



# Simultaneous precipitation of magnesite and lizardite from hydrothermal alteration of olivine under high-carbonate alkalinity

Romain Lafay, German Montes-Hernandez, Emilie Janots, Nathaniel Findling,  
Rodica Chiriac, Francois Toche

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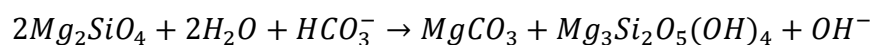
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24 **Abstract**

25           The present study reports original experiments in order to investigate the simultaneous  
26 serpentinization and carbonation of olivine with relevance in Earth systems (e.g. functioning of  
27 hydrothermal fields) or in engineered systems (e.g. ex-situ and in-situ mineral sequestration of  
28 CO<sub>2</sub>). For this case, specific experimental conditions were examined (200°C, saturated vapor  
29 pressure ≈ 16bar, solution/solid weight ratio = 15, olivine grain size < 30μm and high-carbonate  
30 alkalinity ≈ 1M NaHCO<sub>3</sub>). Under these conditions, competitive precipitation of magnesite and  
31 serpentine (preferentially lizardite type) were clearly determined by using conventional analytic  
32 tools (XRD, FESEM, FTIR and TGA); excluding the fate of the iron initially contained in  
33 olivine, the alteration reaction for olivine under high-carbonate alkalinity can be expressed as  
34 follows:



35 This reaction mechanism implied a dissolution process, releasing Mg and Si ions into solution  
36 until supersaturation of solution with respect to magnesite and/or serpentine. The released iron  
37 contained in the olivine has not implied any precipitation of iron oxides or (oxy)hydroxides; in  
38 fact, the released iron was partially oxidized (about 50%) via a simple reduction of water  
39 ( $2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + H_2 + 2OH^-$ ). In this way, the released iron was incorporated in  
40 serpentine (Fe(II) and Fe(III)) and in magnesite (Fe(II)). This latter was clearly determined by  
41 FESEM/EDS chemical analysis on the single magnesite crystals. The nucleation and epitaxial  
42 growth processes at the olivine-fluid interfaces cannot be excluded in our investigated system.

43 The experimental kinetic data fitted by using a kinetic pseudo-second-order model have revealed

44 a retarding process of serpentine formation with respect to magnesite (about three times slower);  
45 in fact, the magnesite seems to reach an apparent stabilization after about 20 days of reaction  
46 while the serpentine follows a progressive slower evolution. We assumed that the magnesite has  
47 reached a fast apparent equilibrium with solution because the available carbonate species are not  
48 renewed from fluid phase as typically constrained in aqueous carbonation experiments where a  
49 given CO<sub>2</sub> pressure is imposed in the system.

50 On the other hand, the reactivity of serpentinized olivine (chrysotile+brucite+small amount of  
51 residual olivine) and high-purity chrysotile at the same above investigated conditions; and the  
52 olivine serpentinization in initial acid pH  $\approx$  0.66 are also reported as complementary information  
53 in this study.

54 These novel experimental results concerning simultaneous serpentinization and aqueous  
55 carbonation of olivine expand the thermodynamic conditions where serpentine and magnesite can  
56 simultaneously precipitate; this could contribute to a better understanding of fluid-rock  
57 interactions in natural active hydrothermal fields on Earth.

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66 **Keywords:** Olivine alteration; High-carbonate alkalinity; Magnesite; Lizardite; Crystal growth;  
67 Hydrothermal systems.

68

69 **1. Introduction**

70 The physicochemical reactions at the solid-fluid interfaces play a crucial role in the global cycle  
71 of major and trace elements in the Earth and other telluric planets. In this way, chemical  
72 weathering, metamorphic reactions, diagenetic reactions, hydrothermalism, volcanic activity,  
73 crystal-melt reactions are important non-limited physicochemical processes that shape the Earth's  
74 surface and sub-surface. However, many physicochemical and textural aspects of these so-called  
75 rock-fluid interactions are still poorly understood. For example, when mantle peridotite is  
76 tectonically exposed with (sub-) surface fluids (e.g. seafloor water and meteoric water), the  
77 olivine and pyroxene anhydrous minerals contained in peridotite are far-from-equilibrium with  
78 respect to fluid composition. In this way, numerous physicochemical reactions at peridotite-fluid  
79 interfaces can take place such as hydration (-OH incorporation or serpentinization) and  
80 carbonation processes if the required temperature and fluid compositions are enough to activate  
81 these reactions; both most important processes directly related to natural H<sub>2</sub> and abiotic methane  
82 production via redox reactions and the formation of other non-limited secondary minerals as it  
83 has been observed in various natural hydrothermal sites (e.g. Logatchev, Rainbow, The Lost  
84 City...) (e.g. Charlou et al., 2002; Allen and Seyfried, 2004; Ludwig et al., 2006; Seyfried Jr. et  
85 al., 2007; McCollom and Bach 2009; Klein et al., 2009 ; Rudge et al., 2010 ; Seyfried Jr., et al.,  
86 2011). Such reducing systems may represent analogues to early Earth environments and may  
87 provide insights into requirements for the emergence of life, probably initiated at the sea floor  
88 (e.g. MacLeod et al., 1994; Charlou et al., 2002; Früh-Green et al., 2003; Kelley et al., 2005). The  
89 field monitoring and ex-situ characterization have revealed complex fluid chemistry and  
90 generally low pH (from 2.8 to 4.3) and high temperature (from 275 to 365°C) in the expelled

91 fluids from various studied ultramafic-hosted hydrothermal systems at the Mid-Atlantic Ridge  
92 (Charlou et al., 2002). Conversely, the expelled fluids at the Lost City field and other sites for  
93 example in continental serpentinization systems (e.g. Samail Ophiolite in Oman) are highly  
94 alkaline (pH>9) and lower temperatures have been monitored/determined (from 55 to 90°C)  
95 (Kelley et al., 2001; Früh-Green et al., 2003; Ludwig et al., 2006; Kelemen et al., 2011). These  
96 surprising measurements and the recent discovery of spectacular carbonate towers at the Lost  
97 City hydrothermal field have stimulated interest in the role of serpentinization and carbonation  
98 processes on the production of hydrogen- and methane-rich fluids and on the biological  
99 communities that may be supported in these environments (Früh-Green et al., 2003; Kelley et al.,  
100 2005; Schrenk et al., 2013). Moreover, at the present time, the ex-situ and in-situ carbonation of  
101 mafic and ultramafic rocks (e.g. basalts and peridotite), extensively available in the oceanic crust  
102 and ophiolites, have been proposed as a promising solution to mitigate the global warming of  
103 Earth's atmosphere related to excessive anthropogenic and natural CO<sub>2</sub> emissions; because Mg-  
104 Ca- or Fe-carbonates resulting from mineral carbonation of CO<sub>2</sub> can remain stable at the  
105 geological time scales as frequently observed in the Earth surface and/or sub-surface (e.g.  
106 Seifritz, 1990; Lackner et al., 1995; Bachu, 2000; Kaszuba et al., 2003; Xu et al., 2004, Kaszuba  
107 et al., 2005; IPCC, 2007; Gerdemann et al., 2007; Kelemen and Matter, 2008; Oelkers et al.,  
108 2008; Montes-Hernandez et al., 2009; Matter and Kelemen, 2009; Kelemen et al., 2011;  
109 Schwarzenbach et al., 2013). In this general context, numerous experimental studies concerning  
110 the serpentinization or carbonation of peridotite (or single olivine) have been recently performed  
111 using batch, semi-continuous or flow-through reactors in order to better understand the reaction  
112 mechanisms and kinetics, reaction and cracking propagation from the grain boundaries, nature  
113 and role of secondary phase formation, potential of hydrogen production, potential for mineral



114 sequestration of CO<sub>2</sub> and role of P, T, pH, solid/fluid ratio and fluid chemistry (e.g. Wunder and  
115 Schreyer, 1997; James et al., 2003; Giammar et al.; 2005; Béarat et al., 2006; Seyfried Jr. et al.,  
116 2007; Andreani et al., 2009; McCollom and Bach, 2009; King et al., 2010; Garcia et al., 2010;  
117 Daval et al., 2011; Hövelmann et al., 2011; Marcaillou et al., 2011; Klein and Garrido, 2011;  
118 Bonfils et al., 2012; Malvoisin et al., 2012; Lafay et al., 2012). However, the competitive and/or  
119 coexistence between serpentinization and carbonation at peridotite-fluid interfaces have been  
120 rarely investigated at the laboratory scale, remarking that serpentinization and carbonation of  
121 peridotite, leading to precipitation of serpentine (e.g. lizardite, chrysotile...) and magnesite (or  
122 hydrated Mg carbonates), could occur simultaneously in natural hydrothermal systems if the  
123 interacting solution is supersaturated with respect to both minerals. For this simple reason, the  
124 main goal of this present study was focussed to determine the simultaneous precipitation of  
125 serpentine and magnesite from hydrothermal alteration of olivine under high-carbonate alkalinity.  
126 For this particular case, specific experimental conditions were used (200°C, saturation vapour  
127 pressure (≈16bar), solution/solid weight ratio (=15), olivine grain size (<30μm) and high-  
128 carbonate alkalinity solution (1M NaHCO<sub>3</sub>)). These experimental conditions were selected with  
129 help of previous-experimental studies, investigating independently the serpentinization or the  
130 carbonation of olivine (e.g. Giammar et al.; 2005; Béarat et al., 2006; Seyfried Jr. et al., 2007;  
131 King et al., 2010; Garcia et al., 2010; Daval et al., 2011; Hövelmann et al., 2011; Marcaillou et  
132 al., 2011; Bonfils et al., 2012; Malvoisin et al., 2012; Lafay et al., 2012). High-purity synthetic  
133 chrysotile and serpentinized olivine (chrysotile + brucite mineral + small amount of residual  
134 olivine) obtained in our laboratory were also used as starting solids in complementary-similar  
135 experiments in order to determine their reactivity under high-alkalinity. As expected, the  
136 chrysotile was slightly altered and brucite quickly transformed to magnesite at the investigated

137 conditions. Various analytical tools such as X-ray diffraction (XRD), Field Emission Gun  
138 Scanning Electron Microscopy (FESEM), Thermogravimetric analyses (TGA/SDTA) and Fourier  
139 Transform Infrared Spectroscopy (FTIR) were used to characterize the solid products. TGA  
140 analyses and the respective 1<sup>st</sup> derivative curves were particularly used to determine with high  
141 accuracy the temporal variation of magnesite and serpentine during olivine alteration.

142

## 143 **2. Materials and Methods**

### 144 *2.1. Preparation of solid reactants*

145 *Olivine grains:* Millimetric grains of olivine San Carlos (Fo<sub>91</sub>) were crushed using a Fritsh  
146 Pulverisette 7 micro-crusher. One class of grain/particle size (particle size < 30 μm) was isolated  
147 by sieving. The samples were washed three times using high-pure water in order to remove the  
148 ultrafine particles that possibly stuck at grain surfaces during crushing step. Optical and electron  
149 microscopy was performed to control the initial state/appearance of olivine surfaces. On the other  
150 hand, high specific surface area (2.3 m<sup>2</sup>/g) was deduced from N<sub>2</sub> adsorption isotherm using  
151 conventional Brunauer–Emmett–Teller (BET) method. This high specific surface area was  
152 probably due to a significant presence of very fine particles (< 1 μm; not verified), not spherical  
153 morphology of grains and significant surface-defects and/or roughness.

