 606, pp.120904. 10.1016/j.chemgeo.2022.120904 . hal-03697883

HAL Id: hal-03697883

<https://hal.univ-lorraine.fr/hal-03697883>

Submitted on 23 Nov 2022

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26 **Abstract**

27

28 Anthropogenic activities have led to a significant accumulation of Pb in the
29 environment, posing a threat to ecosystems. Iron oxides that display magnetic properties are
30 ubiquitous in the environment and Pb partitioning onto these minerals is considered one of the
31 most critical geochemical processes controlling its environmental fate. In anoxic environments,
32 iron oxides undergo redox cycling due to biotic and abiotic routes, resulting in their
33 transformation/dissolution and evolution of their magnetic characteristics. However, there is
34 still a lack of knowledge on the impact of Pb on the dynamic of iron oxides bioreduction.
35 Furthermore, there is little information available regarding the nature of biogenic minerals and
36 their magnetic signatures.

37 Here we incubated Pb-bearing ferrihydrites (Fh_Pb) with various Pb/(Fe + Pb) molar ratios
38 (*i.e.*, 0, 2 and 5%) with the iron-reducing bacterium *Shewanella oneidensis* MR-1, for 21 days.

39 XRD analyses of the initial Fh_Pb displayed characteristic features of Fh and a decrease of
40 magnetization in the presence of Pb. During the bio-reduction process, Pb doping led to a drop
41 in the rate and extent of reduction. At the end of the incubation period, the analysis of the
42 aqueous solutions revealed a minor proportion of Pb in solution, indicating that a significant
43 proportion of the Pb is sorbed onto the biogenic minerals. Magnetite (95%) and siderite (5%)
44 formed during the bioreduction of Fh, while magnetite (~80%) and goethite (~20%) precipitated
45 in the presence of Pb as revealed by transmission Mössbauer spectroscopy. Furthermore, the
46 size of the magnetite particles decreased from about 11 nm in absence of Pb to 6 nm with 2%
47 of Pb-bearing, while 5% of Pb led to particles too small to be quantified with our TEM
48 measurements. The combined effect of the decrease in particle size of magnetite, substitution
49 of Pb and the precipitation of goethite in the Pb-doped assay led to a significant decrease of
50 magnetization at room temperature. Overall, this study highlights the effect of Pb on iron oxides

51 bio-reduction and transformation processes and the sensitivity of magnetism to serve as a
52 monitoring method.

53

54 **Keywords: Pb-bearing ferrihydrite, bioreduction, magnetite, goethite, transmission**
55 **Mössbauer spectroscopy, SQUID**

56

57 1. Introduction

58

59 Anthropogenic activities including mining and smelting have contributed to the release
60 of important levels of lead (Pb) in the environment (Singh and Li, 2014). Lead possesses three
61 oxidation states, Pb(0), Pb(II) and Pb(IV), with Pb(II) being the most frequently encountered
62 form (Abadin et al., 2007). More than 200 mg kg⁻¹ of Pb are commonly measured in
63 contaminated soils, while concentrations lower than 20 mg kg⁻¹ of Pb are generally detected in
64 pristine soils (Gis Sol, 2011; Gutiérrez et al., 2016; Hernandez et al., 2003; Kabata-Pendias and
65 Pendias, 2000; National Academies of Sciences, Engineering, and Medicine, 2017; Villen-
66 Guzman et al., 2018). High levels of Pb poses a threat to human health and ecosystems in the
67 form of contaminated soil and groundwater, and reduce food quality and land arability. In this
68 context, the United States Environmental Protection Agency (US EPA) recommends Pb
69 concentrations in drinking waters below 15 µg L⁻¹ (Martin and Griswold, 2009), while the
70 World Health Organization (WHO) sets a maximum permissible Pb level of 100 mg kg⁻¹ in
71 agricultural soils (Chiroma et al., 2014).

72

73 It was well established that Pb speciation in the environment is largely governed by
74 physicochemical processes. It can precipitate as poorly soluble Pb compounds, can be
75 complexed by organic matter and/or adsorbed on the mineral soil matrix (i.e. carbonate, clays,
76 Mn-and Fe oxides) (Bradl, 2004; Fleming et al., 2013; Jensen et al., 2006; Liu et al., 2020). Fe
77 oxides are of particular interest among the carrier phases of Pb. They are ubiquitous in the
78 environment, accounting for up to 5% in weight of specific fractions (silts, clays) of surface
79 soils and sediments (Journet et al., 2014). They display a high surface area and a reactive
80 surface; hence, they exhibit significant sorption capacities for organic and inorganic species.
81 Thus, Fe oxides exert significant control on the reactivity, speciation, and mobilization of

82 metals and metalloids such as Pb, Ni, Co, As, Sb (Erbs et al., 2010; Frierdich et al., 2011;
83 Zachara et al., 2001; Zegeye et al., 2021). Pb, like other metals, interacts with the surface of
84 Fe oxides and their (hydroxyl) functional groups (Cornell and Schwertmann, 2003). These
85 interactions may lead to the surface adsorption (*via* complexation), or structural incorporation
86 of the metals into the iron oxide crystal, and/or physical isolation within nanosized pores of iron
87 oxides aggregates (Davranche and Bollinger, 2000; Hesterberg et al., 2011; Lu et al., 2011;
88 Seda et al., 2016). Thus, Pb sequestration by iron (oxyhydr)oxides is one of the most critical
89 geochemical processes controlling its environmental fate, transport, and bio-availability
90 (Hassellöv and von der Kammer, 2008).

91 Numerous mineralogical and geochemical studies have proven the occurrence of a
92 significant amount of iron oxides and various heavy metals such as Pb in a polluted environment
93 (Jordanova et al., 2003). Given the magnetic properties of iron oxides, the interaction between
94 metallic pollutants and Fe(III) minerals can be investigated through magnetic and structural
95 measurements. Thus, magnetic approaches have been applied for soil heavy metal content
96 monitoring and pollution assessment during the last decades (Canbay, 2010; Chaparro et al.,
97 2006; Orosun et al., 2020; Schmidt et al., 2005; Wang et al., 2018). Several studies indicated
98 significant positive correlations between soil magnetic parameters (*e.g.*, magnetic
99 susceptibility, MS) and heavy metal contents. For instance, increasing arsenic concentration in
100 the mineral structure led to an elevated magnetic signal (Ouyang et al., 2020). Therefore,
101 magnetic signatures have the potential to detect the level of heavy metal sorbed on iron oxides
102 due to the carrier phase (*i.e.*, iron oxide) magnetic properties.

