

1                   **Effect of Sb on Precipitation of Biogenic Minerals during**  
2                   **the Reduction of Sb-bearing Ferrihydrites**  
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## ABSTRACT

Antimony (Sb) is a naturally occurring element; it is enriched in the environment by anthropogenic activities. Like other metalloid species, Sb partitions to mineral phases such as oxyhydroxides. In reducing environments, Fe(III) may serve as a terminal electron acceptor during dissimilatory iron reduction leading to its transformation. Relatively little is known concerning the effect of Sb(V) on the precipitation of biogenic minerals in relation to microbiologically mediated redox reactions. To further our understanding, Sb-bearing ferrihydrites with variable molar ratios [Sb/(Fe + Sb)] were incubated in the presence of *Shewanella oneidensis* MR-1. A combination of wet chemistry and solid analysis techniques (XRD, Mössbauer and Raman spectroscopies) was used to characterize the reactions.

The Sb loading affected the rate and the extent of bio-reduction compared with pure ferrihydrite. Only a minor fraction of the total Sb was released into the solution by the end of the incubation period, suggesting that the metalloid partitioned mainly in a newly formed phase. Furthermore, XPS analyses showed the presence of Sb(V) and Sb(III) species on the biogenic minerals. Magnetite was the main biogenic precipitate in the absence of Sb(V). Increasing of the molar ratios (Sb/(Fe + Sb)) resulted mainly in the precipitation of carbonated green rust and goethite. Abiotic green rust synthesis carried out in the presence of Sb(V) indicated the latter's stabilizing effect on the green rust structure, as for phosphate species. Thus, it is likely that Sb preserves biogenic green rust, hindering its transformation to more thermodynamically stable phases.

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## 1. INTRODUCTION

Natural deposits (e.g. ores, hot springs) and anthropogenic activities (e.g. mining, road traffic emissions) have led to a significant dispersion of inorganic elements, including antimony (Sb), in the lithosphere (Liu et al., 2010; Anderson, 2012; Okkenhaug et al., 2016; Li et al., 2018; He et al., 2019). There is a small but growing body of evidence that demonstrates the deleterious effect of Sb on biota (Gebel, 1997; Oorts et al., 2008; An and Kim, 2009). As a result, both the United States Environmental Protection Agency (U.S. EPA) and the European Union (E.U.) have listed Sb as a “priority pollutant” (Official Journal L 129, 1976; United States Environmental Protection Agency), which implies the need to assess the behavior Sb(V) in natural settings. In the environment, antimonite [Sb(OH)<sub>3</sub>] and antimonate [Sb(OH)<sub>6</sub><sup>-</sup>] are the dominant chemical species (Filella et al., 2002; Wilson et al., 2010). Antimony has been observed interacting with soil components, in particular, iron oxides (e.g. goethite, lepidocrocite), and it is positively correlated with Fe content (Craw et al., 2004; Mitsunobu et al., 2010a; Takahashi et al., 2010).

Iron oxides display a large surface area and high chemical reactivity given their crystallinity and porosity (Cornell and Schwertmann, 2003). They therefore contribute significantly to the speciation and the fate of elements (e.g. As, Sb) that play a central role in various biogeochemical cycles in soils and sediments (Dixit and Hering, 2003; Borch and Fendorf, 2007; Mitsunobu et al., 2008a; Frierdich and Catalano, 2012a; Ilgen and Trainor, 2012; Okkenhaug et al., 2013; Mallet et al., 2013; Perez et al., 2019). Due to their large specific surface area, iron oxides are considered to be an effective sink for Sb in shooting range soils (Okkenhaug et al., 2016; Okkenhaug et al., 2018). Thus, the properties of these iron oxides have led to the consideration of Fe-based amendments as a potential strategy for the removal and the immobilization of Sb in contaminated areas. In freshwater, Sb is found to

76 be much more mobile in low Fe systems, suggesting that the adsorption or the co-  
77 precipitation with iron oxides is a critical factor controlling Sb dynamics (Mitsunobu et al.,  
78 2010a; Hockmann et al., 2014; Burton et al., 2020). Furthermore, X-ray Absorption Fine  
79 Structure (XAFS) spectroscopic analyses have demonstrated the incorporation of Sb(V) into  
80 the crystallographic structure of iron oxides synthesized in the laboratory, such as goethite  
81 and ferrihydrite (Mitsunobu et al., 2013; Karimian et al., 2019b; Burton et al., 2020). This  
82 structural incorporation has also been reported to occur in natural soil, suggesting that the  
83 substitution of Fe in iron minerals is widespread in the environment (Mitsunobu et al.,  
84 2010b).

85 In subsurface environments, iron oxides are also used as electron acceptors for  
86 dissimilatory iron-reducing bacteria (DIRB) (Lovley, 1993; Coates et al., 1996; Maier and  
87 Myers, 2001; Nealson et al., 2002; Sung et al., 2012). The bio-reduction of Sb-bearing iron  
88 oxide can lead to the potential mobilization into the aqueous phase and (or) the sorption onto  
89 biogenic precipitates of the previously retained Sb(V). DIRB such as *Geobacter sp.* and  
90 *Shewanella sp.* couple the oxidation of an organic (e.g. formate, pyruvate, lactate) or  
91 inorganic (e.g. H<sub>2</sub>) electron source with the reduction of Fe(III) during anaerobic respiration  
92 (Lovley et al., 1993; Lovley, 2000). Subsequently, the Fe(II) generated by bio-reduction is  
93 released into solutions and/or sorbed on mineral surfaces, which leads to the transformation of  
94 Fe-bearing minerals, such as magnetite (Fe<sub>3</sub>O<sub>4</sub>), siderite (FeCO<sub>3</sub>), green rust (GR), goethite  
95 ( $\alpha$ -FeOOH) and lepidocrocite ( $\gamma$ -FeOOH), depending on the biogeochemical conditions  
96 (Kukkadapu et al., 2005; Zegeye et al., 2007; O'Loughlin et al., 2007; Ona-Nguema et al.,  
97 2009; Eusterhues et al., 2014; Muehe et al., 2016).

98 Of these biogenic minerals, GRs are Fe(II-III)-layered double-hydroxysalts constituted  
99 of positively charged layers  $\{\text{FeII}_{(1-x)} \text{FeIII}_x (\text{OH})_2\}^{x+}$ , which alternate with negatively  
100 charged interlayers that include m water molecules per A<sup>n-</sup> anion  $\{(x/n)\text{A}^{n-} \cdot (mx/n)\text{H}_2\text{O}\}^{x-}$

101 (Hansen, 1989; Génin et al., 1996). Two groups of GRs are identified based on X-ray  
102 diffraction (XRD) patterns: green rust 1 (GR1) and green rust 2 (GR2) (Bernal, 1959). Their  
103 structure and composition depend upon the specific anions they incorporate. GR1 is arranged  
104 in rhombohedral geometry and inserts planar or spherical anions (e.g.  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ), whereas  
105 GR2 is arranged in a hexagonal geometry and inserts three-dimensional anions (e.g.  $\text{SO}_4^{2-}$ ,  
106  $\text{SeO}_4^{2-}$ ) (Hansen et al., 1994; Abdelmoula et al., 1996; Refait et al., 1998; Refait et al., 2000;  
107 Simon et al., 2003). GRs have demonstrated their potential ability to interact with Sb(V) with  
108 an inner sphere complex, thus reducing the metalloid's mobility (Mitsunobu et al., 2009).

109         Relatively little is known concerning the effect of Sb(V) on the precipitation of  
110 biogenic minerals such as GRs in relation to microbiologically mediated redox reactions. A  
111 recent study has shown that Sb(V) favors ferrihydrite formation over goethite during the bio-  
112 reduction of Sb(V)-ferrihydrite (Burton et al., 2020). The incorporation of Sb(V) in the iron  
113 oxides' structure was also highlighted. To broaden our understanding of Fe and Sb  
114 biogeochemical cycles, it is pertinent to investigate how various Sb concentrations impact  
115 iron oxide bio-reduction processes and the precipitation of biogenic minerals. Furthermore,  
116 the interaction of Sb(V) with GR1( $\text{CO}_2^{3-}$ ) resulting from the bio-reduction of an Sb(V)-  
117 bearing iron oxide has not been reported previously.

118         Our study aims to investigate the impact of Sb(V) loading on the nature of biogenic  
119 minerals, such as GRs precipitated during the bio-reduction of Sb(V) bearing ferrihydrites. To  
120 achieve this objective, we incubated Sb bearing ferrihydrites with variable molar ratios  
121 (Sb/(Fe + Sb)) with *Shewanella oneidensis* MR-1. We then assessed the following: (i) the  
122 influence of Sb content on the bio-reduction of ferrihydrite (i.e. rate and extent of reduction)  
123 and (ii) the nature of biogenic minerals. Furthermore, we synthesized abiotic GR1( $\text{CO}_3^{2-}$ ) in  
124 the presence of Sb(V) to examine the Sb(V) effect on this mineral formation and stabilization.