154 *High-purity synthetic chrysotile:* 250ml of 1M NaOH solution, 1.302g of silica gel (H<sub>2</sub>SiO<sub>3</sub>) and  
155 5.082g of magnesium chloride hexahydrate (MgCl<sub>2</sub>.6H<sub>2</sub>O) were placed in a Parr *copper alloy*  
156 reactor (autoclave with internal volume of 0.5L). This aqueous reactive system was immediately  
157 stirred using constant mechanical agitation (300 rpm) during the reaction. The aqueous system

158 was then heated at 300°C for 30h by using a heating jacket adapted to the reactor. Based on  
159 several previous experiments, these experimental conditions were optimal to synthesize high-  
160 purity chrysotile with high specific surface area ( $S_{\text{BET}} = 185\text{m}^2\cdot\text{g}^{-1}$ ), more specifically a  
161 mesoporous material (pore size 2 to 50 nm) (Lafay et al., 2013).

162 *Serpentinized olivine (chrysotile+brucite+small amount of residual olivine)*: micrometric grains  
163 of olivine (<30 $\mu\text{m}$ ) were altered in concentrated NaOH solution (1M) at 200°C in static batch  
164 mini-reactors for 30 days. 30 days of olivine-fluid interactions were enough to obtain almost  
165 complete mineral replacement of olivine to chrysotile and brucite. This implied a spatial and  
166 temporal coupling of dissolution and precipitation reactions at the interface between olivine and  
167 chrysotile-brucite minerals. This coupled dissolution-precipitation led to the alteration of starting  
168 olivine grains (so-called primary or parent mineral) to a porous mineral assemblage of chrysotile  
169 and brucite with preservation of the initial olivine grain shape. For more specific details on the  
170 olivine replacement by chrysotile and brucite, including kinetics and reaction steps, refer to Lafay  
171 et al., (2012).

172

## 173 2.2. Preparation of reacting solutions

174 *High-alkaline NaHCO<sub>3</sub> solution (S1)*: This alkaline solution was recovered from magnesite  
175 synthesis that has used Mg(OH)<sub>2</sub> (1mol), NaOH (2mol), high-purity H<sub>2</sub>O (1L) and CO<sub>2</sub> (50bar  
176 equivalent to 2mol in the reactor) as reactants. More details on this synthesis method and  
177 recovery of alkaline solution by centrifugation can be found in Montes-Hernandez et al., (2012).  
178 In summary the recovered solution has a pH of 8.9 (measured at ~20°C), a high concentration of

179 total carbon (=1M) measured by TOC-V<sub>CSN</sub> analyzer and low concentration of Mg (~250mg/L)  
180 measured by ICP-OES. Assuming that all dissolved carbon comes from injected CO<sub>2</sub>, the  
181 Phreeqc equilibrium modeling (Parkhurst and Appelo, 1999) confirms that the recovered solution  
182 is enriched particularly with NaHCO<sub>3</sub> (~1M).

183 *High-alkaline NaHCO<sub>3</sub> solution (S2)*: This solution was obtained by direct capture of CO<sub>2</sub> via  
184 ionic dissociation in a concentrated NaOH solution (2M). Herein, 50bar of CO<sub>2</sub> (~2mol) were  
185 injected into the reaction titanium cell (2L of volume) at ambient temperature (~20°C). The CO<sub>2</sub>  
186 consumption (or pressure drop of CO<sub>2</sub>) and temperature (exothermic reaction) were in-situ  
187 monitored until a macroscopic equilibrium that was reached after about 24h. Then, the residual  
188 CO<sub>2</sub> gas was removed from reactor and the solution was recovered by simple decanting of  
189 supernatant solution. Based on Solvay typical reactions, the following global reactions are  
190 expected:



193 The X-ray diffraction on the recovered solid and the measurements in the solution (pH=8.7 and  
194 TC=0.95M) have confirmed this above reactions.

195

### 196 2.3. Serpentinization-Carbonation experiments

197 In each experiment 1.5 ml of high-alkaline solution (S1 or S2) and 100 mg of olivine (grain  
198 size<30µm) were placed in a Teflon cell reaction (cap-cell also in Teflon). Cell reaction and cap-

199 cell were previously washed by an acidic treatment followed by washing with high-pure water.  
200 This cell reaction was immediately assembled into a steel autoclave without agitation, referred to  
201 as “static batch reactor” and the closed autoclave was placed in a multi-oven (ten independent-  
202 temperature compartments) and heated to 200 °C ( $P_{\text{sat}} \approx 16\text{bar}$ ). Various olivine-fluid reaction  
203 times from 3 h to 60 days were considered in order to determine the serpentinization and  
204 carbonation rates of olivine at the investigated hydrothermal conditions. Complementary  
205 experiments were carried out at the same experimental conditions. Herein, serpentinized olivine  
206 (chrysotile+brucite+small amount of residual olivine) was reacted with *SI* solution (runs: 11 to  
207 15) and high-purity synthetic chrysotile was also reacted with *SI* solution (runs: 6 to 10). All  
208 experiments or runs and some results are summarized in Table 1.

209 At the end of the experiment, the autoclave was quenched in cold water and then disassembled.  
210 The quenching step avoids a significant perturbation of solid reaction products. Conversely, the  
211 chemistry of recovered solutions (pH, ion composition and probably ion speciation) can be  
212 significantly modified by cooling and/or depressuring processes as clearly demonstrated by  
213 modelling for calcite precipitation under hydrothermal conditions (Fritz et al., 2013). For this  
214 reason, the olivine alteration was directly deduced from solid mineral characterization in this  
215 present study. Moreover, for batch experiments, the ion composition and/or concentration are not  
216 directly related to alteration extent for a given mineral(s). In summary, only the pH into the  
217 collected solutions was measured at room temperature ( $\approx 20^\circ\text{C}$ ) “not representative of in-situ pH  
218 during olivine alteration”, these results are also summarized in Table 1. The solid product was  
219 systematically washed in 25ml of high-purity water and separated by centrifugation. Finally, the

220 solid product was directly dried in the centrifugation flask at 90 °C for 24 h. The dry solid  
221 product was recovered for further solid characterizations described below.

#### 222 *2.4. Serpentinization in initial acid pH*

223 Similar to above alteration procedure was performed to investigate the effect of initial acid pH on  
224 the serpentinization process. For this case, the olivine grains (<30µm) were exposed in HCl  
225 solution (S3) (initial pH=0.63) at different duration times (10, 66, 90 and 180 days). These batch  
226 experiments are also summarized in Table 1.

#### 227 *2.5. Characterization of solid products*

228 The following four conventional techniques were used in complementary manner to determine  
229 the mineral composition, morphology of crystals and serpentine polymorphs of reacted samples.

230 *FESEM observations:* Serpentinized-carbonated materials were dispersed by ultrasonic treatment  
231 in absolute ethanol (chemical purity>98%) for five to ten minutes. One or two droplets of the  
232 suspension were then deposited directly on an aluminum support for SEM observations, and  
233 coated with platinum. The morphology of various selected powders was observed using a Zeiss  
234 Ultra 55 field emission gun scanning electron microscope (FESEM) with a maximum spatial  
235 resolution of approximately 1nm at 15kV.

236 *XRD measurements:* X-Ray Powder Diffraction (XRD) analyses were performed using a Siemens  
237 D5000 diffractometer in Bragg-Brentano geometry; equipped with a theta-theta goniometer with  
238 a rotating sample holder. The XRD patterns were collected using Cu  $k\alpha_1$  ( $\lambda_{k\alpha_1}=1.5406\text{Å}$ ) and  $k\alpha_2$   
239 ( $\lambda_{k\alpha_2}=1.5444\text{Å}$ ) radiation in the range  $2\theta = 10 - 70^\circ$  with a step size of  $0.04^\circ$  and a counting time  
240 of 6 seconds per step.

241 *Thermogravimetric analyses:* TGA for all Serpentinized-carbonated samples were performed  
242 with a Mettler Toledo TGA/SDTA 851e instrument under the following conditions: sample mass  
243 of about 10 mg, 150  $\mu$ l alumina crucible with a pinhole, heating rate of  $10^{\circ}\text{C min}^{-1}$ , and inert  $\text{N}_2$   
244 atmosphere of  $50 \text{ ml min}^{-1}$ . Sample mass loss and associated thermal effects were obtained by  
245 TGA/SDTA. In order to identify the different mass loss steps, the TGA first derivative (rate of  
246 mass loss) was used. The TGA apparatus was calibrated in terms of temperature. The melting  
247 points of three compounds (indium, aluminum and copper) obtained from the DTA signals were  
248 used for the sample temperature calibration.

249 *FTIR measurements:* Infrared measurements (in transmission mode) were performed using an IR  
250 microscope Bruker Hyperion 3000. The IR beam was focused through a 15x lens and the typical  
251 size of infrared spot is  $50 \times 50 \text{ mm}^2$ . The light source is a Globar (TM) and the beam splitter is in  
252 KBr. The spectra were measured from  $700$  to  $4000 \text{ cm}^{-1}$  ( $4 \text{ cm}^{-1}$  resolution) with a MCT  
253 monodetector cooled by liquid nitrogen. Samples must be thin (less than  $100 \mu\text{m}$ ) and flat to  
254 avoid absorption band saturation or scattering effects. Sample preparation has involved a careful  
255 crushing of samples in mortar and manual compaction of fine crushed particles between two KBr  
256 windows. In general, five spectra per sample were collected in different zones and/or aggregates  
257 in order to verify their homogeneity/discrepancy.

258

### 259 **3. Results**

#### 260 3.1. Mineral composition of products

261 The conventional analytic techniques (XRD, TGA, FTIR and FESEM) have revealed that the  
262 hydrothermal alteration of olivine using high-carbonate alkalinity solutions, i.e. enriched with

263 CO<sub>2</sub> (*S1* and *S2* solutions), concerns the competitive formation of magnesite and serpentine, in  
264 other words, competitive carbonation and serpentinization processes during olivine alteration was  
265 clearly observed. As expected, both solutions (*S1* and *S2*) have revealed a very similar effect on  
266 the olivine alteration because the mineral composition of products and alteration extent were not  
267 significantly affected for comparable samples. For specific details, refer to mineral composition  
268 evolution summarized in Table 2 for runs 1 to 5 and 16 to 20. Herein, magnesite was observed  
269 from 3 days of reaction until the end of experiment (60 days). Conversely, the formation of  
270 serpentine (preferentially lizardite type) was retarded with respect to magnesite because it was  
271 clearly identified by X-ray diffraction after 10 days of reaction. Chrysotile tubes were also  
272 observed by FESEM, preferentially after 30 days reaction. All these qualitative results are  
273 summarized in the Figure 1, displaying some XRD patterns and some FESEM images for  
274 collected products as the function of reaction time. We note that the experimental duration of 60  
275 days were not enough to transform the available olivine completely into magnesite and serpentine  
276 as qualitatively determined by x-ray diffraction (see XRD pattern after 60 days in Figure 1) and  
277 by infrared spectroscopy (Fig. 2). This latter analytical tool has confirmed a preferential  
278 formation of lizardite polymorph as attested by their two typical stretching infrared modes at 966  
279 and 1085 cm<sup>-1</sup> for Si-O group (see Fig. 2b). These infrared features are clearly different to  
280 infrared features of chrysotile polymorph (Fig. 2c). We remark also that infrared features are in  
281 agreement with FESEM observations, which reveal fine particles with platy morphology for  
282 lizardite (Fig. 1c) and typical tubular morphology for chrysotile (Fig. 1d). In an effort to quantify  
283 “with high-accuracy” the co-formed amount of magnesite and serpentine as a function of time,  
284 the thermogravimetric analysis (TGA) were performed at a specific heating rate of 10°C/min  
285 under 100% N<sub>2</sub> atmosphere (see materials and methods section for more specific details). Herein,



286 the first derivative curve (DTG) was successfully used to delimit the magnesite and serpentine  
287 contents for each reaction-time sample as illustrated in Figure 3. All calculated relative-values for  
288 magnesite and serpentine are summarized in Table 1 and they were also used to determine the  
289 competitive serpentinization and carbonation rates reported in the sub-section 4.2.

