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1 **Revision 2**

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3 **Control of CO₂ on flow and reaction paths in olivine-dominated basements: an**
4 **experimental study**

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36

37 **Abstract**

38

39 The objective of this paper is to quantify the mass transfers involved in the hydrothermal
40 alteration of olivine-rich peridotites in the presence of CO₂-enriched waters, and to determine
41 their effects on the rock hydrodynamic properties. Three flow-through experiments were
42 performed at a temperature of 185 °C and a total pressure of 22.5 ± 2.5 MPa. They consisted
43 in injecting a hydrothermal fluid with different concentrations of carbon dioxide (CO₂ = 6.26,
44 62.6 and 659.7 mmol.L⁻¹ i.e. pCO_2 = 0.1, 1 and 10 MPa, respectively) into cylinders of
45 sintered San Carlos (Arizona, USA) olivine grains. The results show that for low pCO_2
46 conditions (from 0.1 to 1 MPa), olivine is mainly altered into hematite and Mg(Fe)-rich
47 phyllosilicates. Such iddingsitic-type assemblages may clog most of the rock flow paths,
48 resulting in a strong decrease in permeability. Rare Ca-Fe-carbonate minerals also
49 precipitated under these conditions despite the initial Mg-rich system. For higher pCO_2
50 conditions (~10 MPa), olivine is more efficiently altered. A greater amount of poorly
51 crystallized Fe(Mg)-rich phyllosilicates and magnesite is produced, and the carbonation rate
52 of olivine is 3 to 11 times higher than when the pCO_2 is 10 to 100 times lower. Interestingly,
53 the changes in porosity caused by the formation of carbonated and hydrous minerals are small
54 while a strong decrease in permeability is measured during the experiments. The formation of
55 reduced carbon is also observed. It is located preferentially at the inlet, where pH is the
56 lowest. This testifies to a competition between reduction (probably associated with the
57 oxidation of ferrous iron) and carbonation; two processes involved in the fixation of CO₂ in a
58 mineral form. One may speculate that the formation of reduced carbon can also be a
59 significant mechanism of CO₂ sequestration in olivine-dominated basements.

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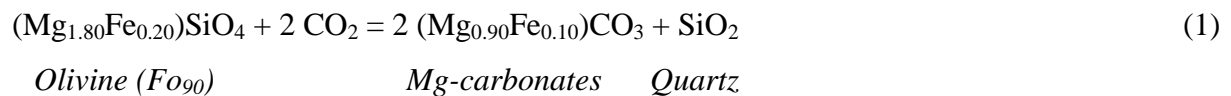
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69 **Keywords:** Olivine, carbonation, reduced carbon, reactive-percolation experiments, porosity,
70 permeability, fluid flow.

71

1. Introduction

Carbonation of mafic and ultramafic rocks (mainly basalts and peridotites) is a widespread process in nature for example, in the past and present oceanic crust and mantle exposed on the seafloor (e.g., Nakamura and Kato, 2004; Ludwig et al., 2006) and within ophiolites (Matter and Kelemen, 2009; Noël et al., 2018). It occurs through the interaction of carbon dioxide (CO₂) with divalent metal ions (Mg²⁺, Fe²⁺, Ca²⁺) contained in mafic silicates (e.g., olivine) to precipitate solid carbonate minerals and quartz (e.g., Oelkers et al., 2008):



Natural carbonation of mafic and ultramafic basements controls part of the Earth's carbon cycle by contributing to the uptake of CO₂ deriving, for example, from the atmosphere, magmatic degassing and C-bearing mineral leaching (Zeebe and Caldeira, 2008; Coggon et al., 2010; Dasgupta and Hirschmann, 2010; Rausch et al., 2013; Kelemen and Manning, 2015). CO₂ mineral trapping in mafic and ultramafic aquifers is also envisioned as a safe way for mitigating carbon anthropogenic emissions to the atmosphere (e.g., Seifritz, 1990). This method is being experimented on a large scale via different pilot sites of CO₂ injection into basaltic reservoirs (Gislason et al., 2010; McGrail et al., 2011).

In both natural and industrial CO₂ geological storage sites, carbon trapping will depend on the mass transfer of solute reactants (products) to (from) reaction interfaces. However, modeling the coupled effects of reactive transport mechanisms during *in situ* mineralization of CO₂ in (ultra-)mafic aquifers is challenging because of the complexity of natural systems and the lack of experimental characterization of the effective mechanisms. Most of the laboratory CO₂ mineralization experiments are conducted in closed reactors (i.e. with no renewing of the solute) and high water-rock ratios (Pokrovsky and Schott, 2000; Giammar et al., 2005; Hänchen et al., 2006; Hänchen et al., 2008; Daval et al., 2011; Kelemen et al., 2011; Klein and McCollom, 2013; Sissmann et al., 2014). Conversely, aquifers are known to be dynamic systems where local chemical equilibria between fluids and minerals are controlled by low water-rock ratios and pore-scale fluid flow (e.g., Steefel et al., 2005). Extensive outcrops of weathered peridotites show different forms and degrees of CO₂ mineralization based on local geological contexts i.e. on small scale variations in the chemistry and hydrodynamic rock properties: carbonates may form large chimneys in deep-sea hydrothermal sites (e.g., Ludwig et al., 2006), travertine deposits from springs in peridotite catchments (Kelemen and Matter, 2008), but also geometrical veins through partially hydrated (Noël et al., 2018) to fully

106 carbonated peridotites, such as ophicalcite (Bernoulli and Weissert, 1985; Schwarzenbach et
107 al., 2013) and listvenite (Hansen et al., 2005; Nasir et al., 2007).

108 In agreement with these natural analogues, some recent reactive percolation experiments
109 conducted on ultramafic cores pointed out the role of fluid flow velocity and pore geometry
110 on the nature and rate of carbonation reactions by controlling chemical microenvironments at
111 the pore scale (Andreani et al., 2009; Godard et al., 2013; Peuble et al., 2015a; Peuble et al.,
112 2015b; Luhmann et al., 2017b). Olivine was proposed to be preferentially dissolved in high
113 flow areas facilitating high fluid-rock disequilibrium conditions while carbonates precipitate
114 mostly in reduced flow zones where diffusion-dominated transport favors the mixing of
115 reactants and their high residence time in the vicinity of the reaction zone (Andreani et al.,
116 2009). Similarly, Peuble et al. (2015b) reported that carbonates grow perpendicular to the
117 main fluid flow direction i.e. where the fluid velocity field tends toward zero promoting
118 cationic supersaturation conditions. Chemical microenvironments may vary in space and time
119 within a porous aquifer depending on its structure, flow paths and successive dissolution-
120 precipitation reactions. For instance, the pH of the fluid increases during its percolation in
121 olivine cores leading to changes in secondary mineralogy marked by the replacement of
122 carbonates by serpentine-type minerals (Peuble et al., 2015b). Likewise, a lateral and
123 temporal variation of CO₂ concentration may also control fluid-rock interaction reactions.
124 Hänchen et al. (2008) observed that the transformation of olivine into magnesite under a
125 partial pressure of CO₂ (pCO_2) of 0.1 MPa and a temperature of 120 °C is slowed down by
126 intermediate reactions: it occurs through the destabilization and/or dissolution of
127 hydromagnesite which itself nucleates from brucite. On the other hand, olivine can be directly
128 dissolved into magnesite at a pCO_2 of 10 MPa for similar temperature conditions (Hänchen et
129 al., 2008). This would induce significant changes in reaction pathways within mafic and
130 ultramafic reservoirs permeated by CO₂ influxes, as CO₂ injection wells in the context of C-
131 sequestration industrial sites.

132 In turn, carbonate formation is likely to have negative feedback effects on fluid flow by
133 decreasing the porosity and permeability of the rock (Oelkers et al., 2008; Jun et al., 2013;
134 Peuble et al., 2015b). The alteration of olivine-dominated basements into carbonates is
135 considered as a volume-increasing process since the volumetric mass density of products
136 (e.g., 3.0 g.cm⁻³ for magnesite) is lower than that of reactants (e.g., 3.3 g.cm⁻³ for olivine)
137 (Deer et al., 1992). As a result, the further carbonation of mafic silicates will rely on cracks,
138 induced by tectonic stresses (Andreani et al., 2007) or by crystal-growth (Jamtveit et al.,
139 2008; Rudge et al., 2010; Kelemen and Hirth, 2012), to preserve fluid pathways in the host

140 rock unless reaction products are leached out by the fluid flow to maintain pore volume and
141 permeability at reaction interfaces (Godard et al., 2013; Peuble et al., 2017).