103 Iron oxides are also the most abundant terminal electron acceptors in several anaerobic
104 subsurface environments for dissimilatory iron-reducing bacteria (DIRB), such as *Geobacter*
105 *sp.* and *Shewanella sp.* (Bleam, 2012). These phylogenetically diverse bacteria can couple the
106 oxidation of an organic (*e.g.*, formate, pyruvate, lactate) or inorganic (*e.g.*, H₂) electron source

107 to the reduction of Fe(III). The Fe(II) generated by the bio-reduction process is either liberated
108 in the solution or further reacts with mineral surfaces and can lead to the precipitation of
109 biogenic minerals such as magnetite (Fe₃O₄), goethite (α -FeOOH) and siderite (FeCO₃) (Han
110 et al., 2018; Hansel et al., 2005, 2003; Pallud et al., 2010; Zachara et al., 2002). Concomitantly,
111 adsorbed or co-precipitated metals, such as Pb, could either be released in the solution or
112 partitioned on the solid phases (*i.e.*, initial iron oxide and/or the biogenic mineral). The
113 mineralogic transformation due to bacterial activity also affects the magnetic signature of the
114 system (Byrne et al., 2015; Porsch et al., 2010).

115 Relatively little is known regarding the effect of Pb on the microbiologically mediated
116 Fe redox reactions, the precipitation of biogenic minerals, and the subsequent redistribution of
117 Pb. It is also of interest to monitor the magnetic signal variation of iron oxides during their
118 incubation with iron-reducing bacteria in order to depict the bio-reduction processes. To
119 broaden our understanding of Fe and Pb biogeochemical cycles and the relevance of magnetic
120 signature measurements, our study aims to investigate how various Pb concentrations impact
121 the bio-reduction of iron oxides, the precipitation of biogenic minerals and their magnetic
122 signals. To this end, we incubated Pb-bearing ferrihydrites with variable molar ratios in the
123 presence of *Shewanella oneidensis* MR-1. With this set-up we aimed to study the changes in:
124 i) the rate and extent of ferrihydrite bioreduction, ii) the redistribution of Pb among the liquid
125 and solid phases, and iii) the nature of the minerals formed upon the bio-reduction and their
126 magnetic signature.

127

128

129 **2. Material and methods**

130

131 All reagents and acids were of analytical grade and solutions were prepared using 18.2 MΩ
132 cm⁻¹ deionized water. Anaerobic experiments and sample collection were conducted under
133 strictly anaerobic conditions in a re-circulating anoxic chamber (Coy Laboratory Products Inc.)
134 where trace amounts of oxygen were scavenged by palladium catalysts. A 98% N₂ + 2% H₂
135 atmosphere was maintained by automatized injection of the gas mixture.

136

137 **2.1. Pb(II)-bearing ferrihydrite synthesis**

138

139 Ferrihydrite was prepared by neutralization of 0.4 M FeCl₃ with 4 M NaOH. Pb-bearing
140 ferrihydrites were synthesized similarly to pristine ferrihydrite except for the addition of PbCl₂
141 (8 to 20 mM PbCl₂ solutions) to the ferric salt before hydrolysis at Pb/(Fe+Pb) molar ratios of
142 0.02 and 0.05 (Schwertmann and Cornell, 2000). These samples will be named Fh, Fh_Pb 0.02,
143 and Fh_Pb 0.05 (or the Fh_Pb series) hereafter. All precipitates were washed free of electrolytes
144 by dialysis (1 nm pore size Spectra/Por® 7 dialysis membranes) until a steady conductivity <
145 20 μS cm⁻¹ was obtained.

146

147 **2.2. Bioreduction of Pb(II)-bearing ferrihydrites**

148

149 *Shewanella oneidensis* MR-1 cells were streaked under aerobic conditions on tryptic soy
150 agar from -80 °C glycerol stock. They were sub-cultured once, and the colonies were used to
151 prepare a suspension to inoculate 400 mL of trypticase soy broth (TSB). Cells were grown
152 aerobically to the exponential growth phase in TSB under agitation at 180 rpm and at 28 °C.

153 They were harvested by centrifugation, washed twice with sterile 0.9% NaCl, and concentrated
154 in the same medium (70 mL).

155 The bio-reduction assays were performed in a mineral medium (Table S1) that was heat
156 sterilized, purged with filter-sterilized N₂ and dispensed into sterile 100 mL serum bottles, in
157 the presence of Fh and Fh_Pb series (6.25 g L⁻¹ initial solids) and crimp sealed with butyl rubber
158 stoppers. Sodium formate, as the sole electron source, and anthraquinone-2,6-disulfonate
159 (AQDS), as an electron shuttle (Watanabe et al., 2009), were sterilized by filtration (filter pore
160 size 0.2 μm), purged with filter-sterilized N₂ and were introduced in the culture medium under
161 aseptic conditions in order to achieve 35 mM and 100 μM respectively in each 80 mL assay. *S.*
162 *oneidensis* MR-1 cell suspensions were added to obtain final concentrations of (1.85 ± 0.15) x
163 10⁹ cell mL⁻¹. The initial pH after mixing all the components was adjusted to ca. 7. The assays
164 were incubated in the dark for 21 days in triplicates at 28°C. The control experiments were cell-
165 free and otherwise identical to the biotic assays.

166

167 2.3 Chemical analyses

168

169 Total Fe and Pb concentrations in the initial solids were quantified using atomic
170 absorption spectroscopy (AAS) after dissolution in 4 M HCl.