290 Complementary experiments using a serpentinized olivine as starting material (runs 11 to 15), i.e.  
291 a mineral material containing chrysotile+brucite+small amount of residual olivine (after Lafay et  
292 al., 2012), have revealed a fast carbonation of existing brucite, leading to magnesite formation  
293 (see Figure 4). Conversely, insignificant structural effect was measured/observed for interacting  
294 chrysotile by using XRD, IR and FESEM. This was experimentally confirmed by using high-  
295 purity chrysotile as starting material in other specific experiments (runs 6 to 10) at the same  
296 hydrothermal conditions as qualitatively measured by infrared spectroscopy (Figure 5). This solid  
297 characterization suggests that chrysotile remains close to equilibrium with respect to interacting  
298 solution at the investigated conditions.

299

## 300 **4. Discussion**

### 301 4.1. Reaction steps

302 In a previous recent study, we reported that the serpentinization of San Carlos olivine  
303 under high-hydroxyl alkalinity “or high-basic conditions” (pH=13.5 ex-situ measured at 20°C)  
304 takes place via mineral replacement of olivine by chrysotile and brucite assemblage, i.e. a spatial  
305 and temporal coupling of dissolution and precipitation reactions at the interface between olivine  
306 and chrysotile–brucite minerals, leading to preservation of external shape of olivine grains  
307 (Figure 6a). For more specific details refer to Lafay et al. 2012. Conversely, in the present study  
308 using the same pressure-temperature conditions, but, using now CO<sub>2</sub>-rich alkaline solutions (*SI*  
15

309 *and S2*) “or high-carbonate alkalinity”, the above mineral replacement reactions has not taken  
310 place. In other terms, the original external shape of olivine grains was not preserved as observed  
311 by FESEM observations (see for ex. Figure 6d). These observations suggest that the super-  
312 saturation for precipitating minerals (magnesite, lizardite and chrysotile) is also reached into the  
313 bulk interacting solution, leading to the precipitation of single magnesite crystals and fine  
314 particles of serpentine from solution, i.e. that the mineral dissolution was temporally and spatially  
315 decoupled of precipitation reactions. However, the nucleation and epitaxial growth processes at  
316 the olivine-fluid interfaces cannot be excluded in our investigated system. As mentioned above,  
317 competitive precipitation of magnesite and serpentine were clearly determined on solid products;  
318 for more simplicity, i.e. excluding the fate of the iron initially contained in olivine, the alteration  
319 reaction for olivine under high-carbonate alkalinity can be expressed as follows:



321 This reaction mechanism implied a dissolution process, releasing Mg and Si ions into solution  
322 until supersaturation of solution with respect to magnesite and/or serpentine. Their kinetic  
323 behavior depends directly on the fluid chemistry such as gradual consumption of dissolved  
324 carbonate species and in-situ OH<sup>-</sup> regeneration in this closed system. This change of fluid  
325 chemistry can probably promote the chrysotile formation at the end of the experiment as  
326 observed on FESEM images (Figure 1 (d)). This is possibly due to a decrease of carbonate  
327 alkalinity (consumption of HCO<sub>3</sub><sup>-</sup>) which is directly proportional to an increase of hydroxyl  
328 alkalinity as illustrated in reaction (2). Moreover, recently Lafay et al. (2012) has reported that  
329 chrysotile formation is favored under high-hydroxyl alkalinity.

330 On the other hand, the released iron contained in the olivine has not implied any precipitation of

331 iron oxides or (oxy)hydroxides for runs 1 to 5 and 16 to 20; in fact, the released iron was partially  
332 oxidized (about 50%) via a simple reduction of water ( $2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + H_2 + 2OH^-$ ).  
333 In this way, the released iron was incorporated in serpentine (as Fe(II) and Fe(III)) and in  
334 magnesite (as Fe(II) only). This latter is clearly determined by FESEM/EDS chemical analysis on  
335 the single magnesite crystals (Figure 7 concerning run 5).

336

#### 337 4.2. Kinetics

338 The kinetic pseudo-first-order and pseudo-second-order models have been widely used to  
339 describe several physicochemical reactions at solid-fluid interfaces such as uptake processes of  
340 ions and molecules, photocatalytic oxidation of organic molecules, sorption of vapour water in/on  
341 clays, osmotic swelling process of clays, aqueous carbonation of alkaline minerals and crystal  
342 growth processes (e.g. Ho and Mckey, 1999; Montes-H and Geraud, 2004; Montes-H, 2005; Ho,  
343 2006; Montes-Hernandez et al., 2009; Montes-Hernandez et al., 2010b). In the present study, the  
344 kinetic pseudo-second-order model was specifically used to describe the kinetic behaviour of  
345 olivine alteration under hydrothermal conditions (reaction 2) by using the variation of formed  
346 mineral(s) content or the alteration extent  $\xi_{extent}$  (%) with time  $t$  (day). As mentioned above,  
347 temporal variation of magnesite and serpentine concerning the reaction (2) was directly  
348 determined by using thermogravimetric measurements (see Fig. 3 and Table 1). These kinetic  
349 data were successfully fitted using a kinetic pseudo-second-order model. This simple model  
350 predicts a fast mass transfer followed by a slow equilibration of mass transfer in closed systems.  
351 The differential form for this kinetic model can be written as follows:

$$352 \frac{d\xi_{extent}}{dt} = k_{alteration}(\xi_{extent,max} - \xi_{extent})^2 \quad (3)$$

353 where  $k_{alteration}$  is the rate constant of olivine alteration [1/% day],  $\xi_{extent,max}$  is the maximum value  
 354 of formed mineral(s) content or alteration extent at apparent equilibrium [%] and  $\xi_{extent}$  is the  
 355 formed mineral(s) content or alteration extent [%] at any time  $t$  [day].

356 The integrated form of Equation (3) for the boundary conditions  $t = 0$  to  $t = t$  and  $\xi_{extent} = 0$  to  
 357  $\xi_{extent} = \xi_{extent}$  is represented by a hyperbolic relationship:

$$358 \quad \xi_{extent} = \frac{\xi_{extent,max} * t}{\left(\frac{1}{k_{alteration} * \xi_{extent,max}}\right) + t} \quad (4)$$

359 Note that the rate constant  $k_{alteration}$  (1/% day) has no physical interpretation. For this reason a new  
 360 parameter can be defined “ $(1/k_{alteration} * \xi_{extent,max}) = t_{1/2}$ ”, which represents the duration after which  
 361 half of the maximum of alteration extent was obtained. The Equation 4 can be then expressed as  
 362 follows:

$$363 \quad \xi_{extent} = \frac{\xi_{extent,max} t}{t_{1/2} + t} \quad (5)$$

364 In the current study,  $t_{1/2}$  is called “half-extent time” and can be used to calculate the initial-rate of  
 365 olivine alteration,  $v_0$  [1/day] by using the following expression:

$$366 \quad v_0 = \frac{\xi_{extent,max}}{100 * t_{1/2}} \quad (6)$$

367 Graphically, the initial rate of olivine alteration  $v_0$  is defined as the slope of the tangent line when  
 368 the time  $t$  tends towards zero on the  $r$  vs.  $t$  curve (see for ex. Montes-Hernandez et al., 2009).

369 A non-linear regression by the least-squares method was performed to determine these two  
 370 kinetic parameters ( $\xi_{extent,max}$  and  $t_{1/2}$ ) from Eq. 5. All values, including correlation factors and  
 371 initial alteration rates  $v_0$  are summarized in Table 2. We note that the alteration rates were

372 normalized with respect to initial specific surface area for olivine fine-grains ( $2.3 \text{ m}^2/\text{g}$ ) deduced  
373 from  $\text{N}_2$  adsorption isotherm and applying the conventional Brunauer–Emmett–Teller (BET)  
374 equation.

375 Competitive carbonation (or magnesite formation) and serpentinization (or serpentine formation)  
376 concerned in the reaction (2) and displayed in Figure 8 confirm a retarding process of serpentine  
377 formation with respect to magnesite (about three times slower); in fact, the magnesite seems to  
378 reach an apparent stabilization after about 20 days of reaction while the serpentine follows a  
379 progressive slower evolution. We assumed that the magnesite reaches a fast apparent equilibrium  
380 with solution because the available carbonate species are not renewed from gas phase as typically  
381 constrained in aqueous carbonation experiments where a given  $\text{CO}_2$  pressure is imposed in the  
382 system (e.g. Bearat et al., 2006). In this way, the serpentinization process remains active until the  
383 end of experiment and the carbonation process seems to be inhibited after about 30 days in the  
384 system as shown in Figure 8. On the other hand, the alteration rate of olivine in presence of  
385 dissolved  $\text{CO}_2$  or under high-carbonate alkalinity ( $1.8636 \times 10^{-9} \text{ mol/m}^2 \text{ s}$ ) is significantly retarded  
386 with respect to a  $\text{CO}_2$ -free system or under high-hydroxyl alkalinity at the same P-T-grain size-  
387 solid/fluid ratio conditions ( $1.6659 \times 10^{-8} \text{ mol/m}^2 \text{ s}$ ) as illustrated in Figure 9. As invoked above,  
388 the chrysotile and brucite were preferentially formed under high-hydroxyl alkalinity and the  
389 original external shape of olivine grains was preserved (Lafay et al., 2012). Conversely, under  
390 high-carbonate alkalinity, lizardite and magnesite were preferentially formed and the original  
391 external shape of olivine grains was not preserved (Figure 6d).