142 Defining the main parameters controlling the development of one suite of chemical and
143 mineralogical reactions at the expense of another, but also their feedback effects on
144 hydrodynamic rock properties is therefore challenging in systems as complex as natural
145 geological porous media where temperature, pressure, composition and permeability will
146 change along flow paths. Numerical simulations allow to integrate the role of coupling
147 between chemistry, transport and fluid flow e.g., JChess geochemical code (Van der Lee et
148 al., 2003) or PhreeqC geochemical code (Parkhurst and Appelo, 2013). However, these
149 modelling tools are designed to handle transport at the Darcy's scale for which the primary
150 upscaling of the flow and transport is implicitly performed. This implies that the local spatial
151 variability of the velocity field (controlled by the Stokes flow) inherent to the geometrical
152 heterogeneity of the connected porosity as well as the local mineralogical heterogeneity are
153 averaged into volumes, named as Representative Elementary Volumes (REV) encompassing
154 several pores. For instance, these models assume (*i*) a full mixing of solutes at the REV scale
155 and comprehensibly a full accessibility of all reactants to reactive surfaces, and (*ii*) a constant
156 residence time of chemical species into the entire REV. The results of the flow-through
157 experiments cited above indicate clearly that these assumptions cannot be considered a priori,
158 i.e. that pore scale heterogeneities are often controlling overall mass transfers for the space
159 and time characteristics under consideration. Yet, the scarcity of experimental data compared
160 to the large variability of potentially realistic situations makes the derivation of reliable
161 upscaling models challenging. For example, it is critical to study the functional dependencies
162 between chemical, hydrodynamic and mechanical processes for experimental configurations
163 with low degree of freedom, in order to characterize the role of surface processes and kinetics
164 versus equilibrium (Pokrovsky and Schott, 2000; Bearat et al., 2006; Daval et al., 2013).

165 In this paper, we present and discuss the results of three reactive percolation experiments
166 conducted on sintered olivine cores at various CO₂ partial pressure (pCO_2). All other
167 characteristics are similar for the three experiments. The objective of this study is to
168 investigate olivine alteration processes under different pCO_2 in order to reproduce the
169 conditions close and far from a CO₂ inflow percolating an ultramafic setting. We aim to
170 characterize the mechanisms controlling fluid chemistry, secondary mineralogy and their
171 consequences on the hydrodynamic rock properties (i.e. porosity and permeability) in the
172 context of CO₂-fluids interactions with ultramafic rocks. Results are compared to previous

173 experimental studies and discussed in the context of natural and anthropically induced
174 hydrothermal systems in ultramafic rocks.

175

176 **2. Methodology**

177

178 *2.1. Experimental protocol*

179

180 Three reactive percolation experiments were performed using the Icare Lab 3 reactive
181 flow-through system (ICARE-RFTS3, Geosciences Montpellier). They were conducted under
182 similar conditions of flow injection rate (0.5 mL.h^{-1}), temperature ($185 \text{ }^\circ\text{C}$) and average
183 pressure ($22.5 \pm 2.5 \text{ MPa}$), but with setting the $p\text{CO}_2$ of the injected fluid at 0.1, 1 and 10 MPa
184 respectively in order to investigate only the effect of changes in CO_2 concentration on fluid-
185 rock interactions.

186 The ICARE-RFTS3 experimental device allows the injection of solutes through
187 permeable samples over the range of pressure and temperature conditions expected in
188 hydrothermal systems and in geological reservoirs targeted for CO_2 sequestration: $P = 0.5 -$
189 40 MPa and $T = 50 - 400 \text{ }^\circ\text{C}$. It is built for exploring mass transfer processes from kinetic-
190 controlled to transport-controlled conditions for samples displaying permeability values
191 ranging from 10^{-20} to 10^{-13} m^2 .

192 ICARE-RFTS3 (Fig. 1) includes (i) a fluid injection system, comprising three computer-
193 controlled motorized dual-piston pumps programmed to achieve the mixing of CO_2 with
194 water and then inject the mixture through the sample at a constant flow rate, (ii) a heated
195 sample-holder, maintaining the sample at the given confinement pressure using a motorized
196 piston pump, (iii) a back pressure controller equipment, composed of a motorized piston
197 pump coupled with a large volume pneumatic dumper, and (iv) an automatic sampling system,
198 allowing to sample $\approx 3 \text{ mL}$ of fluid directly from the rock sample outlet. All surfaces of the
199 ICARE-RFTS3 system in contact with the fluid are made of Hastelloy C22. The motorized
200 piston pumps are equipped with displacement encoders allowing an accurate control of the
201 flow injection rate; fluctuations are less than 0.1% of the flow injection rate. Continuous flow
202 rates ranging from 3.4×10^{-3} to 10^2 mL.h^{-1} ($9.5 \times 10^{-13} - 2.8 \times 10^{-8} \text{ m}^3.\text{s}^{-1}$) can be operated.
203 All pumps, valves and the sampling system are controlled by a LabView® program according
204 to the user requirements. Both axial and radial confining pressures are applied to the sample
205 fitted into a tight Teflon sleeve. The confinement pressure is set to 112% of the inlet fluid
206 pressure during the experiments (from the loading to the unloading of the circuit fluid

207 pressure) in order to minimize deviatoric stresses. During reactive percolation experiments, a
208 porous nickel sinter is positioned upstream of the sample to ensure a homogeneous
209 distribution of the flow.

210 The difference in fluid pressure between the inlet and the outlet of the sample, ΔP (in Pa),
211 is monitored during the experiments using a differential pressure sensor (Rosemount® 3051
212 with an accuracy of 3×10^3 Pa) coupled with two high-resolution pressure sensors (Keller®
213 PA-33x with an accuracy of 3.5×10^4 Pa). Assuming laminar flow conditions, the sample
214 permeability k (in m^2) was calculated from Darcy's law:

$$k = \frac{Q \cdot \mu \cdot L}{S \cdot \Delta P} \quad (2)$$

215 where Q is the flow injection rate ($\text{m}^3 \cdot \text{s}^{-1}$), L and S the length (m) and section area (m^2) of
216 the sample, respectively, and μ is the dynamic fluid viscosity set at 1.5×10^{-4} Pa.s for water at
217 185 °C (Mao and Duan, 2009).

218

219 *2.2. Preparation and composition of olivine cores and injected fluids*

220

221 The percolation experiments were performed on cores (≈ 16 mm length \times 6.35 mm
222 diameter) made of sintered San Carlos (Arizona, USA) olivine grains. The sintering technique
223 was used because it allows obtaining solid aggregates of controlled porosity and composition
224 (Table 1 and Appendix A1).

225 The starting material consisted of millimeter-size grains of San Carlos olivine (Fo₉₀, see
226 Appendix A1). Olivine grains were sorted under binocular microscope to eliminate those
227 having spinels or pyroxenes on their surfaces or as inclusions. The selected grains were
228 crushed and sieved. The 100 – 150 μm olivine fraction was then cleaned ultrasonically for 10
229 min in diluted hydrochloric acid ($\approx 2\%$ HCl) to remove any carbonate grains and finally
230 rinsed in MilliQ-water for 15 min. The cleaning and rinsing procedure was repeated three
231 times before drying the powder at 110 °C for 12 hours. Bulk composition of the resulting
232 olivine powder was analyzed by X-ray fluorescence spectroscopy (Geolabs, Canada) and
233 compared to the composition of the olivine grains measured by electron probe micro-analyzer
234 (EPMA, University of Montpellier; Appendix A1). Bulk and mineral compositions were
235 similar indicating that no contamination occurred during the preparation procedure.

236 Three sintered olivine cores were made using the following procedure. First, the 100 –
237 150 μm fraction of the cleaned olivine powder was pressed at 5 MPa and 25 °C in stainless
238 steel capsules. Then, samples were sintered at a temperature of 1180 °C and a confining

239 pressure of 150 MPa using a gas medium (Ar) high-pressure and high-temperature vessel
240 (Paterson, 1990) at Geosciences Montpellier. For each core, the initial porosity was measured
241 before the percolation experiment using the triple weight method (Dullien, 1979); it ranged
242 between 10.57 and $11.30 \pm 0.10\%$ (Table 1). Experiments were performed on samples named
243 SC1-L, SC2-M and SC3-H, which have similar initial permeability ($1.6 - 4.6 \times 10^{-15} \text{ m}^2$;
244 Table 1).