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## 127 **2. METHODS**

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129 All reagents and acids were of analytical grade and solutions were prepared using 18.2 M $\Omega$   
130 cm<sup>-1</sup> deionized water. Anaerobic experiments (bio-reduction, abiotic GR synthesis and aging),  
131 sample collection (*i.e.* by centrifugation) and sample drying were conducted under strictly  
132 anaerobic conditions in a re-circulating anoxic chamber (Coy Laboratory Products Inc.) in  
133 which trace amounts of oxygen were scavenged by palladium catalysts. A 98% N<sub>2</sub> + 2% H<sub>2</sub>  
134 atmosphere was maintained by the automatized injection of the gas mixture. When needed,  
135 the samples were removed from the anaerobic chamber in an air-tight sample holder for solid  
136 analyses.

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### 138 **2.1 Synthesis of Sb(V)-bearing ferrihydrite**

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140 Ferrihydrite (Fh hereafter) was synthesized by precipitating 0.4 M FeCl<sub>3</sub> with 4 M NaOH  
141 according to the method adapted from Cornell and Schwertmann (2003). When the pH  
142 approached the desired endpoint of the hydrolysis, a solution of 0.5 M NaOH was used to  
143 adjust the pH to = 7.2 ± 0.1. Antimony co-precipitated Fhs were synthesized in similar  
144 fashion, except for the addition of K[Sb(OH)<sub>6</sub>] stock solution to the ferric salt before  
145 hydrolysis at Sb/(Fe + Sb) molar ratios of 0.04, 0.06 and 0.1 (Fh\_Sb0.04, Fh\_Sb0.06 and  
146 Fh\_Sb0.1 hereafter), following a modification of the method used by Mitsunobu et al.  
147 (2010b). All suspensions were allowed to equilibrate for 4 hours after the synthesis and the  
148 pH was readjusted to pH 7.2 with 0.05 M NaOH if necessary. Thereafter, the co-precipitates  
149 were washed six times with Milli-Q water by centrifugation and freeze-dried.

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## 154 2.2 Bio-reduction of Sb(V)-bearing ferrihydrites

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156 Frozen *Shewanella oneidensis* MR-1 cells from a stock (frozen in 20% glycerol at -80  
157 °C) were revived under aerobic conditions on tryptic soy agar. They were sub-cultured once,  
158 and the colonies used to prepare a suspension to inoculate 700 mL of tryptic soy broth. Cells  
159 were grown, continuously agitated at 300 rpm and 30°C, harvested after 14 hours of culture  
160 by centrifugation (10 000 x g at 20°C for 10 minutes), washed twice with sterile 0.9% NaCl,  
161 and concentrated in the same medium. The cells were purged for 30 minutes by bubbling with  
162 filter-sterilized N<sub>2</sub> filtration through a membrane of pore size 0.2 µm, and used to inoculate  
163 batches with ferrihydrite.

164 The bio-reduction were performed in a culture medium composed of 22 mM NH<sub>4</sub>Cl, 1.5 M  
165 NaCl, 1.2 mM KCl, 1.1 mM MgSO<sub>4</sub>•7H<sub>2</sub>O, 0.71 mM nitrilotriacetic acid (NTA), 0.67 M  
166 CaCl<sub>2</sub>, 0.27 mM MnSO<sub>4</sub>•H<sub>2</sub>O, 86 µM ZnCl<sub>2</sub>, 38 µM CoSO<sub>4</sub>•7H<sub>2</sub>O, 32 µM FeSO<sub>4</sub>•7 H<sub>2</sub>O,  
167 9.3µM Na<sub>2</sub>MoO<sub>4</sub> •2 H<sub>2</sub>O, 9.1 µM NiCl<sub>2</sub> •6H<sub>2</sub>O, 6.8 µM Na<sub>2</sub>WO<sub>4</sub>•2 H<sub>2</sub>O, 3.6 µM CuSO<sub>4</sub>•5  
168 H<sub>2</sub>O, 1.9 µM AlK(SO<sub>4</sub>)<sub>2</sub>•12 H<sub>2</sub>O, 1.5 µM H<sub>3</sub>BO<sub>3</sub>. The medium was heat-sterilized and purged  
169 with filter-sterilized N<sub>2</sub>, and dispensed into sterile 100 mL serum bottles in the presence of 0.5  
170 g of Sb-bearing Fh, and crimp sealed using butyl rubber stoppers. Sodium methanoate, as the  
171 sole electron source, and anthraquinone-2,6-disulfonate (AQDS), as an electron shuttle, were  
172 sterilized by filtration (filter pore size 0.2 µm), purged with filter-sterilized N<sub>2</sub>, and introduced  
173 in the culture medium under aseptic conditions in order to achieve 50 mM (i.e. excess of ≈  
174 55% with respect to Fe(III)) and 100 µM respectively in each 80 mL assay. *S. oneidensis*  
175 cell suspensions were added to obtain final concentrations of 1.0 × 10<sup>8</sup> cell mL<sup>-1</sup>. The initial  
176 pH after mixing all the components was 7.2 ± 0.1. The assays were incubated in the dark for

177 25 days, in triplicates. The control experiments were cell-free but otherwise identical to the  
178 biotic assays.

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### 180 2.3 **Precipitation of abiotic GR1(CO<sub>3</sub><sup>2-</sup>)**

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182 Carbonate green rusts were synthesized according to the method adapted from Bocher  
183 et al. (2004). Ferrous sulfate heptahydrate FeSO<sub>4</sub> and ferric sulfate Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> were dissolved  
184 in 30 mL of ultra-pure water with a Fe(II) / Fe(III) ratio of 2:1 and titrated with 30 mL of an  
185 appropriate concentration of a basic solution (NaOH, [OH<sup>-</sup>] / [Fe<sub>t</sub>] = 2, and Na<sub>2</sub>CO<sub>3</sub>, [CO<sub>3</sub><sup>2-</sup>] /  
186 [Fe<sub>t</sub>] = 7/6). Other sets of GR synthesis were conducted by mixing either (i) phosphate  
187 solution (PO<sub>4</sub><sup>3-</sup> / Fe<sub>t</sub> = 0.016) or (ii) Sb<sup>V</sup> solution (Sb(V) / Fe<sub>t</sub> = 0.09) with the ferric/ferrous  
188 solution before the co-precipitation. Phosphate was used to hinder the transformation of GR  
189 and to stabilize the mineral. A further synthesis was run with the Sb(V) solution being added  
190 directly after GR precipitation (~ 10 min) in order to obtain a Sb(V) / Fe<sub>t</sub> ratio of 0.09. The  
191 different precipitates were characterized after one week of aging in an anaerobic chamber.

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### 193 2.4 **Analytical procedure**

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#### 195 2.4.1 *Chemical analyses*

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197 The Sb/(Fe + Sb) molar fractions of the initial Fh minerals were measured by  
198 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) after being dissolved  
199 in acid, (6 M HCl) (Amstaetter et al., 2012).

200 At each time point, samples (0.5 mL) were removed from the bio-reduction assays and  
201 extracted with 4 M HCl in an anaerobic chamber in order to quantify total Fe (Fe<sub>tot</sub>) and total



202 Fe(II) ( $\text{Fe}^{\text{II}}_{\text{tot}}$ ) using the ferrozine method (Viollier et al., 2000). The apparent initial reduction  
203 rates were computed from the first derivative of a nonlinear curve fit (1)

$$204 \quad \%(\text{Fe}^{\text{II}}_{\text{tot}}/\text{Fe}_{\text{tot}})_t = \%(\text{Fe}^{\text{II}}_{\text{tot}}/\text{Fe}_{\text{tot}})_{\text{max}} [1 - \exp(-k_{\text{obs}}t)] \quad (1)$$

205 where  $\%(\text{Fe}^{\text{II}}_{\text{tot}}/\text{Fe}_{\text{tot}})_t$  is the  $(\text{Fe}^{\text{II}}_{\text{tot}}/\text{Fe}_{\text{tot}})$  (%) produced at time  $t$ ,  $\%(\text{Fe}^{\text{II}}_{\text{tot}}/\text{Fe}_{\text{tot}})_{\text{max}}$  is the  
206 maximum  $\%(\text{Fe}^{\text{II}}_{\text{tot}}/\text{Fe}_{\text{tot}})$  observed at the end of the reduction period (i.e. 25 days), and  $k_{\text{obs}}$  is  
207 the pseudo first-order constant.

