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1 **Fe^{III}-substituted brucite: hydrothermal synthesis from (Mg_{0.8},Fe^{II}_{0.2})-brucite,**
2 **crystal chemistry and relevance to the alteration of ultramafic rocks**

3

4

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10

Abstract

11

12 Ferroan brucite, $(\text{Mg,Fe})(\text{OH})_2$, is a common mineral product of serpentinization reactions.
13 The alteration of ferroan brucite under subsurface conditions is expected to form magnetite and
14 hydrogen (H_2). Ferroan brucite, $(\text{Mg}_{0.8}\text{Fe}_{0.2})(\text{OH})_2$, with a grain size of 20 – 100 nm, was synthesized
15 by precipitation of iron salts in the presence of NaOH under sub-anoxic conditions. Both composition
16 and grain size of the synthetic product are similar to those of ferroan brucite found in serpentinized
17 peridotites collected during the Oman Drilling Project. Synthetic ferroan brucite was then reacted in
18 aqueous solutions at 378 and 403 K during 1 to 36 days either in PTFE-lined reactors or in gold
19 capsules placed in externally heated pressure vessels. In gold capsules, ferroan brucite barely reacted
20 and minor magnetite and H_2 were produced. In PTFE-lined reactors, reaction progress over 75%
21 could be achieved with reaction products composed of magnetite, pyroaurite
22 $[\text{Mg}_6\text{Fe}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4.5\text{H}_2\text{O}]$, and a new phase, identified as ferrian brucite
23 $[(\text{Mg}_{0.8}\text{Fe}^{\text{III}}_{0.2})\text{O}_{0.2}(\text{OH})_{1.8}]$ based on the Rietveld refinement of its X-ray powder diffraction data,
24 $\text{Fe}^{\text{III}}/\text{Fe}_{\text{tot}}$ colorimetric determination and thermogravimetric analysis. Ferrian brucite is isostructural
25 to ferroan brucite and displays the same iron/magnesium ratio. However, all iron is trivalent. X-ray
26 diffraction and thermogravimetric data support deprotonation as the mechanism responsible for
27 charge compensating Fe^{II} oxidation ($\text{Fe}^{2+} + \text{OH}^- \Rightarrow \text{Fe}^{3+} + \text{O}^{2-}$). The difference in reaction products
28 obtained with the two types of reactors is attributed to the higher permeability to H_2 (and/or O_2) of
29 the PTFE-lined reactors compared to gold capsules. Ferroan brucite conversion into ferrian brucite
30 was unexpectedly fast and proceeded in a few days. The thermodynamic stability of ferrian brucite is
31 discussed as a function of oxygen fugacity and pH.

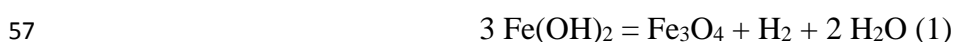
32 **Keywords:** ferroan brucite oxidation, ferrian brucite, serpentinization, low-temperature alteration,
33 H_2 production.

34

35 1 Introduction

36 Seepages of natural H₂-containing gas are encountered onshore in association with ultramafic
37 bodies that interact chemically with meteoritic waters under sub-surface conditions (Neal and Stanger
38 1983; Coveney et al. 1987; Abrajano et al. 1990). Petrographic investigation of Oman ophiolite
39 samples has actually shown that the alteration under subsurface conditions of minerals bearing ferrous
40 iron hosted in partially to fully serpentinized samples can lead to further iron oxidation, probably
41 coupled with H₂ production (Mayhew et al. 2018; Ellison et al. 2021). Among serpentinization
42 mineral products, ferroan brucite appears to be the most reactive in the course of low-temperature
43 alteration processes and has thus been the subject of growing interest as a possible contributor to low
44 temperature H₂ generation which may in turn fuel hydrogenotrophic microbial activity (Malvoisin
45 2015; Jöns et al. 2017; Miller et al. 2017; Klein et al. 2020; Templeton and Ellison 2020).

46 Brucite structure was initially determined by Aminoff (1921) and is composed of layers of
47 edge-sharing octahedra. Subsequent investigations of structural analogues by infrared spectroscopy
48 (Brindley and Kao 1984) and neutron diffraction (Chakoumakos et al. 1997) showed that hydroxyl
49 groups are perpendicular to the layer. Ferroan brucite, (Mg_{1-x}Fe^{II}_x)(OH)₂, preserved in serpentinized
50 peridotites contains significant divalent iron with *x* generally ranging from 0.15 to 0.4 per formula
51 unit in samples collected at mid-ocean ridges, in ophiolites, and in forearc settings (D'Antonio and
52 Kristensen 2004; Bach et al. 2006; Beard et al. 2009; Klein et al. 2009, 2014; Kodolányi and Pettke
53 2011; Kodolányi et al. 2012; Frost et al. 2013; Schwarzenbach et al. 2016; Malvoisin et al. 2020).
54 Thermochemical models have shown that equilibrium between the Fe(OH)₂ component of ferroan
55 brucite and magnetite buffers the H₂ activity (e.g., McCollom and Bach 2009) through the
56 equilibrium:



58 Reaction (1) can also be used to calculate Fe(OH)₂ activity in brucite at a given H₂ partial
59 pressure assuming a ferroan brucite solid-solution model and knowing the thermodynamic parameters
60 of the Fe(OH)₂ end-member. Thermodynamic models involving Fe-bearing brucite that reasonably

61 reproduce natural observations and experimental data have been proposed (Bach and Klein 2009;
62 Klein et al. 2009, 2013; McCollom and Bach 2009; Jöns et al. 2017). On simple thermodynamic
63 grounds, it can be predicted that ferroan brucite initially formed by oceanic serpentinization may
64 further produce H₂ when exposed to meteoric water. According to Reaction (1), potential change in
65 H₂ activity will lead to the production of more magnetite (and additional H₂), thereby consuming the
66 Fe(OH)₂ component of ferroan brucite. Such a change in H₂ activity may occur by dilution due to
67 fluid infiltration, loss to the atmosphere, or consumption through microbial activity (Takai et al. 2004;
68 Petersen et al. 2011; Myagkiy et al. 2020). This simple mechanism of H₂ production through near-
69 surface fluid-rock interactions might be more complicated in natural systems where aqueous fluids
70 contain dissolved species (SO₄²⁻, Cl⁻, HCO₃⁻) and O₂. Oxidation of ferroan brucite may thus yield
71 Fe^{II}/Fe^{III} layered double hydroxides containing chlorine (iowaite; Klein et al. 2020) or CO₂
72 (pyroaurite; Boschi et al. 2017) with or without simultaneous H₂ production.

73 In order to gain insight on the behavior of ferroan brucite when exposed to fluids in subsurface
74 conditions relevant to ophiolite settings, ferroan brucite was synthesized and compared (composition,
75 size, morphology) to natural ferroan brucite from the Oman ophiolite. Synthetic ferroan brucite was
76 then reacted in the presence of water at temperatures close to 373 K, considered here as low
77 temperatures. The characterization of the reaction products with X-ray diffraction, scanning electron
78 microscopy, bulk Fe^{III} determination by colorimetry, and thermogravimetric analysis allowed us to
79 propose phase relationships for ferroan brucite in the naturally relevant FeO-MgO-H₂O+/-O₂ sub-
80 system.

81

82 **2 Materials and Methods**

83 **2.1 Fe^{II}-bearing brucite synthesis**

84 Ferroan brucite with $x \sim 0.2$ was synthesized at ambient conditions based on a method used to
85 synthesize aqueous Fe^{II} precipitates (Olowe and Génin 1991; Gilbert et al. 2008). Ferroan brucite was

86 precipitated from a stoichiometric solution of dissolved Fe^{II} and Mg salts, either sulphate
87 (*MgSO₄·7H₂O* and *FeSO₄·7H₂O*) or chloride (*MgCl₂·6H₂O* and *FeCl₂·4H₂O*). Precipitation occurred
88 after pouring the metal salt solution into a NaOH solution under stirring at ~ 400 rpm. The
89 composition of the mixture is characterized by its *R* ratio defined as $R = \frac{[Fe^{2+}] + [Mg^{2+}]}{[NaOH]}$. Solutions of
90 100 mL with salt concentrations of 0.3 mol.L⁻¹ were mixed with 100 mL solutions with a NaOH
91 concentration of either 0.75 or 6 mol.L⁻¹. This led to 200 mL solutions with *R* = 0.4 and *R* = 0.05,
92 respectively. In order to minimize the oxidation of Fe^{II}, ultrapure water (resistivity of 18.2 MΩ.cm)
93 was boiled under continuous N₂ bubbling prior to all experiments.

94 The precipitate was separated from the solution by ultra-centrifugation in an airtight bottle.
95 The bottle was then opened in a glove box under an Ar atmosphere with a continuous measurement
96 of O₂ level indicating concentration < 10 ppm. The glove box was systematically used in the
97 subsequent steps requiring an inert atmosphere. The precipitate was recovered and rinsed using two
98 different procedures: 1) vacuum enhanced filtration to collect the solid on a 0.8 μm nitrocellulose
99 filter (AAWP filter), followed by washing three to four times with a total of ~ 50 mL degassed
100 ultrapure water without resuspending the solid fraction; and 2) repeated cycles of centrifugation,
101 supernatant removal, resuspension of the powder paste under manual stirring with ~ 150 mL of
102 degassed ultrapure water. Two to four cycles were needed to reach the point where the pH did not
103 longer decrease (10.3 – 10.7 range). This second method was mainly used in the present study due to
104 its convenience.

105 **2.2 Ferroan brucite reactivity experiments**

106 A total of twenty experiments was carried out by reacting Fe-bearing brucite with an aqueous
107 solution in two types of reactors (Table 1). Eighteen experiments were performed with synthetic
108 ferroan brucite loaded with an aqueous solution (Table 1) into 45 mL PTFE-lined vessels (Parr
109 4744TM). Five of these experiments (Runs #01 to #05, Table 1) were performed directly with the
110 ferroan brucite (~ 1 g) recovered after the first centrifugation stage (see the above-described
111 procedure 2). In this case, the starting material was thus neither rinsed nor dried and was reacted

112 under pressure and temperature with the solution (~ 25 g) from which this ferroan brucite precipitated
113 (pH > 13). In all other experiments, the initial ferroan brucite used was rinsed according to one of the
114 above-described protocols. The initial pH of the solution was measured for Runs #10, #19 and #20
115 and found to be close to 10 (i.e., close to the pH range measured for the last rinsing cycle, *see* previous
116 section). The reactors were loaded and sealed in the glove box and Ar atmosphere. They were then
117 placed in an oven regulated within 1 K. Reactivity of ferroan brucite was investigated at two
118 temperatures: 378 and 403 K and at the water vapor pressure (0.12 and 0.27 MPa, respectively). Each
119 experiment was stopped at a specific time ranging from 1 to 36 days (Table 1). Reactors were then
120 opened in the glove box where the solid product was recovered. The final pH of the solution measured
121 for eleven runs (Runs #8-16, #19, and #20) is 9.4 +/- 0.5.

122 Two additional experiments (#17 and #18 in Table 1) were performed by loading in the glove
123 box about 30 mg of ferroan brucite with 100 μ L of degassed ultrapure water in 2 – 3 cm long gold
124 tubes (4.4 mm outer diameter and 4.0 mm inner diameter) welded shut at one end. The open end of
125 the capsule was then squeezed and the capsule transferred outside the glove box for immediate
126 welding. The Au capsule was then placed in a horizontal cold seal pressure vessel for reaction at
127 378 K under a water pressure of 20 MPa. The temperature was measured with a Ni-NiCr
128 thermocouple and regulated within 1 K. At the end of the experiment, the vessel was cooled down
129 under a compressed air stream (see Brunet and Chopin 1995 for experimental details).

130 **2.3 Gas chromatography**

131 H_2 gas contained in the sealed gold capsules (experiments # 17 and # 18) was recovered using
132 the method described in Malvoisin et al. (2013). The recovered gas diluted in Ar was injected with a
133 250 μ L gas-tight syringe in a Clarus 500 gas chromatograph (Perkin ElmerTM) equipped with a
134 polymer filled column (Restek ShinCarbonTM) and a thermal conductivity detector (TCD). Argon was
135 used as carrier gas. Each gas sample was analyzed at least three times consecutively. H_2 detection
136 limit with the gas chromatograph setup was estimated to 10 – 100 ppm. A H_2 blank experiment was
137 performed in a sealed gold capsule with 100 μ L of degassed ultrapure water. After fifteen days at 378

138 K and 20 MPa, no hydrogen was detected in the blank experiment. After gas chromatography
139 analysis, the capsules were opened in the glove box where the solid was dried for several days in the
140 Ar atmosphere before characterization.

141 **2.4 X-ray diffraction (XRD) and Rietveld analysis**

142 Run products were front-loaded as randomly oriented mounts in the glove box using an air-
143 tight holder and analyzed by X-ray diffraction (XRD) with a Bruker D8 diffractometer. XRD patterns
144 were collected from 15 to 80° (2 θ) using CuK α radiation and counting times of 3 s per 0.04° step.
145 After identification of the different mineral phases, XRD patterns were analyzed using the Rietveld
146 technique with the BGMN software (Doebelin and Kleeberg 2015). A non-exhaustive list of
147 independently refined parameters includes: i) the proportions of the different phases present in the
148 samples: ferroan brucite [containing Fe^{II}], pyroaurite [a Fe-containing layered double hydroxide
149 (LDH) structure], magnetite, and ferrian brucite [containing Fe^{III}]; ii) the unit-cell parameters of these
150 phases; iii) the Mg:Fe ratios in ferroan and ferrian brucites if present at > 10 and >25 wt.%,
151 respectively; iv) z-coordinate of the O atom 2d position in ferroan and ferrian brucites (space group
152 $P\bar{3}m1$) if present at >50 wt%; v) preferred orientation of the different phases using spherical harmonic
153 functions if the phase content was sufficient (Doebelin and Kleeberg 2015); vi) size of the coherent
154 scattering domains and strain in the different phases. In particular, the partial occupancy of the mixed
155 (Fe,Mg) site refined in ferroan brucite was constrained both from the variation of the in-plane a unit-
156 cell parameter between values reported for Mg(OH)₂ (brucite – ICDD #44-1482) and Fe(OH)₂
157 (amakinite – ICSD #107289) end-members and from the influence of site mixed occupancy on the
158 intensity distribution between hkl reflections. To our knowledge, no systematic study is available to
159 confirm the validity of Vegard’s law between these two end-members. The remarkably linear
160 relationship existing between the in-plane dimension of brucite-like structures and the ionic radius of
161 the octahedral cation ($R^2 = 0.996$ – Fig. S1) strongly supports the validity of the approach, however.
162 Unit-cell c parameter was not included in the approach owing to the more erratic variation of this
163 dimension with the ionic radius of the octahedral cation (Fig. S1). Intensity distribution between

164 reflections was used as an additional constraint to refine the partial occupancy of the mixed (Fe,Mg)
165 site when proportion of ferroan brucite exceeded 10 wt.%. As no structure model was available for
166 ferrian brucite, unit-cell parameters and Fe contents were refined independently when proportion of
167 ferrian brucite exceeded 25 wt.% and charge compensation was hypothesized to originate either from
168 the presence of octahedral vacancies or from the partial deprotonation of the layered structure as
169 proposed by Genin et al. (2006a) for the octahedral layer of fully oxidized green rust. In the latter
170 case, the partial occupancy of the mixed (Fe,Mg) site was refined using a split site and constraining
171 a complete (Fe+Mg) site occupancy. In the former case, the Fe content was kept constant and similar
172 to that in ferroan brucite (0.17 Fe per octahedral site) and only Mg site occupancy was refined to
173 avoid refinement of cross-correlated parameters related to electron density at the octahedral cation
174 position (overall site occupancy and Mg:Fe ratio).

175 **2.5 SEM imaging**

176 Powders of the starting material and of the run products were mounted on double-sided carbon
177 tape in the glove box under Ar atmosphere. They were then coated under vacuum with a 1 nm thick
178 gold layer and characterized with a field emission gun scanning electron microscope (FEG-SEM;
179 Zeiss Ultra 55) operated at 5 to 10 kV accelerating voltage.

180 **2.6 Thermogravimetric analysis**

181 Thermogravimetric analyses (TGA) were performed using a Mettler-Toledo TGA-DSC3+
182 instrument. Samples were loaded into 100 μ L aluminum crucibles inside the glove box. The crucibles
183 were mechanically sealed in the glove box using a manual press (Mettler-Toledo) and then brought
184 to the instrument. The lid was pierced using a small needle just prior to the measurements to minimize
185 atmosphere exposure. A thermal treatment consisting of a 5 min isotherm at 298.15 K and a
186 subsequent ramp from 298.15 to 873.15 K at 10 K/min was programmed, under a 50 mL/min N₂ flow.
187 The gas produced by the sample during the TGA measurement was analyzed using an IS50 Fourier
188 Transform Infrared (FTIR) spectrometer from Thermo Scientific. The gas was transferred from the
189 outlet of the TGA instrument to the spectrometer using a heated transfer line (573 K). 40 scans were

190 acquired and averaged every 51 s. Absorbance spectra were measured from 4500 to 500 cm^{-1} , with a
191 4 cm^{-1} resolution.