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395 4.3. Role of pH and fluid chemistry

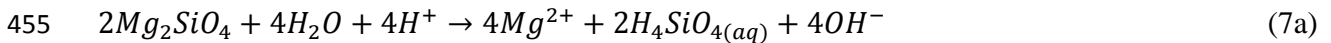
396 In a previous recent study, we demonstrated that high-hydroxyl alkalinity (1M NaOH, pH=13.5  
397 at 20°C) promote a fast serpentinization process of San Carlos olivine (Lafay et al., 2012), if it is  
398 compared with experimental serpentinization of olivine in high-purity water or in salt solution  
399 (seawater analogue) already reported by Malvoisin et al. (2012). This latter study has clearly  
400 described the influence of temperature and initial grain size on the serpentinization rate. In  
401 general, the serpentinization rate increases with a decrease of initial grain size and an increase of  
402 temperature from 200 to 350°C (Malvoisin et al., 2012). However, the serpentinization rate of  
403 olivine can also depend on the fluid/solid ratio, fluid hydrodynamics and fluid chemistry  
404 (including pH) as suggested by field fluid monitoring and modeling studies (e.g Charlou et al.,  
405 2002; Früh-Green et al., 2003; Allen et al., 2004; Ludwig et al., 2006; Seyfried et al., 2011). In  
406 this way, the present study has revealed that a simple change in alkalinity from high-hydroxyl  
407 alkalinity (1M NaOH, pH=13.5 at 20°C) to high-carbonate alkalinity (1M NaHCO<sub>3</sub>, pH=8.9 at  
408 20°C) retards significantly the alteration process of olivine (Figure 9), leading to a preferential  
409 formation of lizardite and magnesite. Moreover, the spatial and temporal coupling of dissolution  
410 and precipitation reactions (or mineral replacement reactions) was not observed under high-  
411 carbonate alkalinity. This means that the fluid chemistry and pH play an important role on the  
412 alteration kinetics, reaction mechanisms and nature of solid-gas products during olivine alteration  
413 in natural hydrothermal systems. The effect of pH on the dissolution rate of olivine and/or of  
414 forsteritic olivine has been assessed using continuous, semi-continuous or discontinuous  
415 experimental systems (e.g. Pokrovsky and Schott, 2000; Rosso and Rimstidt, 2000; Chen and  
416 Brantley, 2000; Hänchen et al., 2006; Daval et al., 2011). However, the effect of pH on the

417 serpentinization rate for olivine is more difficult to be experimentally assessed because it implies  
418 dissolution of primary components followed by precipitation of secondary mineral phases and H<sub>2</sub>  
419 production whether redox reactions are significant (e.g. Marcaillou et al., 2011; Malvoisin et al.,  
420 2012; Lafay et al., 2012). In an effort, to evaluate the pH effect on the serpentinization rate, the  
421 olivine serpentinization was recently investigated under high-hydroxyl alkalinity (pH=13.5 at  
422 20°C) (Lafay et al., 2013). This extreme scenario has provided interesting insights on the kinetics  
423 and reaction mechanism. For example, the magnetite (Fe<sub>3</sub>O<sub>4</sub>) secondary mineral phase, typically  
424 observed from olivine serpentinization in high-purity water at T>200°C (Marcaillou et al. 2011  
425 and Malvoisin et al., 2012) was not observed under high-hydroxyl alkalinity. However, the  
426 magnetite formation during serpentinization is frequently related to redox reactions and/or H<sub>2</sub>  
427 production (McCollom and Bach, 2009; Marcaillou et al., 2011); herein, we note that the H<sub>2</sub>  
428 production is not necessary associated to magnetite precipitation because it can be produced by  
429 simple oxidation of Fe(II) (initially contained in olivine) followed by a simple reduction of water  
430 as expressed by the following coupled oxidation-reduction reaction ( $2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} +$   
431  $H_2 + 2OH^-$ ). In fact, the oxidized iron (Fe(III)) and reduced iron (Fe(II)) can be selectively  
432 incorporated and/or sequestered in major secondary phases (serpentine, brucite, magnesite..) (e.g.  
433 Klein et al., 2009; Lafay et al., 2012; this study); this limits the formation of iron oxides and/or  
434 oxyhydroxides in specific environments. Under high alkalinity, preliminary Mössbauer  
435 spectroscopy measurements (results not shown here) on two selected samples have revealed a  
436 partial iron oxidation ( $\approx 50\%$ ) from Fe(II) to Fe(III) of initial iron contained in olivine. Moreover,  
437 FESEM//EDS chemical analyses have revealed that single crystals of magnesite contain  
438 significant amount of iron. We note that only Fe(II) can be incorporated into magnesite crystals;  
439 this confirms also a partial oxidation. Based on this result, the H<sub>2</sub> production is expected in our  
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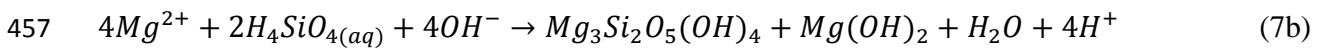
440 system and could be roughly quantified, but, this specific study was mainly oriented on the  
441 simultaneous serpentinization and aqueous carbonation of olivine.

442 On the other hand, some serpentinization experiments (runs 21 to 24 in Table 1) under high-  
443 acidic solutions (initial pH=0.66) have revealed slower serpentinization rates and a more complex  
444 kinetic behavior (sigmoidal kinetic behavior:  $[\xi_{extent} = \xi_{extent,max} / (1 + \exp(-(t - t_{1/2})/b))]$ ) than  
445 under high-hydroxyl alkalinity (Lafay et al., 2012) and under high-carbonate alkalinity (this  
446 study); however, as expected, the pH increases proportionally with serpentinization progress (see  
447 Figure 10), because by definition the dissolution of olivine (ultrabasic rock) in acidic solutions  
448 and in discontinuous (or closed) systems, implies a transient consumption of protons ( $H^+$ ) and the  
449 production of hydroxyl ions ( $OH^-$ ) until the solution supersaturation with respect to serpentine,  
450 brucite and other minor mineral phases (e.g. TOT clays and iron oxides/oxyhydroxides),. The  
451 brucite mineral ( $Mg(OH)_2$ ) is a direct proof of hydroxyl ion production in the system. A  
452 simplified reaction mechanism for serpentinization of olivine in acidic solution and in batch  
453 system, i.e. excluding the fate of initial Fe(II) contained in olivine, can be expressed as follows:

454 Dissolution step,

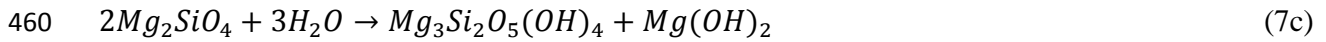


456 Precipitation from solution and/or nucleation-growth processes at olivine-fluid interfaces,



458 The summation of these two reaction steps (7a) and 7(b) gives a classic serpentinization global  
459 reaction for forsteritic olivine as described in many previous studies:





461 This global serpentinization reaction for San Carlos olivine, initiated at low pH (=0.66), is in  
462 agreement with thermogravimetric measurements reported in Table 1 (runs 21 to 24) and in  
463 Figure 10. However, we note that minor other mineral phases were also identified from XRD  
464 patterns in these experiments such as the hydro-hematite and TOT clay (talc type).

465

#### 466 4.4 Is “silica passivating layer” a universal process during olivine alteration?

467 The formation of passivating layers during solid-fluid interfacial processes are widely  
468 documented in materials sciences and chemical engineering areas. For example, in gas-solid  
469 carbonation of alkaline sorbents, the CO<sub>2</sub>-sorbent reaction typically takes place by the formation  
470 of a dense non-porous layer of carbonate (or protective carbonate layer) around the reacting  
471 particles. For these cases, the carbonation reaction is generally stopped before a complete  
472 carbonation (e.g., Fernandez Bertos et al., 2004; Sun et al., 2008; Prigiobbe et al., 2009;  
473 Stendardo and Foscolo, 2009; Huntzinger et al., 2009). Conversely, recent studies have  
474 demonstrated that the formation of a so-called passivating layer of carbonate depend strongly on  
475 the intrinsic textural properties of reacting particles and on the experimental conditions such as  
476 relative humidity, CO<sub>2</sub> pressure, fluid dynamics and temperature (e.g. Beruto and Botter, 2000;  
477 Dheilily et al., 2002; Seo et al., 2007; Zeman, 2008; Montes-Hernandez et al. 2010a and 2010b;  
478 Montes-Hernandez et al., 2012). In this way, the formation of a protective carbonate layer leads  
479 to a physical increase in volume at the grain scale (expansion or swelling process) or a decrease  
480 in porosity (pore closure process) when porous materials are partially carbonated (Fernandez

481 Bertos et al., 2004; Chen et al., 2007; Sun et al., 2008 ). Concerning the olivine aqueous  
482 alteration under acid conditions or under high CO<sub>2</sub> pressure (>20bar), incongruent dissolution  
483 process has been measured, leading to a Si-rich layer alteration profile around reacting olivine  
484 grains (e.g. Wogelius and Walther, 1991; Pokrovsky and Schott, 2000; Rosso and Rimstidt, 2000;  
485 Prigiobbe et al., 2009); its progressive formation generally leads to a passivating effect “limiting  
486 reaction process”. Similar to gas-solid carbonation process, the formation of a silica layer around  
487 the olivine reacting particles could passivate or squarely stopper the interfacial reaction as already  
488 invoked by Daval et al., 2011. However, the mechanistic pathway of its formation is still debated  
489 in the literature; some authors have proposed a polymerization process via an ion-exchange  
490 reaction ( $Mg^{2+} \leftrightarrow 2H^+$ ) and formation of surface ( $\equiv Si(OH)_4$ ) monomers that polymerize to a  
491 porous or non-porous silica layer (e.g. Wogelius and Walther, 1991; Chen and Brantley, 2000;  
492 Pokrovsky and Schott, 2000; Béarat et al., 2006). Conversely, other recent studies have proposed  
493 a temporal and spatial coupling of Si release ( $H_4SiO_{4(aq)}$ ) and silica precipitation process ( $SiO_{2(s)}$   
494 layer) (e.g. Daval et al., 2011), initially proposed by Hellmann et al. (2003) for labradorite  
495 feldspar altered under acid pH. This implies that the silica phase reaches a rapid supersaturation  
496 near of the reacting mineral phase. In this context and based on our recent results (Lafay et al.,  
497 2012 and this study), we assume that a silica passivating layer during alteration of olivine is only  
498 formed under high acid conditions (pH<4), including high CO<sub>2</sub> pressure (>20 bar) because under  
499 high hydroxyl or carbonate alkalinity conditions ( $9 < pH \leq 13.5$ ), the formation of so-called silica  
500 passivating layer was not determined/suspected by XRD, FTIR and TGA measurements. This  
501 observation is in agreement with a previous study and explanations provided by Pokrovsky and  
502 Schott, (2000).

503 **5. Coexistence of carbonation and serpentinization processes: from experimentation to**  
504 **natural systems**

505 In the last decades, the serpentinization of olivine have been intensively investigated at the lab  
506 scale in order to determine the reaction mechanisms and kinetics, the reaction and cracking  
507 propagation from the grain boundaries, its potential for hydrogen production and its implications  
508 on the early Earth life, i.e. its role on the abiotic formation of organic molecules (MacLeod et al.,  
509 1994; James et al., 2003; McCollom and Bach, 2009; Seyfried et al., 2007; Hövelmann et al.,  
510 2011; Marcaillou et al., 2011; Malvoisin et al., 2012; Lafay et al., 2012). Obviously, these studies  
511 have direct relevance in Earth systems, but, they are systematically oriented to investigate the  
512 olivine alteration in high-purity water, in saline water (seawater analogue) or in acidic solutions.  
513 In this way, we demonstrated that the olivine alteration under high alkalinity conditions follows  
514 different reaction mechanisms and the kinetic behaviour is drastically modified as explained  
515 above. On the other hand, direct and indirect aqueous carbonation of olivine is intensively being  
516 investigated in order to determine the best experimental conditions for ex-situ mineral  
517 sequestration of CO<sub>2</sub> using natural olivine. Herein, the Albany Research Centre has reported that  
518 the optimum sequestration reaction conditions observed to date are 1M NaCl + 0.64M NaHCO<sub>3</sub>  
519 at T≈180°C and P<sub>CO<sub>2</sub></sub>≈135 bar (Chen et al., 2006; Béarat et al., 2006; King et al, 2010;Daval et  
520 al., 2011). In this context, Béarat et al. (2006) have concluded that mitigating passivating layer  
521 effectiveness is critical to enhancing carbonation and lowering sequestration process cost.  
522 Inspired on these independent results of olivine serpentinization and aqueous carbonation,  
523 specific novel experimental conditions were used in this study (1M NaHCO<sub>3</sub> solution, pH ≈ 9,  
524 200°C and saturated vapor pressure) in order to investigate a competitive effect between

525 serpentinization and aqueous carbonation of olivine. These simple experimental constraints could  
526 contribute to a better understanding of fluid-rock interactions in natural active hydrothermal  
527 Earth fields such as Samail Ophiolite in Oman, New Caledonia Ophiolite, etc. where a  
528 simultaneous serpentinization and aqueous carbonation processes are currently expected (e.g.  
529 Kelemen and Matter, 2008; Matter and Kelemen, 2009).