208 At the end of the incubation period, 1 mL was withdrawn from the assays, filtered  
209 through 0.22  $\mu\text{m}$  pore filters, and placed in 2 M HCl in an anaerobic chamber to measure the  
210 concentration of Sb in solution ( $\text{Sb}_{\text{sol}}$ ) by Hydride Generation - Atomic Fluorescence  
211 Spectroscopy (HG-AFS). Stibnite was generated in a continuous flow system (PS Analytical's  
212 Millennium Excalibur<sup>TM</sup>) using 0.7%, m/v  $\text{NaBH}_4$  solution (stabilized with 0.1 M NaOH) and  
213 25% v/v HCl as carrier solution. The sample solution (flow rate: 9 mL  $\text{min}^{-1}$ ) and carrier  
214 solution ( $\text{NaBH}_4$  flow rate: 4.5 mL  $\text{min}^{-1}$ ; HCl flow rate: 9 mL  $\text{min}^{-1}$ ) were pumped  
215 simultaneously into the sample valve for mixing. The standard and the sample solution were  
216 prepared in a 30% v/v HCl medium and 1% m/v KI / 0.2% m/v ascorbic acid mix to achieve  
217 the pre-reduction of the Sb(V). The mixture was transferred into the gas-liquid separator, and  
218 the generated gaseous hydrides were transported to the atomizer flame of the AFS. A boosted  
219 discharge hollow cathode lamp (BDHCL) for Sb was used throughout the experiments.

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226 2.4.2 *Solid analyses*

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#### 228 2.4.2.1 X-Ray Diffraction (XRD)

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230 The X-Ray Diffraction (XRD) data of the Fh and Fh\_Sb series and the biogenic  
231 minerals were collected using a Bruker D8 diffractometer equipped with a monochromator  
232 and position-sensitive detector. The X-ray source was a Co anode ( $\lambda = 0.17902$  nm). The  
233 diffractogram was recorded in the  $3 - 84^\circ$   $2\theta$  range, with a  $0.0359^\circ$  step size and collection  
234 time of 3 seconds per point. Crystalline size was calculated using the Scherrer equation (2)

$$235 \quad D = K\lambda/\beta\cos\theta \quad (2)$$

236 where D is the mean size of the crystalline domains, K is a dimensionless shape factor (0.94),  
237  $\lambda$  is the wavelength of the X-ray radiation,  $\beta$  is the line broadening at the full width at half  
238 maximum (FWHM) and  $\theta$  is the Bragg angle of the particular peak of interest.

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#### 240 2.4.2.2 Transmission Mössbauer Spectroscopy (TMS)

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242 Transmission Mössbauer Spectroscopy (TMS) was performed using a  $^{57}\text{Co}$  source to  
243 identify and quantify iron phases and magnetic ordering formed after the bio-reduction of Fh,  
244 Fh\_Sb(0.04), Fh\_Sb(0.06) and Fh\_Sb(0.1).  $^{57}\text{Fe}$  Mössbauer spectra were collected using a  
245 conventional spectrometer in transmission geometry coupled with an Advances Research  
246 Systems (USA) cold head cryostat, equipped with in-house made vibration isolation stand.  
247 The 50 mCi  $^{57}\text{Co}$  in Rh matrix radioactive source was mounted in a constant acceleration  
248 velocity transducer. Solid samples were prepared under an  $\text{N}_2$  atmosphere in an anoxic glove  
249 box (Jacomex) using appropriate amounts (10 mg of powder per  $\text{cm}^2$ ). Measurements were  
250 taken at the wide range of velocity  $\pm 11$   $\text{mm s}^{-1}$  or  $\pm 4$   $\text{mm s}^{-1}$  for experiments at room  
251 temperature (RT). This approach is useful for the unambiguous identification of iron oxides at

252 room temperature and low-temperature studies by comparing the hyperfine split obtained at  
253 low temperature with the spectra measured at room temperature. The hyperfine interaction  
254 parameters were determined by fitting the experimental spectra by a least-squares method  
255 using Recoil software (Lagarec and Rancourt, 1998) with Voigt-based fitting analysis or the  
256 Lorentzian model, except in the case of the appearance of a magnetic order Fe(II) phases  
257 (siderite), whereas the full static Hamiltonian site model was required at very low temperature  
258 (15 K) to solve the mixed hyperfine interactions. Center shifts were reported with respect to  
259 that of 25  $\mu\text{m}$ -thick  $\alpha$ -Fe foil at room temperature.

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#### 261 *2.4.2.3 Raman Spectroscopy*

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263 Raman spectra were collected on a Renishaw inVia™ Qontor® microspectrometer  
264 equipped with a confocal microscope and an Olympus X50 objective (numerical aperture =  
265 0.55). The samples were prepared in an anaerobic chamber and enclosed in an airtight cell  
266 with sapphire windows. 785 nm exciting radiation was used with a laser power below 0.1 mW  
267 for all samples, in order to prevent their degradation. The spot area was a few  $\mu\text{m}^2$ . Several  
268 locations were probed on each sample. The spectral resolution was about  $4\text{ cm}^{-1}$  and the  
269 precision on the wavenumber was below than  $1\text{ cm}^{-1}$ .

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#### 271 *2.4.2.4 X-ray Photoelectron Spectroscopy (XPS)*

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273 The surface physicochemical properties of Fh\_Sb(0.1) were characterized before and  
274 after bio-reduction using X-ray Photoelectron Spectroscopy (XPS). Spectra were recorded on  
275 a Kratos Axis Ultra X-ray photoelectron spectrometer equipped with a monochromatic Al K $\alpha$   
276 source (1486.6 eV) operated at 120 W. Powder samples were deposited onto a copper

277 adhesive tape in an anaerobic chamber and kept in sealed aluminum pouches that were re-  
278 opened in an anaerobic glove box connected to the UHV preparation chamber at  $10^{-7}$  mb. The  
279 analysis area was equal to  $300 \times 700 \mu\text{m}^2$ . The spectra were collected at a take-off angle of  
280  $90^\circ$  and the pressure in the analysis chamber was approximately  $10^{-9}$  mbar. A pass energy of  
281 20 eV was used for the high-resolution spectra. Charge compensation was applied by flooding  
282 low-energy electrons. Binding energies were calibrated by assigning the adventitious carbon  
283 C 1s peak to 284.6 eV. Curve fitting was performed using a Gaussian/Lorentzian (70/30) peak  
284 shape after Shirley's background subtraction and using X-vision 2.2.11 software.

285

#### 286 2.4.2.5 Magnetism

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288 A Quantum Design Superconducting Quantum Interference Device (SQUID) was used to  
289 perform Zero field cooled (ZFC) and field cooled (FC) measurements. The ZFC procedure  
290 consisted of demagnetizing the samples at 300 K using an oscillatory decaying field from 1 T  
291 to zero field (resp. magnetized under 7.5 mT), and then cooling them to 2 K at a rate of 1  
292 K/min. ZFC magnetic moment was then measured while the temperature was ramped back up  
293 from 2 K to 300 K at a rate of 1 K/min under 7.5 mT constant field. The FC procedure  
294 consisted of cooling down the sample from 300K under 7.5 mT and then measuring moment  
295 while heating it from 2 K back up to 300 K.

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### 299 **3. RESULTS**

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#### 301 **3.1 Sb-bearing ferrihydrite characterization**

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303 The Fe and Sb contents of the co-precipitates were measured by ICP-OES; the  
304 concentrations obtained were approximately equal to the initial molar ratio of Sb/(Sb + Fe)  
305 (*i.e.* 0.04, 0.06 and 0.1) used to precipitate the solids. X-ray diffraction was used to  
306 characterize the co-precipitated phases (Fig. 1), and the signal displayed two broad humps (at  
307  $2\theta \sim 41^\circ$  and  $75^\circ$ ) with d-spacing of  $\sim 0.258$  nm and  $\sim 0.149$  nm indicative of Two-line  
308 ferrihydrite. No other Fe(III) oxides were detected. We observed a broadening of the XRD  
309 peaks as the Sb content of the Fh increased; this was due to either a decrease in crystallinity as  
310 a result the incorporation of Sb in the structure of the Fe oxyhydroxide as revealed by  
311 Mitsunobu et al. (2010b) or a decrease in crystallite size as hypothesized in the case of arsenic  
312 substitution (Waychunas et al., 1996).

313

#### 314 **3.2 Microbial bio-reduction of Sb-bearing ferrihydrite**

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316 We quantitatively monitored the bio-reduction of Sb-bearing ferrihydrite series over time.  
317 Bio-reduction started without a lag phase and reached a plateau after 25 days (Fig. 2). No  
318 measurable Fe(III) reduction took place in the non-inoculated treatments (data not shown).  
319 The apparent rate of reduction was  $16.40 \pm 0.07\%$  ( $\text{Fe}_{\text{tot}}^{\text{II}}/\text{Fe}_{\text{tot}}$ )  $\text{day}^{-1}$  for Fh, while the rate  
320 was less than 50% slower for Fh\_Sb (Table 1). Additionally, the extent of reduction reached  $\sim$   
321 35% for pure Fh, and  $\sim 30\%$  for Fh\_Sb(0.04) and Fh\_Sb(0.06), whereas it plateaued at  $\sim 50\%$   
322 for Fh\_Sb(0.1) (Table 1).