192 **2.7 Raman microspectroscopy**

193 Value of x in the ferroan brucite was determined by Raman spectroscopy with a confocal
194 Horiba LabRAM Soleil equipped with a 532 nm laser at ISTERre. The confocal aperture was set at
195 200 μm and the gratings at 600 grooves/mm. Five duplicate spectra were acquired over the 3200-3800
196 cm^{-1} range with a x100 objective. After subtracting the baseline, spectra were fitted with Lorentzian
197 functions to determine the position of the ν_1 O-H stretching band of ferroan brucite. This position was
198 then used to calculate x using the linear relationship from Templeton and Ellison (2020).

199 **2.8 Ferric and ferrous iron quantification in the solid products**

200 For Runs #19 and 20, ferric and ferrous iron contents of the starting ferroan brucite and of its
201 hydrothermal reaction products were determined by colorimetric assay with a $\sim 3\%$ precision.
202 Sample preparation for Fe quantification was performed in a glove box under an Ar atmosphere
203 containing 3 ppmv O_2 . A mass of 103 mg of sample powder was dissolved into 4 mL of 3M HCl
204 according to the protocol proposed in Pan et al. (2020). The resulting solution was first diluted to 50
205 mL with ultrapure water (18.2 M Ω) and then diluted again 10 times in ultrapure water. A 1 mL aliquot
206 of this last solution was mixed with 1 mL of a pH-buffered solution (pH = 3.5); then, 1 mL of ultrapure
207 degassed water and 1 mL of 10^{-2} M O-phenanthroline were successively added for $[\text{Fe}^{2+}]$
208 quantification by spectrophotometric method (Herrera et al. 2007). Stability of aqueous Fe^{2+} in
209 acidified solution (pH ~ 1) has been tested on 0.1 M $\text{Fe}^{\text{II}}\text{Cl}_2$ solutions prepared outside the glove box,
210 with degassed water. No significant aqueous Fe^{2+} oxidation is expected in the time lapse (< 2 h)
211 between dissolution and iron complexation in a glove box with 3 ppmv O_2 . The procedure described
212 above was repeated with 1 mL of hydroxylamine chloride instead of 1 mL of ultrapure degassed water
213 to obtain $[\text{Fe}]_{\text{total}}$; $[\text{Fe}^{3+}]$ was deduced from the difference between $[\text{Fe}]_{\text{total}}$ and $[\text{Fe}^{2+}]$.

2.9 Comparison to a natural ferroan brucite from the Oman ophiolite

A ferroan brucite bearing sample was collected in the Wadi Tayin massif of the Samail Ophiolite during the Oman Drilling Project (sample BA4A-81-1-1-17; Kelemen et al. 2020). Sample mineralogical composition and microstructure are described in detail in Malvoisin et al. (2020, 2021). The sample consists of an extensively serpentinized dunite (serpentinization progress > 80%) containing olivine relicts surrounded by serpentine and ferroan brucite. Magnetite is rare. Malvoisin et al. (2021) have shown that serpentine occurs as ~ 1 μm wide lizardite columns perpendicular to the olivine surface. These columns are embedded in an aggregate of randomly oriented ferroan brucite grains (< 100 nm across). An x value of 0.2762 (95% confidence bounds of 0.2760 and 0.2765) was inferred by Malvoisin et al. (2020) for ferroan brucite composition based on the microprobe analyses of mixtures of lizardite columns and ferroan brucite grains.

225

3 Results

3.1 Characterization of synthetic ferroan brucite

The synthesis protocol led to ferroan brucite production as a single crystalline phase as shown by powder XRD (Fig. 1). The same results were obtained whether chloride or sulfate iron salt was used, and whether the solid products were recovered by vacuum enhanced filtration or centrifugation. Two peaks were identified in the 3200-3800 cm^{-1} range with Raman spectroscopy on sample FeBR_R0.4_Cl_11 (also used as starting material for Run #20; Fig. S2A): the broad peak at ~ 3586 cm^{-1} was attributed to ferroan brucite oxidation in air during measurement, whereas the sharp peak at ~ 3641 cm^{-1} was attributed to the ν_1 O-H stretching band of ferroan brucite. Using the relationship of Templeton and Ellison (2020), the position of this ν_1 O-H stretching band indicates a x value of 0.17 ± 0.05 . Based on Vegard's law, refined unit-cell parameters confirmed the $x \sim 0.2$ composition (Tables S1, S2) that allows also reproducing the experimental distribution of intensities between the different hkl reflections. The FWHM of ferroan brucite diffraction peaks are similar for all synthetic samples and indicative of a 20 - 40 nm crystal size within the **ab** plane (Table 1). The

240 crystal size inferred from XRD data is close to the size of synthetic ferroan brucite platelets (50 - 100
241 nm across with homogeneous size distribution) observed with SEM (Fig. 2A and 2B). In this ferroan
242 brucite, calculated (Mg,Fe)-O bond lengths ($\sim 2.13 \text{ \AA}$ – Table S2) are consistent with the prevalence
243 of divalent cations in the structure. Bond valence calculated with the Valence program (Brown and
244 Altermatt 1985; Brown 2009) and bond-valence parameters from Gagné and Hawthorne (2015)
245 indicate that Fe^{II} atoms would receive 0.348 v.u. from each of its 6 surrounding O atoms. This ensures
246 an almost ideal charge compensation (2.088 v.u.), whereas Mg^{II} atoms would receive 0.308 v.u. from
247 each of the 6 surrounding O atoms. By contrast, bond valence calculated for Fe^{III} cations and a similar
248 Fe-O bond length indicates that these cations would receive only 0.364 v.u. from surrounding O
249 atoms, thus resulting in their strong undersaturation (2.184 v.u.). These charge compensation
250 calculations support the prevalence of Fe^{II} over Fe^{III} in ferroan brucite.

251 Bulk Fe^{III} content has been determined experimentally for the two synthetic ferroan brucite
252 used as initial material in Runs #20 and #19 (Fig. S3). In sample #20, which was prepared using the
253 same protocol as all other syntheses, $\text{Fe}^{\text{III}}/\text{Fe}_{\text{tot}}$ amounts to 0.08(1). Sample #19 was aged in the glove
254 box until the product was covered with a thin pale reddish layer indicative of oxidation. In this
255 extreme case, $\text{Fe}^{\text{III}}/\text{Fe}_{\text{tot}}$ reaches 0.17(1) (Fig. S3). In both cases, these experimentally determined
256 proportions of Fe^{II} and Fe^{III} further support the prevalence of Fe^{II} over Fe^{III} in ferroan brucite.

257 **3.2 Identification and quantification of the products of ferroan brucite reaction in aqueous** 258 **media at $T \leq 403 \text{ K}$**

259 At 378 and 403 K, in PTFE-lined reactors, ferroan brucite was found to react significantly.
260 Indeed, after one week of experiment, 20 – 30 wt.% of ferroan brucite have reacted at both
261 temperatures (Table 1). For a duration of about a month, up to 80 – 90 wt.% of ferroan brucite has
262 reacted at the two temperatures (Table 1). The two experiments performed in gold capsules yielded
263 strikingly different results, ferroan brucite having barely reacted even after 26 d at 378 K (Table 1).
264 In this case, only two reaction products were identified, magnetite [3.2(2) – 3.9(3) wt.%] and

265 pyroaurite [0.4(3) – 5.4(19) wt.%], a ferromagnesian LDH with interlayer water and carbonate anions
266 (Allmann 1968), nominally $\text{Fe}_2\text{Mg}_6(\text{OH})_{16}(\text{CO}_3)\cdot 4.5\text{H}_2\text{O}$.

267 The ferric iron content of the reaction products from PTFE-lined reactors has been
268 experimentally determined for Experiments #19 and #20 which were specifically designed to quantify
269 the oxidation of iron in the course of the ferroan brucite reaction. The starting material of Run #19
270 was purposely oxidized leading to a $\text{Fe}^{\text{III}}/\text{Fe}_{\text{tot}}$ ratio of 0.17(1) (Fig. S3). This ratio increased to 0.92(1)
271 after hydrothermal treatment for 32 days at 378 K (Run #19). Like for all other experiments, the
272 starting material of Run #20 [$\text{Fe}^{\text{III}}/\text{Fe}_{\text{tot}}$ ratio of 0.08(1)] was prepared to avoid as much as possible
273 oxygen contamination. After hydrothermal treatment for 32 days at 378 K (Run #20) a $\text{Fe}^{\text{III}}/\text{Fe}_{\text{tot}}$ ratio
274 of 0.87(5) was measured in the reaction product (Fig. S3). Both experiments indicate that Fe is mainly
275 present as Fe^{III} in reaction products of ferroan brucite.

276 Refinement of unit-cell parameters of ferroan brucite remaining in reaction products indicates
277 that its Fe content (x) after reaction is similar to that of the starting material (~ 0.2). Magnetite was
278 found in almost all run products (0.9 – 4.1 wt.%), even in experiments having lasted less than a week
279 (Table 1). Pyroaurite was identified by XRD in all experiments but in proportions close to the
280 detection limit ($\sim 0.2 - 0.3$ wt.%) for Runs #04, #05 and #18 (Table 1). In all other runs, quantitative
281 phase analysis yielded pyroaurite proportions of ~ 5 to ~ 30 wt.% depending on run duration and
282 water-to-rock ratio. Another layered phase was present whose peak positions are similar to those of
283 the initial ferroan brucite, although slightly shifted towards higher angles (Fig. 3B). This phase was
284 assumed to be isostructural to ferroan brucite but with shorter unit-cell parameters, most likely as a
285 consequence of Fe^{II} oxidation shown by the initial quick formation of pyroaurite, and will hereafter
286 be referred to as ferrian brucite. Progressive replacement of ferroan brucite by ferrian brucite is
287 illustrated on Fig. 3A where the time evolution of the XRD pattern of the run product is displayed.
288 Accordingly, a satisfactory fit to the data was obtained assuming a contribution from this ferrian
289 brucite structure (Fig. S4). SEM images (Fig. 2C) showed that ferrian brucite displayed the same
290 habitus as starting ferroan brucite (Fig. 2A and 2B) with platelets of larger size however (~ 400 nm).

291 3.3 Crystal chemistry of ferrian brucite

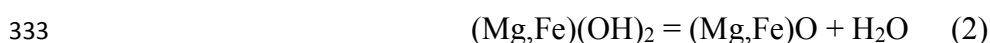
292 For Run #03, in which ferrian brucite accounts for ~ 75% of the reaction products, its unit-
293 cell parameters and atomic positions were refined to further constrain its crystal chemistry, and more
294 especially its Fe/Mg ratio and Fe valence. Refined unit-cell parameters ($a = 3.1255(5) \text{ \AA}$, $c =$
295 $4.6774(13) \text{ \AA}$; space group $P\bar{3}m1$ – Tables S1, S3) suggest the presence of ~ 15% Fe^{III} in the ferrian
296 structure using brucite and fully oxidized green rust (Fe^{III}₆O₁₂H₈CO₃) as end members for Vegard's
297 law ($a = 3.1442 \text{ \AA}$ – ICDD #44-1482 – and $a = 3.01 \text{ \AA}$ – Génin et al. 2006a – respectively). Validity
298 of Vegard's law between these two end-members is supported by the extension of the linear regression
299 between the in-plane a dimension of brucite-like structures and the ionic radius of the octahedral
300 cations to include Fe^{III} ($R^2 = 0.994$ – Fig. S5). Validity of Vegard's law for the in-plane a parameter
301 of mixed (Fe^{III},Mg^{II}) octahedral layers is further supported by the consistency between calculated and
302 experimentally measured a unit-cell parameters of (Fe^{III},Mg^{II})-LDHs of similar layer composition.
303 The a parameter calculated by Elmoubarki et al. (2017) for a LDH [Fe^{III}_{0.27}Mg^{II}_{0.73}(OH)₂ – 3.108 Å]
304 is indeed equivalent to their experimentally determined value of 3.11 Å, and similar to the 3.109 Å a
305 unit-cell parameter of pyroaurite (Fe^{III}_{0.25}Mg^{II}_{0.75}(OH)₂ – ICDD #1-70-2150). In addition, the Fe
306 content refined independently for ferrian brucite from intensity distribution of its hkl reflections is
307 ~ 0.17, a content similar to that of the initial brucite suggesting that all / most of ferroan brucite initial
308 Fe^{II} was oxidized to Fe^{III}. The complete oxidation of Fe in ferrian brucite is supported further by the
309 consistency of Fe^{III}/Fe_{tot} ratios determined experimentally and calculated from quantitative phase
310 analysis for Runs #19 and #20 (Fig. S3 and Table S4, respectively). In addition, evolution of layer O
311 atomic coordinate (Table S3) and of in-plane unit-cell parameters in ferrian brucite compared to
312 ferroan brucite led to a significant shortening of the (Mg,Fe)-O bond length from ~ 2.13 Å in the
313 initial ferroan brucite to ~ 2.08 Å in ferrian brucite. The resulting increase in the Fe-O bond valence
314 calculated for Fe^{III}-O in ferrian brucite (0.418 v.u.) compared to Fe^{II}-O in ferroan brucite (0.348 v.u.)
315 is consistent with the sole presence of Fe^{III} in ferrian brucite (Fe^{III} receives 2.508 v.u. from the 6

316 surrounding O atoms), especially as Mg remains the dominant cation (~80%) in ferrian brucite, thus
317 preventing shortening further the average (Mg,Fe)-O bond length.

318 In this model, compensation of the increased positive charge induced by Fe^{II} oxidation was
319 assumed to be achieved by partial deprotonation of the structure, as proposed by Genin et al. (2006a)
320 for oxidized green rust, leading to a (Fe^{III}_yMg_{1-y})(OH_(1-y/2))₂ structural formula. Another alternative
321 for charge compensation is the creation of Mg octahedral vacancies. This alternative structure model
322 was assessed for ferrian brucite by refining the partial occupancy of a mixed [Fe_{0.17}Mg_w] octahedral
323 site for Run #03. The refined [Fe_{0.17}Mg_{0.80(2)}] average cationic composition of this site is ~ 1.0 and
324 supports the absence of octahedral vacancies. This alternative model was thus rejected and it was
325 concluded that deprotonation charge-compensates Fe^{II} oxidation in the initial ferroan brucite.

326 **3.4 Thermogravimetric analysis of ferroan brucite and ferrian brucite rich samples**

327 Evolution of sample mass as a function of temperature measured by TGA and its derivative
328 are displayed in Fig. 4 for ferroan brucite (synthesized from chloride salts) and for Runs #09 and #15
329 which both contained over 30 wt.% ferrian brucite (Table 1). Ferroan brucite exhibits two mass loss
330 events. The first one occurred below 461 K (Fig. 4A) which is interpreted as departure of physisorbed
331 water (6.2 wt.%), whereas a second mass loss of much higher amplitude occurred between 500 and
332 700 K and is interpreted as dehydroxylation of ferroan brucite (Reaction 2):



334 This temperature range of dehydroxylation is consistent with thermogravimetric data on
335 synthetic brucite, Mg(OH)₂, which was found to dehydroxylate in the 550 – 700 K range (Turner et
336 al. 1963; Klein et al. 2020).

337 In comparison, TGA analysis of reaction products shows a more limited mass loss (2.9 wt.%)
338 due to physisorbed water that may be related to the larger grain size (smaller surface area). An
339 additional mass loss (2.3 wt.%) is observed from 461 – 505 K (Fig. 4B and 4C). It is most likely
340 related to the dehydration of pyroaurite interlayers that contain H₂O in addition to CO₃²⁻ anions.

341 Indeed, based on 4.5 H₂O per formula unit, pyroaurite structural water represents 2.9 wt.% of the total
342 TGA weight loss (Run #15, calculated with 24.3 wt.% pyroaurite as given by Rietveld refinement).
343 In the reaction products, the main mass loss event was found to shift towards higher temperature
344 when the ferrian brucite content in the sample increased, from 660 K for the ferroan brucite starting
345 material up to 692 K for Run #15 (Fig. 4D). This event is expected to include the dehydroxylation of
346 both ferrian brucite / pyroaurite and of residual ferroan brucite. Dehydroxylation of pyroaurite and
347 ferrian brucite are expected to occur in the same temperature range since they have identical
348 octahedral layer composition. Coupled infrared spectroscopy indicated that CO₂ from pyroaurite was
349 also mostly released over this temperature range. The increase in the temperature of the main mass
350 loss event with respect to single-phase ferroan brucite could be related either to a grain size effect
351 with ferrian brucite and pyroaurite having larger grain size than starting (Mg_{0.8}Fe_{0.2})(OH)₂ and/or to
352 the valence modification in the octahedral layer due to the presence of trivalent Fe.

353 **3.5 Natural ferroan brucite from Oman**

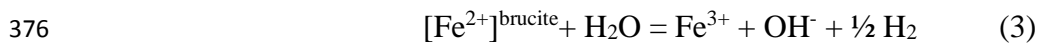
354 Powder diffraction patterns and Raman spectroscopy of natural serpentinite sample show the
355 presence of ferroan brucite and serpentine (Fig. 1B and S2B – Wadi Tayin massif, Samail ophiolite).
356 Ferrian brucite was not detected. The comparison between the powder diffraction patterns of the
357 synthetic product and that of ferroan brucite from the natural serpentinite sample shows that the lattice
358 parameters are the same and that diffraction peak widths are similar, indicative of crystallite sizes in
359 the order of 30 to 100 nm in the **ab** plane. Raman spectroscopy in the 3200-3800 cm⁻¹ range on the
360 natural sample reveals peaks similar to those observed for synthetic ferroan brucite but slightly shifted
361 at ~ 3594 cm⁻¹ for the broad peak and at ~ 3632 cm⁻¹ for the sharp peak (ν_1 O-H stretching band; Fig.
362 S2B). Using the relationship of Templeton and Ellison (2020), the position of this ν_1 O-H stretching
363 band indicates a x value of 0.287 ± 0.03 . This latter value is consistent with results from electron
364 microprobe analysis on the same sample yielding $x = 0.276$ (Malvoisin et al. 2020). SEM
365 characterization of both sample types confirmed the grain size derived from XRD data analysis.