171 At each time point, the assays were shaken to ensure homogeneity of the slurries before
172 sampling and extraction with 4 M HCl. Total Fe(II) (Fe(II)_{tot}) was determined by the ferrozine
173 method (Viollier et al., 2000). The same procedure was used to measure total Fe (Fe_{tot}) but after
174 reduction of the samples with hydroxylamine hydrochloride. The apparent reduction rate was
175 computed from the first derivative of a nonlinear curve fit (Eq. 1).

$$\%(Fe(II)_{tot}/Fe_{tot})_t = \%(Fe(II)_{tot}/Fe_{tot})_{max} \times [1 - e^{-k_{obs} \times t}] \quad (1)$$

176 Where $\%(\text{Fe(II)}_{\text{tot}}/\text{Fe}_{\text{tot}})_t$ is the $(\text{Fe(II)}_{\text{tot}}/\text{Fe}_{\text{tot}})$ (%) produced at time t , $\%(\text{Fe(II)}_{\text{tot}}/\text{Fe}_{\text{tot}})_{\text{max}}$ is the
177 maximum $\%(\text{Fe(II)}_{\text{tot}}/\text{Fe}_{\text{tot}})$ observed at the end of the reduction period (*i.e.*, 21 days), and k_{obs}
178 is the pseudo first-order constant.

179 At the end of the incubation period, 1 mL was withdrawn from the assays, filtered through 0.22
180 μm pore filters and acidified in 2 M HCl to measure Pb in the aqueous phase by AAS.

181

182 **2.4 Characterization of the solid phase**

183

184 Powder X-ray diffraction (XRD) was performed using D8 Bruker diffractometer
185 equipped with a monochromator, a position-sensitive detector and a Co anode ($K\alpha_1 = 0.178897$
186 nm radiation). The diffractograms were recorded in the $3\text{--}80^\circ$ 2θ range and a 0.03° 2θ step size
187 with a collecting time of 3 s per point, using sample holders equipped with glass domes and
188 filled under a glovebox to maintain the samples under a N_2 atmosphere. Phase identification
189 was performed using the software DIFFRAC.EVA.

190 TEM observations and selected area electron diffraction (SAED) were carried out using
191 a Philips CM200 TEM (200 kV) at the end of the incubation period (*i.e.*, 21 days). One drop of
192 the suspension was laid on an amorphous carbon-coated grid and loaded into the analysis holder
193 of the microscope under 10^{-8} Torr vacuum.

194 *SQUID* Magnetic measurements were performed using Quantum Design
195 Superconducting Quantum Interference Device (SQUID). Magnetization versus magnetic field
196 hysteresis loops were measured at 300 K and 2 K with field sweep range up to 7 T. Zero field
197 cooled (ZFC) and field cooled (FC) measurements were also performed. The ZFC procedure
198 was as follows: The sample were demagnetized at 300 K using an oscillatory decaying field
199 from 1 T to zero field and then cooled to 2 K with a rate of 1 K min^{-1} . Afterwards ZFC magnetic
200 moments were measured while the temperature was ramped back up from 2 K to 300 K at a

201 rate of 1 K min⁻¹ under 7.5 mT constant field. The FC procedure consists in cooling down the
202 sample from 300K under 7.5 mT and then measuring moment while heating it up from 2 K
203 back to 300 K.

204

205 *⁵⁷Fe Mössbauer spectroscopy* Transmission Mössbauer spectroscopy was performed
206 between 298 K and 11 K with a constant acceleration Mössbauer spectrometer, 512
207 multichannel analyzer (Halder Electronic GmbH), and a 50 mCi source of ⁵⁷Co in Rh maintained
208 at room temperature (RT). Data were obtained from appropriate amounts (10 mg of Fe per cm²)
209 of solid samples to get optimal experimental conditions. Analyzes were carried out between
210 ambient and 11 K on the ARS cryostat (Advanced Research Systems, Macungie USA) equipped
211 with vibration isolation stand developed in the LCPME laboratory. Mössbauer spectra were
212 collected in transmission mode. The 50 mCi source of ⁵⁷Co in Rh matrix was maintained at
213 room temperature and mounted at end of a Mössbauer velocity transducer. The spectrometers
214 were calibrated with a 25 µm foil of α-Fe at RT. Spectra were computer-fitted (recoil Software,
215 Ottawa University) with the Voigt-based fitting model for paramagnetic sites corresponding to
216 doublet which have a distributions of quadrupole splittings (QSDs) and magnetic sites
217 corresponding to sextet which have a distribution of magnetic hyperfine fields (HFDs), as
218 implemented in the Recoil software.

219

220 3 Results and discussion

221 3.1 Fh_Pb series characterization

222

223 The XRD pattern for the pristine Fh and Pb-bearing Fh (Fh_Pb(0.02) and Fh_Pb(0.05))
224 display only two diffraction peaks, at about 0.149 and 0.258 nm (Figure 1) (Schwertmann and
225 Cornell, 2000). However, in the presence of Pb, we observe a shift of the most intense
226 diffraction lines (*i.e.*, 0.258) to higher *d* values relative to the peak of the pristine Fh. In addition,
227 the patterns of the Pb-bearing Fh indicate a line broadening which may imply either a decrease
228 of the crystallite size or the incorporation of Pb in the Fh structure, lowering its crystallinity.
229 No other peak indicative of additional phases was observed in the diffraction data.

230 The Fe and Pb contents of the co-precipitates were measured by AAS, and the obtained
231 concentrations were approximately equal to the initial molar ratio of Pb/(Pb+Fe) (*i.e.*, 0.02, and
232 0.05) used to precipitate the solids.

233

234 To gain more insight into the influence of Pb-doping on ferrihydrite magnetic properties,
235 we performed both isothermal magnetization versus field loops at different temperatures and
236 ZFC/FC magnetization versus temperature measurements, on Fh, Fh_Pb(0.02) and
237 Fh_Pb(0.05). At 250 K, Fh shows a linear increase of magnetization with field intensity with a
238 slope of $1.5 \text{ A m}^2 \text{ kg}^{-1} \text{ T}^{-1}$ (Figure 2a). The same linear behavior is observed for Fh with 2%
239 and 5% Pb but with a smaller slope, down to $1.1 \text{ A m}^2 \text{ kg}^{-1} \text{ T}^{-1}$ for 5% Pb. These results suggest
240 that the moment of Fh decreases when adding Pb. In recent experiments on Sb-doping of Fh,
241 whose chemical and structural characterization is reported in Zegeye et al. (2021), we also
242 observed a similar trend (Figure 3a). As the concentration in Sb increases from 0 to 10%, the
243 slope of the magnetic susceptibility at 250 K decreases from 1.45 to $0.65 \text{ A m}^2 \text{ kg}^{-1} \text{ T}^{-1}$.