323           After 25 days of incubation, only a minor fraction - less than 0.5% - of the Sb ions  
324 were present in the aqueous phase irrespective of the molar ratio Sb/(Sb + Fe) of the initial  
325 Fhs.

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### 327 3.3    **Biogenic minerals**

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329 The mineralogical transformation of Fh and Fh\_Sb series was monitored after the incubation  
330 period using a suite of spectroscopic techniques.

331

#### 332 3.3.1 *Biogenic minerals formed by Sb free Fh bio-reduction*

333           The biogenic minerals displayed X-ray diffraction peaks with d-spacing characteristic  
334 of magnetite and siderite (Fig. 3). Based on the FWHM of the strongest peaks at  $d = 0.251$   
335 (hkl: 311) and  $0.294$  nm (hkl: 220), the estimated crystalline size of the magnetite was  $9.4$  nm  
336 which is in the same range as the sizes observed in bio-reduction experiments described in the  
337 literature (Kukkadapu et al., 2005; Byrne et al., 2011).

338           We performed Mössbauer temperature profiles at room temperature (RT),  $143$  K,  $78$  K  
339 and  $15$  K (Fig. 4) to identify and quantify the biogenic minerals precipitated during Fh bio-  
340 reduction. At RT and  $143$  K, Mössbauer spectra are complex, with the superposition of a  
341 paramagnetic doublet as well as the significant broadening of a magnetic component. At RT  
342 the quadrupole doublet is characterized by large center shifts (CS) and a quadrupole splitting  
343 ( $\Delta$ ) values of  $1.14$  mm s<sup>-1</sup> and  $1.92$  mm s<sup>-1</sup> respectively, which are similar to those published  
344 for siderite at room temperature, i.e. CS =  $1.14$  mm s<sup>-1</sup> and  $\Delta = 1.98$  mm s<sup>-1</sup> (Génin et al.,  
345 2002). The magnetic component was fitted using two distributions of the hyperfine magnetic  
346 field with widened lines, possibly due to magnetite observed using XRD. We fitted this  
347 component with two broad overlapping sextets with two weak mean magnetic fields at  $40.8$  T

348 and 13.2 T respectively. However, the two sextets are usually clearly defined and fitted with a  
349 Lorentzian model when dealing with large-particle magnetite. This discrepancy in the line  
350 shape of the Mössbauer spectrum at RT is due to the small particle size (less than 20 nm),  
351 which may induce a greater distribution in the magnetic behavior (Silva et al., 2013; Alves et  
352 al., 2016).

353 During cooling, the spectral features of the magnetic component change considerably. At 77  
354 K, the ferrous doublet of the siderite phase observed at RT remains and the CS and the  $\Delta$   
355 increase as expected for the hyperfine parameters of the Fe(II), and adopt a high spin  
356 configuration at the octahedral site. The magnetic contribution of the spectrum exhibits five  
357 sextets that were deconvoluted using a Lorentzian model; they correspond to the five iron  
358 sites observed for magnetite below the Verwey temperature (Srivastava et al., 1981;  
359 Vandenberghe et al., 2000). At 15 K, the spectrum becomes more complex in its central part.  
360 This indicates that all the carbonate-containing Fe(II) sites are now magnetically ordered and  
361 represented by an octet versus paramagnetic doublet at 77 K (Maitte et al., 2015). Modelling  
362 of this spectrum component, using the software package Recoil (Lagarec and Rancourt,  
363 1998), is intricate, owing to the mixing of states, particularly given the fact that, for Fe(II)  
364 compounds below magnetic transition, the electric quadrupole and magnetic hyperfine  
365 interactions are generally of the same order of magnitude. Thus, it is not likely that this  
366 component can be analyzed in terms of six-line patterns (sextets) as is the case for the  
367 magnetism of ferric compounds (Duboscq et al., 2020). The octet comprises eight lines that  
368 have to be computed fully by solving the eigenvalues of the full Hamiltonian. The octet is  
369 characterized by hyperfine parameters (Table 2), a CS of  $1.76 \text{ mm s}^{-1}$ , electric quadrupole  
370 interaction ( $e^2qQ/2$ ) of  $2.72 \text{ mm s}^{-1}$ , and a hyperfine field  $H$  of 18.7 T typical of Fe(II) in  
371 siderite (Maitte et al., 2015). The relative abundance of siderite was  $\sim 9 \%$ .

372 The second interesting feature in the spectrum at 15 K is the appearance of resonance  
373 lines on the high energies which correspond, after spectral deconvolution, to the five sextets  
374 S1, S2, S3, S4 and S5. Their hyperfine parameters, listed in Table 2, are consistent with those  
375 generally reported for magnetite of five-sextets as observed in the literature (Srivastava et al.,  
376 1981) at low temperature. Moreover, the particle size constraints generate the phenomenon of  
377 superparamagnetism and influence the magnetic properties, which could explain the gradual  
378 evolution with regards to temperature from a broad sextet component to sharp sextets as the  
379 temperature decreases. This behavior is typical of superparamagnetic particles (Goya et al.,  
380 2003), and may be related to the widening of the diffraction lines assigned to magnetite by  
381 XRD (Fig. 3). The relative abundance of magnetite was ~ 91 %.

382 The Raman spectra realized at different locations on the sample (analyzed spot size of  
383 a few  $\mu\text{m}$ ) exhibited a strong band at  $680\text{ cm}^{-1}$  and a weaker one in the region of  $310\text{ cm}^{-1}$ ,  
384 indicating the precipitation of magnetite (Fig. A1) (Shebanova and Lazor, 2003; Jubb and  
385 Allen, 2010). Additional bands at  $280$ ,  $725$  and  $1084\text{ cm}^{-1}$  were attributed to siderite (Fig. A1)  
386 (Hanesch, 2009; Maitte et al., 2015). The fact that different locations display a different  
387 mineral indicates that the system is heterogeneous, and that various mineral precipitation  
388 pathways are involved.

389

### 390 3.3.2 *Biogenic minerals formed by Fh\_Sb bio-reduction*

391 Neither magnetite nor siderite was detected as a result of the transformation of Sb-  
392 bearing minerals at the level discernible by XRD (Fig. 3). Instead, the d-spacing displayed the  
393 sharp diffraction peaks of green rust 1 (GR1) and goethite as biogenic minerals irrespective of  
394 the Sb/(Fe + Sb) molar ratio. Peaks of an unidentified mineral (indicated by \*) were also  
395 present on the diffractograms independently of the Sb/(Sb + Fe) molar ratio of the initial Fhs.  
396 No evidence for the formation of other Sb-hosting minerals such as hydroxyferroromeite or



397 Fe- and Sb-bearing minerals such as tripuyhite was detected. Based on the experimental  
398 setup, the reduction medium composition and the electron source used in our study (i.e.  
399 methanoate), the precipitated GR1 is likely a carbonated GR ( $\text{GR1}(\text{CO}_3^{2-})$ ) as described  
400 elsewhere (Ona-Nguema et al., 2004; Zegeye et al., 2007; O'Loughlin et al., 2007).  
401 We used the FWHM of the strongest peaks at  $d = 0.755 \text{ nm}$  (hkl : 003) and  $d = 0.378 \text{ nm}$  (hkl  
402 : 006) to estimate the average GR1 crystal size. Our goal was not to determine the exact  
403 crystal size but to monitor any variation due to the loading of Sb(V). The estimated crystal  
404 sizes of the  $\text{GR1}(\text{CO}_3^{2-})$  bio-precipitated from the Fh\_Sb(0.04), Fh\_Sb(0.06) and Fh\_Sb(0.1)  
405 bio-reductions were 77 nm, 40 nm and 66 nm for respectively.

406 At room temperature, the Mössbauer spectra Fh\_Sb(0.04), Fh\_Sb(0.06), and  
407 Fh\_Sb(0.1) were computer fitted with 5, 3 and 5 quadrupole doublets respectively (Fig. A2).  
408 Their hyperfine parameters are typical of ferrous and ferric cations (Table A1), but their  
409 mineralogical identification remains difficult. Nevertheless, the presence of  $\text{GR1}(\text{CO}_3^{2-})$  and  
410 superparamagnetic goethite phases cannot be ruled out on the basis of the XRD  
411 characterization.

412 Iron oxides are often sensitive to effects such as small particle size in the nanometer range,  
413 which complicates their identification and characterization. These constraints require  
414 Mössbauer spectra to be recorded at a lower temperature. At 15 K, all the Fh\_Sb(0.04),  
415 Fh\_Sb(0.06) and Fh\_Sb(0.1) samples displayed magnetically ordered components on which  
416 paramagnetic doublets were superimposed (Fig. 5). The magnetic components exhibit broad  
417 and asymmetric lines with a distribution of the hyperfine magnetic fields centered on three  
418 components at 45 T, 47.5 T and 49.4 T. The quadrupole shift obtained ( $-0.22 \text{ mm s}^{-1}$ ) is  
419 characteristic of goethite, also identified by XRD but with widened lines. The broadening of  
420 magnetic lines is the result of relaxation effects of the smallest particles and/or a poor

421 crystallinity. This could explain the spectral behavior observed at RT, with a significant  
422 doublet suspected as being superparamagnetic goethite (Kone et al., 2009).