245 The inlet fluid was a mineral water (Volvic[®]) mixed with various concentrations of
246 gaseous CO₂. The Volvic[®] water was selected because of its chemical composition that is
247 stable and typical of aquifers containing mafic minerals (e.g., olivine) under low temperature
248 conditions (50 – 200 °C; Table 2 and Appendix A2). The rationale was to reproduce chemical
249 conditions similar to those anticipated for CO₂ industrial storage in igneous basements, close
250 and far from an injection site. The Volvic[®] water was first vacuumed for three hours at room
251 temperature to degas it and thus reproduce anoxic conditions. Then it was mixed with gaseous
252 CO₂ at 30 MPa and 25 °C by repeated back-and-forth pumping between two out of the three
253 injection pumps for three hours (Fig. 1). The pH of Volvic[®] water at 25 °C is 7.0. After
254 mixing with CO₂, the inlet fluid pH at 185 °C and 22.5 ± 2.5 MPa was calculated using
255 PhreeqC and the Lawrence Livermore National Laboratory ‘thermo.com.V8.R6.230’
256 thermodynamic database (Parkhurst and Appelo, 2013): pH = 4.5, 3.9 and 3.4 for the
257 experiments SC1-L (experiment at the lowest $p\text{CO}_2 = 0.1$ MPa; $\text{CO}_2 = 6.26 \text{ mmol.L}^{-1}$), SC2-
258 M (experiment at medium $p\text{CO}_2 = 1$ MPa; $\text{CO}_2 = 62.6 \text{ mmol.L}^{-1}$) and SC3-H (experiment at
259 the highest $p\text{CO}_2 = 10$ MPa; $\text{CO}_2 = 659.7 \text{ mmol.L}^{-1}$), respectively.

260

261 *2.3. Analytical methods*

262

263 The chemical composition of the inlet and outlet fluids was measured on an Agilent 7700x
264 inductively coupled plasma – mass spectrometer (ICP–MS) at Geosciences Montpellier
265 (AETE platform, France). All fluids were previously diluted by two in an acidified MilliQ-
266 water ($\approx 2\%$ of nitric acid). Indium (1 ppb) was used as an internal standard during analyses.
267 Both accuracy and reproducibility of the measurements were assessed with the SLRS-5 water
268 standard. The analytical results were within the range of compiled values (Yeghicheyan et al.,
269 2013). The external reproducibility was better than 5% for all measured elements. The Si, Mg,
270 Fe and Ca concentrations of the inlet and outlet fluids and of the SLRS-5 water standard are
271 reported in Table 2 and in the Supplementary Materials (Appendix A3).

272 Both composition and mineralogy of the reacted aggregates were characterized with the
273 methodology described thereafter. Samples magnetic susceptibility was measured before and
274 after each experiment on a Bartington–MS2 meter susceptibility system operating at 0.565
275 kHz for values ranging from 1×10^{-8} to $9999 \times 10^{-8} \text{ m}^3 \cdot \text{Kg}^{-1}$ with an uncertainty of $\approx 1\%$
276 (Geosciences Montpellier).

277 After magnetic susceptibility measurements, the reacted cores were longitudinally sawn
278 into two semi-cylindrical halves. The first half was polished for microscopic and
279 spectroscopic characterizations (scanning electron microscopy, Raman spectroscopy and
280 electron probe micro-analyzer) according to the protocol described in detail in Peuble et al.
281 (2015a). The second half was crushed for bulk powder analyses (Mössbauer spectroscopy and
282 bulk rock carbon and hydrogen measurements).

283 Polished sections were described optically, then backscattered (BSE) and secondary
284 electron (SE) images were collected on a FEI Quanta FEG 200 scanning electron microscope
285 (SEM) using an acceleration voltage of 15 kV and an ambient pressure of 0.45 torr
286 (University of Montpellier, France).

287 Secondary minerals have been also identified on LabRam Aramis IR2 (Charles Gerhardt
288 Institute, Montpellier, France) and XploRa (Laboratory of Geology of Lyon, France) confocal
289 Raman spectrometers (Jobin-Yvon SA, Horiba, France); both equipped with a charge-coupled
290 device (CCD) detector. Raman analyses were performed with 473 nm (LabRam Aramis IR2)
291 and 532 nm (XploRa) radiations from diode lasers generating less than 1 mW. The spectra
292 resolution is $\pm 2 \text{ cm}^{-1}$. Before analyses, Raman spectrometers were calibrated using a
293 crystalline silicon thin-section showing a large band at $521 \pm 2 \text{ cm}^{-1}$.

294 The composition of primary and secondary minerals was measured on carbon-coated
295 polished sections (thus precluding further investigations on C-phases) using a Cameca SX-
296 100 EPMA (University of Montpellier) equipped with five wavelength-dispersive X-ray
297 spectrometers (WDS). Analyses were done at an acceleration potential of 20 kV and a beam
298 current of 10 nA. Results are summarized in Appendix A1.

299 The presence (or lack) of ferric iron in the reacted samples was measured by Mössbauer
300 spectroscopy at the Charles Gerhardt Institute (Montpellier, France) with a detection limit of
301 $\approx 2\%$. Mössbauer data were acquired at ambient temperature on $\approx 200 \text{ mg}$ bulk rock powders
302 in the constant acceleration mode. ^{57}Fe Mössbauer spectra were obtained using a source of
303 ^{57}Co in rhodium metal. The spectrometer was operated using a triangular velocity waveform.
304 Gamma rays were detected with a NaI scintillation detector. Spectra were fitted with a
305 combination of Lorentzian lines then used to determine the spectral parameters i.e. the isomer

306 shift (IS), the electric quadrupole splitting (QS), the full line width at half maximum (LW)
307 and the relative resonance areas (A) of different components of the absorption patterns (see
308 Appendix A4). The magnetic hyperfine field (H) is absent in the case of these samples
309 confirming the paramagnetic character of the analyzed phases.

310 Bulk carbon (in inorganic and organic form) and water compositions were determined
311 using step-heating experiments (Javoy and Pineau, 1991; Pineau and Javoy, 1994) at the IPGP
312 (Institut de Physique du Globe de Paris, France) on ≈ 100 mg aliquots. First, powders were
313 loaded in a quartz tube connected to a vacuum line and degassed one night at room
314 temperature. A vertical cylindrical furnace (with a temperature stability of ± 2 °C) was then
315 used to heat progressively the samples at 100 °C for 1 hour to eliminate all surface
316 contaminants e.g., water and other adsorbed compounds. Finally, samples were heated 1 hour
317 at 700 °C and 1 hour at 1100 °C to extract the carbon trapped in the organic and inorganic
318 form respectively. Heating was made under an oxygen atmosphere raised up to 0.4 MPa after
319 30 min of reaction. Liquid nitrogen was used to cryogenically separate and collect gaseous
320 CO₂ and H₂O. The amount of CO₂ was quantified using a Toepler® pressure gauge with a
321 detection limit of 0.05%. Carbon and water analyses were duplicated to ensure the
322 reproducibility of the data.

323

324 **3. Results**

325

326 *3.1. Permeability*

327

328 All reactive percolation experiments displayed a reduction in sample permeability from
329 initial values of $1.6 - 4.6 \times 10^{-15}$ m² (Table 1) down to 0.075×10^{-15} m² (SC1-L), 0.019×10^{-15}
330 m² (SC2-M) and 0.005×10^{-15} m² (SC3-H; Fig. 2). In detail, the way in which permeability
331 decreased varied from one experiment to the other.

332 The permeability of experiment SC1-L decreased slightly in the early hours of injection
333 ($dk/dt = 1.40 \times 10^{-17}$ m².h⁻¹) before dropping down to 0.08×10^{-15} m² at $t \approx 36$ h and declining
334 slightly again until the end of fluid injection ($dk/dt = 6.30 \times 10^{-19}$ m².h⁻¹).

335 Experiment SC2-M is characterized by four periods of fast permeability drop starting at t
336 ≈ 13 h ($dk/dt = 1.40 \times 10^{-15}$ m².h⁻¹), $t \approx 54$ h ($dk/dt = 5.62 \times 10^{-16}$ m².h⁻¹), $t \approx 84$ h ($dk/dt = 9.29$
337 $\times 10^{-17}$ m².h⁻¹) and $t \approx 107$ h ($dk/dt = 2.10 \times 10^{-16}$ m².h⁻¹). These periods were separated by four
338 intervals of low permeability decrease of about 13, 41, 30 and 23 hours, respectively.

339 The permeability of experiment SC3-H is marked by a slow and almost constant decrease
340 of 135 hours ($dk/dt = 1.5 \times 10^{-17} \text{ m}^2\cdot\text{h}^{-1}$), then accelerating sharply at $dk/dt = 4.3 \times 10^{-17} \text{ m}^2\cdot\text{h}^{-1}$.
341 After 168 hours, the decrease in permeability slowed down to $dk/dt = 1.4 \times 10^{-18} \text{ m}^2\cdot\text{h}^{-1}$ until
342 the end of injection.