244

245 The linear $M(H)$ curve shown in Figure 2a and Figure 3a at 250 K is typical of a
246 paramagnetic material. Although a Néel temperature for 2-line ferrihydrite of about 350 K was
247 once extracted from neutron reflectivity experiments (Seehra et al., 2000), for nanometer-size
248 ferrihydrite particles, several studies demonstrated an additional paramagnetic-like signal for
249 temperature much lower than 350 K. It is attributed to the presence of uncompensated surficial
250 spins (Guyodo et al., 2006; Punnoose et al., 2004) either from reduced coordination and broken
251 exchange bonds (Knyazev et al., 2021) or the depletion of Fe and enrichment of OH groups
252 (Michel et al., 2010; Hiemstra, 2018) on the ferrihydrite nanoparticles surface. The magnetic
253 susceptibility measured here around $1.5 \text{ A m}^2 \text{ kg}^{-1} \text{ T}^{-1}$ at 250 K for Fh matches values reported
254 in Punnoose et al. (2004). In the same article, the authors found a decrease of the moment per
255 particle of 35% for 5% Ir or Mo doping. For Pb and Sb, from the slopes of the paramagnetic
256 $M(H)$ loop in Figure 2a and Figure 3a, we obtain a decrease of 27% and 35%, respectively. This
257 is consistent with a general scenario where the surface Fe(III) of ferrihydrite nanoparticles is
258 preferably substituted by the dopant, as already reported for Co doping (Stolyar et al., 2017).
259 So, unlike magnetic dopants that can improve exchange (Stolyar et al., 2017), we conclude that
260 non-magnetic dopants such as Pb and Sb could reduce the exchange coupling between
261 ferrihydrite uncompensated spins and therefore lead to a decrease in the moment per particle.

262

263 Next, we measured $M(H)$ loops at 2 K. For all three concentrations of Pb (as well as for
264 samples in the Sb-bearing ferrihydrite series), the loop was a S-type hysteresis loop without any
265 magnetic saturation even under 7 T field. A typical example is shown for 2% Pb-doping in inset
266 of Figure 2a. Magnetization reversal steps also occurred at low magnetic field. Both features
267 are the signature of spin glass systems (Ghosh et al., 2017; Mydosh, 2014) where the magnetic
268 moments are driven by strong dipolar interactions (Berquó et al., 2009; Seehra et al., 2000)
269 and/or surface electronic exchange coupling. This is typical of dense assemblies of

270 agglomerated nanoparticles (Fiorani and Peddis, 2014; Fraerman and Sapozhnikov, 2002;
271 Mydosh, 2014) and was already experimentally revealed in agglomerated ferrihydrite
272 nanoparticles (Duarte et al., 2006; Punnoose et al., 2004). The superspin-glass behaviour of our
273 ferrihydrite nanoparticles assemblies is confirmed by the ZFC/FC curves presented in Figure
274 2b and inset of Figure 3b (De Toro et al., 2013; Duarte et al., 2006; Fiorani and Peddis, 2014).
275 The difference between ZFC and FC characterizes the difference of randomness in the
276 collective random freezing of ferrihydrite particle moments depending on the field-induced
277 symmetry breaking below a critical temperature, so-called spin-glass transition temperature
278 (T_g). It is to be noted that the curve for pure Fh in the Pb-doping series does not show a parabolic
279 shape below T_g (Figure 2b), unlike typical spin-glass system and unlike the pure Fh sample in
280 the Sb-doping series (Zegeye et al., 2021). We have no clear explanation for this discrepancy
281 since all the other curves match very well the superspin-glass scenario. As depicted in Figure
282 3b, T_g decreases when the dopant concentration increases for the ferrihydrite Pb-series and for
283 the ferrihydrite Sb-series. Moreover, the height of the dip below T_g decreases as the dopant
284 concentration increases. It can be seen in the normalized plot of $M/M(T_g)$ value as a function
285 of temperature (inset of Figure 3b). The ferrihydrite nanoparticle diameter does not vary much
286 with a few percent of doping. Furthermore, the interparticle interaction energy is much larger
287 than the individual particle anisotropy energy in a strongly interacting superspin-glass system.
288 We conclude that the dip height and T_g change must originate mainly from the gradual
289 reduction of the ferrihydrite inter-particles interaction because of the decrease of each particle
290 moment when adding Pb or Sb dopant.

291

292 **3.2 Bioreduction of the Fh_Pb series and Pb partitioning**

293

294 We monitored the bioreduction of the Pb-bearing Fh series for 21 days (Figure 4). No
295 measurable Fe(III) reduction took place in the cell-free assays. The presence of Pb decreased
296 the rate and extent of reduction (Figure 4a). The apparent reduction rate was 0.07 ± 0.01
297 $(\text{Fe(II)}_{\text{tot}}/\text{Fe}_{\text{tot}}) \text{ day}^{-1}$ for assays run with Fh, while it decreased to 0.014 ± 0.001 $(\text{Fe(II)}_{\text{tot}}/\text{Fe}_{\text{tot}})$
298 day^{-1} for those run with Fh_Pb(0.05). Thus, the reduction rate declined by 15% for every molar
299 ratio increase of 0.01 in Pb-bearing Fh (Figure 4b). Although the linear decrease tends to
300 indicate a complete inhibition of the reduction for a higher Pb/(PB + Fe) molar ratio relative to
301 our study, further assays will be necessary to conclude on the impact of lead loading, higher
302 than 5%, on the bioreduction process. The precipitation of Pb with Fh alters the
303 physicochemical properties of Fh, as shown for other elements (Ekstrom et al., 2010; Erbs et
304 al., 2010). The decrease of the reduction rate observed in this study may be related to a
305 significant decrease of reactive sites in the Fh surface due to Pb loading. This trend is consistent
306 with bioreduction data presented by Ekstrom et al., 2010 and Fredrickson et al., 2001 that
307 showed a decrease of the reduction rate with increasing Al or Ni content for substituted Fh.
308 Fh is a metastable mineral and transforms to a thermodynamically stable phase such as goethite
309 and magnetite in the presence of Fe(II) (Benali et al., 2001; Boland et al., 2014; Hansel et al.,
310 2005; Pedersen et al., 2005; Williams and Scherer, 2004). The extent of reduction reached 35%
311 for Fh (Figure 4), indicating that 35% of Fe(II) was enough to induce its mineralogical
312 transformation. On the other hand, the extent of reduction levelled around 25% irrespective of
313 the Pb/(Fe+Pb) molar ratio. Lower Fe(II) concentrations are thus required to induce Fh
314 transformation via Fe(II) catalyzed dissolution-reprecipitation in the presence of Pb, indicating
315 higher lability of Fh_Pb in the concentration range tested in this study. These results indicate
316 that the presence of Pb decreased the Fe(II)/Fe(III) ratio required to induce Fh transformation
317 compared to that of Fh.