423 The paramagnetic components were fitted with two quadrupole doublets (D1 and D2).  
424 Doublet D1 with values of  $CS = 1.21 \text{ mm s}^{-1}$  and  $\Delta = 2.9 \text{ mm s}^{-1}$  differs from doublet D2  
425 with smaller values for  $CS (0.38 \text{ mm s}^{-1})$  and  $\Delta (0.74 \text{ mm s}^{-1})$ , which are ascribed to  
426  $(GR1(CO_3^{2-}))$  (Génin et al., 2006). It is also possible to detect another magnetic component  
427 appearing as an octet characterized by hyperfine parameters (Table 2) with a  $CS$  of  $1.52 \text{ mm}$   
428  $\text{s}^{-1}$ , electric quadrupole interaction ( $e^2qQ/2$ ) of  $2.47 \text{ mm s}^{-1}$  and a hyperfine field  $H$  of  $11 \text{ T}$ ,  
429 which is typical of  $Fe(II)$  in probable association with  $Sb$ . This component unambiguously  
430 distinguishes it from both siderite, which has a much higher magnetic field, and  $GR1(CO_3^{2-})$ ,  
431 which is a mixed-valence (ferrous-ferric) compound leading to two magnetic ordering  
432 temperatures,  $5.2$  and  $7 \text{ K}$  (Rusch et al., 2008). The relative abundance of  $GR1(CO_3^{2-})$  and of  
433 unspecified  $Fe(II)$  species increases with the increase of  $Sb(V)$  loading (Table 2).

434 We performed field cooled (FC) and zero-field cooled (ZFC) moment measurement  
435 (Fig. A3). FC and ZFC curves overlap from  $300 \text{ K}$  down to approximately  $15 \text{ K}$ . At  
436 temperatures lower than  $15 \text{ K}$ , there are two maxima in the ZFC curve. In a system including  
437 particles, such maxima are usually associated with the blocking process of particles, thus  
438 determining the onset of superparamagnetic behavior (Néel, 1949; Brown, 1963). The  
439 blocking temperatures estimated for the maximum magnetization of ZFC curves were  $10.5 \text{ K}$   
440 and  $4.9 \text{ K}$ . We expect that these two blocking temperatures are relative to the two main  
441 minerals detected by Mössbauer spectroscopy and XRD, namely goethite and green rust.

442 The characterization by Raman spectroscopy of different locations on the biogenic  
443 minerals precipitated from the Fh\_Sb series samples revealed different biogenic minerals  
444 (Fig. 6A). Thus, the results exhibited strong bands at  $435$  and  $510 \text{ cm}^{-1}$  and a weak band at  
445  $220 \text{ cm}^{-1}$ , characteristics of  $GR1(CO_3^{2-})$  (Legrand et al., 2001b; Refait et al., 2011). We also

446 observed bands related to the precipitation of magnetite and siderite that were not detected by  
447 XRD, implying that these phases were present as minor species.

448 XPS analysis was carried out to investigate the chemical composition of the surface of  
449 biogenic solid, with special emphasis on determining the chemical speciation of Fe, Sb and C.  
450 The Fe 2p, Sb 3d and C 1s spectra of unreacted and bio-reacted Fh\_Sb(0.1) samples are  
451 compared in Fig. 7. The Fe 2p high-resolution spectrum of unreacted ferrihydrite Fh\_Sb(0.1)  
452 displays a maximum at  $\sim 711.0$  eV and a broad satellite peak at  $\sim 719$  eV, as is commonly  
453 observed for Fe(III) species in iron (oxyhydr)oxides (Mallet et al., 2013; Fan et al., 2016).  
454 Four multiplet peaks at 710.2, 711.3, 712.4 and 713.5 (FWHM = 1.3 eV) and peak area ratios  
455 relative to the first Fe(III)-O component of 1.1, 0.69 and 0.38 respectively were used to fit the  
456  $2p_{3/2}$  spectrum in agreement with Gupta and Sen, 1974; Gupta and Sen, 1975 predictions (Fig.  
457 7A, top). An additional surface peak at 714.7 eV is required to fit the data (Grosvenor et al.,  
458 2004).

459 A slight shift of the Fe  $2p_{3/2}$  maximum component towards lower binding energy is observed,  
460 and the satellite peak characteristic of Fe(III) species is strongly attenuated (Fig. 7A, bottom).  
461 In addition to the four Fe(III) multiplet peaks, three multiplet peaks located at 708.6, 709.6  
462 and 710.7 eV that characterize the presence of Fe(II) are required to fit the spectra of the  
463 Fh\_Sb(0.1) bio-reduced sample (Fig. 7A, bottom). The peak area ratio of the multiplet  
464 components relative to the first Fe(II)-O component is 1.1 and 0.5, and the FWHM is 1.6 eV.  
465 The presence of Fe(II) in the bio-reduced sample agrees well with the formation of GR1 (and  
466 minor amounts of magnetite and siderite) as observed in the XRD and TMS characterizations.  
467 The binding energy of Sb(III) and Sb(V) compounds bonded to oxygen species are too close  
468 to allow individual quantification (Fig. 7B). Previous studies have reported that the binding  
469 energy of Sb  $3d_{3/2}$  core for Sb(III) and Sb(V) within antimonite oxides were usually 538.8-  
470 539.4 and 539.8-541.7 eV respectively (Huang and Ruiz, 2006; Mittal et al., 2011). The

471 binding energy of Sb 3d<sub>5/2</sub> peak position of unreacted Fh\_Sb(0.1) at 540.0 eV agrees well  
472 with that reported for Sb(V)-O species (Fig 7B, top). Interestingly, the Sb 3d<sub>3/2</sub> peak of the  
473 bio-reduced sample shifted to a slightly lower binding energy of 539.6 eV which may  
474 cautiously suggest that some reduction of Sb(V) into Sb(III) occurred at the surface of the  
475 sample (Fig 7B, bottom). In particular, Xu et al. (2011) reported Sb 3d<sub>3/2</sub> binding energy of  
476 539.7 eV for Sb(III) sorption onto goethite.

477 Lastly, the C 1s peak of unreacted Fh\_Sb(0.1) is usually fitted with the components at 284.6  
478 eV, 286.1 eV and 288.7 attributed to C-C, H, C-O and C=O, -O environments (Fig. 7C, top).  
479 The presence of carbon reflects some surface contamination often observed in XPS  
480 experiments. Bio-reduced samples show a significant increase in the carbonate components  
481 located at 288.0 eV (Fig. 7C, bottom), in agreement with the formation of GR1(CO<sub>3</sub><sup>2-</sup>) as  
482 observed by XRD and TMS.

483

### 484 3.3.3 Stability of abiotic GR1(CO<sub>3</sub><sup>2-</sup>)

485

486 GR1(CO<sub>3</sub><sup>2-</sup>) was synthesized as described by Bocher et al. (2004) and aged for one week  
487 before being analyzed by Raman spectroscopy (Fig. 6B). The GR1(CO<sub>3</sub><sup>2-</sup>) synthesized  
488 without any additive (i.e. PO<sub>4</sub><sup>3-</sup> or Sb(V)) had transformed by the end of the aging time (Fig.  
489 6B a). The Raman spectrum displayed a strong band at 670 cm<sup>-1</sup>, which is assigned to  
490 magnetite. Similarly, the study carried out by Bocher et al. (2004) demonstrated the  
491 transformation of GR1(CO<sub>3</sub><sup>2-</sup>) toward magnetite (Fe<sub>3</sub>O<sub>4</sub>) and ferrous hydroxide (Fe(OH)<sub>2</sub>).  
492 Moreover, Guilbaud et al. (2013) used the same procedure to synthesize GR1(CO<sub>3</sub><sup>2-</sup>) and  
493 observed its transformation towards magnetite after 69 hours of aging. The Raman spectrum  
494 of the GR1(CO<sub>3</sub><sup>2-</sup>) synthesized in the presence of phosphate with an PO<sub>4</sub><sup>3-</sup> / Fe<sub>t</sub> ratio of 0.016,  
495 exhibited two strong bands at 435 and 510 cm<sup>-1</sup> and a weak band at 220 cm<sup>-1</sup>, indicating the

496 occurrence of  $\text{GR1}(\text{CO}_3^{2-})$  (Fig. 6B b). No specific band of either magnetite or of siderite was  
497 detected. This result agrees with the data produced by Benali et al. (2001) and Bocher et al.  
498 (2004), where the presence of phosphate stabilized the mixed-valence mineral and hindered  
499 mineralogic transformation. When the  $\text{GR1}(\text{CO}_3^{2-})$  precipitation occurred in the presence of  
500  $\text{Sb}(\text{V})$ , the Raman spectrum exhibited the two strong bands at 435, and  $510 \text{ cm}^{-1}$   
501 characteristics of  $\text{GR1}(\text{CO}_3^{2-})$  plus an additional unassigned phase, probably an iron-bearing  
502 solid doped with Sb (Fig. 6B d, e). However, when the  $\text{Sb}(\text{V})$  was added after the  
503 precipitation ( $\sim 10 \text{ min}$ ) the characteristic Raman bands of  $\text{GR1}(\text{CO}_3^{2-})$  and magnetite were  
504 observed (Fig. 6B c).