343

344 3.2. Fluid chemistry

345

346 The outlet fluids composition at the time of sampling (Fig. 3) denotes the value integrated
347 over the volume of fluids having flowed and reacted with the olivine cores over the 6 hours of
348 reactive percolation experiments preceding sampling (each fluid sample is 3 mL and fluid flux
349 Q is $0.5 \text{ mL}\cdot\text{h}^{-1}$). The three experiments were marked by significant changes with time in the
350 outlet fluids composition compared to the injected CO_2 -water. First, all outlet fluids displayed
351 enrichments in the three major components of olivine (i.e. Si, Mg and Fe; Fig. 3a,b,c)
352 testifying to the dissolution of the Mg-silicate during the experiments. Second, the sampled
353 outlet fluids were (or became) depleted in Ca indicating the trapping of this element in the
354 percolated cores through the precipitation of Ca-bearing mineral(s) (Fig. 3d). However, the
355 amount of cations released or trapped per time unit varied between the experiments. It should
356 be noted that the outlet fluids sampled at the earliest stages of all experiments (time of
357 sampling $< 20\text{h}$) systematically displayed chemical compositions at odds with the overall
358 chemical trends showed later in the experiments. These variations are controlled by the
359 dissolution of a minor fraction of small grains produced during the preparation of olivine
360 aggregates (Andreani et al., 2009; Godard et al., 2013; Peuble et al., 2015b). These initial
361 processes will not be discussed in details thereafter and we will mainly focus our analysis to t
362 $> 20\text{h}$.

363 Experiment SC1-L (lowest concentration in $\text{CO}_2 = 6.26 \text{ mmol}\cdot\text{L}^{-1}$) showed a slight
364 increase in the outlet concentrations of Si (from 43.7 to 62.0 ppm), Mg (from 13.5 to 14.8
365 ppm) and Fe (from 0.2 to 0.7 ppm). But the amount of Mg and Fe is low compared to that of
366 Si and to the olivine stoichiometry; the molar ratios of $(\text{Mg}/\text{Si})_{(\text{outlet-inlet})}$ and $(\text{Fe}/\text{Si})_{(\text{outlet-inlet})}$ in
367 sampled fluids are 0.15 and 0.01, respectively. This indicates either that the dissolution of
368 olivine was non-stoichiometric or, more probably, that some of the Mg and Fe released upon
369 olivine dissolution remained trapped in the percolated core. The concentrations of Ca, brought
370 in by the inlet fluid, decreased with time from 12.6 to 10.8 ppm in the sampled fluids. This
371 decrease, particularly marked in the first 48 hours of injection (Fig. 3d), suggests that the
372 outlet fluids Ca composition is partly controlled by cation trapping mechanisms. It is worth

373 noting that the change in chemistry observed in the outlet fluids after 48 hours is close in time
374 to the change in permeability recorded in experiment SC1-L at $t \approx 36$ h.

375 During experiment SC2-M (medium concentration in $\text{CO}_2 = 62.6 \text{ mmol.L}^{-1}$), Si, Mg and
376 Fe also displayed an increase in their outlet concentrations with time. However, Si
377 concentrations were high (107 to 261 ppm) and their variations erratic (peaks observed at $t \approx$
378 13, 83, 134 and 147 hours; Figure 3a) compared to experiment SC1-L. Mg concentrations
379 increased steadily during about 48 hours before stabilizing around 25 ppm. The increase in Fe
380 concentrations followed two plateaus, the first at ≈ 0.3 ppm (from 13 to 109 hours) and the
381 second at ≈ 0.5 ppm (after 122 hours). Compared to experiment SC1-L, Ca concentration
382 values in experiment SC2-M were overall low, decreasing from 12.2 to 9.1 ppm over time.
383 Chemical trends of Si, Mg, Fe and Ca were interpreted as indicating both dissolution of
384 olivine and trapping of Mg, Fe and Ca in the percolated core. Molar ratios of $(\text{Mg/Si})_{(\text{outlet-inlet})}$
385 and $(\text{Fe/Si})_{(\text{outlet-inlet})}$ were low compared to experiment SC1-L with values of 0.09 and 0.002,
386 respectively; suggesting that the mechanisms controlling the trapping of Mg and Fe were
387 overall more efficient in experiment SC2-M. The irregular and abrupt changes in fluid
388 chemistry during experiment SC2-M also suggest that complex feedback processes between
389 these trapping mechanisms, olivine dissolution and fluid fluxes occurred. For instance, the
390 increase in Mg relative to Si in the first 48 hours suggests that Mg-trapping became less
391 efficient than olivine dissolution yet this period is associated to a strong permeability drop.
392 After 122 hours, the experiment is marked by an increase in Si, Fe and, to a lesser extent, in
393 Ca revealing a further decrease in trapping efficiency while olivine dissolution continued and
394 permeability remained stable.

395 Compared with experiments SC1-L and SC2-M, the outlet fluids sampled in experiment
396 SC3-H (highest concentration in $\text{CO}_2 = 659.7 \text{ mmol.L}^{-1}$) are depleted in Fe, but enriched in
397 Mg compared to experiments SC1-L and SC2-M, and in Si compared to experiment SC1-L.
398 Fluid time series are also distinguished by contrasting chemical variations defining two time
399 periods (Fig. 3). The first period, from the start to $t \approx 144$ h, is characterized by large changes
400 in the concentrations of all elements: Si concentrations increased rapidly then stabilized at \approx
401 82 ppm at $t \approx 38$ h; Mg concentrations increased sharply at the beginning then slower after \approx
402 38h before reaching a peak at 64.1 ppm (at $t \approx 70$ h) and decreasing down to 38.3 ppm; Fe
403 concentrations were strongly depleted (< 0.03 ppm) except for a peak (up to 0.19 ppm)
404 between 96 and 140 hours; Ca concentrations showed a strong increase during the first hours
405 until a peak (10.5 ppm) was reached at $t \approx 45$ h followed by a decrease down to 4.7 ppm (at $t \approx$
406 135h). In contrast, the second period, starting after $t \approx 144$ h, is characterized by little to no

407 variations in fluid chemistry. Only Si showed a slow increase up to ≈ 106 ppm and Mg
408 displayed a slight increase at ≈ 45 ppm after 216 hours. Molar ratios of $(\text{Mg}/\text{Si})_{(\text{outlet-inlet})}$ and
409 $(\text{Fe}/\text{Si})_{(\text{outlet-inlet})}$ were low in the SC3-H sampled fluids (0.54 and 0.0005, respectively)
410 suggesting an efficient trapping of Mg and Fe in the olivine aggregate. However, in contrast
411 to the low $p\text{CO}_2$ experiments, $(\text{Mg}/\text{Si})_{(\text{outlet-inlet})}$ changed significantly from 0.70 to 0.43 after t
412 $\approx 144\text{h}$ indicating either a higher release of Si relative to Mg during the dissolution of olivine
413 and/or a more efficient trapping of Mg (together with Ca) during the second period of
414 experiment SC3-H. These chemical changes are associated to variations in rock
415 hydrodynamic properties; the first period is characterized by slow changes in permeability
416 while a significant drop in permeability marks the second period.

417

418 *3.3. Characterization of the reacted samples*

419

420 Optical observations shows that the three rock samples remained mainly composed of
421 olivine after the percolation experiments. However, the initial green olivine crystals are
422 covered by a red hue decreasing in intensity away from the inlet (Fig. 4). The red hue coating
423 increases with the CO_2 partial pressure value used in the experiment; it extends to few mm^2 in
424 sample SC1-L, three-quarters of sample length for sample SC2-M and the whole sample for
425 sample SC3-H.

426 At the micrometric scale, SEM analyses allow the identification of secondary minerals in
427 the three percolated cores (Fig. 5 and Appendix A1). For the lowest $p\text{CO}_2$ experiments (SC1-
428 L, SC2-M), some pores contain clusters of an amorphous phyllosilicate enriched in $\text{Mg} \pm \text{Fe}$
429 (Fig. 5a and Appendix A1). Raman analyses suggest that this phase may represent a poorly
430 crystallized precursor of Mg-Fe-rich hydrous minerals such as Fe(III)-rich serpentine (Fig. 6),
431 which is commonly observed in the earliest stages of serpentinization (Andreani et al., 2013).
432 It has Raman peaks comparable to those of lizardite, with a band at 1104 cm^{-1} (Auzende et al.,
433 2004), and those of iddingsite, a Fe(III)-rich olivine alteration product having a non-definite
434 crystal structure, with a first band observed between 611 and 663 cm^{-1} and a second in the O-
435 H bonds spectral region from 3500 to 3600 cm^{-1} (Kuebler, 2013). This alteration product is
436 probably localized at the surface of olivine grains, since olivine peaks are also identified on
437 the Raman spectrum at 824 and 857 cm^{-1} (Cnopnras, 1991). It is associated with hematite
438 showing four Raman bands at 224 , 300 , 411 and 1322 cm^{-1} (De Faria et al., 1997). Both
439 hydrous phases and iron oxides are found preferentially along the olivine rims located in the
440 vicinity of the inlet; they account for the red hue covering the reacted samples (Fig. 4).