## 530 **6. Implications for in-situ carbonation of peridotite for CO<sub>2</sub> storage**

531 Unregulated CO<sub>2</sub> emissions into the Earth's atmosphere (about 22x10<sup>9</sup> ton CO<sub>2</sub>/year), caused  
532 mainly by fossil fuel combustion, have led to concerns about global warming. To maintain the  
533 atmospheric CO<sub>2</sub> level below 500 ppm, CO<sub>2</sub> emissions will have to be stabilized at current levels,  
534 although they are forecast to double over the next 50 years (Allwood et al., 2010). Capture from  
535 individual industrial sources and long-term geological storage are realistic and available ways of  
536 reducing CO<sub>2</sub> emissions because large volumes of this gas can be stored in various deep  
537 geological formations (e.g. Knauss et al., 2005; Friedmann, 2007; IPCC, 2007; Bachu, 2008).  
538 Recently, Kelemen and Matter (2008) have proposed the in-situ carbonation of peridotite for CO<sub>2</sub>  
539 storage, i.e. the injection of purified CO<sub>2</sub> in peridotite massifs. This conceptual methodology  
540 requires obviously drilling, hydraulic fracturing, the use of NaHCO<sub>3</sub> as catalyst, pumping fluid  
541 and preheating fluid for the first heating step. In this way, the authors have estimated very fast  
542 carbonation of peridotite compared with natural peridotite hydration and carbonation in the  
543 Samail Ophiolite (Oman) and have reported that the in-situ carbonation of peridotite could  
544 consume >1 billion tons of CO<sub>2</sub> per year in Oman alone. In this context, the basic research in the  
545 coming years on the simultaneous hydration (and/or serpentinization) and carbonation rates of  
546 peridotite "from strategic fields" could have relevant implications for this promising potential

547 alternative for CO<sub>2</sub> storage. In addition, sophisticated experimental setups could be designed to  
548 evaluate hydraulic fracturing and reactive percolation in fractured-porous media under high  
549 confinement pressure and temperature in order to evaluate the swelling process and associated  
550 micro-fracturing related to hydration and/or carbonation processes of peridotite. Technically, this  
551 is feasible because various percolation experiments simulating the reactivity of supercritical CO<sub>2</sub>  
552 have already been reported (e.g. Le Guen et al., 2007; Andreani et al., 2009).

553

## 554 **7. Conclusion**

555 The coexistence of serpentinization and aqueous carbonation of ultrabasic rocks has up to now  
556 not been investigated at laboratory scale and various questions still remain unanswered  
557 concerning its mechanistic pathways in natural systems, mainly under high alkalinity. In response  
558 to this scientific gap, this study provides new insights on competitive serpentinization and  
559 aqueous carbonation of olivine under high-carbonate alkalinity. In this way, we quantified a  
560 retarding process of serpentine formation with respect to magnesite (about three times slower) by  
561 using a simple kinetic pseudo-second-order model; in fact, the magnesite seems to reach an  
562 apparent stabilization after about 20 days of reaction while the serpentine follows a progressive  
563 slower evolution. We assumed that the magnesite has reached a fast apparent equilibrium with  
564 solution because the available carbonate species are not renewed from fluid phase as typically  
565 constrained in aqueous carbonation experiments where a given CO<sub>2</sub> pressure is imposed in the  
566 system. In summary, we demonstrated that a simple change of fluid chemistry (including pH) has  
567 a significant impact on the reaction mechanism and kinetics for olivine alteration at a given  
568 temperature. Some FESEM/EDS chemical analyses and preliminary Mössbauer measurements

569 have revealed that about 50% of initial Fe(II) was oxidized to Fe(III). The not oxidized iron in  
570 solution (Fe(II)) from reacting olivine was preferentially incorporated into magnesite crystals.  
571 This means a classic hydrogen production via a simple water reduction. The full quantification of  
572 redox reactions during simultaneous serpentinization and carbonation of olivine and peridotite  
573 under high carbonate alkalinity remains a future challenge.

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- 810 Zeman F. (2008) Effect of steam hydration on performance of lime sorbent for CO<sub>2</sub> capture. *Int.*  
811 *J. Greenhouse Gas Control* **2**, 203-209.

812

813 Table 1. Summary of experimental conditions and thermogravimetric analyses (TGA)

Run #	Starting material	Time (days)	Solution	pH		Product amount (%) from TGA			
				initial	final	Serpentine	Magnesite	Brucite	Residual olivine
1	Ol	3	S1	8.9	9.17	4.0	12.8	-	83.2
2	Ol	10	S1	8.9	9.38	21.6	14.9	-	63.5
3	Ol	20	S1	8.9	9.63	18.5	25.5	-	56.0
4	Ol	33	S1	8.9	9.55	27.0	23.7	-	49.3
5	Ol	60	S1	8.9	9.58	40.6	26.6	-	32.8
6	Ctl	3	S1	8.9	9.05	95.4	4.6	-	-
7	Ctl	11	S1	8.9	9.18	95.4	4.6	-	-
8	Ctl	22	S1	8.9	9.25	95.8	4.2	-	-
9	Ctl	32	S1	8.9	9.19	95.7	4.3	-	-
10	Ctl	78	S1	8.9	8.83	96.8	3.2	-	-
11	Ctl+bru	3	S1	8.9	9.57	82.9	17.1	-	-
12	Ctl+bru	10	S1	8.9	9.57	82.6	17.4	-	-
13	Ctl+bru	20	S1	8.9	9.59	83.6	16.4	-	-
14	Ctl+bru	33	S1	8.9	9.58	81.3	18.7	-	-
15	Ctl+bru	60	S1	8.9	9.66	79.0	21.0	-	-
16	Ol	3	S2	8.7	9	2.8	10.1	-	87.0
17	Ol	10	S2	8.7	9.4	19.6	16.6	-	63.8
18	Ol	20	S2	8.7	9.45	26.7	22.8	-	50.5
19	Ol	23	S2	8.7	9.49	24.8	20.9	-	54.4
20	Ol	60	S2	8.7	9.57	46.7	23.0	-	30.3
21	Ol	10	S3	0.63	4.77	3.8	-	<1	96.2
22	Ol	66	S3	0.63	6.37	14.5	-	<1	85.5
23	Ol	90	S3	0.63	7.29	33.1	-	5	62.9
24	Ol	183	S3	0.63	7.95	71.4	-	7.9	20.7

814 All experiments were carried out at 200°C and saturated vapor pressure. Fluid/solid weight ratio  
815 is always  $\approx 15$ . S1 and S2 are high-carbonate alkalinity solutions ( $\approx 1\text{M NaHCO}_3$ ). S3 is an  
816 acid solution ( $\text{pH} \approx 0.63$ ) prepared by dilution of concentrated HCl solution (10% v/v). pH is ex-  
817 situ measured at room temperature  $\approx 20^\circ\text{C}$ . Ol: olivine; Ctl: chrysotile; bru: brucite.

818

819 Table 2. Summary of kinetic parameters for simultaneous serpentinization and aqueous

820 carbonation of olivine, including alteration of olivine under high carbonate and hydroxyl  
 821 alkalinity.

Process	$\xi_{extent, max}$ (%)	$t_{1/2}$ days	$v_0$ 1/s	R <sup>2</sup>
$2Mg_2SiO_4 + 2H_2O + HCO_3^- \rightarrow MgCO_3 + Mg_3Si_2O_5(OH)_4 + OH^-$				
Serpentine formation	65±13	33±13.4	<b>2.3x10<sup>-7</sup></b>	0.90
Magnesite formation	27±1.7	4.8±1.3	<b>6.5x10<sup>-7</sup></b>	0.85
Alteration	81±5.2	14±2.5	<b>6.6x10<sup>-7</sup></b> =1.8636x10 <sup>-9</sup> mol/m <sup>2</sup> s	0.96
$2Mg_2SiO_4 + 3H_2O \rightarrow Mg(OH)_2 + Mg_3Si_2O_5(OH)_4$				
Alteration	105±5.5	2±0.46	<b>5.9x10<sup>-6</sup></b> =1.6659x10 <sup>-8</sup> mol/m <sup>2</sup> s	0.96
Alteration (initiated in acid pH)	83±7.0*	99±10*	<b>9.7x10<sup>-8</sup>**</b> =2.7389x10 <sup>-10</sup> mol/m <sup>2</sup> s	0.99*

822  $\xi_{extent, max}$  is the maximum value of mineral(s) content or alteration extent at apparent equilibrium  
 823 and  $t_{1/2}$  is the half-content time determined by using a kinetic pseudo-second-order model.  $v_0$  is  
 824 the initial reaction rate ( $v_0 = \xi_{extent, max} / t_{1/2} * 100$ ). \*: values obtained from fitting of a sigmoidal  
 825 equation ( $\xi_{extent} = \xi_{extent, max} / (1 + \exp(-(t - t_{1/2}) / b))$ ). \*\*: effective reaction rate after the so-called  
 826 incubation period (or induction time) in sigmoidal kinetic behaviors. The alteration rates were  
 827 normalized with respect to initial specific surface area for olivine fine-grains (2.3 m<sup>2</sup>/g).