366

367 4 Discussion

368 4.1 Magnetite and H₂ formation

369 When reacted in gold capsules that are known to be impermeable to H₂ below 623 K (Chou
370 1986), synthetic ferroan brucite only barely reacted and the identified run products were magnetite
371 (3.2(2) - 3.9(3) wt.% – Table 1), pyroaurite, and H₂. The amount of H₂ gas produced during Runs #17
372 and #18 ranged from 2.87 ± 0.46 to 8.49 ± 1.5 nanomoles leading to [H₂,aq] comprised between 28.7
373 ± 4.6 and 84.9 ± 15 μmol/L at 20 MPa and 378 K. This amount of H₂ recovered is three orders of
374 magnitude lower than expected if all the magnetite in the run products would have formed from
375 ferroan brucite oxidation according to the following equation:



377 Based on the magnetite content of Runs #19 and #20, for which the Fe^{III} content of the starting
378 ferroan-brucite material was analyzed, it can thus be concluded that magnetite mainly derived from
379 trivalent iron present in the starting material (~ 10% of Fe_{tot}).

380 4.2 Ferroan brucite oxidation to ferrian brucite and pyroaurite

381 The reaction of ferroan brucite in PTFE reactors mostly involved Fe^{II} oxidation to Fe^{III} and
382 the formation of ferrian brucite. As for the above experiments in sealed gold capsules (Runs #17 and
383 #18), ~ 3 - 4 wt.% of magnetite has formed, most likely from Fe^{III} present in the starting material (and
384 O₂ contamination). This Fe^{III} did not form hematite that could have been produced if more oxidizing
385 conditions had prevailed in the experimental setup. Similarly, lepidocrocite or goethite that are easily
386 formed in air from Fe(OH)₂ (Olowe and Génin 1991; Gilbert et al. 2008) were not detected.

387 The formation of ferrian brucite in PTFE reactor and its absence in experiments performed in
388 gold capsules at the same temperature, duration and absence of stirring, can be interpreted as
389 reflecting different RedOx conditions in the two setups. Whereas gold capsules are not permeable to
390 H₂ at the temperatures of the present experiments (378 – 403 K), PTFE reactors with a PTFE seal are
391 known to be more permeable to gases, and even to store gases in the PTFE macro-porosity (Vacher

392 et al. 2019). In PTFE reactors where significant outward H₂ diffusion and/or inward O₂ diffusion
393 cannot be avoided, RedOx conditions occurred to be favorable to the oxidation of Fe^{II} contained in
394 ferroan brucite layer to form ferrian brucite.

395 At 378 K, the ferroan brucite transformation to ferrian brucite seemed to follow zero-order
396 kinetics irrespective of the reaction medium, i.e., ultrapure degassed water or ferroan brucite synthesis
397 solution (Fig. 5). Magnetite and pyroaurite formed before ferrian brucite in the early stage of the
398 experiments in both aqueous media. Departure from zero-order kinetics of the ferroan-to-ferrian
399 brucite transformation in the first 3 days of experiments may thus be interpreted as the result of rapid
400 pyroaurite (and possibly magnetite) formation. This early transformation of ferroan brucite can be
401 considered as fast since it proceeded at the day scale at temperatures relevant to subsurface conditions.

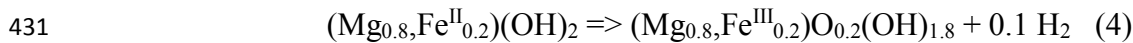
402 The amount of pyroaurite product appears to be proportional to the water-to-rock ratio
403 indicating that the main source of CO₂ is likely the CO₂ dissolved in the added solution (Table 1).
404 Indeed, CO₂ is highly soluble at elevated pH in NaOH solutions (Yoo et al. 2013 and references
405 therein). This strong partitioning of CO₂ into pyroaurite confirms the potential of this mineral as
406 efficient CO₂ sink in rocks or mine tailing containing Fe-brucite (e.g., Assima et al. 2014; Boschi et
407 al. 2017; Turvey et al. 2018). The low concentration (~ 2 wt.%) or even the absence of pyroaurite in
408 experiments performed in sealed gold-capsule where the highest H₂ pressure has been attained might
409 result from a combination of low water-to-rock ratio and of reducing conditions that hindered or
410 prevented the oxidation of Fe^{II} to Fe^{III} in ferroan brucite and the associated formation of pyroaurite
411 (Fe^{III},Mg)(OH)₂ octahedral layer.

412 **4.3 Transformation mechanisms of ferroan brucite into ferrian brucite**

413 The similarity between initial ferroan brucite and ferrian brucite product in terms of
414 constitutive crystallite sizes, suggests that changes affecting the octahedral layer remained limited to
415 Fe^{II} oxidation and to the induced partial deprotonation to compensate for the increased cationic
416 charge. This similarity and similar Fe/Mg ratios determined in ferroan and ferrian brucites both
417 indicate an isomorphic oxidation process. Rietveld refinement of ferrian brucite indicated little or no

418 octahedral vacancies, thus supporting deprotonation of the hydroxyl groups ($\text{Fe}^{2+} + \text{OH}^- = \text{Fe}^{3+} + \text{O}^{2-}$
 419) as the mechanism balancing the charge resulting from Fe^{II} oxidation in brucite octahedral layers.

420 Based on the phase proportions and their estimated standard deviations (esd) derived from
 421 Rietveld refinement and considering the following nominal compositions, $(\text{Mg}_{0.81}\text{Fe}^{\text{II}}_{0.19})(\text{OH})_2$,
 422 $(\text{Mg}_{0.83}\text{Fe}^{\text{III}}_{0.17})\text{O}_{0.17}(\text{OH})_{1.83}$ and $\text{Mg}_6\text{Fe}^{\text{III}}_2(\text{CO}_3)(\text{OH})_{16.4.5}\text{H}_2\text{O}$ for ferroan brucite, ferrian brucite
 423 and pyroaurite, respectively, a theoretical total mass loss (H_2O and CO_2) of 28.9(8) wt.% was
 424 calculated for Run #15. This prediction agrees well with the experimental total mass loss of Run #15
 425 which amounts to 27.2(2) wt.% after subtraction of the contribution of physisorbed water. For
 426 comparison, the alternative model which considers a ferrian brucite composition with octahedral
 427 vacancies, $(\text{Mg}_{0.76}\square_{0.08}\text{Fe}^{\text{III}}_{0.16})(\text{OH})_2$, would lead to a total mass loss of 30.6(8) wt.%. TGA data thus
 428 support further the deprotonation model to charge balance the presence of Fe^{III} in the octahedral sheets
 429 of ferrian brucite consistent with the Rietveld refinement of XRD data. The equation to describe the
 430 oxidation of ferroan brucite is thus most likely:



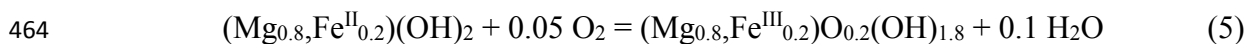
432 In the same chemical system, fougérite which belongs to the green rust mineral group also
 433 possesses a structure based on brucite-like octahedral sheets with interlayer water molecules and
 434 anion(s). The structural formula of fougérite is $[\text{Fe}^{\text{II}}_{1-z}\text{Fe}^{\text{III}}_z \text{Mg}_y(\text{OH})_{2+2y}]^{+z} [z/nA^{-n} \cdot m\text{H}_2\text{O}]^{-z}$ where A
 435 is the interlayer anion (OH^- , Cl^- , CO_3^{2-} , SO_4^{2-}) and n its valency (Trolard et al. 2007). The charge
 436 excess of the octahedral sheet is compensated for by the presence of interlayer anions. Génin et al.
 437 (2006b) consistently showed that the oxidation of synthetic (CO_3^{2-}) green rust can be achieved
 438 following the general substitution scheme $\text{Fe}^{\text{II}}_{6(1-z)}\text{Fe}^{\text{III}}_{6z}\text{O}_{12}\text{H}_{2(7-3z)}\text{CO}_3$ which involves charge
 439 compensation by progressive deprotonation.

440

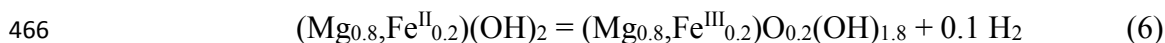
441 5 Implications

442 5.1 Ferrian brucite stability in the FeO-MgO-H₂O+/-O₂ system

443 The oxidation of $\text{Fe}(\text{OH})_2$ in air (high oxygen fugacity; $f\text{O}_2$) produces goethite, lepidocrocite,
444 or hematite ($\alpha\text{-FeOOH}$, $\gamma\text{-FeOOH}$, and $\alpha\text{-Fe}_2\text{O}_3$, respectively; Gilbert et al. 2008). The experiments
445 in gold capsules performed at 378 K confirmed that under low $f\text{O}_2$ conditions, H_2 is produced during
446 ferroan brucite oxidation. Under these conditions, the only oxidized reaction product was magnetite,
447 suggesting that reaction (1) led to H_2 production, even though the presence of trivalent iron in the
448 starting material also significantly contributed to magnetite formation (Ellison et al. 2021; Mayhew
449 et al. 2013; Miller et al. 2017). In the PTFE reactors, ferrian brucite was formed and the $f\text{O}_2$ was thus
450 intermediate between that of sealed gold capsules and air (intermediate $f\text{O}_2$). It cannot be concluded
451 at this stage whether ferrian brucite was a stable or a metastable phase. It can however be deduced
452 from its coexistence with magnetite observed in PTFE experiments that its stability/metastability field
453 should fall in a $f\text{O}_2$ range comprised between the stability fields of ferroan brucite and of hematite.
454 To confirm this statement, the thermodynamic properties of ferrian brucite, $(\text{Mg}_{1-x}, \text{Fe}^{\text{III}}_x)\text{O}_x(\text{OH})_{2-x}$,
455 were computed from a linear combination of the thermodynamic properties of goethite and brucite
456 with the slop16.dat database (Fig. 6). Obviously, such an approximation is fraught with uncertainty.
457 The effect of changing the Gibbs energy of formation (ΔG°_f) of ferrian brucite in the calculation by
458 ± 10 kJ/mol was thus considered. Within that range of ΔG°_f , the topology remains unchanged and
459 ferrian brucite is always found to occur at $f\text{O}_2$ comprised between those of ferroan brucite and
460 hematite stability fields (Fig. 6). However, the uncertainty on the thermodynamic parameters does
461 not allow to determine if O_2 or H_2 is the dominant gas species in the stability field of ferrian brucite
462 (Fig. 6). It is thus still unclear whether ferrian brucite formed in PTFE-lined reactors at the expense
463 of ferroan brucite by consuming O_2 or by producing H_2 , according to one of the following reactions:



465 or



467 One should note that Tosca et al. (2008) observed H₂ production during Fe(OH)₂ conversion into
468 green rust-CO₃, which, as shown above, shares crystallographic properties with ferrian brucite.
469 Additional experiments in the FeO-MgO-H₂O+/-O₂ system are still needed to constrain the exact
470 range of *f*O₂-T conditions under which ferrian brucite may be expected to occur in nature.

471 **5.2 Ferroan brucite oxidation kinetics**

472 Mineral replacement reactions generally proceed through dissolution and precipitation which are
473 mineral-surface dependent leading to non-constant replacement rates (Putnis 2002; Malvoisin et al.
474 2012). The conversion from ferroan to ferrian brucite appeared here to follow zero-order kinetics,
475 indicating that reaction rate is not controlled by this common dissolution-precipitation process. The
476 fact that ferrian brucite is likely stable at relatively low H₂ partial pressure (Fig. 6) implies that
477 Reaction (6) cannot reach large extent in closed system. H₂ partial pressure should indeed remain low
478 to maintain the system in the stability field of ferrian brucite. Large reaction extents as those observed
479 here (e.g., > 75%) would thus require extraction of at least part of the H₂ produced according to
480 Reaction (6). As a result, ferroan to ferrian brucite conversion was likely controlled by the rate of H₂
481 permeation through the PTFE reactor. This latter rate is expected to be constant (and the reaction
482 kinetics of zero order) if H₂ permeates into an infinite gas reservoir, which is a reasonable
483 approximation for the room in which the experiments were conducted. A symmetrical scenario
484 involving atmospheric O₂ permeation into the reactor would yield similar results and cannot be ruled
485 out at this stage to account for ferrian brucite formation.

486 This being said, ferroan brucite oxidation into ferrian brucite and/or pyroaurite revealed to be
487 remarkably fast even at temperatures as low as 378 K. Indeed, about half of the starting ferroan brucite
488 converted into ferrian brucite after 15 days and more than 90% reacted after 36 days (Table 1). Ferrian
489 brucite and pyroaurite (like other LDH containing different anions) are based on the same structural
490 arrangement composed of brucite-like octahedral layers. They actually differ only in the way
491 octahedral Fe^{III} is charge balanced: incorporation of an interlayer anion (CO₃²⁻, Cl⁻, SO₄²⁻) group or
492 partial deprotonation of the brucite-like layer, respectively. The fact that these two charge-balance

493 mechanisms do not involve recrystallization of the octahedral layer might explain why they are
494 effective at a temperature as low as 378 K and on a day – week timescale (Fig. 5).

495 Although ferrian brucite may well no be a stable phase in the FeO-MgO-H₂O+/-O₂ system,
496 the relatively fast transformation of ferroan into ferrian brucite makes the latter a likely metastable
497 state in the ferroan brucite reaction process into Fe(III)-bearing oxides/hydroxides according to
498 Ostwald's rule of stages. It must be noted that deprotonation coupled to iron oxidation in brucite
499 layers is also relevant to clay minerals such as smectite (Drits and Manceau 2000; Manceau et al.
500 2000). Interestingly, this process was found to occur in soils at a relative short timescale of several
501 months.

502 **5.3 Why ferrian brucite has never been reported in ophiolites?**

503 The reddish color and chemical analyses of brucite in some natural samples indicate ferroan
504 brucite oxidation (Beard and Hopkinson 2000; Beard and Frost 2016; Ellison et al. 2021). However,
505 the presence of ferrian brucite was not confirmed by mineralogical analysis and ferric
506 (oxyhydr)oxides could lead to the same characteristics. The ubiquitous presence of anions in natural
507 fluids (e.g., seawater, meteoric waters) likely favors the formation of green rust group minerals over
508 that of ferrian brucite. In addition to pyroaurite discussed above, iowaite (Mg₆Fe^{III}₂Cl₂(OH)₁₆·4H₂O;
509 Kohls and Rodda 1967) is another LDH reported in serpentized peridotites (Heling and Schwarz
510 1992; Gibson et al. 1996; Bach et al. 2004; D'Antonio and Kristensen 2004; Sharp and Barnes 2004;
511 Moll et al. 2007; Bonifacie et al. 2008; Kodolányi and Pettke 2011; Kodolányi et al. 2012; Albers et
512 al. 2020). It occurs in samples collected at mid-ocean ridges, on passive margins and in ophiolites
513 where it is generally associated at the submicrometer scale with ferroan brucite (Klein et al. 2020).
514 Heling and Schwarz (1992) proposed that iowaite forms from brucite with iron oxidation charge-
515 balanced by interlayer Cl⁻. This reaction is thought to occur under the oxidizing conditions associated
516 to weathering at low temperature (Bach et al. 2004). However, methane was reported in seamounts
517 where iowaite was found (Heling and Schwarz 1992), suggesting that iowaite formation, similarly to
518 ferrian brucite formation in the experiments reported here, does not necessarily involve oxidizing

519 conditions. Similarly, Génin et al. (2006b) and Ruby et al. (2010) determined Eh-pH diagrams in
520 which naturally occurring green rust group minerals (mixed valence Fe^{II},Fe^{III} LDHs) are stable in the
521 same field as molecular hydrogen.

522

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526 **CRediT authorship contribution statement**

527 **William Carlin:** Methodology, Investigation, Data Curation, Writing – Original Draft,
528 Visualization. **Benjamin Malvoisin:** Conceptualization, Formal analysis, Writing – Original Draft,
529 Writing – Review & Editing, Supervision, Visualization. **Bruno Lanson:** Methodology, Software,
530 Investigation, Writing – Review & Editing, Visualization. **Fabrice Brunet:** Conceptualization,
531 Formal analysis, Writing – Original Draft, Writing – Review & Editing, Supervision. **Nathaniel**
532 **Findling:** Methodology, Software. **Martine Lanson:** Methodology, Investigation. **Valérie Magnin:**
533 Investigation. **Tiphaine Fargetton:** Review and Supervision. **Laurent Jeannin:** Review and
534 Supervision. **Olivier Lhote:** Project administration.

535 **Declaration of Competing Interest**

536 The authors declare no known competing financial interests or personal relationships that
537 could have appeared to influence the work reported in this article.