441 Samples SC1-L and SC2-M contain also micro-grains of silica, Mg-Fe-bearing calcite
442 ($\text{Ca}_{0.95}\text{Mg}_{0.03}\text{Fe}_{0.02}\text{CO}_3$) and minor siderite ($\text{Fe}_{0.95}\text{Mg}_{0.04}\text{Ca}_{0.01}\text{CO}_3$) that are distributed evenly
443 along the percolated cores (Fig. 5b-c and Appendix A1).

444 In sample SC3-H, some olivine surfaces exhibit dissolution features forming conical-
445 shaped etch-pits with a maximum length of 1 μm (Fig. 5d-e). Etch-pits are observed along the
446 dissolved olivine surfaces in large pores (10-50 μm) and within the micro-fissures ($< 5 \mu\text{m}$)
447 that were probably induced by the sample preparation (Peuble et al., 2015a). Sample SC3-H
448 also displays large Mg-carbonate crystals ($\text{Mg}_{0.91}\text{Ca}_{0.07}\text{Fe}_{0.02}\text{CO}_3$) forming a matrix of several
449 tens of μm in the pores (Fig. 5f and Appendix A1). This carbonate was identified as
450 magnesite with the typical Raman peak of C-O bonds observed at 1094 cm^{-1} and three minor
451 peaks at 209, 325 and 738 cm^{-1} (Rividi et al., 2010 – see Figure 9). In addition to magnesite, a
452 poorly crystallized phyllosilicate enriched in $\text{Fe} \pm \text{Mg}$ was also characterized in sample SC3-
453 H (Fig. 5d and Appendix A1). This phase forms a dense network of curled fibers similar to
454 the proto-serpentine observed in previous flow-through experiments (Godard et al., 2013). Its
455 Raman spectrum is comparable to the poorly crystallized phase identified in samples SC1-L
456 and SC2-M, forming an assemblage of hydrous minerals and hematite at the olivine grains
457 surface (Fig. 6). The attenuation of the Raman peaks of olivine compared to this proto-
458 serpentine precursor suggests a greater degree of crystallization of the latter in experiment
459 SC3-H than in experiments SC1-L and SC2-M (Kuebler, 2009).

460 Black grains were observed in pores located close to the inlet in the three reacted samples
461 ($< 5 \text{ mm}$ - see Figs. 4 and 8). These micron-size grains ($< 20 \mu\text{m}$) were identified as carbon
462 from the D and G bands observed at respective values of 1310 and 1520 cm^{-1} on Raman
463 spectra (e.g., Galvez et al., 2013). Carbon grains have a symmetrical G band in Raman
464 analyses indicative of a poorly ordered crystallographic structure also referred to as
465 turbostratic. Reduced turbostratic carbon or graphene is commonly reported under low
466 temperature conditions i.e. $< 400 \text{ }^\circ\text{C}$ (Audier et al., 1981; Beyssac et al., 2003).

467 Magnetic susceptibility and Mössbauer analyses were realized on a subset of powders.
468 They show that the precipitation of ferric iron is minimal in the three reacted cores in spite of
469 the change of color observed optically. Samples magnetic susceptibility did not change
470 significantly during reactive percolation experiments suggesting that magnetite did not
471 precipitate during CO_2 -fluids injection (see Table 1). Mössbauer measurements identified no
472 ferric iron impurities in the reacted powders in the limit of $\approx 2\%$ (see Fig. 9 and Appendix
473 A4). Note that all Mössbauer spectra were fitted using two doublets (components 1 and 2
474 corresponding to the M1 and M2 sites of olivine), both having the parameters of high spin

475 Fe²⁺ occupying octahedral sites in the olivine crystals. The isomer shifts and the quadrupole
476 splitting are similar to the reported values for olivine (Dyar et al., 2006). The only differences
477 between these samples are the line widths and the relative fractions of components 1 and 2,
478 which are both within the uncertainty of Mössbauer analyses (i.e. less than $\approx 2\%$ relative to
479 the total iron content).

480 Bulk rock hydrogen and carbon analyses indicate that reacted samples were systematically
481 enriched in these two elements relative to the initial olivine (Table 3 and Appendix A5). This
482 is consistent with the presence of secondary hydrous and carbon-bearing phases revealed by
483 the petrological and mineralogical analyses of reacted samples. Bulk powder measurements
484 also show that carbon is present in both inorganic and organic forms in reacted samples SC2-
485 M and SC3-H. Inorganic carbon (carbonates) is dominant after the highest pCO_2 experiment:
486 it represents 97% of the total carbon measured in sample SC3-H. In contrast, inorganic carbon
487 represents only $\sim 40\%$ of the measured total carbon in sample SC2-M; the remaining fraction
488 being organic (i.e. reduced) carbon, which suggests less favorable conditions for carbonates
489 precipitation under a lower pCO_2 .

490

491 *3.4 Mass estimates of dissolved and precipitated minerals*

492

493 Both olivine and secondary minerals are mainly composed of Si, Mg, Fe and Ca. The
494 mass balance calculation (expressed as oxides mass) of these cations comparing inlet and
495 outlet fluids provides a first insight of the volatile-free bulk mass lost or gained by the
496 ultramafic cores during the experiments (Peuble et al., 2015b). Calculations indicate a total
497 mass loss of 0.22, 1.60 and 2.39% relative to the initial samples mass in experiments SC1-L,
498 SC2-M and SC3-H, respectively (Appendix A6), even though the Ca brought in by fluids is
499 trapped into the samples.

500 Hydrous minerals, oxides and carbonates were identified as secondary phases in the
501 percolated aggregates. Some identified minerals display unreferenced compositions (such as
502 the hydrous phases interpreted as serpentine precursors), albeit they all contain at least Si, Mg,
503 Fe or Ca. Furthermore, bulk analyses could not be used directly to quantify the amount of
504 carbon and hydrogen trapped in reacted samples. First, due to technical problems, hydrogen
505 was not analyzed in one of the samples (sample SC3-H). Second, the distribution of hydrogen
506 and organic and inorganic carbon in sample SC1-L may have been affected by leakage of
507 containment fluid (MilliQ-water in equilibrium with the atmosphere) into the sample Teflon
508 sleeve, when the experiment was stopped ($t \approx 93\text{h}$). For these reasons, the quantification of

509 dissolved and trapped phases was done only on the basis of fluid time series. In such
510 conditions, estimating the actual mass change of the samples during reactions requires making
511 conjectures on the distribution of cations in secondary minerals (Andreani et al., 2009). For
512 this study, we assume that:

513 (i) The excess of Si measured in the outlet fluids, i.e. $Si_{(\text{outlet-inlet})}$, equals to the Si released
514 by the dissolution of olivine only. In other words, we assumed that the amount of Si trapped
515 in the samples is negligible even if Si-rich secondary phases precipitated in the reacted cores.
516 The calculated mass of dissolved olivine is thus a minimal estimate. Accordingly, we
517 calculated a concentration model of the outlet fluids for Mg and Fe involving the mass of
518 these elements released by olivine dissolution and the mass brought in by the injected fluid.
519 The measured deficits in Mg and Fe relative to this concentration model allow estimating the
520 mass of trapped minerals.

521 (ii) Fe was trapped in carbonates during experiments SC1-L and SC2-M, and Mg was
522 sequestered as magnesite in experiment SC3-H. All Ca was incorporated into carbonates in
523 the three experiments (Fe-bearing calcite in samples SC1-L and SC2-M; Ca-bearing
524 magnesite in sample SC3-H).

525 (iii) The contribution of hydrous silicate minerals associated to (proto-)serpentinization of
526 olivine was approximated from pure end-member components that have been described as
527 ‘precursor phases’ of serpentine minerals: brucite ($Mg(OH)_2$) for the Mg(Fe)-rich
528 phyllosilicates in experiments SC1-L and SC2-M (e.g., Ferry, 2000; Tutolo et al., 2018);
529 goethite ($FeO(OH)$) for the Fe(Mg)-rich phyllosilicates in experiment SC3-H (Delvigne et al.,
530 1979; Lee et al., 2015).