318 After the 21d-bioreduction, the concentration of Pb in solution was significantly lower than that
319 initially associated with Fh ($Pb_{\text{solution}}/Pb_{\text{initial}} < 1\%$) (Table S2). These results suggest that a
320 substantial amount of Pb is associated with secondary minerals. We hypothesize that adsorption
321 and coprecipitation of Pb occur during bioreduction through three processes: i) the adsorption
322 of Pb ions on the surface, structural defects and nano-pores of biogenic minerals (Vu et al.,
323 2013, 2010), ii) the incorporation within the structure of biogenic minerals due to olation and
324 oxolation processes occurring upon their formation (Dai et al., 2017; Hu et al., 2012; Scheck et
325 al., 2016), and iii) the occlusion of Pb ions in the porosity of the aggregates formed by newly
326 precipitated minerals. Similarly, Vu et al. (2010) observed that Pb partitioned mainly into the
327 solid phase during the transformation Pb-bearing Fh into hematite.

328

329 **3.3 Biogenic minerals formed by the bioreduction of the Fh_Pb series**

330

331 The secondary minerals formed after 21 days of bioreduction were investigated by XRD
332 (Figure 5), TEM (Figure 6) and TMS (Figure 7, Table 1). XRD results revealed the precipitation
333 of magnetite in the Pb-free assay while magnetite and goethite were detected in the assays with
334 Pb. Neither ferrihydrite signature nor Pb precipitates crystalized were identified in the systems
335 after the incubation period. The XRD characterizations are in line with TEM observations.

336 We performed TMS analyses to identify and quantify the biogenic minerals. Transmission
337 Mössbauer spectroscopy has been proved to be a very suitable tool to identify the reduction-
338 oxidation states, structural and magnetic properties of iron-bearing materials, especially iron
339 oxides (Murad and Cashion, 2004; Vandenberghe et al., 2000). Iron oxides that were formed in
340 the ambient environment, often have certain characteristics that may exert a major influence on
341 their magnetic properties (size effects), and consequently also on their Mössbauer spectra
342 (Rakotomalala Robinson et al., 2019). However, because nanostructured materials and in

343 particular iron oxides substituted in foreign element can adopt an organization into a
344 nanostructure, they may have parameters that deviate noticeably from those obtained in bulk
345 materials. Such deviations include higher quadrupole splitting and line widths, in the
346 paramagnetic state; and lower magnetic ordering temperatures and hyperfine fields, in the
347 magnetically ordered state. However, because temperature reduction also has an effect on these
348 deviations, the Mössbauer spectra of the biogenic minerals formed in the bio-reduced Fh,
349 Fh_Pb(0.02) and Fh_Pb(0.05) systems were recorded at 128 K (Figure 7a). The TMS measured
350 at 128 K of the bioreduced Fh (without Pb) exhibited a quadrupole doublet of siderite in low
351 abundance, characterized by center shift (CS) and D values of 1.32 and 2.32 mm.s⁻¹ respectively
352 (Benali et al., 2001) and magnetically ordered components attributable to magnetite, also
353 identified at 77 K (Figure S1). Fh_Pb(0.02) systems exhibited mainly a magnetically ordered
354 components with three distributions of hyperfine fields that consists of a broad sextet
355 corresponding respectively to magnetite and goethite, as are indicated by their associated
356 hyperfine parameters in Table 1. The spectrum of the bioreduced Fh_Pb(0.05) system showed
357 a complex magnetic structure which superimposed on a broad absorption envelope. For this last
358 bioreduced sample, spectral fits were obtained assuming the overlapping of spectral signatures
359 of superparamagnetic magnetite (quadrupolar doublet and singlet), magnetic magnetite (two
360 distributions of hyperfine fields, corresponding to Fe(III) ions in tetrahedral sites and to Fe(II)
361 and Fe(III) in octahedral sites) and goethite. Mössbauer temperature profiles (Figure 7b) for the
362 bioreduction Fh_Pb(0.05) system were used to consolidate the presence and attribution of the
363 previously suggested phases. The room temperature Mössbauer spectrum (Figure 7a) was fitted
364 with one quadrupole D1 doublets, one broad singlet and two sextets with broadened lines width
365 (Table 1). When the temperature decreases between 128 and 11 K, we observe a gradual
366 evolution from broad single line and complex magnetic structure with asymmetrically
367 broadened components, modelled by distribution of magnetic hyperfine fields; to magnetic

368 structure fitted with six components, using the Lorentzian-shape lines model (Rancourt, 1998).
369 The sextet characterized by magnetic field of 484 kOe and negative quadrupole shift ε (-0.14
370 mm s⁻¹) is attributed to goethite (Benali et al., 2001; Murad and Johnston, 1987) while the five
371 other sextets can be assigned to magnetite as established for this mineral at very low temperature
372 in the literature (Vandenberghe et al., 2000).