538 **Data availability**

539 The data presented in this study are available on request from the corresponding author.

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546 **References**

- 547 Abrajano, T.A., Sturchio, N.C., Kennedy, B.M., Lyon, G.L., Muehlenbachs, K., Bohlke, J.K., 1990.
548 Geochemistry of reduced gas related to serpentinization of the Zambales ophiolite,
549 Philippines. *Appl. Geochem.* 5, 625–630. [https://doi.org/10.1016/0883-2927\(90\)90060-I](https://doi.org/10.1016/0883-2927(90)90060-I)
- 550 Albers, E., Kahl, W.-A., Beyer, L., Bach, W., 2020. Variant across-forearc compositions of slab-
551 fluids recorded by serpentinites: Implications on the mobilization of FMEs from an active
552 subduction zone (Mariana forearc). *Lithos* 364–365, 105525.
553 <https://doi.org/10.1016/j.lithos.2020.105525>
- 554 Allmann, R., 1968. The crystal structure of pyroaurite. *Acta Crystallogr. B* 24, 972–977.
555 <https://doi.org/10.1107/S0567740868003511>
- 556 Aminoff, G., 1921. XXV. Über die Struktur des Magnesiumhydroxydes. *Z. Krist.-Cryst. Mater.* 56,
557 506–509. <https://doi.org/10.1524/zkri.1921.56.1.506>
- 558 Assima, G.P., Larachi, F., Molson, J., Beaudoin, G., 2014. Comparative study of five Québec
559 ultramafic mining residues for use in direct ambient carbon dioxide mineral sequestration.
560 *Chem. Eng. J.* 245, 56–64. <https://doi.org/10.1016/j.cej.2014.02.010>
- 561 Bach, W., Garrido, C.J., Paulick, H., Harvey, J., Rosner, M., 2004. Seawater-peridotite interactions:
562 First insights from ODP Leg 209, MAR 15°N. *Geochem. Geophys. Geosyst.* 5.
563 <https://doi.org/10.1029/2004GC000744>
- 564 Bach, W., Klein, F., 2009. The petrology of seafloor rodingites: Insights from geochemical reaction
565 path modeling. *Lithos* 112, 103–117. <https://doi.org/10.1016/j.lithos.2008.10.022>
- 566 Bach, W., Paulick, H., Garrido, C.J., Ildefonse, B., Meurer, W.P., Humphris, S.E., 2006. Unraveling
567 the sequence of serpentinization reactions: petrography, mineral chemistry, and petrophysics
568 of serpentinites from MAR 15°N (ODP Leg 209, Site 1274). *Geophys. Res. Lett.* 33, L13306.
569 <https://doi.org/10.1029/2006GL025681>
- 570 Beard, J.S., Frost, B.R., 2016. The stoichiometric effects of ferric iron substitutions in serpentine from
571 microprobe data. *Int. Geol. Rev.* 59, 541–547.
572 <https://doi.org/10.1080/00206814.2016.1197803>
- 573 Beard, J.S., Frost, B.R., Fryer, P., McCaig, A., Searle, R., Ildefonse, B., Zinin, P., Sharma, S.K., 2009.
574 Onset and progression of serpentinization and magnetite formation in olivine-rich troctolite
575 from IODP Hole U1309D. *J. Petrol.* 50, 387–403. <https://doi.org/10.1093/petrology/egp004>
- 576 Beard, J.S., Hopkinson, L., 2000. A fossil, serpentinization-related hydrothermal vent, Ocean Drilling
577 Program Leg 173, Site 1068 (Iberia abyssal plain): Some aspects of mineral and fluid
578 chemistry. *J. Geophys. Res.* 105, 16527–16539. <https://doi.org/10.1029/2000JB900073>
- 579 Bonifacie, M., Busigny, V., Mével, C., Philippot, P., Agrinier, P., Jendrzejewski, N., Scambelluri,
580 M., Javoy, M., 2008. Chlorine isotopic composition in seafloor serpentinites and high-
581 pressure metaperidotites. Insights into oceanic serpentinization and subduction processes.
582 *Geochim. Cosmochim. Ac.* 72, 126–139. <https://doi.org/10.1016/j.gca.2007.10.010>
- 583 Boschi, C., Dini, A., Baneschi, I., Bedini, F., Perchiazzi, N., Cavallo, A., 2017. Brucite-driven CO₂
584 uptake in serpentinized dunites (Ligurian Ophiolites, Montecastelli, Tuscany). *Lithos* 288–
585 289, 264–281. <https://doi.org/10.1016/j.lithos.2017.07.005>

- 586 Brindley, G.W., Kao, C.-C., 1984. Structural and IR relations among brucite-like divalent metal
587 hydroxides. *Phys. Chem. Miner.* 10, 187–191. <https://doi.org/10.1007/BF00311476>
- 588 Brown, I.D., 2009. Recent developments in the methods and applications of the bond valence model.
589 *Chem. Rev.* 109, 6858–6919. <https://doi.org/10.1021/cr900053k>
- 590 Brown, I.D., Altermatt, D., 1985. Bond-valence parameters obtained from a systematic analysis of
591 the Inorganic Crystal Structure Database. *Acta Crystallogr. B* 41, 244–247.
592 <https://doi.org/10.1107/S0108768185002063>
- 593 Brunet, F., Chopin, C., 1995. Bearthite, $\text{Ca}_2\text{Al}(\text{PO}_4)_2\text{OH}$: stability, thermodynamic properties and
594 phase relations. *Contr. Mineral. Petrol.* 121, 258–266. <https://doi.org/10.1007/BF02688241>
- 595 Chakoumakos, B.C., Loong, C.-K., Schultz, A.J., 1997. Low-Temperature Structure and Dynamics
596 of Brucite. *J. Phys. Chem. B* 101, 9458–9462. <https://doi.org/10.1021/jp972225a>
- 597 Chou, I.-M., 1986. Permeability of precious metals to hydrogen at 2kb total pressure and elevated
598 temperatures. *Am J Sci* 286, 638–658. <https://doi.org/10.2475/ajs.286.8.638>
- 599 Coveney, R., Goebel, E., Zeller, E., Dreschhoff, G., Angino, E., 1987. Serpentinization and the origin
600 of hydrogen gas in Kansas. *AAPG Bull.* 71, 39–48. [https://doi.org/10.1306/94886D3F-1704-
601 11D7-8645000102C1865D](https://doi.org/10.1306/94886D3F-1704-11D7-8645000102C1865D)
- 602 D'Antonio, M., Kristensen, M.B., 2004. Serpentine and brucite of ultramafic clasts from the South
603 Chamorro Seamount (Ocean Drilling Program Leg 195, Site 1200): inferences for the
604 serpentinization of the Mariana forearc mantle. *Mineral. Mag.* 68, 887–904.
605 <https://doi.org/10.1180/0026461046860229>
- 606 de Obeso, J.C., Kelemen, P.B., 2020. Major element mobility during serpentinization, oxidation and
607 weathering of mantle peridotite at low temperatures. *Phil. Trans. R. Soc. A* 378, 20180433.
608 <https://doi.org/10.1098/rsta.2018.0433>
- 609 Doebelin, N., Kleeberg, R., 2015. Profex : a graphical user interface for the Rietveld refinement
610 program BGMN. *J. Appl. Crystallogr.* 48, 1573–1580.
611 <https://doi.org/10.1107/S1600576715014685>
- 612 Drits, V.A., Manceau, A., 2000. A model for the mechanism of Fe^{3+} to Fe^{2+} reduction in dioctahedral
613 smectites. *Clay Clay Miner.* 48, 185–195. <https://doi.org/10.1346/CCMN.2000.0480204>
- 614 Ellison, E.T., Templeton, A.S., Zeigler, S.D., Mayhew, L.E., Kelemen, P.B., Matter, J.M., The Oman
615 Drilling Project Science Party, 2021. Low- temperature hydrogen formation during aqueous
616 alteration of serpentinized peridotite in the Samail ophiolite. *J. Geophys. Res. Solid Earth* 126.
617 <https://doi.org/10.1029/2021JB021981>
- 618 Elmoubarki, R., Mahjoubi, F.Z., Elhalil, A., Tounsadi, H., Abdennouri, M., Sadiq, M., Qourzal, S.,
619 Zouhri, A., Barka, N., 2017. Ni/Fe and Mg/Fe layered double hydroxides and their calcined
620 derivatives: preparation, characterization and application on textile dyes removal. *J. Mater.
621 Res. Technol.* 6, 271–283. <https://doi.org/10.1016/j.jmrt.2016.09.007>
- 622 Frost, B.R., Evans, K.A., Swapp, S.M., Beard, J.S., Mothersole, F.E., 2013. The process of
623 serpentinization in dunite from New Caledonia. *Lithos* 178, 24–39.
624 <https://doi.org/10.1016/j.lithos.2013.02.002>

- 625 Gagné, O.C., Hawthorne, F.C., 2015. Comprehensive derivation of bond-valence parameters for ion
626 pairs involving oxygen. *Acta Crystallogr. B* 71, 562–578.
627 <https://doi.org/10.1107/S2052520615016297>
- 628 Génin, J.-M.R., Ruby, C., Upadhyay, C., 2006a. Structure and thermodynamics of ferrous,
629 stoichiometric and ferric oxyhydroxycarbonate green rusts; redox flexibility and fougérite
630 mineral. *Solid State Sci.* 8, 1330–1343.
631 <https://doi.org/10.1016/j.solidstatesciences.2006.05.010>
- 632 Génin, J.-M.R., Ruby, C., Géhin, A., Refait, P., 2006b. Synthesis of green rusts by oxidation of
633 Fe(OH)₂, their products of oxidation and reduction of ferric oxyhydroxides; –pH Pourbaix
634 diagrams. *C. R. Geosci.* 338, 433–446. <https://doi.org/10.1016/j.crte.2006.04.004>
- 635 Gibson, I.L., Beslier, M.O., Cornen, G., Milliken, K.L., Seifert, K.E., 1996. Major-and trace-element
636 seawater alteration profiles in serpentinite formed during the development of the Iberia
637 Margin, Site 897. *Proceedings-Ocean Drilling Program Scientific Results* 149, 519–528.
- 638 Gilbert, F., Refait, P., Lévêque, F., Remazeilles, C., Conforto, E., 2008. Synthesis of goethite from
639 Fe(OH)₂ precipitates: Influence of Fe(II) concentration and stirring speed. *J. Phys. Chem.*
640 *Solids* 69, 2124–2130. <https://doi.org/10.1016/j.jpccs.2008.03.010>
- 641 Heling, D., Schwarz, A., 1992. Iowaite in serpentinite muds at Sites 778, 779, 780, and 784: a possible
642 cause for the low chlorinity of pore waters, in: *Proc. Ocean Drill. Prog., Sci. Results* 125, 313–
643 323. <https://doi.org/10.2973/odp.proc.sr.125.176.1992>
- 644 Herrera, L., Ruiz, P., Aguillon, J.C., Fehrmann, A., 2007. A new spectrophotometric method for the
645 determination of ferrous iron in the presence of ferric iron. *J. Chem. Technol. Biotechnol.* 44,
646 171–181. <https://doi.org/10.1002/jctb.280440302>
- 647 Jöns, N., Kahl, W.-A., Bach, W., 2017. Reaction-induced porosity and onset of low-temperature
648 carbonation in abyssal peridotites: Insights from 3D high-resolution microtomography. *Lithos*
649 268–271, 274–284. <https://doi.org/10.1016/j.lithos.2016.11.014>
- 650 Kelemen, P.B., Matter, J.M., Teagle, D.A.H., Coggon, J.A., Oman Drilling Science Team, 2020.
651 Oman Drilling Project: Scientific Drilling in the Samail Ophiolite, Sultanate of Oman.
652 *Proceedings of the Oman Drilling Project.* <https://doi.org/10.14379/OmanDP.proc.2020>.
- 653 Klein, F., Bach, W., Humphris, S.E., Kahl, W.-A., Jöns, N., Moskowitz, B., Berquo, T.S., 2014.
654 Magnetite in seafloor serpentinite--Some like it hot. *Geology* 42, 135–138.
655 <https://doi.org/10.1130/G35068.1>
- 656 Klein, F., Bach, W., Jöns, N., McCollom, T., Moskowitz, B., Berquó, T., 2009. Iron partitioning and
657 hydrogen generation during serpentinization of abyssal peridotites from 15°N on the Mid-
658 Atlantic ridge. *Geochim. Cosmochim. Ac.* 73, 6868–6893.
659 <https://doi.org/10.1016/j.gca.2009.08.021>
- 660 Klein, F., Bach, W., McCollom, T.M., 2013. Compositional controls on hydrogen generation during
661 serpentinization of ultramafic rocks. *Lithos* 178, 55–69.
662 <https://doi.org/10.1016/j.lithos.2013.03.008>
- 663 Klein, F., Humphris, S.E., Bach, W., 2020. Brucite formation and dissolution in oceanic serpentinite.
664 *Geochem. Persp. Lett.* 1–5. <https://doi.org/10.7185/geochemlet.2035>

- 665 Kodolányi, J., Pettke, T., 2011. Loss of trace elements from serpentinites during fluid-assisted
666 transformation of chrysotile to antigorite — An example from Guatemala. *Chem. Geol.* 284,
667 351–362. <https://doi.org/10.1016/j.chemgeo.2011.03.016>
- 668 Kodolányi, J., Pettke, T., Spandler, C., Kamber, B.S., Gméling, K., 2012. Geochemistry of ocean
669 floor and fore-arc serpentinites: constraints on the ultramafic input to subduction zones. *J.*
670 *Petrol.* 53, 235–270. <https://doi.org/10.1093/petrology/egr058>
- 671 Kohls, D.W., Rodda, J.L., 1967. Iowaite, a new hydrous magnesium hydroxide-ferric oxychloride
672 from the Precambrian of Iowa. *Am. Mineral.* 52, 1261–1271.
- 673 Malvoisin, B., 2015. Mass transfer in the oceanic lithosphere: Serpentinization is not isochemical.
674 *Earth Planet. Sc. Lett.* 430, 75–85. <https://doi.org/10.1016/j.epsl.2015.07.043>
- 675 Malvoisin, B., Auzende, A.-L., Kelemen, P.B., 2021. Nanostructure of serpentinisation products:
676 Importance for water transport and low-temperature alteration. *Earth Planet. Sc. Lett.* 576,
677 117212. <https://doi.org/10.1016/j.epsl.2021.117212>
- 678 Malvoisin, B., Brunet, F., Carlut, J., Montes-Hernandez, G., Findling, N., Lanson, M., Vidal, O.,
679 Bottero, J.-Y., Goffé, B., 2013. High-purity hydrogen gas from the reaction between BOF
680 steel slag and water in the 473–673 K range. *Int. J. Hydrogen Energ.* 38, 7382–7393.
681 <https://doi.org/10.1016/j.ijhydene.2013.03.163>
- 682 Malvoisin, B., Brunet, F., Carlut, J., Rouméjon, S., Cannat, M., 2012. Serpentinization of oceanic
683 peridotites: 2. Kinetics and processes of San Carlos olivine hydrothermal alteration. *J.*
684 *Geophys. Res.* 117. <https://doi.org/10.1029/2011JB008842>
- 685 Malvoisin, B., Zhang, C., Müntener, O., Baumgartner, L.P., Kelemen, P.B., Oman Drilling Project
686 Science Party, 2020. Measurement of volume change and mass transfer during
687 serpentinization: insights from the Oman drilling project. *J. Geophys. Res. Solid Earth* 125.
688 <https://doi.org/10.1029/2019JB018877>
- 689 Manceau, A., Lanson, B., Drits, V.A., Chateigner, D., Gates, W.P., Wu, J., Huo, D., Stucki, J.W.,
690 2000. Oxidation-reduction mechanism of iron in dioctahedral smectites: I. Crystal chemistry
691 of oxidized reference nontronites. *Am. Mineral.* 85, 133–152. [https://doi.org/10.2138/am-](https://doi.org/10.2138/am-2000-0114)
692 [2000-0114](https://doi.org/10.2138/am-2000-0114)
- 693 Mayhew, L.E., Ellison, E.T., Miller, H.M., Kelemen, P.B., Templeton, A.S., 2018. Iron
694 transformations during low temperature alteration of variably serpentinized rocks from the
695 Samail ophiolite, Oman. *Geochim. Cosmochim. Ac.* 222, 704–728,
696 <https://doi.org/10.1016/j.gca.2017.11.023>.
- 697 McCollom, T.M., Bach, W., 2009. Thermodynamic constraints on hydrogen generation during
698 serpentinization of ultramafic rocks. *Geochim. Cosmochim. Ac.* 73, 856–875.
699 <https://doi.org/10.1016/j.gca.2008.10.032>
- 700 Miller, H.M., Mayhew, L.E., Ellison, E.T., Kelemen, P., Kubo, M., Templeton, A.S., 2017. Low
701 temperature hydrogen production during experimental hydration of partially-serpentinized
702 dunite. *Geochim. Cosmochim. Ac.* 209, 161–183. <https://doi.org/10.1016/j.gca.2017.04.022>
- 703 Moll, M., Paulick, H., Suhr, G., Bach, W., 2007. Data report: microprobe analyses of primary phases
704 (olivine, pyroxene, and spinel) and alteration products (serpentine, iowaite, talc, magnetite,
705 and sulfides) in Holes 1268A, 1272A, and 1274A. In Kelemen, P.B., Kikawa, E., and Miller,