531 The calculated mass of dissolved olivine is 8.34, 63.17 and 62.94 mg in experiments SC1-
532 L, SC2-M and SC3-H, respectively. This represents a mass loss of 0.48, 3.69 and 4.31%
533 relative to the initial mass of samples SC1-L, SC2-M and SC3-H, respectively (Table 4 and
534 Fig. 10). The calculated mass of hydrous Mg-phases in samples SC1-L and SC2-M is 6.82
535 and 54.08 mg, respectively; this indicates a gain of mass of 0.40 and 3.15% relative to their
536 initial mass, respectively. The calculated mass of hydrous Fe-phases in sample SC3-H is 7.28
537 mg, corresponding to a relative mass gain of 0.50%. The total mass of carbonates is 1.30, 9.98
538 and 45.60 mg in samples SC1-L, SC2-M and SC3-H, respectively, representing a relative
539 mass gain of 0.08, 0.58 and 3.12%.

540 Petrological observations and bulk rock analyses indicated that organic carbon was
541 present in the reacted samples. Bulk rock analyses showed that the carbon content of the
542 initial olivine was below the detection limit, so the only source of carbon is the CO_2 -bearing

543 injected fluid. In order to evaluate the amount of organic carbon in the three reacted samples,
544 we assumed that (i) the measured ratios of organic and inorganic carbon for samples SC3-H
545 and SC2-M were representative of the actual distribution of carbonates versus reduced carbon
546 in the samples, and (ii) the ratio of organic and inorganic carbon in sample SC1-L was the
547 same as that of sample SC2-M. Based on the calculated masses of carbonates, the total mass
548 of reduced carbon is 0.19, 1.77 and 0.20 mg in samples SC1-L, SC2-M and SC3-H,
549 respectively and corresponds to a relative mass gain of 0.01, 0.10 and 0.01%, respectively.

550 Based on these calculations, the mass balance between dissolved olivine and precipitated
551 secondary minerals (hydrous phases, reduced carbon and carbonates) led to a negligible total
552 mass change of the cores: a relative mass gain of 0.01 and 0.14% for samples SC1-L and
553 SC2-M, respectively, and a relative mass loss of 0.68% for sample SC3-H. They also indicate
554 that the alteration of olivine into carbon-bearing phases (reduced carbon and carbonates)
555 resulted in a total sequestration of CO₂ of 0.07, 0.60 and 1.66 wt.% in experiments SC1-L,
556 SC2-M and SC3-H, respectively (see Table 4). These values are consistent with bulk rock
557 data measured of samples SC2-M and SC3-H (Fig. 10), which validates a posteriori the
558 assumptions made for the mass balance. Calculations also showed that only 10.5, 4.8 and
559 0.5% of the total amount of CO₂ injected in samples SC1-L, SC2-M and SC3-H respectively,
560 remained trapped as carbon-bearing products (reduced carbon and carbonates). This implies
561 that the percolating fluids were still enriched in CO₂ at the cores outlet.

562

563 *3.5. Porosity variation during olivine alteration*

564

565 Changes in rock porosity induced by the percolation of CO₂-fluids in the ultramafic cores
566 can be inferred from the calculated mineral masses. A volumetric mass density of 3.3 g.cm⁻³
567 was assumed for olivine (Deer et al., 1992). The total volume of carbonates was assessed from
568 the volumetric mass density of calcite ($\rho_{calcite} = 2.7 \text{ g.cm}^{-3}$) and siderite ($\rho_{siderite} = 3.9 \text{ g.cm}^{-3}$)
569 in experiments SC1-L and SC2-M, and of magnesite ($\rho_{magnesite} = 3.0 \text{ g.cm}^{-3}$) in
570 experiment SC3-H (Deer et al., 1992). Two end-member scenarios were used to estimate the
571 volume of hydrous phases considering the density of their expected precursors (brucite in
572 samples SC1-L and SC2-M ($\rho_{brucite} = 2.4 \text{ g.cm}^{-3}$); goethite in sample SC3-H ($\rho_{goethite} = 4.3$
573 g.cm^{-3})) or that of lizardite as a serpentine-type mineral ($\rho_{lizardite} = 2.6 \text{ g.cm}^{-3}$) (Deer et al.,
574 1992). The precipitation of reduced carbon was considered as negligible.

575 Results show that changes in porosity are relatively small during the percolation
576 experiments (Table 4, Fig. 10c and Appendix A7). Samples porosity was reduced from
577 10.96% to 10.80% in experiment SC1-L and from 11.30% to 9.89% in experiment SC2-M
578 according to the different scenarios of carbonate formation (calcite or siderite) and hydration
579 (brucite or lizardite). Compared to the initial samples porosity, these results correspond to a
580 maximum porosity change of ~1% and ~12% in experiments SC1-L and SC2-M, respectively.
581 In experiment SC3-H, the porosity increased by ~5% (from 10.57 to 11.11%) or ~3% (from
582 10.57 to 10.86%) considering the precipitation of magnesite and goethite or the precipitation
583 of magnesite and lizardite, respectively.

584

585 **4. Discussion**

586

587 All reacted samples show the alteration of olivine into secondary minerals. However, the
588 nature and rate of dissolution and precipitation reactions are variable depending on the inlet
589 fluid pCO_2 . The experiments with the lowest pCO_2 (0.1 – 1 MPa i.e. $CO_2 = 6.26 - 62.6$
590 $mmol.L^{-1}$) are characterized by the formation of Mg(Fe)-rich phyllosilicates associated with
591 Ca- and Fe-carbonates. The high pCO_2 experiment (10 MPa i.e. $CO_2 = 659.7 mmol.L^{-1}$)
592 involves the precipitation of magnesite and Fe(Mg)-rich phyllosilicates. All percolated cores
593 contain hematite and reduced carbon. Hereafter, we will discuss the role of CO_2 on the
594 hydrothermal alteration of olivine and the fate of carbon in the ultramafic aggregates.

595

596 *4.1. Alteration of olivine and formation of carbonates during low CO_2 concentration* 597 *experiments (6.26 – 62.6 $mmol.L^{-1}$)*

598

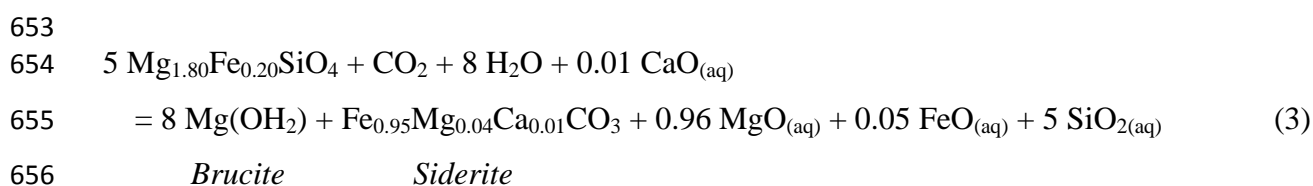
599 The comparison of experiments SC1-L and SC2-M shows an increase in the mean
600 dissolution rate of olivine with CO_2 partial pressure: $1.43 \times 10^{-8} s^{-1}$ at $pCO_2 = 0.1$ MPa
601 (sample SC1-L); $6.55 \times 10^{-8} s^{-1}$ at $pCO_2 = 1$ MPa (sample SC2-M). These results are
602 consistent with previous studies reporting the effect of CO_2 concentration on olivine
603 dissolution rates by controlling the activity of H^+ ions in the solution (Rosso and Rimstidt,
604 2000; Hänchen et al., 2006). H^+ ions are assumed to govern the kinetics of olivine dissolution
605 by favoring the protonation of Mg–O and Fe–O bonds (in Mg–O–Si and Fe–O–Si
606 arrangements) to form Mg and Fe complexes associated with silicic acid (Casey and Bunker,
607 1990; Wogelius and Walther, 1990; Pokrovsky and Schott, 2000). In our study, the
608 dissolution rate of olivine is correlated to the activity of protons in the fluid: it is multiplied by

609 4.6 when the H^+ concentration is quadrupled between experiments SC1-L ($H^+ = 0.04 \text{ mmol.L}^{-1}$)
610 ¹) and SC2-M ($H^+ = 0.16 \text{ mmol.L}^{-1}$) based on PhreeqC calculations (Parkhurst and Appelo,
611 2013). However, the outlet concentrations of Si showed that the dissolution rate of olivine
612 evolved differently between these two experiments: it reached rapidly a steady state in
613 experiment SC1-L while it fluctuated throughout experiment SC2-M.