373 The precipitation of various secondary minerals implies that different mechanisms are involved
374 in the transformation of Fh. In the bioreduced Fh system 95% of magnetite formed along with
375 only 5% of siderite. Siderite precipitated neither during the bioreduction of Fh_Pb(0.02) nor
376 Fh_Pb(0.05), which contained 78% of magnetite plus 22% of goethite, and 81% of magnetite
377 plus 19% of goethite respectively. Magnetite precipitates either by the crystallization of
378 dissolved Fe(II) and Fe(III) ions after the dissolution of Fh or by a solid-state conversion of Fh
379 (Hansel et al., 2003; Jolivet et al., 2004; Tronc et al., 1992). The solid-state conversion results
380 from Fe(II) adsorption onto Fh surface and forming a short-range ordered material with mixed-
381 valence and exhibiting fast electron mobility. This electron mobility induces rearrangements of
382 the local structure and spinel ordering (Gorski and Scherer, 2009; Jolivet et al., 2004; Tamaura
383 et al., 1983; Tronc et al., 1992; Williams and Scherer, 2004). The presence of magnetite in the
384 bioreduced Fh_Pb(0.05) system was not detected by XRD analysis, while equivalent amounts
385 of magnetite formed in the bioreduced Pb-bearing systems as revealed by TMS (Table 1). This
386 discrepancy may be related to the size of the magnetite particles. The shape and size of the
387 magnetite obtained are detailed in Table S3. The particle size distribution for magnetite was
388 centered around 11.04 ± 2.31 nm (n = 150) and 6.03 ± 1.50 nm (n = 155) in the bioreduced Fh
389 and Fh_Pb(0.02) systems, respectively. These particles size are in line with previous biogenic
390 magnetite formed during the reduction of ferrihydrite by *Shewanella* species (Kukkadapu et al.,
391 2005; Zachara et al., 2002; Zegeye et al., 2021). However, in the bioreduced Fh_Pb(0.05)
392 system, magnetite particles exhibited a superparamagnetic signature suggesting that the size of

393 these nano particles are smaller than that observed in the Fh_Pb(0.02) assays, making their
394 detection by XRD difficult. Additionally, the presence of goethite hindered the accurate
395 determination of the size of magnetite particles by TEM. Indeed, the size of magnetite particles
396 can vary according to the pH, ionic strength, and presence of magnetite foreign ions in solution.
397 Indeed, the presence of other ions than Fe(II) slows down the electron mobility within Fe(II)-
398 adsorbed Fh, and in turn perturbs the formation of magnetite by solid-state conversion (Jolivet
399 et al., 2004; Tronc et al., 1992). Thus, the formation of specific species (corner- and/or edge-
400 sharing complexes) on the surface of magnetite influences its nucleation and growth, as
401 revealed by Wang et al. (2008), investigating the formation of magnetite in the presence of
402 As(III). The adsorption of foreign ions on magnetite nuclei may decrease interfacial tension,
403 which is the particle growth driving force (Vayssières et al., 1998) limiting the diffusion of
404 soluble species toward magnetite surface and thus inhibiting the growth of magnetite particles
405 (Wang et al., 2008). We assume Pb induced such growth inhibition of the magnetite particles
406 in the bioreduced systems containing Pb, hampering the detection of the magnetite formed in
407 the bioreduced Fh_Pb(0.05) systems with XRD analysis.

408 The precipitation of goethite may occur after the dissolution of ferrihydrite and the
409 crystallization of the dissolved Fe(III) ions with a planar tetramer ($[M_4(OH)_{12}(OH_2)_4]^0$) as
410 intermediary product, prior to its condensation by olation and oxolation reactions (Jolivet et al.,
411 2004). The bioreduction kinetic of the Pb-bearing Fhs were slower compared to the pristine
412 ferrihydrite bioreduction kinetic. This is due to the blocking of Fh surface reactive sites by Pb.
413 In addition, this induces a lower production of Fe(II) ions, leading to lower Fe(II)/Fe(III) ratio
414 (< 0.1 mM Fe(II)/g Fh) and enabling the formation of goethite in the Pb-bearing systems.

415 The precipitation of 5% of siderite in the bioreduced Fh system may be explained by a local
416 high concentration of Fe(II) and HCO_3^- in micro-aggregate where the mass transfer is slowed
417 down (Pallud et al., 2010).

418

419 The magnetic properties of the dried product of bioreduction of Fh series namely
420 biored_Fh, biored_Fh_Pb(0.02) and biored_Fh_Pb(0.05) were investigated by SQUID.
421 Moment per mass versus field are plotted for 300 K and 5 K in Figure 8. At 300 K, all the
422 samples show curves which can be fitted with Langevin functions characteristic of
423 superparamagnetic behaviour of nanoparticles; this is consistent with bio-formed 5 to 20 nm-
424 sized magnetite particles (Knobel et al., 2007; Mikhaylova et al., 2004) The magnetic
425 susceptibility decreases with increase in Pb concentration, which is consistent with the decrease
426 of particle size and therefore magneto-crystalline anisotropy energy. Moreover, the
427 magnetization at 4 T decreases monotonically with the amount of initial Pb dopant up to 5%.
428 When cooled down to 5 K, the hysteresis loop opens up for the bioreduced Fh, Fh_Pb(0.02),
429 and Fh_Pb(0.05) systems, with coercivity of the order of 30 mT. The low squareness of the
430 hysteresis loops, characterized by a remanent magnetization smaller than half of the saturation
431 magnetization, indicates a significant dipolar or ferromagnetic interaction between the
432 nanoparticles. This is not a surprise since the sample is dried and the nanoparticles aggregated.
433 More interestingly, the magnetization at 4 T (near saturation) at 5 K decreases from 82 A.m².kg⁻¹
434 down to 32 A.m².kg⁻¹ with 5%. The value for the bioreduced Fh system agrees with the
435 magnetization of pure magnetite nanoparticles at 5 K reported in the literature (Byrne et al.,
436 2013; Deepak et al., 2015). To explain the decrease of moment with Pb-content in Fh, we must
437 study how the magnetic moment is perturbed by the formation about 20% goethite particles, as
438 characterized by Mössbauer measurements. Goethite particles (Figure 6c) are anti-
439 ferromagnetic with a Neel temperature of 400 K (Forsyth et al., 1968) and carry no net
440 magnetization, unless their diameter is lower than few nanometer (Brok et al., 2014) which is
441 not the case here. Therefore, with Pb doped in Fh and the occurrence of 20% goethite, the
442 overall moment per mass must decrease compared to almost 100% of magnetite for the undoped