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## 507 **4. DISCUSSION**

508

### 509 *4.1 Rate and extent of bio-reduction and Sb partitioning*

510

511 The bio-reduction of Fh was not inhibited by Sb(V), which is in line with recent work  
512 by Burton et al. (2019). It was expected that Sb(V) loading, like other elements substitutions,  
513 would alter the physicochemical properties of the Fh (Tsapin et al., 1996; Fredrickson et al.,  
514 2001; Jentzsch and Penn, 2006; Ekstrom et al., 2010; Frierdich and Catalano, 2012b; Massey  
515 et al., 2014), and consequently affects the rate and the extent of bio-reduction. In this study,  
516 the rate of reduction decreased by ~ 50% in the presence of Sb(V) independently of the  
517 Sb/(Sb+Fe) molar ratio (Table 1, Fig. 2). The observed decrease in the rate of reduction may  
518 be related to the decline of a significant number of reactive sites on the Fh surface due to  
519 Sb(V) loading (Fredrickson et al., 2001; Ekstrom et al., 2010; Voegelin et al., 2019).

520 Fh is a metastable mineral that transforms promptly to more thermodynamically stable  
521 phases such as magnetite and goethite when reacted with Fe(II) (Hansel et al., 2005; Pedersen  
522 et al., 2005) under anoxic and non-sulfidic conditions. Electron transfer between surface-  
523 associated Fe(II) and structural Fe(III) has been shown to initiate the dissolution of Fh and the  
524 precipitation of a thermodynamically stable secondary minerals (Williams and Scherer, 2004;  
525 Yang et al., 2010; Boland et al., 2014). The bio-generation and sorption on the Fh surface of  
526 the minimum amount of Fe(II) necessary to trigger Fh transformation would hamper the bio-  
527 reduction process. In the present study, the assays run with an Sb/(Sb+Fe) molar ratio inferior  
528 to 0.06 displayed the same extent of reduction as that of pure Fh (Table 1, Fig. 2). The  
529 transformation of the host mineral was induced by ~ 35% of bio-generated Fe(II), which  
530 subsequently halted the bio-reduction process. This result indicates that Sb(V) loading with an

531 Sb/(Sb+Fe) molar ratio of up to 0.06 has a minimal effect on Fh\_Sb lability or reducibility  
532 compared with pure Fh.  
533 The extent of reduction of Fh\_Sb(0.1) reached ~ 50%, indicating that a higher Fe(II) loading  
534 was required to induce Fh\_Sb(0.1) transformation (Table 1, Fig. 2). It may be considered that  
535 this Sb loading probably reduced the lability or reducibility of the Fh\_Sb(0.1) by likely  
536 decreasing the transfer of electrons between the bio-generated Fe(II) and the Fh\_Sb(0.1). A  
537 higher Fe(II) concentration was thus needed to trigger Fh\_Sb(0.1) transformation (Williams  
538 and Scherer, 2004; Masue-Slowey et al., 2011; Friedrich et al., 2012). The inhibitory effect of  
539 a high Sb(V) concentration (0.25 mmol of Sb(V) per gram of goethite) was also observed  
540 during the Fe(II)-catalyzed recrystallization of goethite (Burton et al., 2020). The amount of  
541 Sb(V) in the Fh\_Sb(0.1) probably increased the extent of reduction by likely retarding the  
542 mineralogical transformation of the Fh\_Sb(0.1) and preserving the Fh\_Sb(0.1) surface area  
543 for further reduction (Masue-Slowey et al., 2011).

544 At the end of the bio-reduction period, a minor fraction of Sb(V) was measured in the  
545 solution. Our results indicate that a substantial amount of Sb(V) was probably associated with  
546 secondary minerals, in line with the data observed elsewhere under biotic and abiotic  
547 conditions (Mitsunobu et al., 2010b; Burton et al., 2019; Karimian et al., 2019a). We  
548 hypothesize that a significant proportion of Sb(V) was likely adsorbed on the newly formed  
549 Fe(II) minerals or otherwise occluded within aggregates of biogenic minerals. Based on  
550 earlier reported data for the incorporation of Sb(V) into iron-bearing minerals (Mitsunobu et  
551 al., 2013b; Karimian et al., 2017; Burton et al., 2019; Burton et al., 2020), we assume that  
552 Sb(V) may structurally substitute for Fe(III) in the secondary minerals due to the similarity in  
553 ion size (Fe: 0.65 Å; Sb: 0.60 Å). The fact that Fe-O and Sb-O bond distances are in the  
554 same range (Fe-O: 1.97-2 Å; Sb-O: 1.91 Å) in the Fe<sup>III</sup>O<sub>6</sub> and Sb<sup>V</sup>O<sub>6</sub> octahedra (Mitsunobu et  
555 al., 2010b; Mitsunobu et al., 2013b) further supports this assumption. Mössbauer analyses

556 indicated the precipitation of an unidentified Fe(II)-bearing solid. Given our experimental  
557 conditions, the composition of the reduction medium, and hyperfine parameters, this non-  
558 identified solid could plausibly be constituted of Sb, which could be an additional reason for  
559 the low amount of Sb present in the aqueous phase.

560 A slight reduction of the solid associated Sb(V) to Sb(III) was observed by the XPS  
561 analyses (Fig. 7B); this may have been triggered by electron transfer from Fe(II). Karimian et  
562 al. (2019b) noted that humic acids (HA) and an Fe(II)-rich environment induced a substantial  
563 reduction of Sb(V) by the potential formation of a ternary complex composed of Fe(II), HA  
564 and Sb(V), thereby facilitating the electron transfer. Fe(II)-(III) minerals such as magnetite  
565 are also able to reduce Sb(V) to Sb(III), as reported by Kirsch et al. (2008). The spiking of  
566 Sb(V) during the precipitation of  $\text{GR}_2(\text{SO}_4^{2-})$  triggered its adsorption on the newly formed  
567  $\text{GR}_2(\text{SO}_4^{2-})$  and its reduction to Sb(III). However, no reduction of Sb(V) was observed when  
568 the latter was supplemented in the medium after the precipitation of  $\text{GR}_2(\text{SO}_4^{2-})$  (Mitsunobu  
569 et al., 2008b; Mitsunobu et al., 2009). Although there is no data in the literature describing the  
570 interaction of  $\text{GR}_1(\text{CO}_3^{2-})$  and Sb(V), the slight reduction observed in our study was probably  
571 induced by the Fe(II) / Fe(III) complex during the precipitation of  $\text{GR}_1(\text{CO}_3^{2-})$ .

572

#### 573 4.2 *Precipitation of biogenic minerals*

574

575 No detectable biogenic mineral was observed in the control assays (without bacteria),  
576 whatever the Sb loading. This observation is in line with previous studies showing that the  
577 transformation of Fh to a thermodynamically more stable mineral necessitates a long period  
578 (months or years) in our experimental conditions (i.e. near-neutral pH and room temperature)  
579 (Schwertmann et al., 2004).

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#### *4.2.1 Biogenic minerals formed by bio-reduction of Sb-free Fh*

The ratio of electron donor to electron acceptor is a significant parameter, as it impacts the Fe(II) to Fe(III) fraction that controls the nature of the biogenic minerals in the reduction media. Indeed, a lower Fe(II) / Fe(III) ratio ( $< 1.0$  mmol Fe(II)/g Fh) promotes the precipitation of ferric phases, such as lepidocrocite and goethite. At the same time, a higher ratio leads to the precipitation of ferrous and ferrous/ferric phases such as siderite, magnetite and GR (Hansel et al., 2003; Yang et al., 2010). In this study, we conducted the Fh bio-reduction experiments with an excess of electron source, and the resulting biogenic minerals were magnetite (91%) and siderite (9%) (Fig. 8). Iron oxides particles have a high affinity to bacteria cells walls and associated extracellular polymeric substances (Fein et al., 1997; Lower et al., 2001; Luef et al., 2013), leading to the formation of aggregated structures. Furthermore, the Fh drying procedure used in this study entails the aggregation of Fh particles (Gilbert et al., 2009). Such bio-inorganic structures are likely to lead to the formation of micro-environments establishing distinct chemical and redox zones relative to the bulk solution (Zegeye et al., 2010; Luef et al., 2013). Similar conditions may induce the precipitation of various biogenic minerals due to the occurrence of a differential Fe(II) gradient. In the literature, the precipitation of siderite is commonly observed in the presence of an  $\text{HCO}_3^-$  buffered medium (Fredrickson et al., 1998) or in an atmosphere containing  $\text{CO}_2$  (Roh et al., 2003), which was not the case in our experimental setup. As siderite precipitation requires high local bicarbonate concentration, we hypothesized that its formation occurs in the micro-environments of aggregates where the mass transfer is probably limited or slowed down, thereby allowing the simultaneous accumulation of both Fe(II) and bicarbonate (Pallud et al., 2010).