614 In porous media, the dissolution rate of olivine is controlled by local chemical equilibrium
615 conditions, which are themselves determined by the mass transfer of solutes to reactive sites,
616 the adsorption of such chemical species at the Mg-silicate surface and the residence time of
617 fluids at mineral interfaces (Peuble et al., 2015b). Accordingly, we postulate that the injection
618 of a low concentration of H^+ ions in experiment SC1-L ($pCO_2 = 0.1 \text{ MPa}$) allowed the
619 dissolution rate of olivine to rapidly achieve a steady state at the sample scale, independently
620 of the rock hydrodynamic properties. In experiment SC2-M, CO_2 concentrations were 10
621 times greater ($pCO_2 = 1 \text{ MPa}$), which increased the difference to equilibrium between olivine
622 and fluids. During this experiment, the olivine dissolution rate never reached a steady state.
623 We speculate that this rate varied locally and temporally along the percolated core depending
624 on local fluid flow conditions and reactive surface areas.

625 Unlike the dissolution of olivine, the outlet concentrations of Ca and Fe suggest that the
626 precipitation rate of Ca-carbonates and Fe-bearing phases (carbonates and oxides) reached a
627 steady state in both low pCO_2 experiments (except for Fe in sample SC1-L). The precipitation
628 of Ca- and Fe- carbonates (i.e. calcite and siderite) appears contradictory with the Mg-rich
629 composition of the initial ultramafic system (olivine FO_{90}). Furthermore, the outlet fluids of
630 low pCO_2 experiments do contain magnesium coming from the dissolution of olivine (Fig.
631 3b), and PhreeqC geochemical simulations indicate that they are supersaturated with respect
632 to magnesite (Parkhurst and Appelo, 2013). These inconsistencies highlight the competitive
633 processes in the precipitation kinetics between Mg-, Ca- and Fe-carbonates, due to the
634 different chemical affinities of Mg^{2+} , Ca^{2+} and Fe^{2+} ions with water (e.g., Pokrovsky and
635 Schott, 2002). Mg^{2+} has a highly hydrated character compared to Ca^{2+} and Fe^{2+} (Pokrovsky
636 and Schott, 2002; Schott et al., 2009; Gautier, 2012). Hänchen et al. (2008) observed that the
637 crystallization of magnesite is generally hindered by the intermediate precipitation of hydrous
638 Mg-carbonates (e.g., nesquehonite, hydromagnesite) especially under low CO_2 partial
639 pressure conditions ($< 0.3 \text{ MPa}$). Hence, the precipitation rate of magnesite can be up to six
640 orders of magnitude slower than that of other carbonates such as calcite (Saldi et al., 2009;
641 Saldi et al., 2012). Because of these thermo-kinetic restrictions, the Mg-rich samples SC1-L
642 and SC2-M promoted the crystallization of calcite and siderite at the expense of magnesite.

643 This means that the potential for CO₂ mineralization in olivine-dominated basements under
 644 low *p*CO₂ conditions (0.1 – 1 MPa) is primarily regulated by the amount of iron provided by
 645 the mafic silicate and the amount of calcium brought in by the percolating fluids; both
 646 mechanisms favoring the precipitation of siderite ± calcite. Magnesium is mainly incorporated
 647 into transient, hydrous and amorphous phases (Mg(Fe)-rich (proto-)phyllosilicates) that
 648 probably developed from the destabilization of brucite, as it is commonly reported during
 649 serpentinization of olivine (Delvigne et al., 1979; Escario et al., 2018; Tutolo et al., 2018).
 650 Thus, if we tentatively extrapolate these results to ultramafic reservoirs infiltrated by
 651 relatively low *p*CO₂ waters, we can model the hydrothermal alteration of olivine in areas
 652 located far from the CO₂ input by the following reaction:



657
 658 Under low CO₂ concentrations (here defined as being ≤ 62.6 mmol.L⁻¹), the dissolution of
 659 five moles of olivine produces eight moles of hydrous minerals (e.g., brucite) but only one
 660 mole of Fe-carbonates. Such olivine alteration products (especially brucite) may then induce
 661 negative feedback effects on the completion of the reaction (Malvoisin and Brunet, 2014), but
 662 also on the hydrodynamic properties of the rock. Indeed, differential pressure measurements
 663 revealed a sharp decrease in the permeability of samples SC1-L and SC2-M even though
 664 porosity values display little change over time. This suggests that the decrease in permeability
 665 is primarily controlled by the structure of secondary minerals (mainly the hydrous phases)
 666 clogging fluid pathways in the host rock, in agreement with the results obtained in previous
 667 flow-through serpentinization experiments for similar fluid flow conditions (Godard et al.,
 668 2013; Peuble et al., 2015b; Farough et al., 2016; Luhmann et al., 2017a).

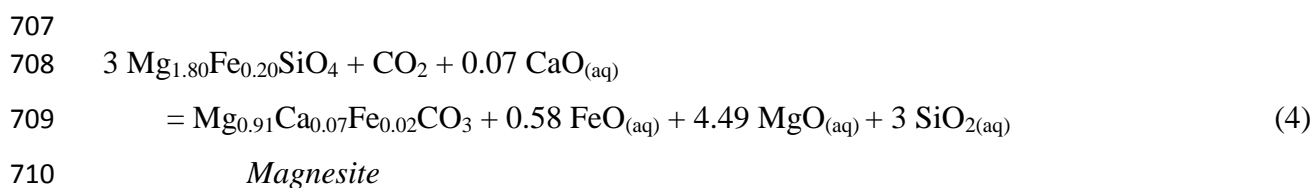
669
 670 *4.2. Alteration of olivine and formation of carbonates during a high CO₂ concentration*
 671 *experiment (659.7 mmol.L⁻¹)*

672
 673 High *p*CO₂ experiment SC3-H has probably the highest dissolution rate of olivine, and
 674 paradoxically, lower Si outlet fluid concentrations than in experiment SC2-M. The strong
 675 dissolution of olivine in sample SC3-H is characterized by abundant etch-pits, similar to those
 676 described on several experimental (e.g., Grandstaff, 1978; Malvoisin et al., 2012; King et al.,

677 2014; Peuble et al., 2015a) and natural samples (Velbel and Ranck, 2008; Velbel, 2009), and
 678 attributed to an anisotropic dissolution of the Mg-silicate (King et al., 2014; Peuble et al.,
 679 2015a). The relatively low concentrations of Si in this experiment can be ascribed to the
 680 development of large Fe(Mg)-rich phyllosilicates (Fig. 5d), trapping part of the Si released
 681 upon olivine dissolution. As for the hydrous minerals of low pCO_2 experiments, these
 682 phyllosilicates are presumably transitional phases formed before serpentinization. However,
 683 their formation appears to be related to the pCO_2 since the largest phyllosilicates were
 684 observed in sample SC3-H. We postulate that the use of a higher concentration of CO_2 in this
 685 experiment has facilitated the growth of these phases by increasing the dissolution rate of
 686 olivine under lower pH conditions (Wogelius and Walther, 1990; Hänchen et al., 2006;
 687 Prigiobbe et al., 2009).

688 The identified serpentine precursors resemble an iddingsitized form of olivine according
 689 to optical, microscopic and Raman observations (Figs. 4-6). Iddingsitization of olivine is an
 690 oxidation and hydration reaction leading to the conservation of Si, the loss of Mg (that is
 691 leached out from the olivine surfaces) and the gain of Fe (being preferentially converted into
 692 ferric iron) in weathered ultramafic rocks (Delvigne et al., 1979). The more prominent
 693 serpentine precursors in sample SC3-H (compared to samples SC1-L and SC2-M) have
 694 depleted the percolating fluids in Si and Fe relative to Mg suggesting an underestimation of
 695 the olivine dissolution rate in sample SC3-H (compared to samples SC1-L and SC2-M). They
 696 also promoted the concentration of ferric iron micro-particles (hematite) along dissolved
 697 olivine surfaces. These Fe-oxides may then have acted as preferential nuclei for the
 698 polymerization of Fe(Mg)-rich phyllosilicates, as it was previously observed during late
 699 stages of olivine iddingsitization (Lee et al., 2015).

700 In sample SC3-H, most of the Mg released upon olivine dissolution was incorporated into
 701 a large matrix of magnesite (Fig. 5f). These results confirm that a high concentration of CO_2
 702 ($659.7 \text{ mmol.L}^{-1}$), resulting in a high dissolution rate of olivine and consequently a high
 703 concentration of Mg^{2+} in the fluid, is required to overcome the difficulty of Mg-carbonates
 704 precipitation (due to the highly hydrated character of Mg^{2+} compared with Ca^{2+} and Fe^{2+} ions
 705 - see discussion before). Under these conditions, the main alteration reaction of olivine is
 706 dominated by the formation of magnesite according to the following reaction:



711

712 The comparison of reactions (3) and (4) shows that, for every mole of CO₂ converted into
713 carbonates, five moles of olivine need to be dissolved in the low pCO_2 experiments but only
714 three in the high pCO_2 experiment. This demonstrates a greater potential of olivine to trap
715 CO₂ as carbonates when the inlet fluid has a higher partial pressure of CO₂.