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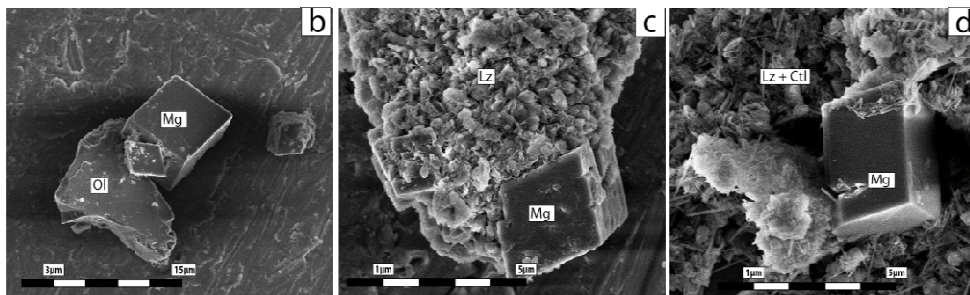
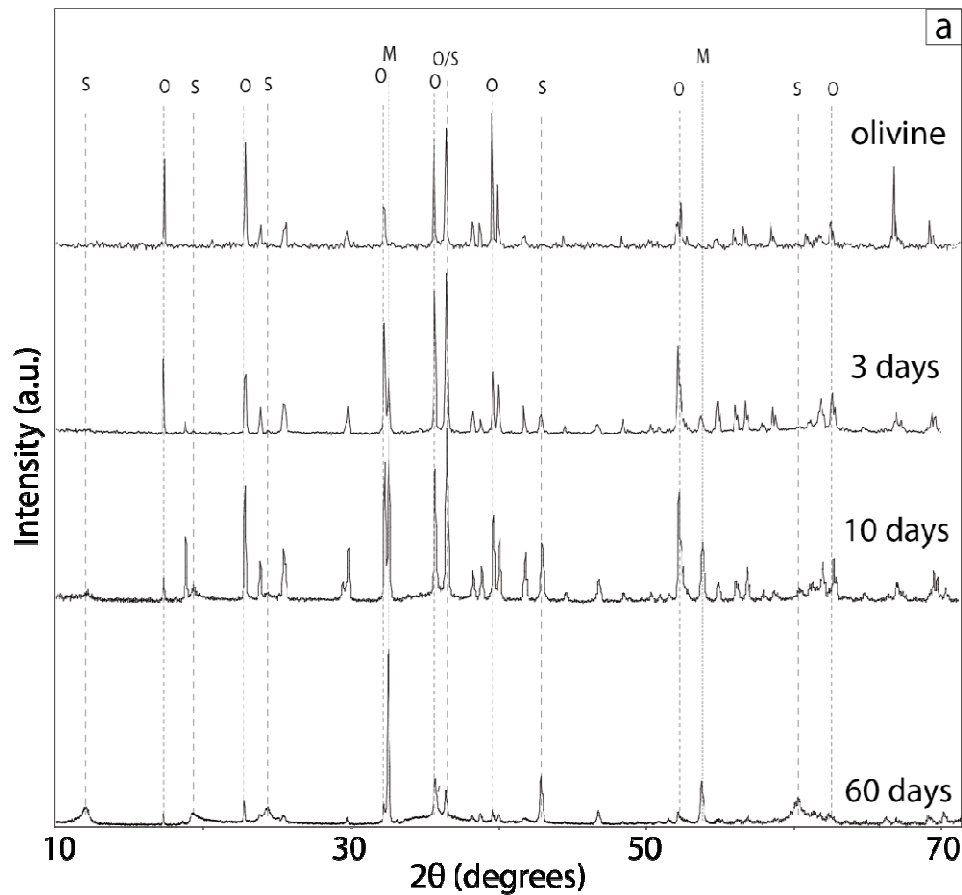
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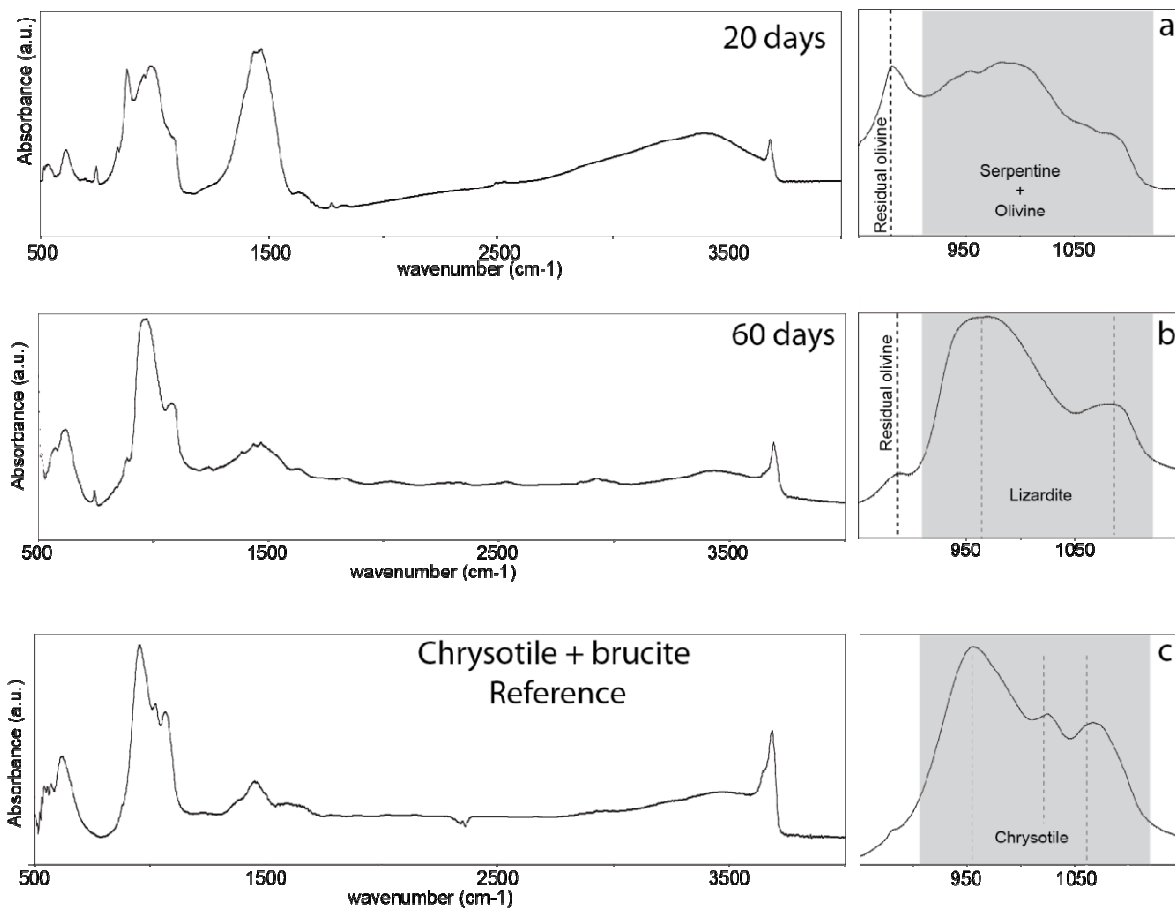


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837 Figure 1. (a) Experimental x-ray diffraction patterns for starting olivine and for products at  
 838 different reaction time (3 days: run 1; 10 days: run 2 and 60 days: run 5); S: serpentine, O:  
 839 olivine, M: magnesite. (b), (c) and (d) FESEM images showing the coexistence of magnesite  
 840 (Mg) and serpentine (lizardite: Lz and chrysotile: Ctl) during olivine (Ol) alteration after 3 days  
 841 “run 1” (b), 10 days “run 2” (c) and 60 days “run 5” (d).

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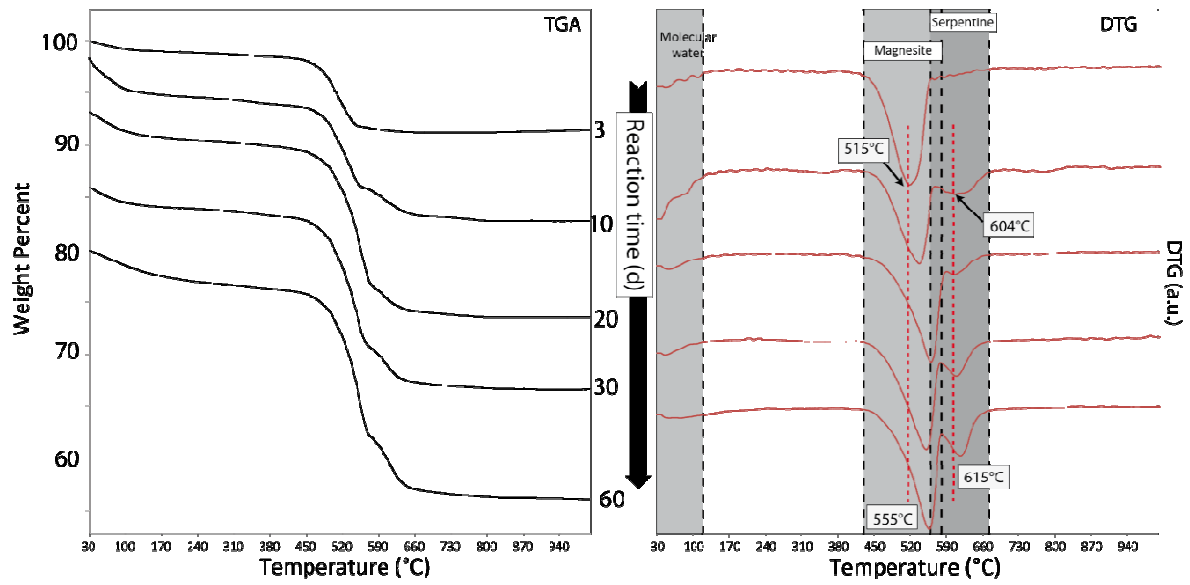
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846 Figure 2. Infrared measurements (in transmission option) showing a preferential lizardite  
 847 formation under high-carbonate alkalinity (panel a “run 3” and b “run 5”) as attested by their two  
 848 typical stretching infrared modes at 966 and 1085  $\text{cm}^{-1}$  for Si-O group (panel b). These infrared  
 849 features are clearly different to infrared features of chrysotile polymorph (panel c).

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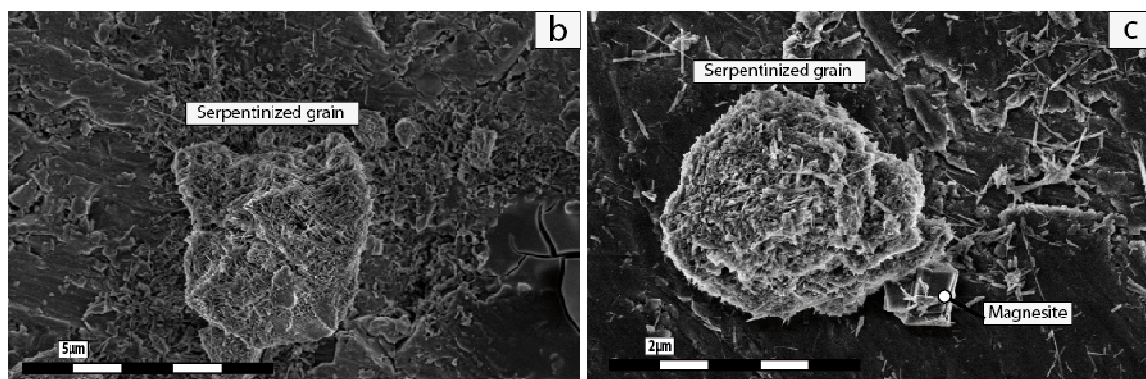
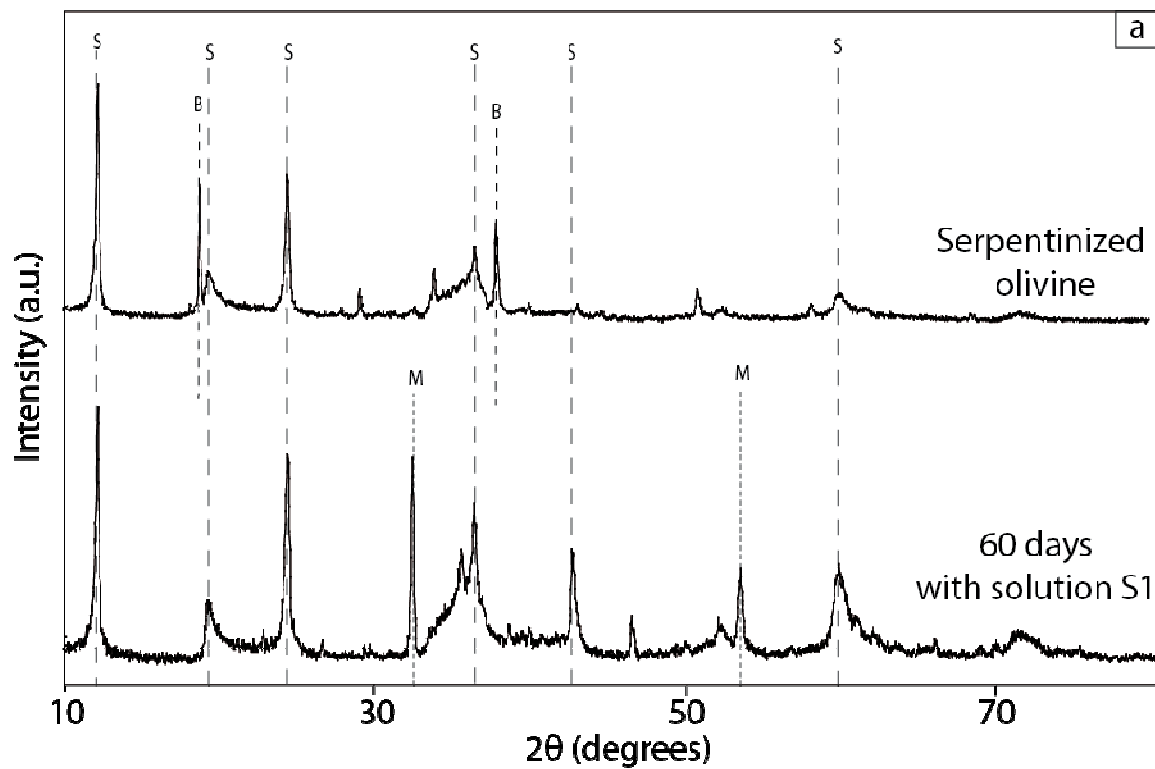
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856 Figure 3. Thermogravimetric analyses (TGA) on the samples collected at different reaction time  
 857 and its respective 1<sup>st</sup> derivative curve (DTG) that enables a temporal quantification of coexisting  
 858 magnesite and serpentine in the samples (runs 1 to 5, see also Table 1 than summarize all TGA  
 859 values ). Magnesite and serpentine decomposition seem to be shifted from 515 to 555°C and from  
 860 604 to 615°C, respectively (DTG graphs); probably due to a progressive crystal size evolution  
 861 and/or mineral proportion.