- 706 D.J. (Eds.), Proc. ODP, Sci. Results 209: College Station, TX (Ocean Drilling Program), 1–
707 13. <https://doi.org/10.2973/odp.proc.sr.209.003.2007>.
- 708 Myagkiy, A., Brunet, F., Popov, C., Krüger, R., Guimarães, H., Sousa, R. S., Charlet, L., Moretti, I.,
709 2020. H₂ dynamics in the soil of a H₂-emitting zone (São Francisco Basin, Brazil): Microbial
710 uptake quantification and reactive transport modelling. *Applied Geochemistry* 112, 104474.
711 <https://doi.org/10.1016/j.apgeochem.2019.104474>.
- 712 Neal, C., Stanger, G., 1983. Hydrogen generation from mantle source rocks in Oman. *Earth Planet.*
713 *Sc. Lett.* 66, 315–320. [https://doi.org/10.1016/0012-821X\(83\)90144-9](https://doi.org/10.1016/0012-821X(83)90144-9)
- 714 Olowe, A.A., Génin, J.M.R., 1991. The mechanism of oxidation of ferrous hydroxide in sulphated
715 aqueous media: Importance of the initial ratio of the reactants. *Corros. Sci.* 32, 965–984.
716 [https://doi.org/10.1016/0010-938X\(91\)90016-I](https://doi.org/10.1016/0010-938X(91)90016-I)
- 717 Pan, Z., Bártoová, B., LaGrange, T., Butorin, S.M., Hyatt, N.C., Stennett, M.C., Kvashnina, K.O.,
718 Bernier-Latmani, R., 2020. Nanoscale mechanism of UO₂ formation through uranium
719 reduction by magnetite. *Nat. Commun.* 11, 4001. [https://doi.org/10.1038/s41467-020-17795-](https://doi.org/10.1038/s41467-020-17795-0)
720 [0](https://doi.org/10.1038/s41467-020-17795-0)
- 721 Petersen, J.M., Zielinski, F.U., Pape, T., Seifert, R., Moraru, C., Amann, R., Hourdez, S., Girguis,
722 P.R., Wankel, S.D., Barbe, V., Pelletier, E., Fink, D., Borowski, C., Bach, W., Dubilier, N.,
723 2011. Hydrogen is an energy source for hydrothermal vent symbioses. *Nature* 476, 176–180.
724 <https://doi.org/10.1038/nature10325>
- 725 Putnis, A., 2002. Mineral replacement reactions: from macroscopic observations to microscopic
726 mechanisms. *Mineral. Mag.* 66, 689–708. <https://doi.org/10.1180/0026461026650056>
- 727 Ruby, C., Abdelmoula, M., Naille, S., Renard, A., Khare, V., Ona-Nguema, G., Morin, G., Génin, J.-
728 M.R., 2010. Oxidation modes and thermodynamics of FeII–III oxyhydroxycarbonate green
729 rust: Dissolution–precipitation versus in situ deprotonation. *Geochim. Cosmochim. Ac.* 74,
730 953–966. <https://doi.org/10.1016/j.gca.2009.10.030>
- 731 Schwarzenbach, E.M., Caddick, M.J., Beard, J.S., Bodnar, R.J., 2016. Serpentinization, element
732 transfer, and the progressive development of zoning in veins: evidence from a partially
733 serpentinized harzburgite. *Contrib. Mineral. Petrol.* 171, 5. [https://doi.org/10.1007/s00410-](https://doi.org/10.1007/s00410-015-1219-3)
734 [015-1219-3](https://doi.org/10.1007/s00410-015-1219-3)
- 735 Sharp, Z.D., Barnes, J.D., 2004. Water-soluble chlorides in massive seafloor serpentinites: a source
736 of chloride in subduction zones. *Earth Planet. Sc. Lett.* 226, 243–254.
737 <https://doi.org/10.1016/j.epsl.2004.06.016>
- 738 Takai, K., Gamo, T., Tsunogai, U., Nakayama, N., Hirayama, H., Nealson, K.H., Horikoshi, K., 2004.
739 Geochemical and microbiological evidence for a hydrogen-based, hyperthermophilic
740 subsurface lithoautotrophic microbial ecosystem (HyperSLiME) beneath an active deep-sea
741 hydrothermal field. *Extremophiles* 8, 269–282. <https://doi.org/10.1007/s00792-004-0386-3>
- 742 Templeton, A.S., Ellison, E.T., 2020. Formation and loss of metastable brucite: does Fe(II)-bearing
743 brucite support microbial activity in serpentinizing ecosystems? *Phil. Trans. R. Soc. A* 378,
744 20180423. <https://doi.org/10.1098/rsta.2018.0423>

- 745 Tosca, N.J., Ahmed, I.A.M., Tutolo, B.M., Ashpitel, A., Hurowitz, J.A., 2018. Magnetite authigenesis
746 and the warming of early Mars. *Nature Geosci.* 11, 635–639. [https://doi.org/10.1038/s41561-](https://doi.org/10.1038/s41561-018-0203-8)
747 [018-0203-8](https://doi.org/10.1038/s41561-018-0203-8)
- 748 Trolard, F., Bourrié, G., Abdelmoula, M., Refait, P., Feder, F., 2007. Fougérite, a new mineral of the
749 pyroaurite-iowaite group: description and crystal structure. *Clay Clay Miner.* 55, 323–334.
750 <https://doi.org/10.1346/CCMN.2007.0550308>
- 751 Turner, R.C., Hoffman, I., Chen, D., 1963. Thermogravimetry of the dehydration of Mg(OH)₂. *Can.*
752 *J. Chem.* 41, 243–251. <https://doi.org/10.1139/v63-039>
- 753 Turvey, C.C., Wilson, S.A., Hamilton, J.L., Tait, A.W., McCutcheon, J., Beinlich, A., Fallon, S.J.,
754 Dipple, G.M., Southam, G., 2018. Hydrotalcites and hydrated Mg-carbonates as carbon sinks
755 in serpentinite mineral wastes from the Woodsreef chrysotile mine, New South Wales,
756 Australia: Controls on carbonate mineralogy and efficiency of CO₂ air capture in mine
757 tailings. *Int. J. Greenh. Gas Con.* 79, 38–60. <https://doi.org/10.1016/j.ijggc.2018.09.015>
- 758 Vacher, L.G., Truche, L., Faure, F., Tissandier, L., Mosser-Ruck, R., Marrocchi, Y., 2019.
759 Deciphering the conditions of tochilinite and cronstedtite formation in CM chondrites from
760 low temperature hydrothermal experiments. *Meteorit. Planet. Sci.* 54, 1870–1889.
761 <https://doi.org/10.1111/maps.13317>
- 762 Yoo, M., Han, S.-J., Wee, J.-H., 2013. Carbon dioxide capture capacity of sodium hydroxide aqueous
763 solution. *J. Environ. Manage.* 114. <https://doi.org/10.1016/j.jenvman.2012.10.061>
- 764

Figure captions

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767 **Fig. 1.** X-ray diffraction patterns of ferroan brucite ($\text{CuK}\alpha$ radiation). (A) Synthetic product
768 obtained by precipitation of chloride salts. (B) Natural sample from the Oman ophiolite (B). The
769 main Bragg's reflexions of ferroan brucite are marked with vertical dashed lines. S: serpentine
770 minerals.

771 **Fig. 2.** Back-scattered electron micrographs of the starting material and reaction products. A and B:
772 Starting material where ferroan brucite occurs as ~ 50 to 100 nm wide platelets. C: Reaction
773 product from PTFE reactor (Run # 15) showing ~ 400 nm wide platelets composed of the
774 aggregation of smaller crystallites. (D) Nanometric euhedral magnetite precipitating at the surface
775 of platelets (Run #15). mag: magnetite.

776 **Fig. 3.** X-ray diffraction patterns ($\text{CuK}\alpha$) of ferroan brucite reaction products (PTFE reactors)
777 displayed from bottom to top with increasing run duration. A: Full XRD patterns with labeled phases;
778 B: Enlargement of $[36 - 40^\circ]$ 2-theta region to emphasize the shift of the (101) reflexion of ferroan
779 brucite as the result of iron oxidation. Bragg's reflexions of ferroan and ferrian brucites are marked
780 with vertical dashed lines and vertical long-dashed lines, respectively. Phase names as in Table 1.
781 From bottom to top, XRD patterns correspond to ferroan brucite starting material followed by the
782 powder XRD of Runs #06 to #10 (Table 1).

783 **Fig. 4.** Thermogravimetric analysis of the ferroan brucite starting material and of two ferrian brucite
784 rich samples. (A) Synthetic ferroan brucite weight loss during thermogravimetric analysis (solid line).
785 From ambient to 461 K, physisorbed water is mainly released. (B) Ferrian brucite rich sample (Run
786 #15) weight loss during thermogravimetric analysis (dotted-dashed line). Weight loss between 461
787 and 505 K could be attributed to pyroaurite structural (interlayer) water loss. (C) Comparison of TGA
788 data for starting material (solid line) and reaction products from Runs #09 (dashed line) and #15
789 (dotted-dashed line). (D) Weight loss first derivative (smoothed with sliding mean method) for

790 starting material (solid line) and reaction products from Runs #09 (dashed line) and #15 (dotted-
791 dashed line). Heating rate: 10 K/min. For C and D, light grey zones indicate the temperature ranges
792 where evolved CO₂ has been detected. TGA data up to 1273 K have been collected on Run #15 and
793 no significant mass loss was observed above 873 K.

794 **Fig. 5.** Time evolution of phase proportions at 378 K as determined using quantitative phase analysis
795 on the reaction products. Black lines: Runs #06 to #10 (ferroan brucite synthesized from Cl-solutions
796 and reacted with ultrapure degassed water); Grey lines: Runs #01 to #03 (ferroan brucite synthesized
797 with SO₄-solution and reacted in the synthesis solution). Abbreviations: Fe^{II}-brc: ferroan brucite; pyr:
798 pyroaurite; mag: magnetite; Fe^{III}-brc: ferrian brucite.

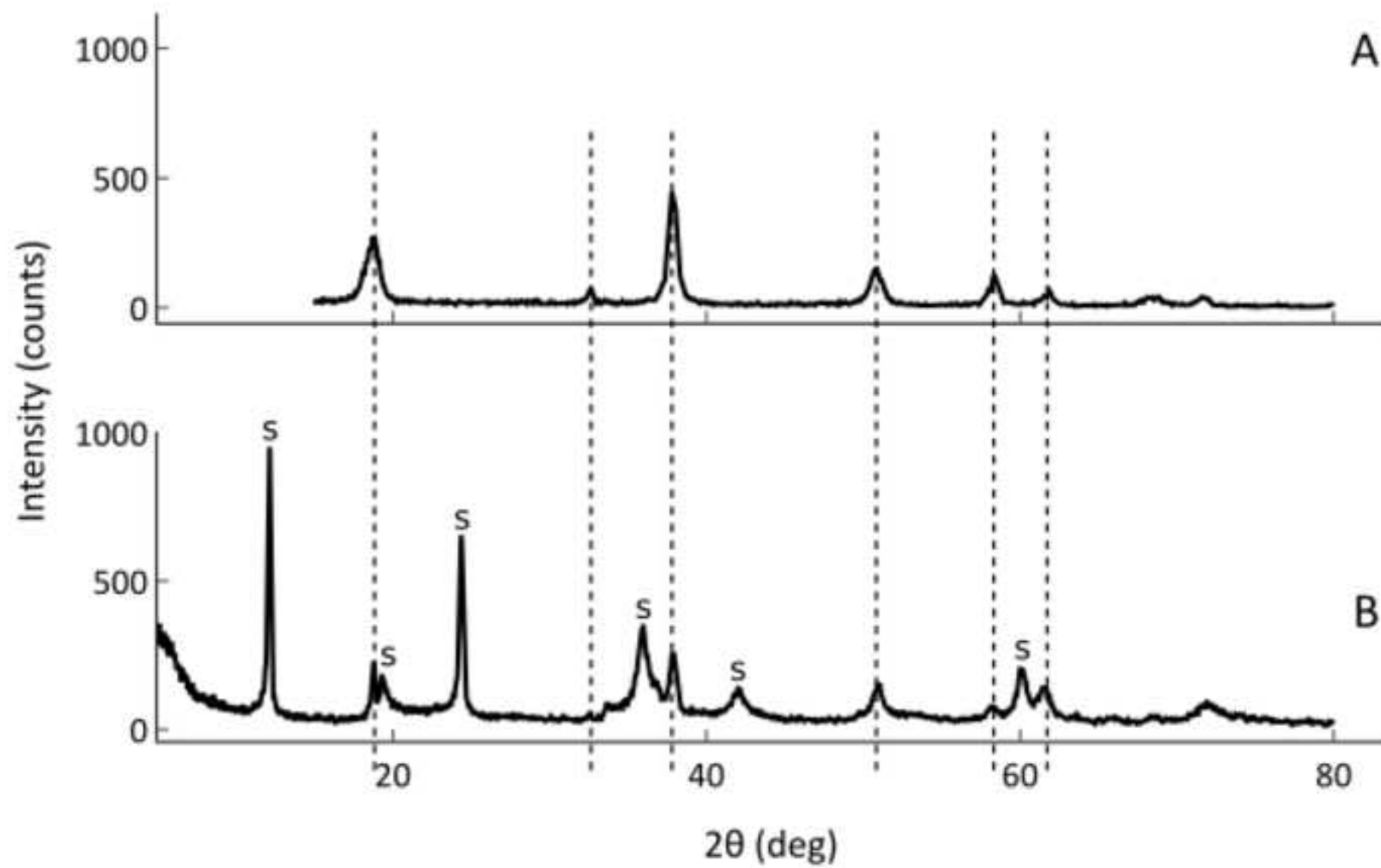
799 **Fig. 6.** Eh-pH Pourbaix diagram of iron phases in a Mg-bearing aqueous system ($a_{Mg^{2+}} = 10^{-3}$ mol/L)
800 at 378 K. The stability fields of ferroan and ferrian brucite are displayed for $x = 0.2$ by considering
801 ideal solid solutions. Computations were performed with the slop16.dat database
802 (<https://gitlab.com/ENKI-portal/geopig/-/blob/master/slop/slop16.dat>) and the properties for
803 Fe(OH)₂ given in Klein et al. (2013). Diagrams were computed by excluding ferrian brucite (solid
804 line), using a solid solution computed from goethite and brucite thermodynamic properties (dotted
805 line), and for Gibbs energy of formation 10 kJ/mol below (dashed line) and above (dashed-dotted
806 line) this latter solid solution.