606 On the other hand, magnetite precipitation is thought to involve a topotactic transformation  
607 process (Tronc et al., 1992; Pedersen et al., 2005; Usman et al., 2018). The sorption of Fe(II)  
608 generated by bacterial activity induces interfacial electron transfer to the structural Fe(III) and  
609 catalyzes the subsequent precipitation of magnetite as the thermodynamically more stable  
610 phase.

611

#### 612 4.2.2 Biogenic minerals formed by Fh\_Sb bio-reduction

613

614 The bio-reduction of Sb-bearing Fh led mainly to the precipitation of GR1(CO<sub>3</sub><sup>2-</sup>),  
615 goethite and an unidentified Fe(II)-bearing solid irrespective of the Sb/Fe ratio. However, the  
616 relative abundance of this unidentified Fe(II) bearing solid rises with the increase of Sb  
617 loading (Fig. 8). Its relative abundance was ~ 7% and reached ~ 17% for the assays run with  
618 Fh\_Sb(0.04) and Fh\_Sb(0.1) respectively (Fig. 8). While which secondary minerals form  
619 depends on the partitioning of the Fe(II) between aqueous and solid associated forms, the  
620 presence of Sb also seems to orient the nature of the biogenic minerals. The precipitation of  
621 magnetite as a very minor phase (Fig. 6A) may be a consequence of the presence of Sb(V).  
622 Fe(II) was generated almost to its maximum concentration just after four days of incubation in  
623 the absence of Sb(V). The generation of a high Fe(II) concentration in a very short time  
624 shifted the precipitation toward magnetite, as witnessed elsewhere in the literature (Ona-  
625 Nguema et al., 2002). The presence of Sb(V) reduced the rate of reduction by 50%, resulting  
626 in slower production of Fe(II) over time and consequently hindering the formation of  
627 magnetite.

628 In a recent study focusing on the same topic (*i.e.* the bio-reduction of Sb bearing  
629 ferrihydrite), feroxyhyte ( $\delta'$ -FeOOH) and goethite were the main biogenic minerals (Burton et  
630 al., 2019). The main difference between the two studies is that in Burton et al. (2019) the

631 electron source was in deficit relative to ferrihydrite concentration. As a result, the Fe(II)  
632 concentration produced in their research was lower, thus providing the chemical condition for  
633 the precipitation of Fe(III)-bearing biogenic minerals. In the current study, however, the  
634 excess of electron source permitted a more substantial input of Fe(II), allowing the  
635 precipitation of both GR1(CO<sub>3</sub><sup>2-</sup>) and goethite. These observations are in agreement with  
636 Hansel et al. (2003), who showed a threshold for segregating the formation of magnetite and  
637 goethite based on the Fe(II) / Fe(III) ratio in a biotic and abiotic systems.

638 It is commonly accepted that the precipitation of ferrous hydroxides, Fe(III) oxides and  
639 oxyhydroxides is the result of the condensation phenomena of iron cations initially present in  
640 aqueous solution. Jolivet et al. (2004) described the different steps involved in these  
641 precipitation processes and revealed how the structure of polymeric precursors determines the  
642 nucleation and growth of the solid phases in a Fe-H<sub>2</sub>O system. These authors posited that  
643 growth of goethite by the dissolution/crystallization process might be interpreted as taking  
644 place on the basis of the planar tetramer [M<sub>4</sub>(OH)<sub>12</sub> (OH<sub>2</sub>)<sub>4</sub>]<sub>0</sub>. In our study, the  
645 superparamagnetic goethite, identified by Mössbauer analysis, appears to be in line with these  
646 mechanisms based on the precipitation of nanosized solid phases. We assumed that the ZFC  
647 maxima at 10.5 K (Fig A3) originates from goethite (Guyodo et al., 2003; Barrero et al.,  
648 2006), and considering an anisotropy constant of 103 J m<sup>-3</sup>, we calculated the average  
649 goethite volume, corresponding to a sphere of about 20 nm diameter. This calculated particle  
650 size agrees with the intriguing line shapes of the Mössbauer spectrum obtained at RT. Indeed,  
651 as was expected for a poorly crystallized goethite, we observed a total absence of any  
652 magnetic signal (sextet) which would suggest the presence of nano-crystalline goethite in a  
653 superparamagnetic state (Janot et al., 1968; Olowe et al., 1990).

654 As GR1(CO<sub>3</sub><sup>2-</sup>) double-layered structure bears Fe(II), Fe(III) and CO<sub>3</sub><sup>2-</sup>, we hypothesized that  
655 its formation was governed by a dissolution/precipitation process. The intriguing feature is

656 that  $\text{GR1}(\text{CO}_3^{2-})$  is a metastable mineral that transforms relatively quickly ( $> 24$  h) into a  
657 thermodynamically more stable mineral such as magnetite or goethite, depending on the  
658 geochemical conditions (Benali et al., 2001; Guilbaud et al., 2013). However, the increased  
659 Sb(V) loading in our system tended to favor the precipitation of  $\text{GR1}(\text{CO}_3^{2-})$  rather than  
660 goethite (Fig. 8): thus, the relative abundance of goethite declined by 25% when the Sb/(Fe +  
661 Sb) molar ratios were raised from 0.06 to 0.1, even though goethite has a much lower  
662 standard-state Gibbs energy ( $- 489.8 \pm 1.2$  kJ/mol) (Hiemstra, 2015) than of  $\text{GR1}(\text{CO}_3^{2-})$  ( $-$   
663  $4044.24$  kJ/mol) (Drissi et al., 1995). Given the higher thermodynamic stability of goethite  
664 compared with  $\text{GR1}(\text{CO}_3^{2-})$ , it was reasonable to assume that the system would move to  
665 goethite. In addition,  $\text{GR1}(\text{CO}_3^{2-})$  needs to be in equilibrium with aqueous Fe(II) in order to  
666 circumvent any mineralogical transformation. But this aqueous Fe(II) would be depleted by  
667 sorption on the goethite surface, thereby inducing the dissolution of  $\text{GR1}(\text{CO}_3^{2-})$ . For  
668 example, Ona-Nguema et al. (2002) demonstrated the depletion of aqueous Fe(II) which was  
669 in equilibrium with  $\text{GR1}(\text{CO}_3^{2-})$  by sorption on the remaining lepidocrocite surface, thereby  
670 inducing the dissolution of  $\text{GR1}(\text{CO}_3^{2-})$  and the precipitation of magnetite in a biotic system.  
671 Similarly, under anoxic conditions,  $\text{GR1}(\text{CO}_3^{2-})$  transforms into magnetite,  $\text{Fe}(\text{OH})_2$  or  
672 siderite (Benali et al., 2001), but in the presence of phosphate it is likely that the adsorption of  
673 the latter species upon the lateral faces of abiotic  $\text{GR1}(\text{CO}_3^{2-})$  crystals likely hindered this  
674 transformation, by acting as a physical barrier (Bocher et al., 2004). Mitsunobu et al. (2009)  
675 also observed the stabilization of abiotic  $\text{GR2}(\text{SO}_4^{2-})$  when precipitated in the presence of  
676 Sb(V). The adsorption of Sb(V) on the edge sites of  $\text{GR2}(\text{SO}_4^{2-})$  with an inner sphere complex  
677 was the main parameter hampering its transformation toward magnetite. To the authors'  
678 knowledge, no comparable information regarding Sb(V) and  $\text{GR1}(\text{CO}_3^{2-})$  is available. We  
679 therefore hypothesized that the adsorption of Sb(V) species on the  $\text{GR1}(\text{CO}_3^{2-})$  crystals  
680 hampered its dissolution by acting as a physical barrier. The observation, after the ageing

681 period, of magnetite and GR1(CO<sub>3</sub><sup>2-</sup>) when Sb(V) was added after GR1(CO<sub>3</sub><sup>2-</sup>) precipitation  
682 implies that the stabilizing effect of Sb(V) is probably more marked when Sb(V) and iron are  
683 co-precipitated together. Stabilization efficiency seems to be related to the interaction of  
684 Sb(V) and iron during the GR1(CO<sub>3</sub><sup>2-</sup>) crystallite formation rather than to Sb(V) adsorption  
685 after the crystal growth (Fig 6B).