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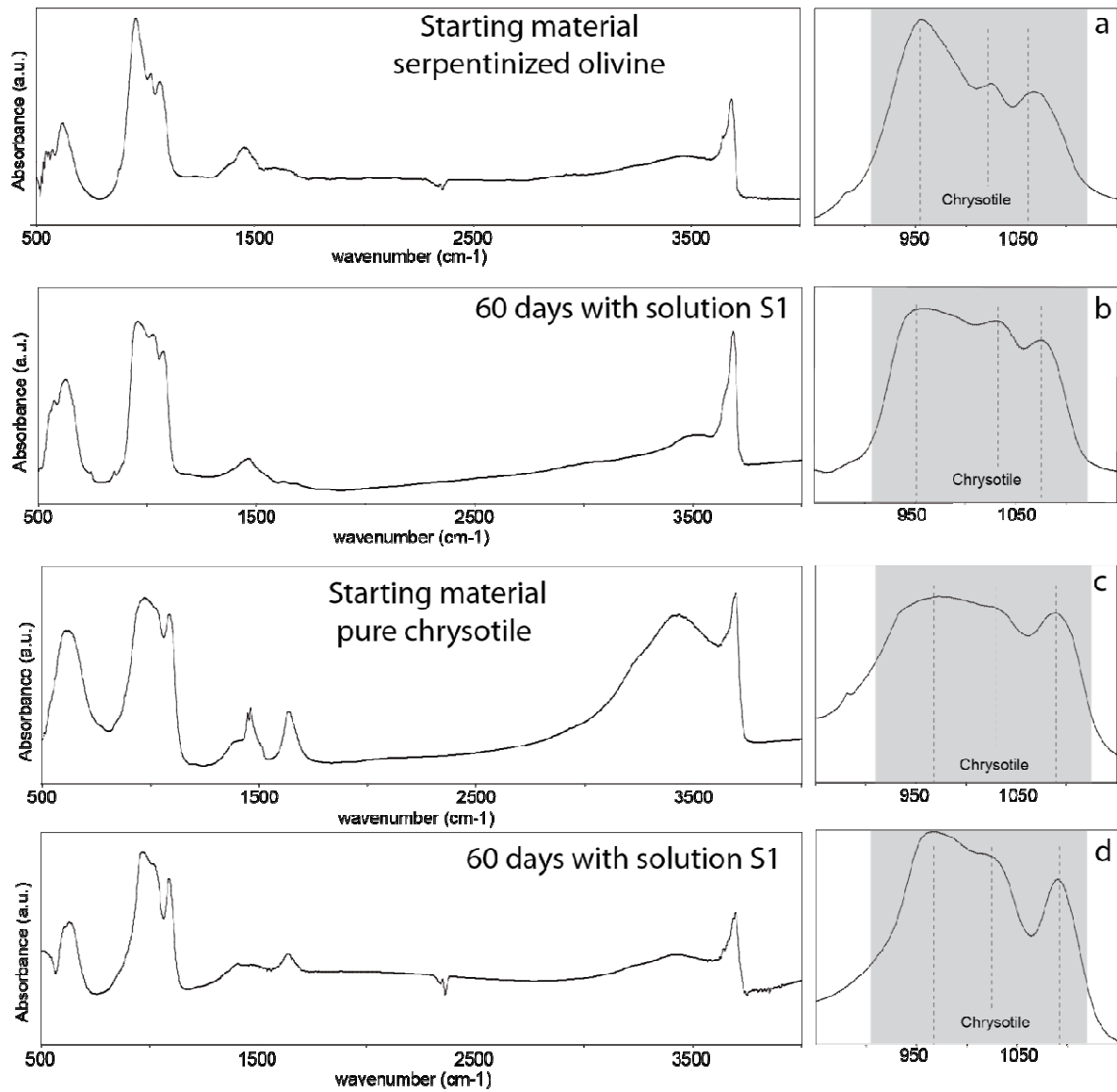
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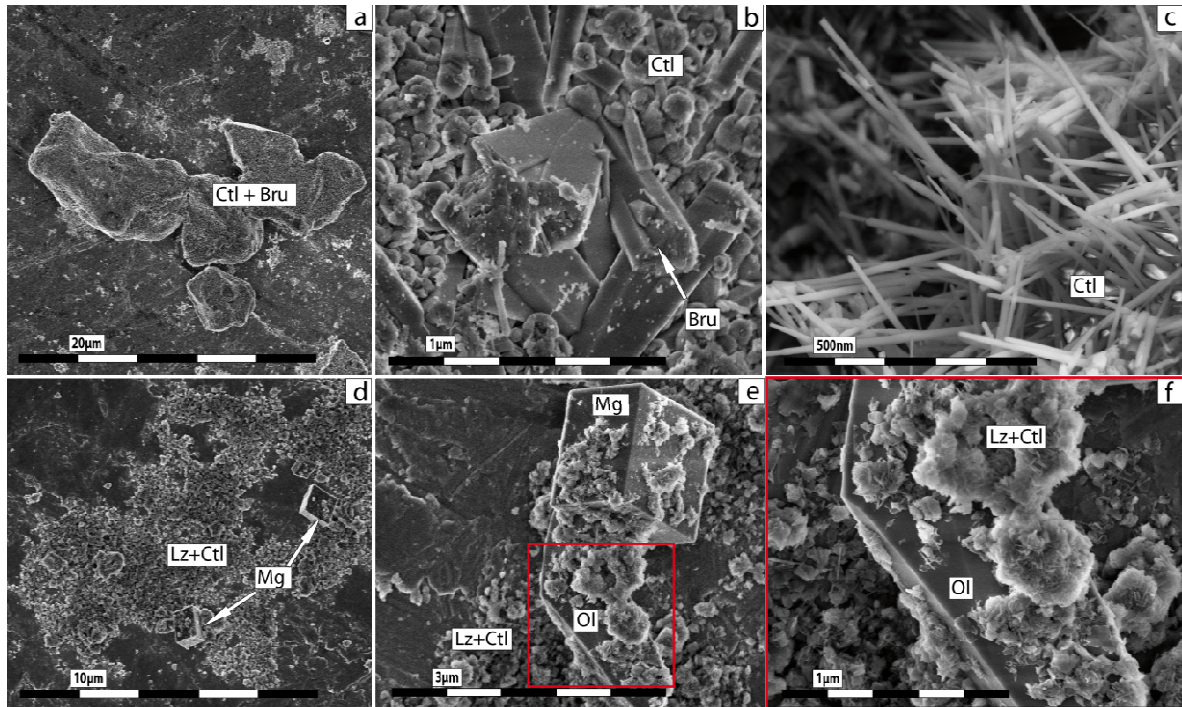
866 Figure 4. Reactivity of serpentinized olivine (chrysotile+brucite+small amount of residual olivine  
 867 as starting material) in high-carbonate alkalinity at 200°C. XRD patterns for starting material and  
 868 after 60 days of reaction (run 15) show only brucite-to-magnesite transformation (a) in agreement  
 869 with FESEM observations. (b) Starting material and (c) after 60 days of reaction (run 15).



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871 Figure 5. Infrared measurements confirming slight or insignificant structural changes in reacted  
 872 chrysotile in high-carbonate alkalinity at 200°C. Two cases, chrysotile contained in the  
 873 serpentinized olivine (panels: (a): starting material and (b): after 60 days of reaction “run 15”)  
 874 and high-purity synthetic chrysotile (panels: (c): starting material and (d): after 60 days of  
 875 reaction “run 10”).





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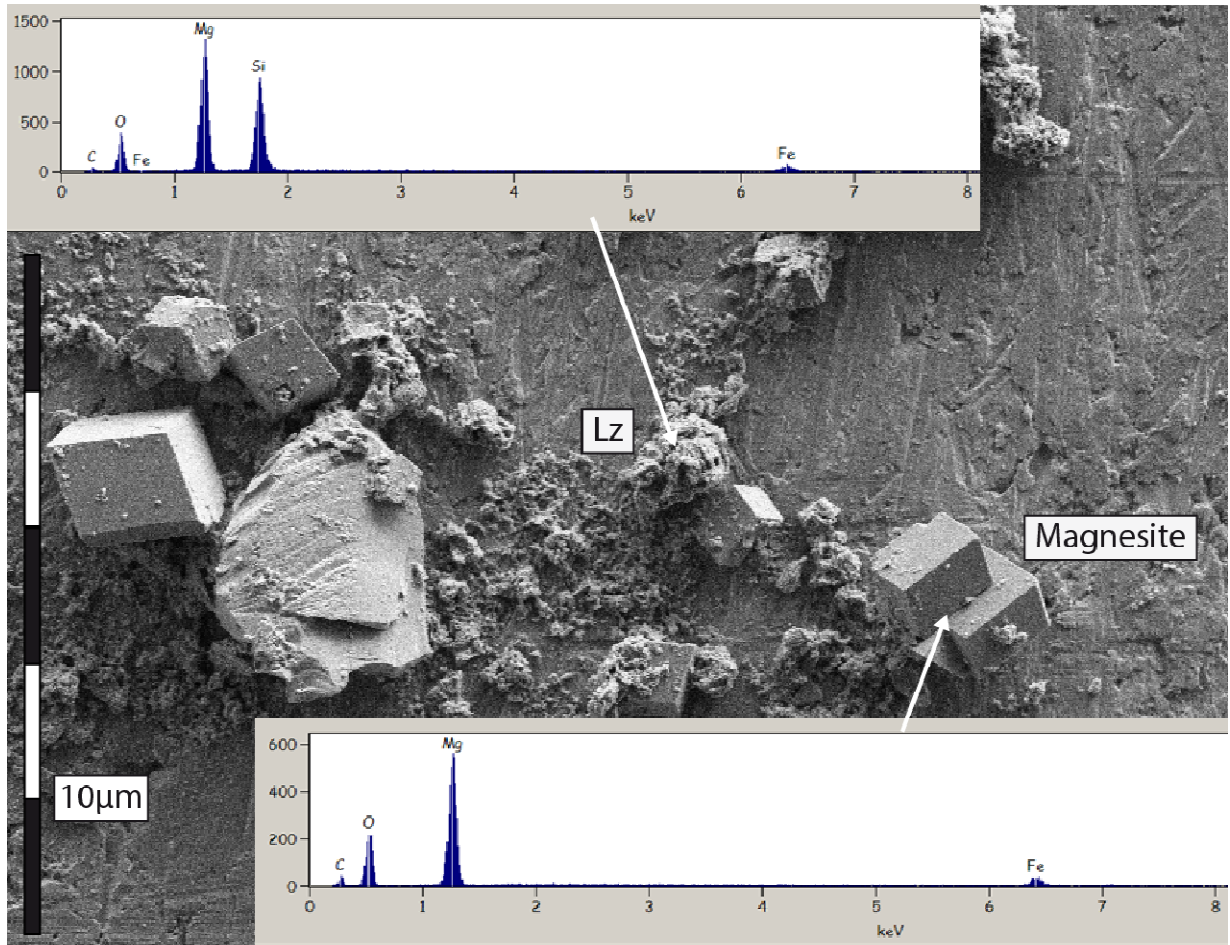
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881 Figure 6. FESEM images: (a), (b) and (c) show mineral replacement of olivine by chrysotile and  
 882 brucite under high-hydroxyl alkalinity, implying the preservation of original external shape of  
 883 olivine grains (image (a), see also Lafay et al. 2012). (d), (e) and (f) show the coexistence of  
 884 magnesite and serpentine precipitation during olivine alteration under high-carbonate alkalinity  
 885 without preservation of original external shape of olivine grains (run 5).