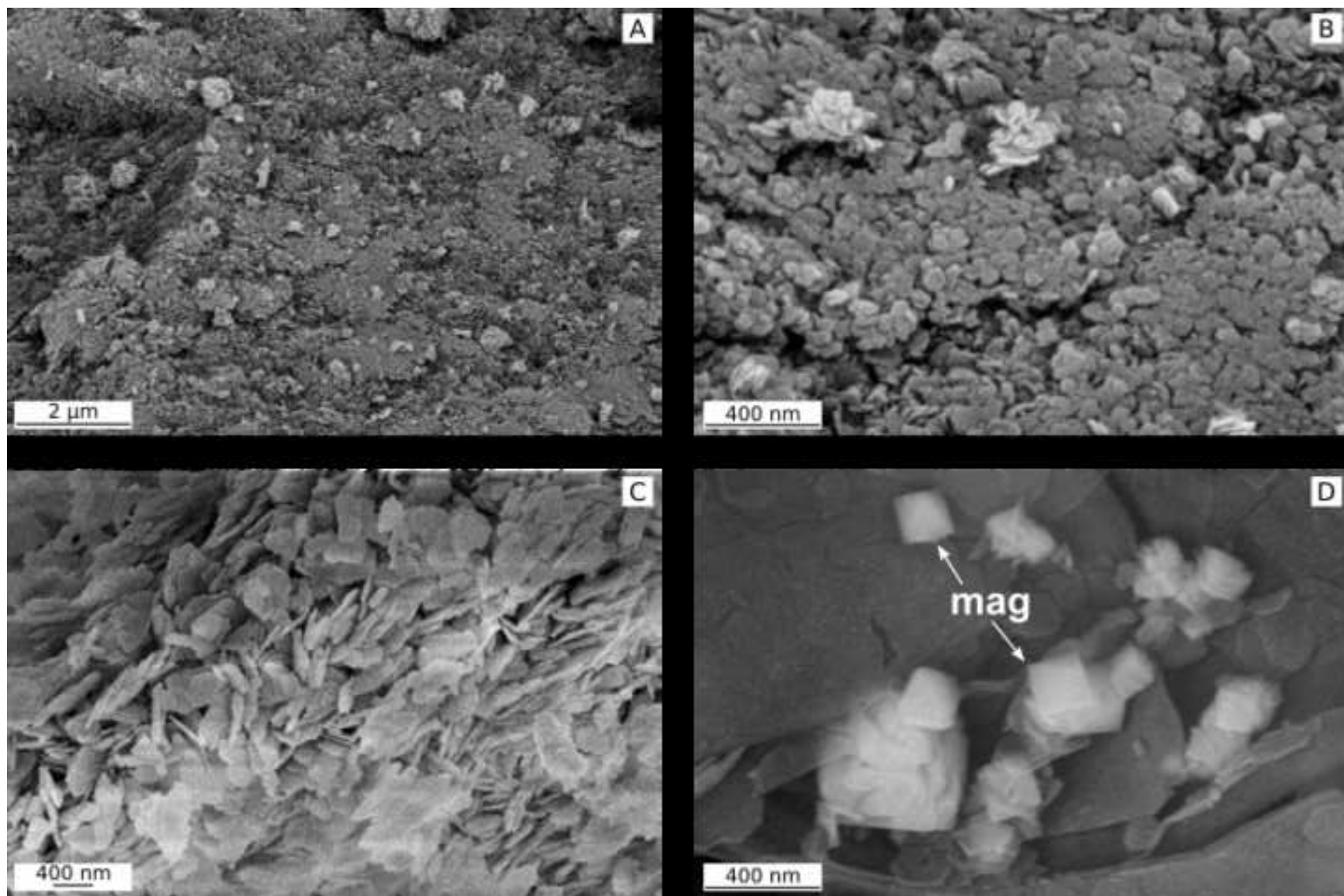
Highlights

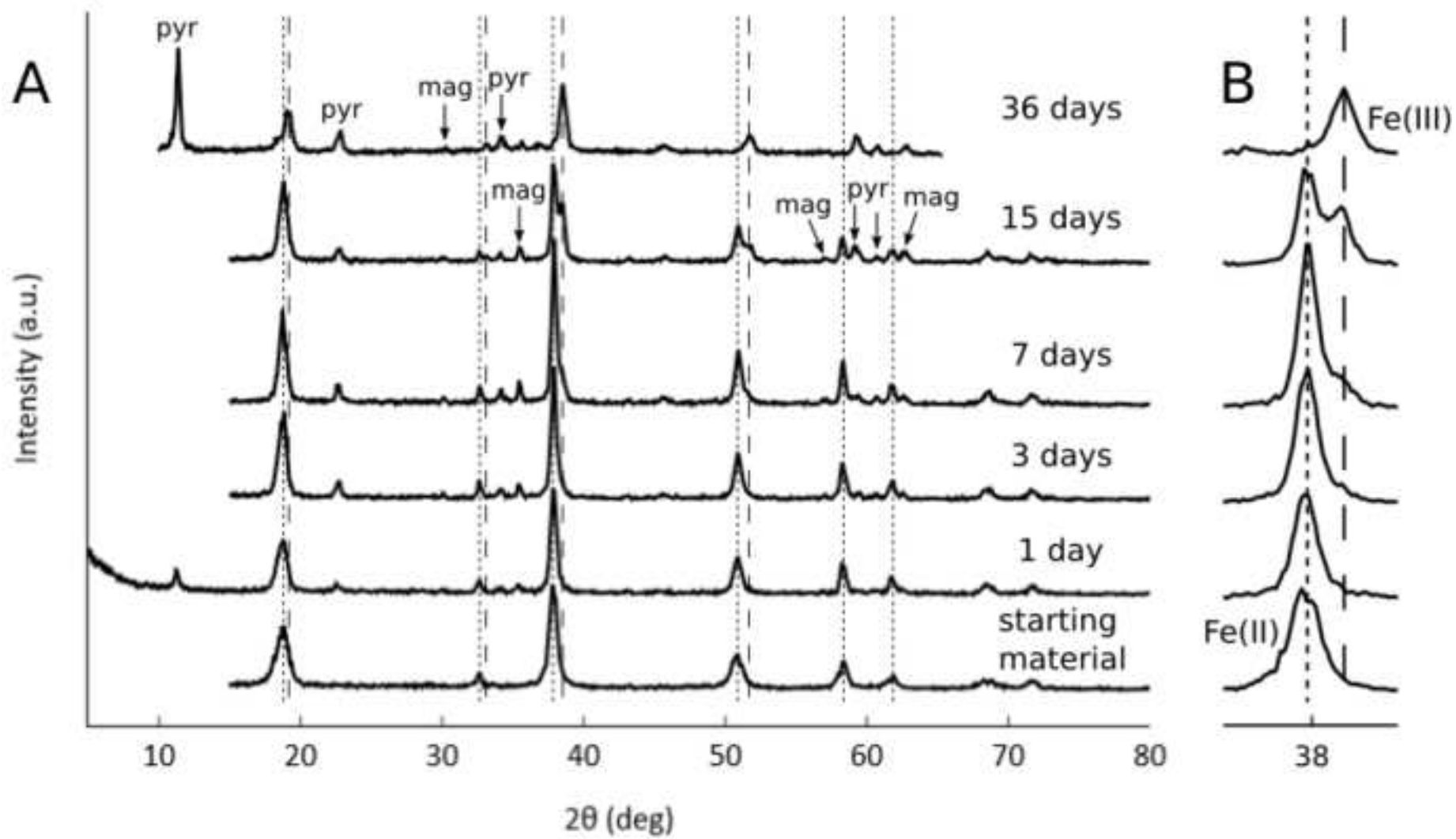
- Reaction of synthetic ferroan brucite, a serpentinization product, at temperatures below 403 K
- Ferrian brucite is formed from ferroan brucite oxidation under intermediate oxygen fugacity
- Ferrian brucite is isostructural to ferroan brucite and has the same Fe/Mg ratio
- Deprotonation of ferrian brucite layer is responsible for charge compensating Fe^{II} oxidation
- In the presence of common anions (Cl⁻, CO₃²⁻), LDHs are formed from ferroan brucite oxidation

Run number / name	Temperature (K)	Pressure (MPa)	Duration (days)	W/R	Ferroan brc (wt.%)	Pyr (wt.%)	Mag (wt.%)	Ferrian brc (wt.%)	Ferroan brc xFe (mol.%)	CSD (110) (nm)	Ferrian brc xFe (mol.%)	CSD (110) (nm)
starting material "FeBR_R0.4_S_2": salt type = SO4, ferroan brc with xFe = 21.6(3) and CSD (110) = 33(2) nm ; reactor: PTFE ; fluid: synthesis solution												
#01 / FeBR_R0.4_S_M105_8d	378	L/V	8	N.D.	89.9(8)	10.2(8)			21.7(2)	56(5)		
#02 / FeBR_R0.4_S_M105_15d	378	L/V	15	N.D.	63.8(13)	7.5(11)	0.9(2)	27.8(15)	23.5(4)	54(9)	27.8(15)	44(10)
#03 / FeBR_R0.4_S_M105_31d	378	L/V	31	N.D.	16.7(11)	8.0(15)	1.5(2)	73.8(17)	19.1(10)	57(24)	15.2(20)	51(5)
starting material "FeBR_R0.05_S": salt type = SO4, ferroan brc with xFe = 22.8(4) and CSD (110) = 33(5) nm ; reactor: PTFE ; fluid: synthesis solution												
#04 / FeBR_R0.05_S_M105_7d	378	L/V	7	N.D.	86.1(19)	0.4(1)	0.3(1)	13.3(19)	20.8(2)	62(7)	17	14(2)
#05 / FeBR_R0.05_S_M105_31d	378	L/V	31	N.D.	70.5(15)	0.3(3)	2.6(4)	26.7(15)	23.6(4)	41(5)	17	48(12)
starting material "FeBR_R0.4_Cl_2": salt type = Cl, ferroan brc with xFe = 17.4(4) and CSD (110) = 22(1) nm ; reactor: PTFE ; fluid: ultrapure degassed water												
#06 / FeBR_R0.4_Cl_1d	378	L/V	1	100	91.9(13)	6.0(13)	2.1(2)		16.6(4)	19(1)		
#07 / FeBR_R0.4_Cl_3d	378	L/V	3	100	80.4(14)	17.0(14)	2.6(2)		19.3(3)	61(10)		
#08 / FeBR_R0.4_Cl_7d	378	L/V	7	100	67.8(14)	17.3(14)	3.6(2)	11.3(10)	19.0(3)	95(22)	17	16(2)
#09 / FeBR_R0.4_Cl_15d	378	L/V	15	100	52.9(12)	13.5(16)	3.7(2)	29.9(11)	20.2(4)	71(17)	16.1(30)	40(5)
#10 / FeBR_R0.4_Cl_36d*	378	L/V	36	100	5.8(11)	30.6(14)	2.9(3)	60.7(17)	20	14(5)	19.3(36)	58(11)
starting material "FeBR_R0.05_Cl": salt type = Cl, ferroan brc with xFe = 19.4(3) and CSD (110) = 30(2) nm ; reactor: PTFE ; fluid: ultrapure degassed water												
#11 / FeBR_R0.05_Cl_1d	403	L/V	1	100	77.6(8)	19.8(8)	2.6(2)		20.1(3)	68(10)		
#12 / FeBR_R0.05_Cl_3d	403	L/V	3	100	72.8(8)	24.0(8)	3.2(3)		18.9(3)	60(8)		
#13 / FeBR_R0.05_Cl_7d	403	L/V	7	100	75.4(7)	19.6(7)	4.0(2)	1.0(3)	18.1(2)	76(12)	17	
#14 / FeBR_R0.05_Cl_15d	403	L/V	15	100	59.4(8)	22.9(6)	3.8(2)	13.9(9)	17.5(2)	104(23)	17	23(3)
#15 / FeBR_R0.05_Cl_31d	403	L/V	31	100	22.8(9)	24.3(7)	3.8(2)	49.4(10)	19.3(6)	31(4)	17.1(25)	105(24)
#16 / FeBR_R0.05_Cl_w-r25_3d	403	L/V	3	25	90.0(6)	7.0(5)	3.0(2)		18.8(3)	41(5)		
starting material "FeBR_R0.4_Cl_7_centrifugation": salt type = Cl, ferroan brc with xFe = 16.2(4) and CSD (110) = 24(2) nm ; reactor: gold capsule ; fluid: ultrapure degassed water												
#17 / FeBR_R0.4_Cl_caps1_105deg_15d	378	20	15	3.13	91.5(19)	5.4(19)	3.2(2)		11.0(4)	44(3)		
#18 / FeBR_R0.4_Cl_caps2_105deg_26d	378	20	26	3.23	95.7(4)	0.4(3)	3.9(3)		13.3(6)	16(1)		
starting material "FeBR_R0.4_Cl_10": salt type = Cl, ferroan brc with xFe = 19.1(5) and CSD (110) = 17.1(8) nm ; reactor: PTFE ; fluid: ultrapure degassed water												
#19 / FeBR_R0.4_Cl_10_32d	378	L/V	32	100	9.5(15)	16.6(9)	5.9(4)	68.0(18)	20		13.9(32)	53(10)
starting material "FeBR_R0.4_Cl_11": salt type = Cl, ferroan brc with xFe = 20.5(4) and CSD (110) = 17.9(8) nm ; reactor: PTFE ; fluid: ultrapure degassed water												
#20 / FeBR_R0.4_Cl_11_32d	378	L/V	32	100	17.8(4)	10.3(7)	4.2(3)	67.7(16)	19.3(12)	46(17)	18.0(28)	38(4)

Table 1. List of all experiments sorted by starting material and experimental setup. Mass proportions, xFe and grain sizes are inferred from Rietveld refinement. Numbers in parentheses are standard deviations associated with the refinement. W/R: water to rock ratio ; Ferroan brc: brucite containing Fe(II) ; Pyr: pyroaurite ; Mag: magnetite ; Ferrian brc: brucite containing Fe(III) ; xFe = Fetot/Fetot+Mg ; SO₄ : sulfate salts used for ferroan brucite synthesis ; Cl : chloride salts used for ferroan brucite synthesis ; R : see text ; * : starting material "FeBR_R0.4_Cl_5": salt type = Cl, ferroan brc with x = 23.1(6) and CSD (110) = 14(1) nm