686

### 687 *4.3 Geochemical significance*

688

689 While this study addresses the effect of Sb (V) on the bio-reduction of Fh and the  
690 resulting secondary minerals, our results may also be of interest in improving our  
691 understanding of the mobility of Sb in the presence of iron-reducing bacteria. In natural soils,  
692 antimony has been shown to be closely associated with iron oxides. Adsorption and  
693 precipitation reactions with Fe(III) oxides play a crucial role in controlling the mobility and  
694 the fate of Sb(V) in natural settings.

695 In subsurface environments, seasonal water table oscillation caused by rainfall and irrigation  
696 establishes oxic-anoxic cycles. Under reducing conditions, the iron oxides may undergo  
697 dissolution and mineralogy transformation upon reaction with iron-reducing bacteria that can  
698 potentially affect the fate and the mobility of sorbed Sb(V). During Sb(V)-bearing bio-  
699 reduction of Fh, goethite and ferrihydrite formation is observed in carbon-deficient setups  
700 (Burton et al., 2019). In contrast, goethite and GR1(CO<sub>3</sub><sup>2-</sup>) is precipitated in carbon-rich  
701 systems (this study). In both cases, Sb(V) partitioned mainly to secondary minerals,  
702 suggesting that labile organic carbon's availability does not affect Sb(V) 's sorption into the  
703 structure of secondary minerals. Furthermore, even a partial formation of Fe(II) can trigger  
704 the mineralogical transformation of iron oxide and lead to Sb(V) sorption in a crystallized  
705 secondary mineral. At redox transitions zones, iron oxides undergo numerous redox cycling

706 that will likely lead to the precipitation of various secondary minerals displaying different  
707 affinity to Sb(V) depending on their properties. Ultimately, Sb(V) repartitioning and  
708 speciation will vary among environments but should be controlled by the flux of Fe(II) which  
709 dictates the secondary minerals' nature.

710 Our study also demonstrates that Sb(V)-loading affects the mineralogy of secondary minerals  
711 indicating that Sb(V) concentration controls the Fe(II) flux. The increase of Sb(V) led to an  
712 substantial Fe(II) formation ( $\text{Fe(II)/Fe}_{\text{tot}} \sim 0.5$ ) leading to the simultaneous rise of metastable  
713  $\text{GR1}(\text{CO}_3^{2-})$  and a decrease of goethite. The Sb(V) sorption on  $\text{GR1}(\text{CO}_3^{2-})$  seems to drive the  
714 mineral's stability. In contaminated subsurface environments,  $\text{GR1}(\text{CO}_3^{2-})$  displays the ability  
715 to remove arsenic (As) species and to be a host phase for As (Perez et al., 2021). It is,  
716 therefore, necessary to study the fate of Sb(V) sorbed on  $\text{GR1}(\text{CO}_3^{2-})$  particles to decipher the  
717 role played by these metastable Fe(II)/Fe(III) minerals in natural settings in regards to the  
718 (im)mobilization of metalloids. Our study's significance is that the parameters governing the  
719 biogeochemical flux of Fe(II) should be understood before considering iron oxides and  
720 secondary minerals as a reliable Sb(V) sink for long-term storage in Sb-contaminated  
721 environments.

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## 725 **5. CONCLUSIONS**

726

727 This study highlights how Sb affects the rate and the extent of Fh bio-reduction as well as  
728 the nature of biogenic minerals. By using complementary characterization methods, we were  
729 able to capture the precipitation of a relative abundance of various biogenic minerals with a  
730 relative abundance that were governed by multiple biomineralization pathways. The presence  
731 of Sb reduced by almost 50% the rate of bio-reduction and enhanced the extent of reduction  
732 of Fh with a Sb/(Sb + Fe) molar ratio of 0.1. Note should also be taken of the total Fh  
733 transformation irrespective of the Sb(V) concentration. Thus, magnetite precipitated in the  
734 absence of Sb(V), while GR1(CO<sub>3</sub><sup>2-</sup>), goethite and an unidentified Fe(II)-Sb-bearing solid  
735 formed in its presence. Importantly, this study shows that the efficiency of Sb in stabilizing  
736 the metastable GR1(CO<sub>3</sub><sup>2-</sup>) by mitigating its mineralogical transformation toward a  
737 thermodynamically more stable mineral such as goethite. The question raised by this study is,  
738 how does Sb(V) interact with GR1(CO<sub>3</sub><sup>2-</sup>) crystals? A natural next step would be to carry out  
739 research to reveal the interaction of Sb(V) with GR1(CO<sub>3</sub><sup>2-</sup>) at the crystallographic level.

740

741

742 **ACKNOWLEDGEMENTS:**

743           This work has been supported by the French National Research Agency through the  
744 national “Investissements d’Avenir” programme under the reference ANR-10-LABX-21-01 /  
745 LABEX RESSOURCES21 and EC2CO 2017.

746           We would like to thank Aurélien Renard of the Spectroscopy and Microscopy Core  
747 Facility of SMI LCPME (Université de Lorraine, CNRS, LCPME – [http://www.lcpme.cnrs-](http://www.lcpme.cnrs-nancy.fr)  
748 [nancy.fr](http://www.lcpme.cnrs-nancy.fr)) for XPS analyses and Renaud Gley of the Université de Lorraine, CNRS, LIEC for  
749 XRD analyses.

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1130 **FIGURES CAPTIONS**

1131

1132 **Figure 1:** X-ray diffraction pattern of Fh (black line) and Sb substituted Fh (Fh\_Sb(0.04) blue  
1133 line, Fh\_Sb(0.06) red line and Fh\_Sb(0.1) green line). The two maxima (0.258 nm and 0.149  
1134 nm) are consistent with 2-line Fh.

1135

1136 **Figure 2:** Bio-reduction of Fh (black symbols) and Sb substituted Fh, (Fh\_Sb(0.04)  
1137 Fh\_Sb(0.06) and Fh\_Sb(0.1) blue, red and green symbols respectively) measured as  
1138  $Fe(II)_{tot}/Fe_{tot}$ . The initial rate of reduction was computed from the first derivation of a  
1139 nonlinear curve fit represented by the dotted lines. Errors bars represent standard deviation of  
1140 three triplicates batches incubations.

1141

1142 **Figure 3:** X-ray diffractograms of microbially reduced Fh (black line) and Sb substituted Fh.  
1143 (Fh\_Sb(0.04), Fh\_Sb(0.06) Fh\_Sb(0.1) blue, red and green lines respectively. “GR1”: green  
1144 rust 1, “M”: magnetite, “S”: siderite and “\*” unidentified phase.

1145

1146 **Figure 4:** TMS spectra of solid phases obtained after the bio-reduction of Fh at different  
1147 temperature. Black dots: experimental data; red dashed line: global fitted curve; solid line:  
1148 components.

1149

1150 **Figure 5:** Raman spectra of biogenic and abiotic minerals **A:** Raman spectra for two locations  
1151 (red and black spectra) on bio-reduced Fh\_Sb(0.04) sample and two locations (green and blue  
1152 spectra) on bio-reduced Fh\_Sb(0.1) sample. **B:** Raman spectra of (a) abiotic GR1 precipitate,  
1153 (b) abiotic GR1 precipitate with phosphate, (c) abiotic GR1 precipitate and addition of Sb(V)  
1154 ~ 10 minutes after the precipitation, (d), (e) two locations for abiotic GR1 precipitated with



1155 Sb(V). The analyses were done after a week of aging. M: Magnetite, S: siderite, GR: Green  
1156 Rust, ?: unassigned phase.

1157

1158 **Figure 6:** TMS spectra of solid phases obtained after the bio-reduction of Sb substituted Fh at  
1159 16 K. Black dots: experimental data; red dashed line: global fitted curve; solid line:  
1160 components.

1161

1162 **Figure 7:** XPS high resolution spectra of (A) Fe2p<sub>3/2</sub> core level before (upper panel) and after  
1163 bio-reduction (lower level), (B) Sb 3d<sub>5/2</sub> core level before (upper panel) and after bio-  
1164 reduction (lower level), (C) C1s core level before (upper panel) and after bio-reduction (lower  
1165 level).

1166

1167 **Figure 8:** Relative abundance distribution of biogenic minerals as a function of Sb/(Sb + Fe)  
1168 based on Mössbauer data.

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#### 1171 **TABLES CAPTIONS:**

1172

1173 **Table 1:** Rate and extent of Fh and substituted Fh bio-reduction. Aqueous Sb were measured  
1174 at the end of the bio-reduction period (*i.e.* 25 days). Numbers in parenthesis are the standard  
1175 deviation of triplicates analyses.

1176

1177 **Table 2:** Mössbauer hyperfine parameters at 15 K and relative abundance of components in  
1178 bio-reduced Fh and bio-reduced Fh\_Sb series. CS = center shift relative to  $\alpha$ -iron at room

1179 temperature,  $\Delta(\epsilon)$  = Quadrupole splitting (shift), H = magnetic hyperfine field, RA = Relative  
1180 abundance.

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1182