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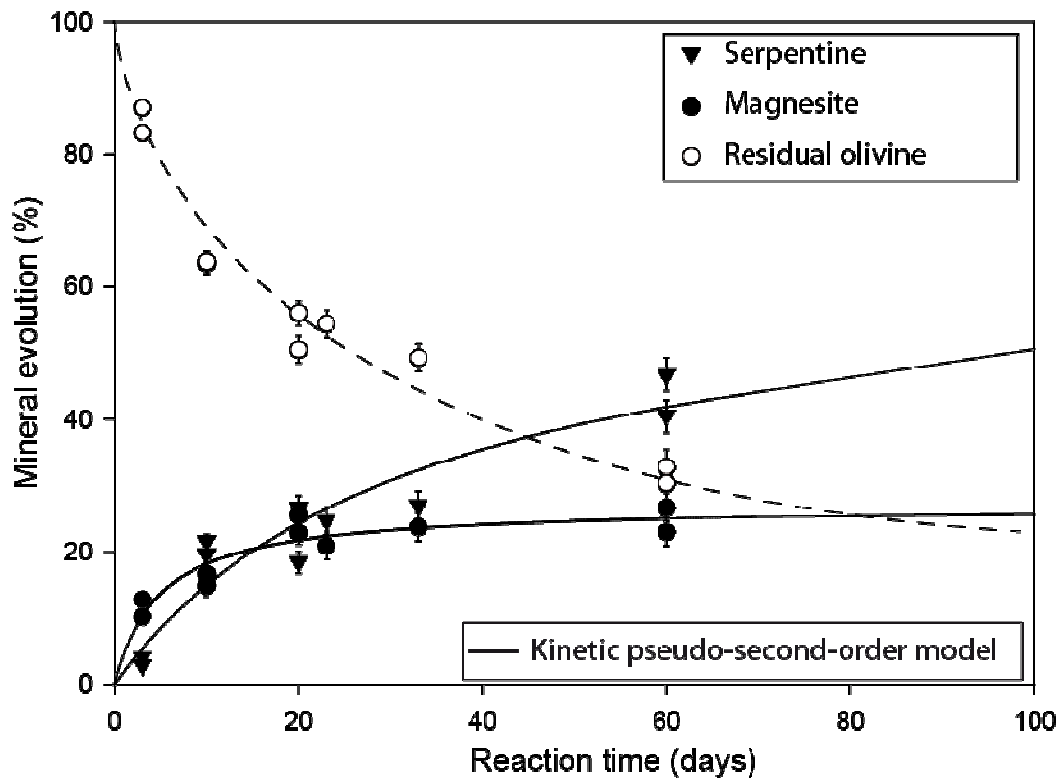
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889 Figure 7. FESEM/EDS chemical analyses have revealed complex fate of released iron initially  
 890 contained in San Carlos olivine. Iron content in magnesite suggests partial iron oxidation via  
 891 water reduction (sample concerning the run 5).

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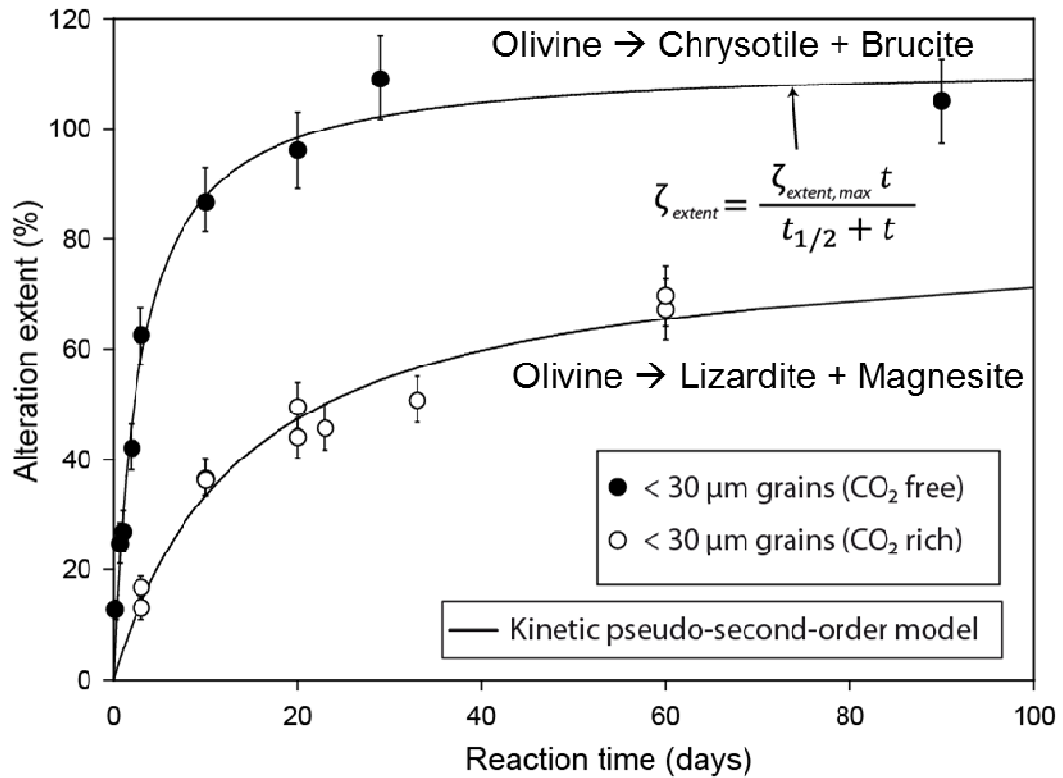
896 Figure 8. Competitive kinetic behavior of magnesite and serpentine during olivine alteration  
 897 under high-carbonate alkalinity (runs 1 to 5 and 16 to 20). Experimental kinetic data for  
 898 magnesite and serpentine were fitted by using a kinetic pseudo-second-order model and kinetic  
 899 parameters are reported in Table 2.

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907 Figure 9. Alteration kinetic of olivine under high-hydroxyl alkalinity (circles filled) (from Lafay

908 et al., 2012) and under high-carbonate alkalinity (open circles) (from runs 1 to 5 and 16 to 20).

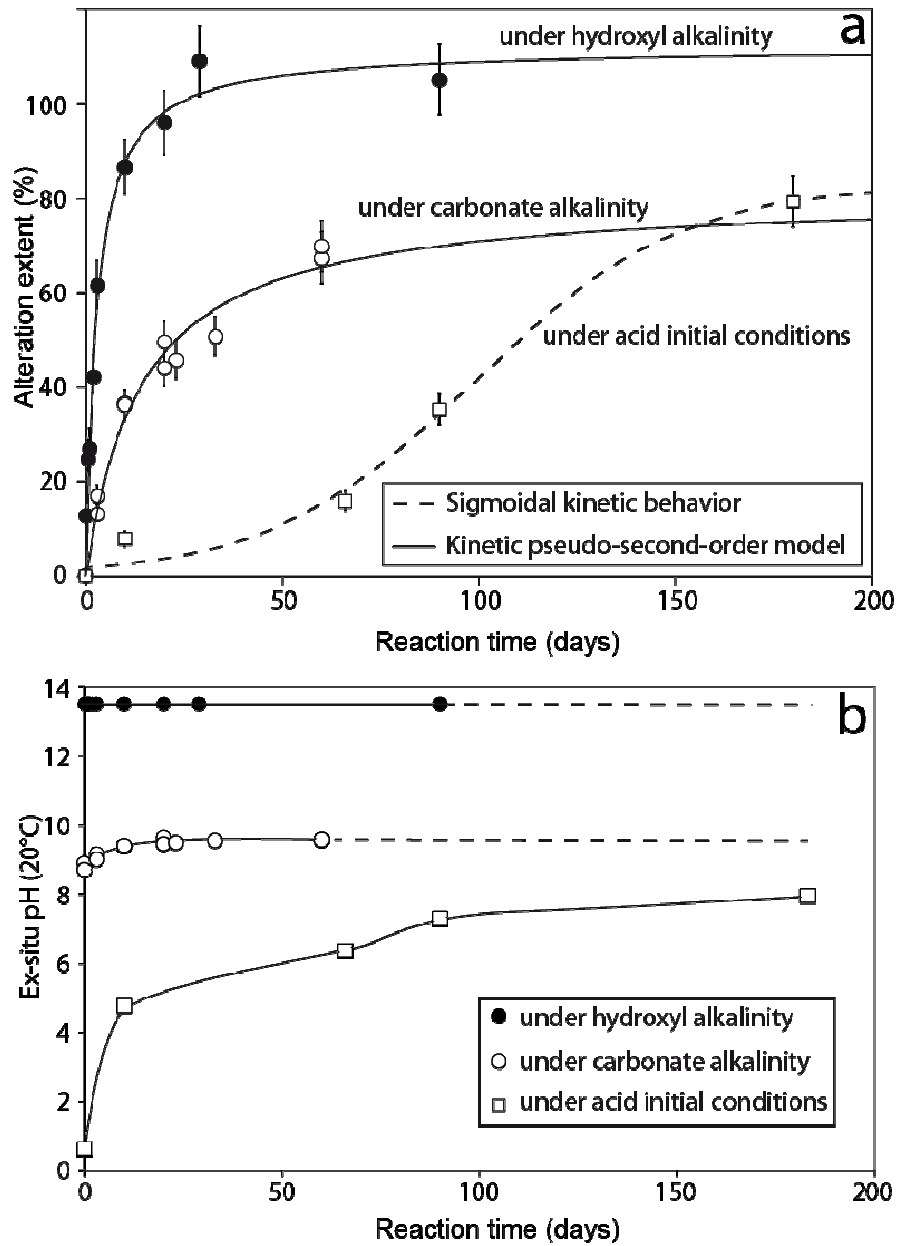
909 Experimental kinetic data were fitted by using a kinetic pseudo-second-order model and kinetic

910 parameters are reported in Table 2.

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915 Figure 10. (a) Alteration kinetic of olivine under high-hydroxyl alkalinity (circles filled) (from  
 916 Lafay et al. 2012), under high-carbonate alkalinity (open circles) (from runs 1 to 5 and 16 to 20)  
 917 and initiated in acid pH (open squares) (from runs 21 to 24). (b) pH evolution for each scenario  
 918 measured ex-situ at room temperature  $\approx 20^{\circ}\text{C}$ .