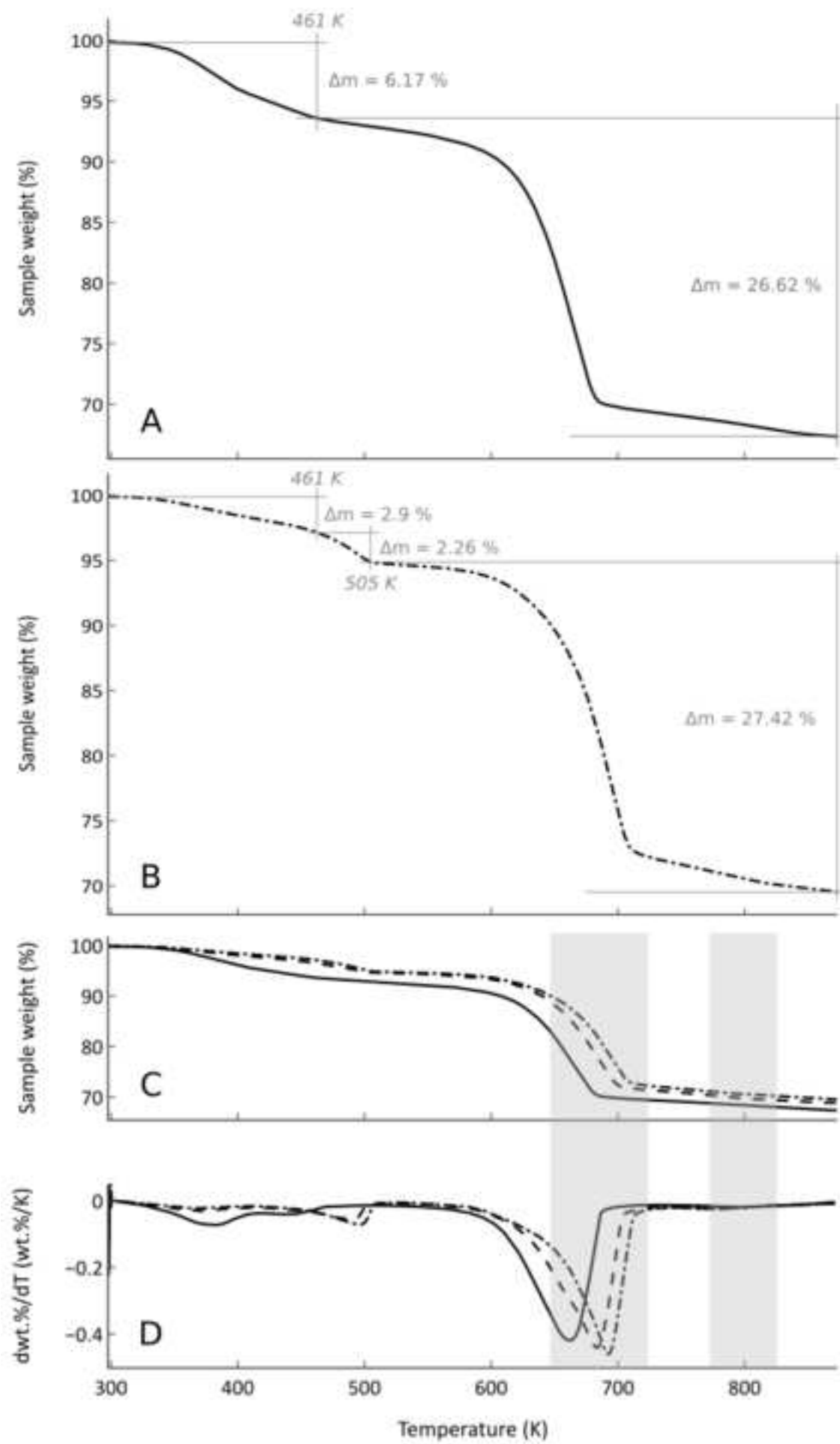


Figure 5

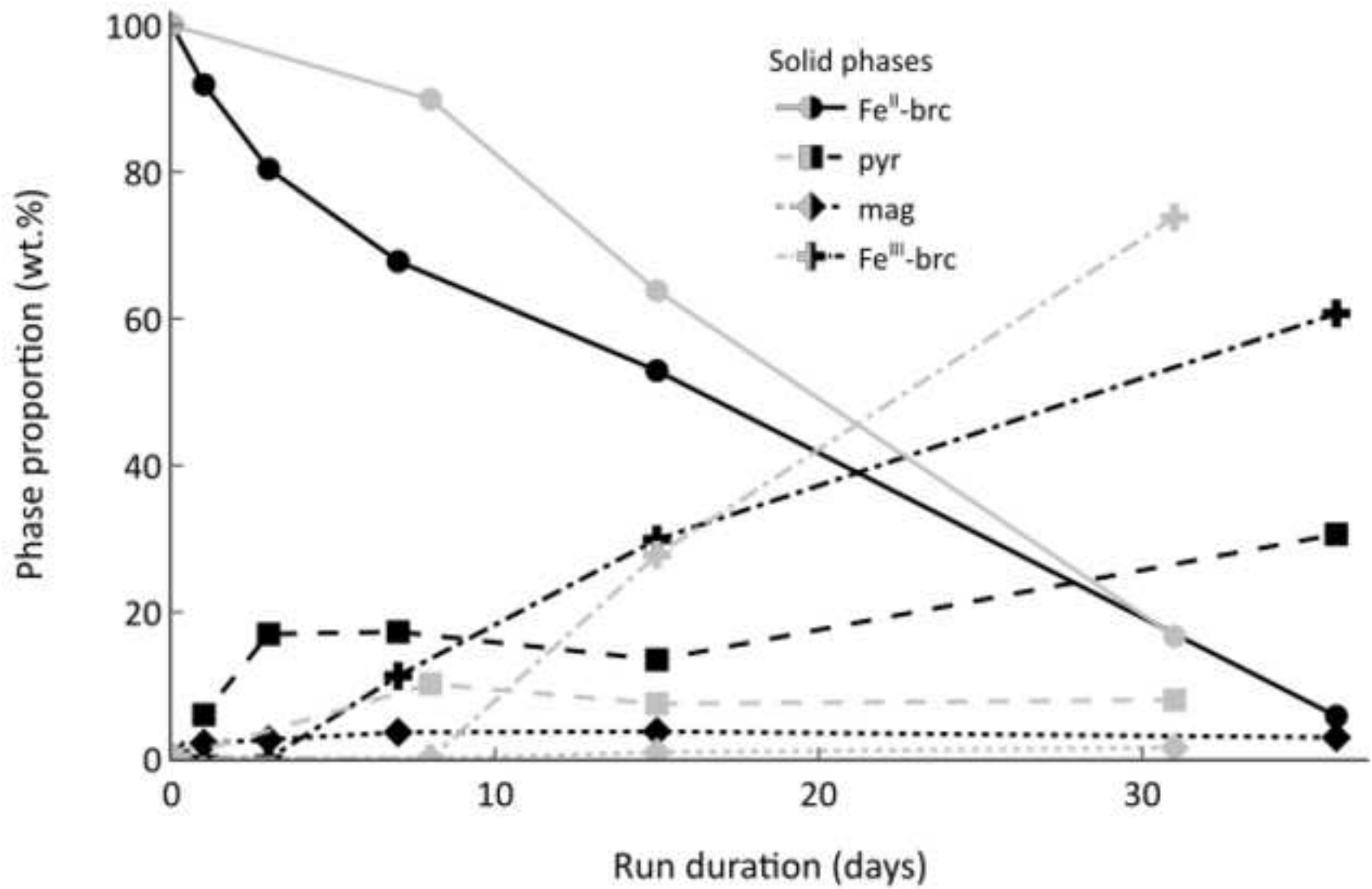
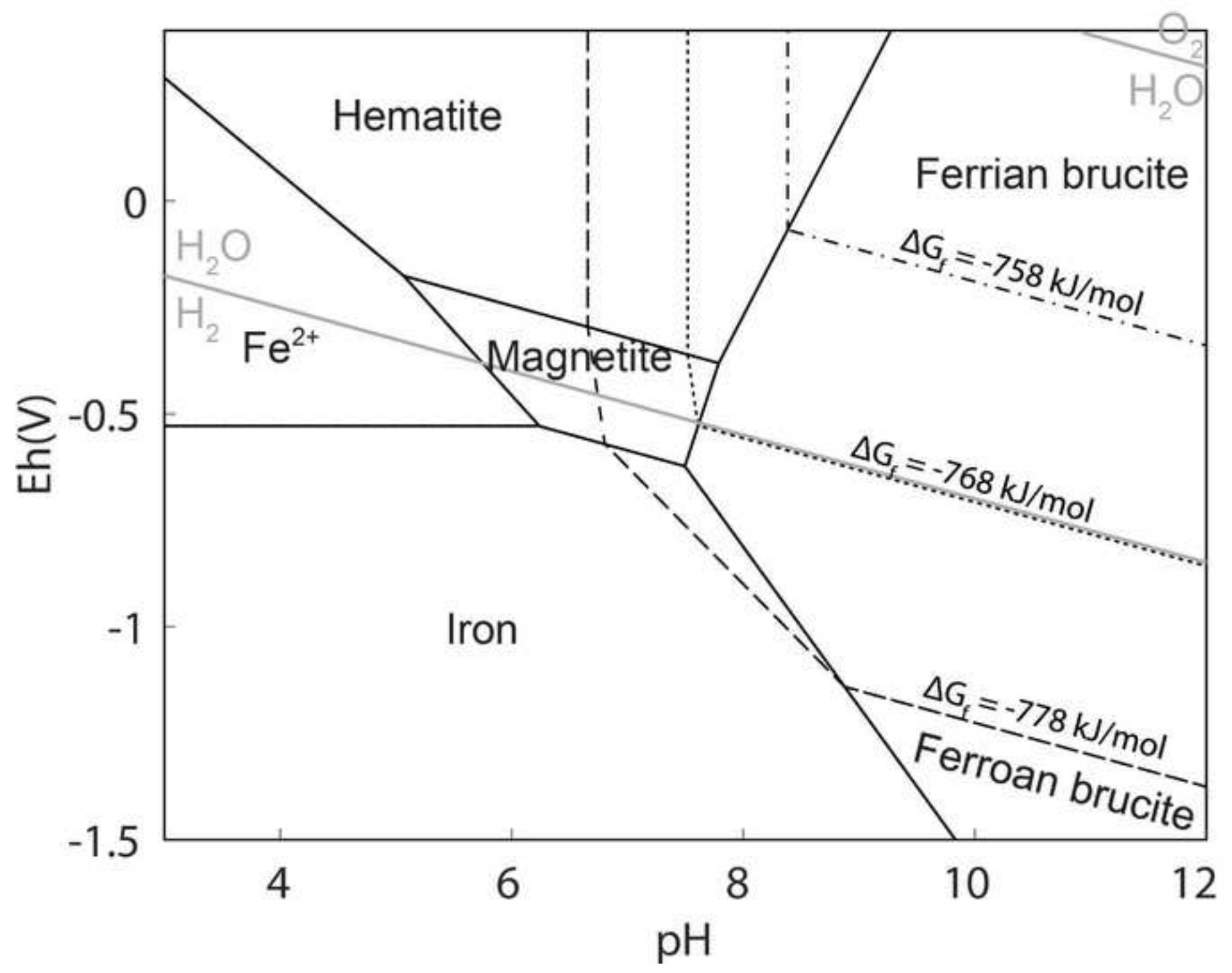


Figure 6



1 **Fe^{III}-substituted brucite: hydrothermal synthesis from (Mg_{0.8},Fe^{II}_{0.2})-brucite,**
2 **crystal chemistry and relevance to the alteration of ultramafic rocks**

3

4

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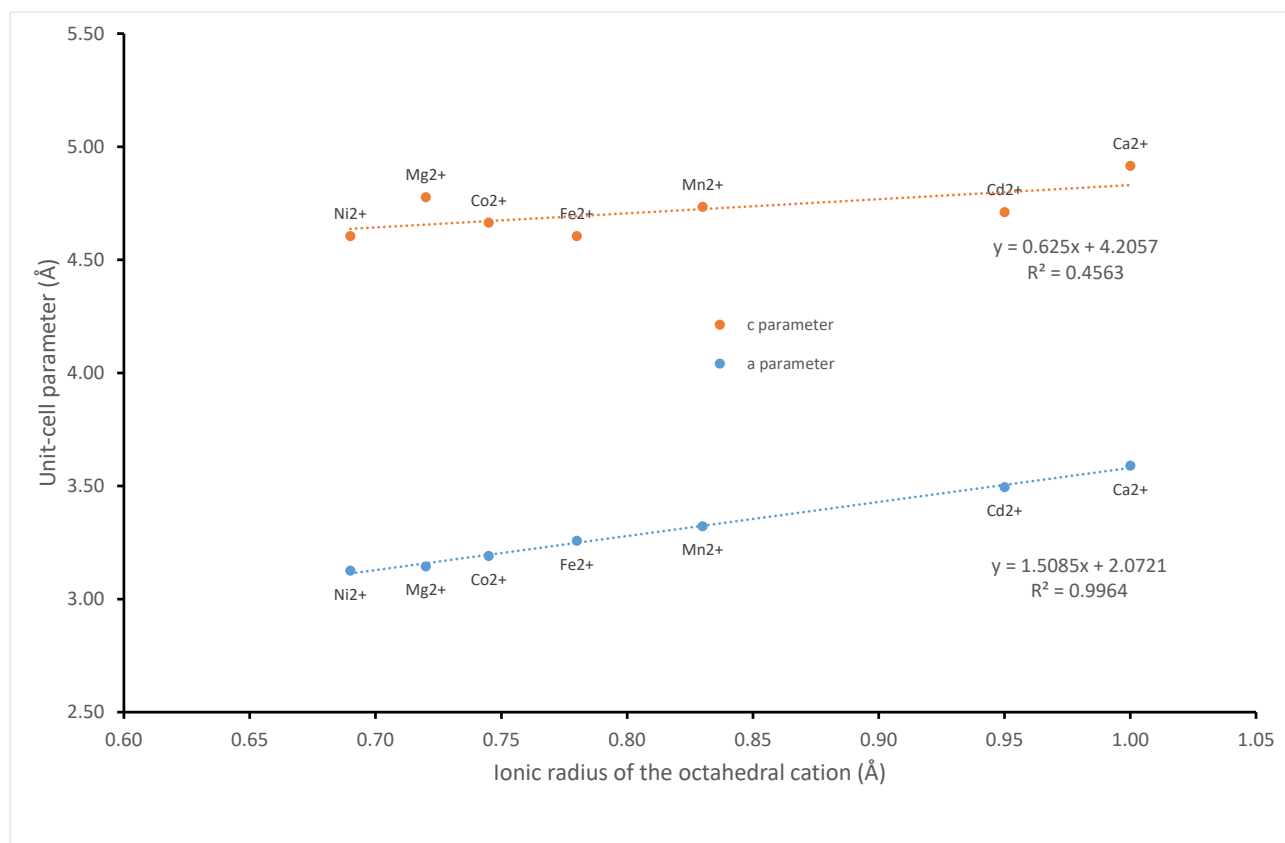
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Supplementary information

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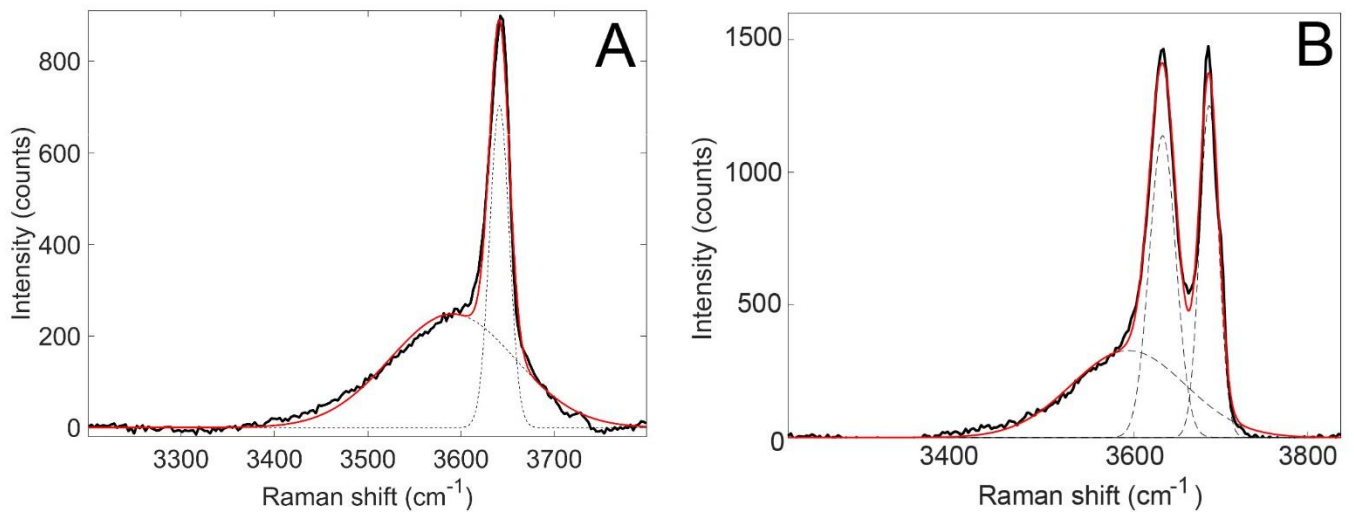
15 **Details for Rietveld refinements on ferroan and ferrian brucite**



16

17 **Fig. S1.** Evolution of in-plane *a* and out-of-plane *c* unit-cell parameters in brucite-like structures as a
 18 function of the ionic radius of octahedral cation. Ionic radii from Shannon (1976). Unit-cell
 19 parameters from ICDD database: portlandite-Ca(OH)₂ #44-1481; Cd(OH)₂ #31-228; pyrochroite-
 20 Mn(OH)₂ #1-73-1133; β-Co(OH)₂ #30-443; brucite-Mg(OH)₂ #44-1482; theophrastite-Ni(OH)₂ #14-
 21 117; amakinite-Fe(OH)₂ from Wyckoff (1963).

22



23

24 **Fig. S2.** Raman spectra of (A) synthetic and (B) natural ferroan brucites. The spectra were fitted with
 25 Lorentzian functions (dashed lines), and their sum is displayed with the solid red curve. The peak at
 26 3641 cm^{-1} in A and at 3632 cm^{-1} in B was attributed to the ν_1 OH-stretching band of ferroan brucite.
 27 Its position is used to determine the Fe content of ferroan brucite (x) using the calibration of
 28 Templeton and Ellison (2020). The broad peak at $\sim 3590\text{ cm}^{-1}$ was attributed to ferroan brucite
 29 oxidation in air during measurement. **A.** Synthetic ferroan brucite (sample FeBR_R0.4_Cl_11) for
 30 which $x = 0.17 \pm 0.05$ (from Raman spectroscopy). **B.** Oman sample BA4A-81-1-1-17 for which $x =$
 31 0.287 ± 0.03 . The peak at 3686 cm^{-1} with a shoulder at 3700 cm^{-1} (Auzende et al., 2004) corresponds
 32 to lizardite that is intermixed with ferroan brucite at the submicrometer scale.

33

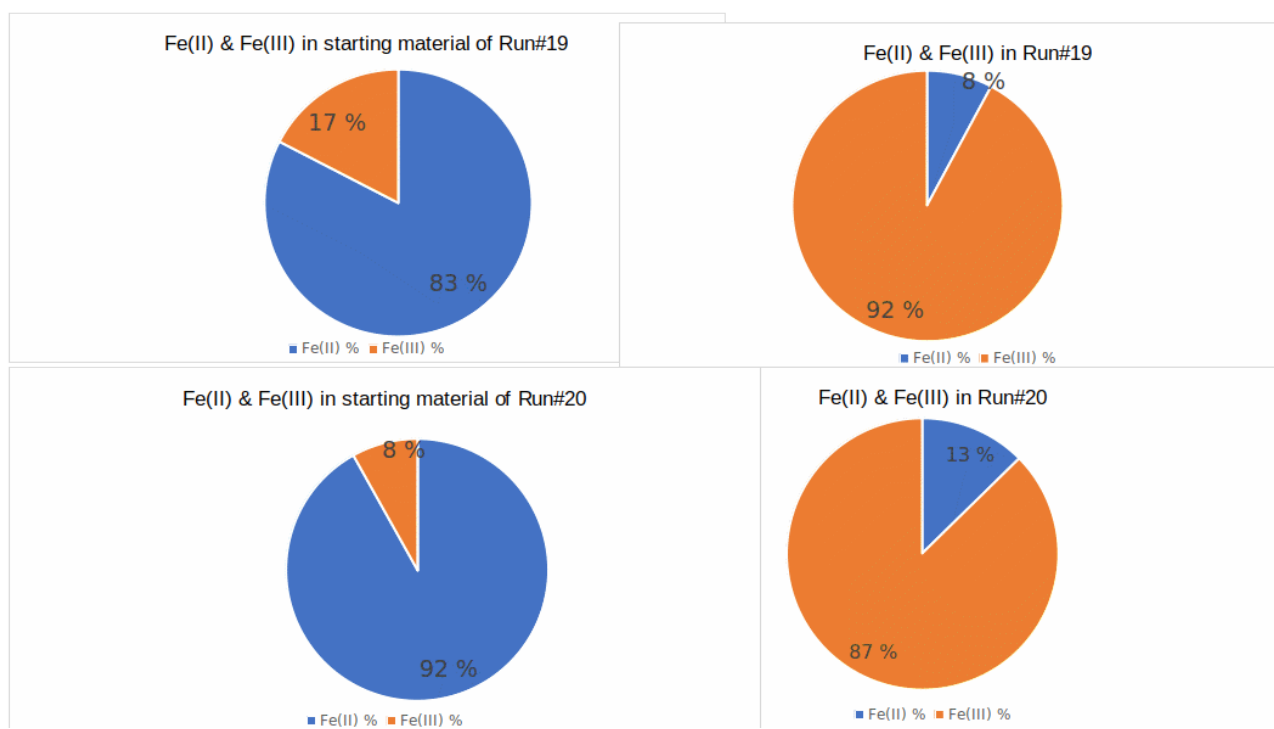
34 **Implications of the Fe^{III} and Fe^{II} determination performed on Runs #19 and #20**

35 Both starting material and reaction products of Runs #19 and #20 have been analyzed for their
36 Fe^{III} and Fe^{II} contents (Fig. S3). The starting material of Run #19 has been aged in the glove box until
37 a thin reddish film was visible. The Fe^{III} content of this starting material can thus be considered as an
38 upper bound. For comparison, the starting material of Run #20 has been prepared with the same care
39 with respect to O₂ contamination as all the other starting materials used in this study. Despite this
40 care, ~ 8 wt. % of Fe^{III} is present in the starting material.