443 sample. In Figure 8d, we compare the measured moment per mass with the weighted average
444 moment considering $82 \text{ A}\cdot\text{m}^2\cdot\text{kg}^{-1}$ for magnetite particle, zero moment for goethite particles
445 and the goethite/magnetite ratio, namely 0/100, 22/78 and 19/81 for the bio-reduced Fh,
446 Fh_Pb(0.02) and Fh_Pb(0.05) systems respectively. The experimental decrease is still larger
447 than the calculated value. The additional loss of moment originates from the combination of
448 two independent phenomena. From the one hand, as quantified by TEM, the magnetite
449 nanoparticle diameter decreases with increasing the amount of Pb. A decrease of diameter of
450 11 nm to 6 nm as obtained with 2% Pb doping was already found to produce up to 10% decrease
451 of magnetization at saturation at 5K (Caruntu et al., 2007; Kolhatkar et al., 2013). On the other
452 hand, the Pb-doping of the magnetite itself can strongly affect the magnetization at 5 K. Deepak
453 et al. (2015) reported that substitution of 5 to 10% Fe by Mn or Ni in magnetite leads to a
454 decrease of 10 to 20% of the moment per mass (Deepak et al., 2015), while Padalia et al. (2016)
455 reported a moment decrease of 20% for a Ce doping of up to 1.5% (Padalia et al., 2016). With
456 our current data, we cannot quantify the relative impact of these two effects, but both must play
457 a role.

458 The low squareness of the hysteresis loops at 5 K, characterized by a remanent
459 magnetization smaller than half of the saturation magnetization, reflects the significant dipolar
460 or ferromagnetic interaction between the nanoparticles due to nanoparticles aggregation. It is
461 to note that the coercivity increases monotonically from 27 mT to 38 mT for the bio-reduced Fh
462 system to the bio-reduced Fh_Pb(0.05) one. On the one hand, the decrease of moment, due to
463 change in magnetite/goethite ratio lowers the dipolar and/or ferromagnetic interactions between
464 particles. Consequently, the coercivity is indeed expected to increase. On the other hand, the
465 decrease of magnetite moment produced by the Pb-doping of magnetite must also increase the
466 coercivity due to a smaller Zeeman energy (Padalia et al., 2016).

467 To further study the change in magnetic features of the bioreduction product of Pb-polluted Fh
468 as a function of the level of Pb-doping, we performed ZFC/FC curves measurements, as shown
469 in Figure 9. For the ZFC measurement, each sample was demagnetized at 300 K and then cooled
470 to 2 K. Afterwards ZFC magnetic moments were measured while the temperature was ramped
471 back up from 2 K to 300 K under 7.5 mT constant field. The FC procedure consists in cooling
472 down the sample from 300K under 7.5 mT and then measuring moment while heating it up
473 from 2 K back to 300 K. The curves show clear difference as compared with the ferrihydrite
474 ones previous to bioreduction (see Figure 2b). Although the produced particles are still strongly
475 interacting, the FC curves show no sign of spin-glass behavior at low temperature. The
476 bioreduced Fh and Fh_Pb(0.02) systems do not exhibit signature superparamagnetic peaks
477 neither, at least not below 150 K (Figure 9). The magnetization is continuously increasing as
478 the temperature increases. Such behaviour is typical of strongly interacting nanoparticles.
479 Similar results have been obtained in Byrne et al. (2013) on interacting magnetite nanoparticles
480 having about 10 nm diameter. Strong inter-particle interactions lead to an effective volume
481 much larger than the actual nanoparticle volume, as measured with TEM; this leads to a mixed
482 behaviour between long- and short-range interacting spins and superparamagnetism. We now
483 turn attention to the ZFC/FC curve for the bioreduced Fh_Pb(0.05) system (Figure 9). ZFC and
484 FC separate around 25 K near a peak in ZFC. Such peak (humping) in ZFC, while FC is still
485 increasing, is signature of superparamagnetic behaviour in the particles for temperature higher
486 than the peak, so called blocking temperature (Bean and Livingston, 1959). In the simplest
487 model, blocking temperature (T_b) occurs when the thermal activation energy ($k_B T$) and the
488 uniaxial anisotropy energy KV (where K is the anisotropy constant and V the nanoparticle
489 volume) of non-interacting particles equalize. In Figure 9, we find T_b is about 25 K. Such value
490 would correspond to a magnetite nanoparticle of 7 nm diameter if we consider an uniaxial
491 anisotropy of $1.4 \cdot 10^4 \text{ J m}^{-3}$ (Byrne et al., 2013; Tournus and Tamion, 2011). This size is

492 consistent with the TEM results in Figure 6. Indeed, strong interaction between particles
493 artificially increases the blocking temperature such that 7 nm is an upper limit for the real
494 nanoparticle diameter.

495

496 **3.4 Environmental significance**

497

498 Given the ecological and environmental importance of bacterial Fe(III) reduction, the
499 subsequent biotransformation of iron oxide has a broader implication than just the cycling of
500 iron. The varying properties of secondary minerals such as crystallinity, solubility or surface
501 area influence the mobility of pollutants such as Pb initially associated with iron oxides. While
502 this study addresses the bioreduction of Pb-bearing Fh at the laboratory scale, our results may
503 be of interest in improving our understanding of the fate of Pb in natural settings and the
504 evolution of Fh's magnetic properties during its transformation. When extending the results of
505 this study to the environment, it is critical to keep in mind the abundance of organic and
506 inorganic species and geochemical conditions likely to affect the bioreduction process, the
507 nature of the biogenic minerals, their properties, and the fate of Pb.

508 In natural setting, Fh particles are considered to precipitate first during hydrolysis of Fe(III) but
509 are thermodynamically unstable with respect to more crystalline iron oxides. Fh particles are
510 therefore estimated as the most important Fe(III) pool in sustaining the metabolism of Fe(III)-
511 reducing bacteria. However, in our study, the presence of Pb decreased the rate and the extent
512 of bioreduction. This implies that Pb-bearing Fh particles are likely less bioavailable for
513 microbial respiration in contaminated environments.

514 A wide range of pollutants such as Pb may sorb on iron oxides in nature. Given that iron oxides
515 are commonly the terminal electron acceptors to iron-reducing bacteria, the fate of adsorbed
516 pollutants is often coupled to bacterial activity. There is a potential re-partitioning and release

517 of associated pollutants during Fe(II) induced transformation. Our study's trend indicates that
518 Pb remains mainly associated with biogenic minerals, which suggests that iron-reducing
519 activity may not mobilize Pb in the aqueous phase in natural settings. Furthermore, we
520 measured a distinct magnetic signature between the biogenic minerals formed by Fh's
521 bioreduction bearing different amounts of Pb. The macroscopic magnetometry measurement
522 are in agreement with TMS data. Thus, these results highlight that magnetic measurement could
523 be a cost-effective methodology to screen polluted environments as suggested elsewhere
524 (Porsch et al., 2014, 2010).

525

526 4 Conclusion

527

528 Lead sequestration by iron (oxyhydr)oxides is recognized to be one of the most critical
529 geochemical processes controlling its environmental fate, transport, and bio-availability.
530 However, there is still a lack of knowledge on the impact of Pb on the bioreduction process of
531 iron oxides and the subsequent precipitation of biogenic minerals.

532 Our study highlights that Pb doping decreased the rate and extent of microbially
533 catalyzed Fh reduction. Indeed, the reduction rate declined by 15% for every Pb/(Pb + Fe) molar
534 ratio increase of 0.01 in Pb-bearing Fh, and the extent of reduction declined of 10% irrespective
535 of the Pb/(Pb + Fe) molar ratio compared to that of pure Fh. Lower Fe(II) concentrations are
536 thus required to induce Fh transformation *via* Fe(II) catalyzed dissolution-reprecipitation in the
537 presence of Pb, indicating that the presence of Pb decreased the Fe(II)/Fe(III) ratio required to
538 induce Fh transformation compared to that of Fh.

539 The catalyzed secondary mineralization led to 95% magnetite and 5% siderite precipitation in
540 the Fh system, while ~80% magnetite and ~20% goethite formed in the Fh_Pb systems. At the
541 end of the bioreduction, less than 1% of Pb was measured in the aqueous phase indicating that
542 a significant amount of Pb was associated with the biogenic minerals. The magnetite particles
543 formed from the bioreduction of Fh_Pb(0.05) displayed a superparamagnetic property. These
544 results reveal that Pb may influence the secondary mineralization pathway by decreasing the
545 flux of Fe(II) and hampering the growth of magnetite particles.

546 Furthermore, the presence of Pb drastically affects the magnetic signal and features of Fh
547 samples after bioreduction. Given the sensitivity of macroscopic magnetometry measurements,
548 this method, in support of classical techniques, may be of interest to characterize the presence
549 of metals such as Pb in redox active environments.

550

551 **Acknowledgements**

552

553 This work is part of the «SIGMABIO» project, funded by the Lorraine University of
554 Excellence. The acquisition of the Quantum Design Superconducting Quantum Interference
555 Device (SQUID) used for measurements was supported by the «SONOMA» project co-funded
556 by FEDER-FSE Lorraine et Massif des Vosges 2014-2020, a European Union Program. The
557 authors wish to acknowledge, Renaud Gley and Sylvie Migot for their support in XRD and
558 TEM analyses.

559

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841

842 **Figure captions**

843

844 Figure 1: X-ray diffraction pattern of pure Fh, Fh_Pb(0.02) and Fh_Pb(0.05).

845

846 Figure 2: Mass magnetization versus field (A) and temperature (B) obtained for pure (Fh) and
847 substituted Fh (Fh_Pb(0.02) and Fh_Pb(0.05)). Insert in (A), presents the 2 K hysteresis-loop
848 curve of Fh_Pb(0.02).

849

850 Figure 3: Mass magnetization versus field (A) obtained for Sb-bearing Fh (Zegeye et al., 2021)
851 presented here for comparison purpose, and (B) the evolution of spin glass transition
852 temperature (T_g) as a function of % of Pb or Sb with insert displaying mass magnetization
853 versus temperature for the Fh_Sb series.

854

855 Figure 4: Bioreduction of Fh series over time. (A) Bioreduction of Fh (circle symbols),
856 Fh_Pb(0.02) and Fh_Pb(0.05) square and triangle symbols, respectively. The initial rate of
857 reduction was computed from the derivative of a nonlinear curve fit represented by the dotted
858 lines. (B) Bacterial Fe(III) reduction rates versus % Pb/(Fe + Pb) molar ratio. Error bars
859 represent the standard deviation of triplicate microbial reduction assays.

860

861 Figure 5: X-ray diffraction pattern of bioreduced Fh, Fh_Pb(0.02) and Fh_Pb(0.05).

862

863 Figure 6: TEM images of bioreduced Fh (A), Fh_Pb(0.02) (B) and (C) Fh_Pb(0.05), after 21
864 days of incubation displaying the formation of magnetite and goethite. Inserts represent the size
865 distributions obtained for magnetite particles. The mean magnetite particles sizes were of 11.04
866 ± 2.31 nm ($n = 150$) and 6.03 ± 1.50 nm ($n = 155$) for the bioreduced Fh and bioreduced

867 Fh_Pb(0.02) respectively. The presence of goethite impeded to determine the size of magnetite
868 particles in the Fh_Pb(0.05) system (Table S3).

869

870 Figure 7: Mössbauer spectra of the secondary minerals formed after the 21 days of bioreduction.
871 (A) bioreduced Fh, Fh_Pb(0.02) and Fh_Pb(0.05) at 128 K , and (B) Fh_Pb(0.05) system at 11,
872 79, 128 and 298 K. Hyperfine parameters corresponding to these spectra are presented in Table
873 1.

874

875 Figure 8: Mass magnetization versus field of bioreduced (A) Fh, (B) Fh_Pb(0.02) and (C)
876 Fh_Pb(0.05). Inserts represents zooms of the mass magnetization versus field. (D) Evolution of
877 the experimental 5 K (black squares) and calculated (white circles) mass magnetization of
878 bioreduced Fh, Fh_Pb(0.02) and Fh_Pb(0.05) versus % of Pb. The dashed line shows the mass
879 magnetization of bulk magnetite.

880

881 Figure 9: Mass magnetization versus temperature of bioreduced Fh (blue), Fh_Pb(0.02) (red)
882 and Fh_Pb(0.05) (green).

883