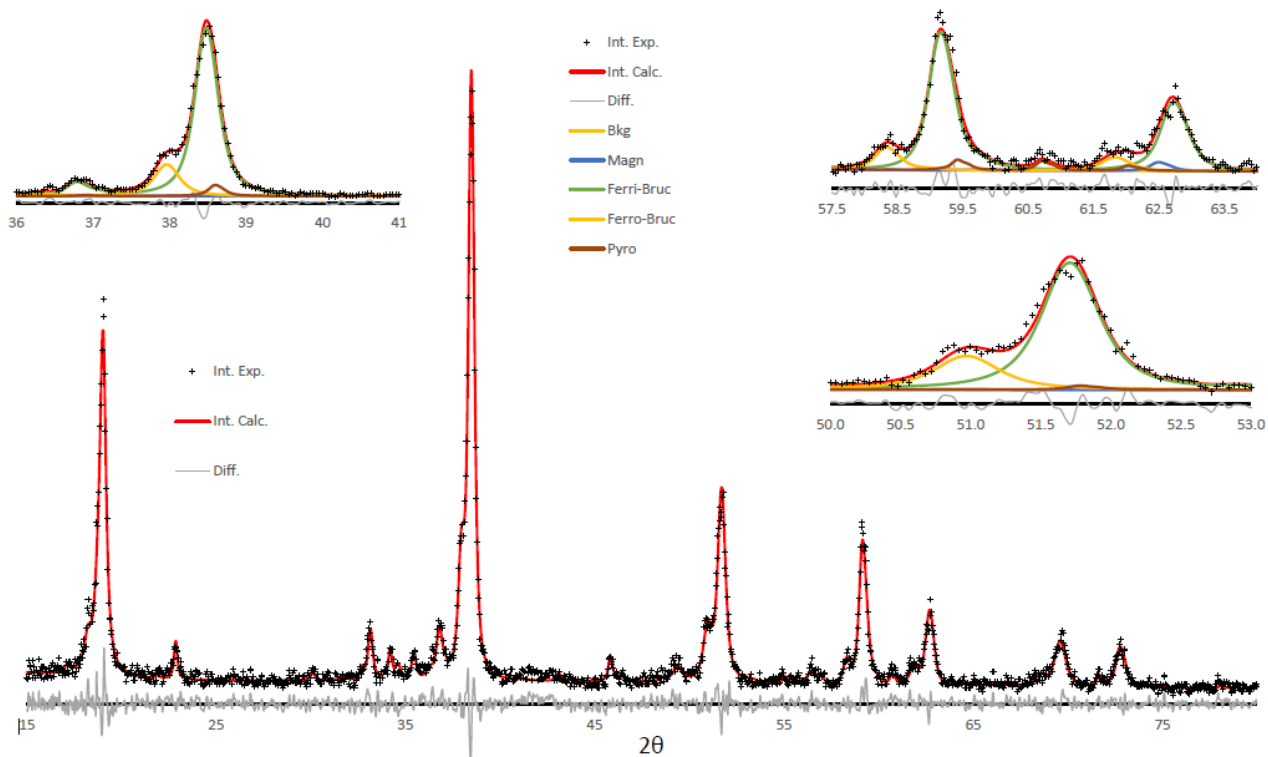
41 Assuming that all Fe^{III} present in the starting material would readily produce magnetite, an
42 expected wt.% of magnetite for Runs #19 and #20, of 6.4 and 2.9 is calculated which compares
43 relatively well with the magnetite content derived from Rietveld analysis of the XRPD data of 5.9
44 and 4.2 wt.%, respectively.

45 The expected Fe^{III}/Fe_{tot} ratio in Runs #19 and #20 can be calculated from the Rietveld analysis
46 of the XRPD data (Table S4) which provides both phase compositions and proportions. Pyroaurite
47 composition was assumed to be ideal (Mg:Fe ratio of 3:1) because the refined value of its in-plane
48 unit-cell parameter *a* scatters very little [3.1112(13)-3.1170(70) for all samples with > 10% pyroaurite
49 – data not shown] close to the ideal 3.109 Å value.

50 For the run product of Run #19, Fe^{III}/Fe_{tot} = 0.82(9) to be compared with the measured value
51 of 0.92(6) (Fig. S3). For Run #20, Fe^{III}/Fe_{tot} = 0.79(6) to be compared with the measured value of
52 0.87(5) (Fig. S3). The Fe^{III} and Fe^{II} contents of Runs #19 and #20 are therefore in good agreement
53 with the phase composition/structural model that has been used for Rietveld refinement.



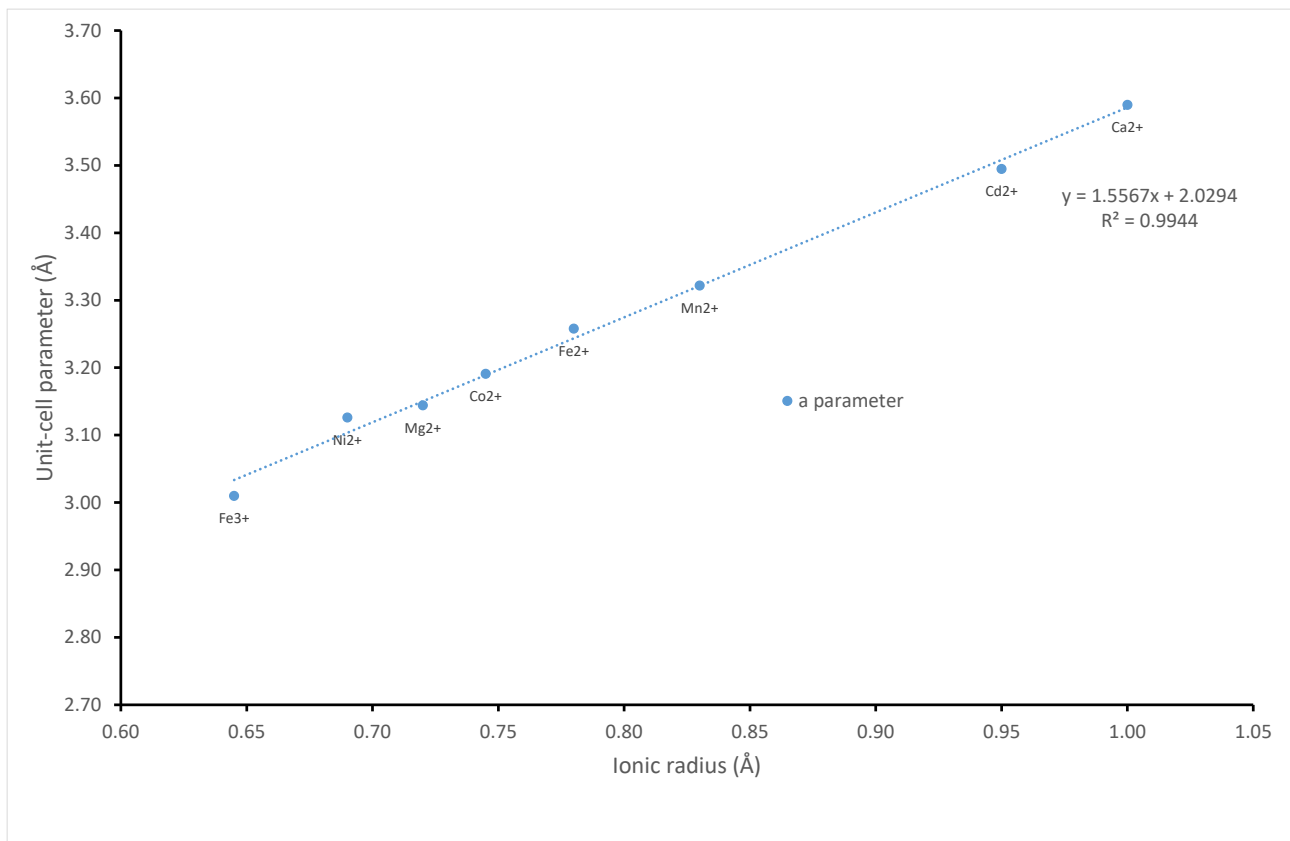
54 **Fig. S3.** Results of the colorimetric determination of Fe^{II} and Fe^{III} relative abundances in starting
 55 materials (left) and reaction products (right) for Runs #19 and #20 (top and bottom, respectively).



56

57 **Fig. S4.** Rietveld refinement of X-ray diffraction data from Run #03 reaction products. Zoomed
 58 frames show the contribution of each phase. *Int. Exp.*: Measured intensity; *Int. Calc.*: Calculated
 59 intensity; *Diff.*: Difference between measured and calculated intensities; *Bkg*: Background

60



61

62 **Fig. S5.** Extension of the regression between in-plane *a* unit-cell parameters of brucite-like structures
 63 and the ionic radius of divalent octahedral cation to include Fe^{III}. Values for divalent cations as in
 64 Fig. S1; unit-cell parameters for fully oxidized green rust (Fe^{III}₆O₁₂H₈CO₃) from Génin et al. (2006).

65 **Table S1.** Crystal parameters refined for ferroan and ferrian brucite and Rietveld refinement details.

Phase / Sample	a (Å)	c (Å)	V (Å ³)	Z	R_p (%)	R_{wp} (%)	R_{exp} (%)	GoF
Ferroan brucite (s.g. #164 $P\bar{3}m1$)								
FeBR_R0.4_S_2	3.1699(4)	4.744(1)	41.29	1	12.2	16.1	18.2	0.88
FeBR_R0.4_Cl_2	3.1651(6)	4.751(2)	41.22	1	15.9	21.0	17.9	1.18
Ferrian brucite (s.g. #164 $P\bar{3}m1$)								
#03 / FeBR_R0.4_S_M105-2_31d	3.1255(5)	4.6774(13)	39.57	1	10.3	13.5	16.6	0.82
#10 / FeBR_R0.4_Cl_36d	3.1259(5)	4.6759(18)	39.57	1	11.8	15.2	15.6	0.97
Notes: a and c : Unit-cell parameters; V : Cell volume; Z : Formula units per cell; R_p : Unweighted profile R-factor; R_{wp} : Weighted profile R-factor; R_{exp} : Expected R-factor ; GoF : Goodness of fit.								

66

67

68 **Table S2.** Fractional atomic coordinates, isotropic displacement parameters and selected interatomic bond distances (Å) for ferroan and ferrian brucite.

Phase / Sample	Site - Position	x	y	z	B_{iso} (Å ²)	Occ.	(Mg1,Fe1)-O1 (Å)
Ferroan brucite / FeBR_R0.4_S_2	Mg1 – 1a	0	0	0	0.48	0.774(4)	
	Fe ^{II} 1 – 1a	0	0	0	0.48	0.226(4)	2.121(8)
	O1 – 2d	1/3	2/3	0.226(3)	0.82	1	
Ferroan brucite / FeBR_R0.4_Cl_2	Mg1 – 1a	0	0	0	0.48	0.816(5)	
	Fe ^{II} 1 – 1a	0	0	0	0.48	0.184(5)	2.139(8)
	O1 – 2d	1/3	2/3	0.234(3)	0.82	1	
Ferrian brucite #03 / FeBR_R0.4_S_M105-2_31d	Mg1 – 1a	0	0	0	0.48	0.842(20)	
	Fe ^{III} 1 – 1a	0	0	0	0.48	0.152(20)	2.087(8)
	O1 – 2d	1/3	2/3	0.224(3)	0.82	1	
Ferrian brucite #10 / FeBR_R0.4_Cl_36d	Mg1 – 1a	0	0	0	0.48	0.807(36)	
	Fe ^{III} 1 – 1a	0	0	0	0.48	0.193(36)	2.080(10)
	O1 – 2d	1/3	2/3	0.221(4)	0.82	1	

70 **Table S3.** Results of the Rietveld refinements performed on reaction products from all experiments.

Run number / Sample name	Ferrian brucite				Fit quality estimates		
	a param. (Å)	c param. (Å)	z (fraction of c param.)	CSD 110 (nm)	Rwp	Rexp	GoF
#01 / FeBR_R0.4_S_M105_8d					16.6	17.9	0.93
#02 / FeBR_R0.4_S_M105_15d	3.1276(8)	4.6703(24)	0.222	44(10)	19.4	19.0	1.02
#03 / FeBR_R0.4_S_M105_31d	3.1255(5)	4.6774(13)	0.224(3)	51(5)	13.5	16.6	0.82
#04 / FeBR_R0.05_S_M105_7d	3.1383(39)	4.7157(31)	0.222	14(2)	14.7	18.4	0.8
#05 / FeBR_R0.05_S_M105_31d	3.1354(9)	4.6891(32)	0.222	48(12)	21.3	20.2	1.06
#06 / FeBR_R0.4_Cl_1d					18.3	17.6	1.03
#07 / FeBR_R0.4_Cl_3d					16.3	18.0	0.91
#08 / FeBR_R0.4_Cl_7d	3.1298(19)	4.6674(41)	0.222	16(2)	15.6	17.0	0.92
#09 / FeBR_R0.4_Cl_15d	3.1244(56)	4.6723(20)	0.222	40(5)	15.1	18.2	0.83
#10 / FeBR_R0.4_Cl_36d	3.1259(5)	4.6759(18)	0.221(4)	58(11)	15.2	15.6	0.97
#11 / FeBR_R0.05_Cl_1d					17.8	19.9	0.89
#12 / FeBR_R0.05_Cl_3d					18.2	19.7	0.92
#13 / FeBR_R0.05_Cl_7d	3.1167(24)	4.6712(41)	0.222		16.1	18.9	0.85
#14 / FeBR_R0.05_Cl_15d	3.1282(12)	4.6789(37)	0.222	23(3)	15.5	17.8	0.87
#15 / FeBR_R0.05_Cl_31d	3.1294(5)	4.6817(12)	0.220(3)	105(24)	17.0	18.9	0.90
#16 / FeBR_R0.05_Cl_w-r25_3d					15.4	18.1	0.85
#17 / FeBR_R0.4_Cl_caps1_105deg_15d					18.2	18.5	0.98
#18 / FeBR_R0.4_Cl_caps2_105deg_26d					15.3	17.4	0.88
#19 / FeBR_R0.4_Cl_10_32d	3.1273(6)	4.6859(21)	0.218(4)	53(10)	29.6	28.7	1.03
#20 / FeBR_R0.4_Cl_11_32d	3.1246(7)	4.6733(21)	0.226(4)	38(4)	29.8	28.2	1.05

Note: a and c: ferrian brucite unit-cell parameters (space group $P\bar{3}m1$); z: z-coordinate of the O atom 2d position (space group $P\bar{3}m1$); CSD: size of the coherent scattering domains along 110; Rwp: Weighted profile R-factor; Rexp: Expected R-factor ; GoF: Goodness of fit.

72 **Table S4.** Fe^{III}/Fe_{tot} ratio calculated from phase composition and relative proportions derived from
 73 the quantitative phase analysis of reaction products from Runs #19 & #20.

Mineral	Structural formula	Rel. Prop.		
		wt.%	nFe ²⁺	nFe ³⁺
Ferroan Brucite	Mg _{0.8} Fe _{0.2} (OH) ₂	9.5(15)	0.029	
Pyroaurite	Mg ₆ Fe ³⁺ ₂ (OH) ₁₆ [CO ₃] · 4.5H ₂ O	16.6(9)		0.049
Ferrian Brucite	Mg _{0.86} Fe _{0.14} O _{0.14} (OH) _{1.86}	68.0(18)		0.151
Magnetite	Fe ²⁺ O · Fe ³⁺ ₂ O ₃	5.9(4)	0.025	0.051
		Sum	0.055(6)	0.252(10)
Run #19			Fe ³⁺ /Fe _{tot}	0.82(9)

Mineral	Formula	Rel. Prop.		
		wt.%	nFe ²⁺	nFe ³⁺
Ferroan Brucite	Mg _{0.81} Fe _{0.19} (OH) ₂	17.8(4)	0.052	
Pyroaurite	Mg ₆ Fe ³⁺ ₂ (OH) ₁₆ [CO ₃] · 4.5H ₂ O	10.3(7)	0	0.031
Ferrian Brucite	Mg _{0.82} Fe _{0.18} O _{0.18} (OH) _{1.82}	67.7(16)	0	0.191
Magnetite	Fe ²⁺ O · Fe ³⁺ ₂ O ₃	4.2(3)	0.018	0.036
		Sum	0.070(3)	0.258(9)
Run #20			Fe ³⁺ /Fe _{tot}	0.79(6)

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76 **References**

- 77 Auzende, A. L., Daniel, I., Reynard, B., Lemaire, C., Guyot, F. (2004). High-pressure behaviour of
78 serpentine minerals: a Raman spectroscopic study. *Phys. Chem. Miner.*, 31, 269-277.
79 <https://doi.org/10.1007/s00269-004-0384-0>
- 80 Génin, J.-M.R., Ruby, C., Upadhyay, C., 2006. Structure and thermodynamics of ferrous,
81 stoichiometric and ferric oxyhydroxycarbonate green rusts; redox flexibility and fougérite
82 mineral. *Solid State Sci* 8, 1330–1343.
83 <https://doi.org/10.1016/j.solidstatesciences.2006.05.010>
- 84 Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic distances in
85 halides and chalcogenides. *Acta Cryst A* 32, 751–767.
86 <https://doi.org/10.1107/S0567739476001551>
- 87 Templeton, A.S., Ellison, E.T., 2020. Formation and loss of metastable brucite: does Fe(II)-bearing
88 brucite support microbial activity in serpentinizing ecosystems? *Phil. Trans. R. Soc. A* 378,
89 20180423. <https://doi.org/10.1098/rsta.2018.0423>
- 90 Wyckoff, R.W.G., 1963. *Crystal structures*. Interscience publishers New York.

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