716 Magnesite is associated with Fe(Mg)-rich phyllosilicates in sample SC3-H. However, the
717 outlet concentration values of Mg, Fe and Ca indicate that these two secondary minerals
718 precipitated at different times in the ultramafic core. The sharp decrease in Fe outlet
719 concentrations coupled with the increasing release of Mg in the first hours of injection suggest
720 an almost immediate polymerization of serpentine fibrous precursors. This process then
721 slowed down after 84 hours, with the increase in Fe outlet concentrations up to ≈ 0.19 ppm.
722 At $t \approx 45$ h, magnesite began to crystallize by first incorporating calcium, then magnesium and
723 iron, resulting in a significant decrease in the outlet concentrations of Ca, Mg and Fe after $t \approx$
724 45, 71 and 116 hours, respectively. These concentrations stabilized after 135 hours, indicating
725 that the olivine carbonation rate rapidly reached a steady state in the percolated aggregate.

726 The onset of the stable carbonation of olivine is correlated with a linear decrease in
727 permeability after 135 hours in sample SC3-H. As in low pCO_2 experiments, this correlation
728 attests to negative feedback effects of some olivine alteration products on rock flow paths by
729 reducing pore hydraulic radius and increasing pore tortuosity over time. However, the
730 porosity of sample SC3-H increased throughout the injection whatever the scenarios
731 considered (Fig. 10c). These results suggest first that the overall decrease in rock pore volume
732 during magnesite and serpentine precursors precipitation is (at least temporarily and locally)
733 offset by the porosity created upon olivine dissolution, maintaining fluid renewal at reaction
734 front interfaces (Peuble et al., 2017). They also show that the decrease in permeability
735 recorded during experiment SC3-H is not controlled by the crystallization of secondary
736 minerals. The decrease in permeability is most likely attributed to the heterogeneous
737 distribution of these secondary minerals in the percolated core, which affects primarily the
738 major fluid pathways.

739

740 *4.3. Oxidation of olivine ferrous iron and the fate of carbon*

741

742 The characterization of reacted samples revealed the presence of reduced carbon, trapping
743 from 0.04% (sample SC3-H) to 0.17% (sample SC2-M) of the CO₂ injected into the
744 percolated olivine aggregates (Fig. 8 and Table 3). To our knowledge, it is the first time that

745 reduced carbon was measured after olivine alteration experiments in presence of CO₂-bearing
746 fluids although it is observed in oceanic and ophiolitic serpentinites (Ménez et al., 2012;
747 Galvez et al., 2013; Sforza et al., 2018), sometimes in association to carbonates
748 (Schwarzenbach et al., 2016). Also, it is worth to note that the precipitation of reduced carbon
749 has been previously reported after another set of reactive percolation experiments using a
750 different set-up and flow-bench (Luquot et al., 2012). These reactive percolation experiments
751 consisted in injecting of CO₂-bearing brines ($pCO_2 = 6$ MPa; $CO_2 = 402$ mmol.L⁻¹) into
752 chlorite/zeolite-rich sandstones at T=95 °C and P=10 MPa. They produced reduced carbon
753 grains with the same poorly organized crystallographic structure as those observed in our
754 samples. Luquot et al. (2012) proposed that these carbon grains were formed after
755 concomitant reduction of the injected CO₂ in association to the oxidation of ferrous iron in
756 chlorite. The oxidation of iron liberates electrons (Eq. 5), inducing locally a more reduced
757 environment, which in turn would favor carbon reduction (Eq. 6).



760 The oxidation of Fe²⁺ during serpentinization is often associated to the abiotic generation
761 of H₂ produced from H₂O reduction. Subsequently, H₂ can react with CO₂ to form a wide
762 range of reduced carbon species including condensed carbonaceous matter (Galvez et al.,
763 2013; Martinez et al., 2017; Sforza et al., 2018) and possibly methane (McCollom, 2016).
764 Some studies have shown that the production of reduced carbon-bearing phases may be
765 kinetically favored in serpentinizing ultramafic systems when metal alloys are present (Horita
766 and Berndt, 1999; Fu et al., 2008; Lazar et al., 2012) because they act as catalysts.
767 Accordingly, we can question the fact that the sintered nickel porous disk positioned
768 upstream of the olivine sample can have acted similarly during our experiments thus favoring
769 the formation of reduced carbon phases albeit, to our knowledge, Ni-Fe alloys have been
770 shown to act as catalysts of the methane production only (Horita and Berndt, 1999).
771 Alternatively, Milesi et al. (2016) recently demonstrated on the basis of thermodynamical
772 calculations that solid carbonaceous material can be formed during serpentinization without
773 catalysts. Furthermore, they showed that the compositions of fluids sampled in ultramafic-
774 hosted hydrothermal vents were consistent with an equilibrium between CO_{2(aq)} and some
775 condensed carbon phases, thus suggesting that these reactions are probably of major
776 importance in ultramafic basements along oceanic spreading centers.

777 During our experiments, the presence of hematite and iddingsite at the olivine surface
778 indicates that oxidation of ferrous iron did occur at the fluid/mineral interface. The pH and pE

779 of the inlet fluids were calculated using the PhreeqC geochemical code (Parkhurst and
780 Appelo, 2013); pH values of 4.5, 3.9 and 3.4 and pE values of 5.4, 6.5 and 7.3 were estimated
781 for experiments SC1-L, SC2-M and SC3-H, respectively. When reported on a pE-pH stability
782 diagram of Fe- and C-species, hematite is thermodynamically stable for the conditions
783 characterizing the inlet fluid, which is consistent with a reaction of Fe^{2+} oxidation at the
784 sample inlet (Figure 11a, b, and c). This oxidation reaction is probably balanced by the
785 reduction of CO_2 into carbon, promoting a strong decrease in the fluid pE down to -2.6, -1.4
786 and -0.3 in experiments SC1-L, SC2-M and SC3-H, respectively. So, assuming that pH stays
787 low and constant (e.g., at the onset of the reaction or close to the CO_2 injection point), carbon
788 reduction could be favored over water reduction (and hydrogen production) (Figure 11d, e,
789 and f), in contrast to what is classically suggested in the literature to balance the oxidation of
790 ferrous iron during serpentinization (Klein et al., 2009). However, the field of stability of
791 carbon is very narrow and olivine dissolution will increase the pH of reacting fluids
792 downstream, consuming H^+ ions in the solutions (Pokrovsky and Schott, 2000; Escario et al.,
793 2018). The observation of carbonates in samples SC1-L, SC2-M and SC3-H suggests an
794 increase of the fluid pH to at least values of 6.3, 5.4 and 4.8, respectively. The precipitation of
795 hydrous phases (Fe(Mg)-rich phyllosilicates) requires an increase of pH to at least values of
796 6.6 in experiments SC1-L – SC2-M and of 7.5 in experiment SC3-H (Fig. 11a-c). This two-
797 step mechanism (redox reactions followed by dissolution-precipitation reactions), by which
798 reactions along flow paths are controlled by feedback processes between the dissolution of
799 olivine and the changes in fluid composition (including pH), could explain both the limited
800 distribution of reduced carbon, observed only in the pores close to the inlet (Fig. 8), and the
801 predominance of carbonate and hydrous phases in the reacted samples. It is worth noticing
802 that carbonate (magnesite) precipitation conditions are favored in the high pCO_2 experiment
803 (minimum pE-pH variations), which could explain the observed high carbonation efficiency
804 in sample SC3-H.

805 Thermodynamic modeling suggests that carbon reduction is strongly controlled by the low
806 pH of fluids, a condition that is rarely met in natural carbonate bearing serpentinizing
807 ultramafic basements, which are dominated by alkaline fluids (Ludwig et al., 2006;
808 Chavagnac et al., 2013; Milesi et al., 2016). This process should however be taken into
809 account when predicting the fate of carbon in the case of a CO_2 -injection experiment in an
810 ultramafic basement.

811

812 **5. Summary and conclusions**

813
814 This experimental study explores the role of CO₂ and fluid flow on the hydrothermal
815 alteration of olivine. Results provide new information to characterize the fluid-rock reactions
816 in the case of an ultramafic aquifer pervaded by CO₂-rich hydrothermal waters. It is the first
817 step to improve the parameterization of future numerical models specifically by allowing the
818 measurement of macroscopic characteristics of the mass transfer mechanisms resulting from
819 complex coupled flow-reaction pore scale processes.

820 Far from the CO₂ input i.e. under low pCO_2 conditions (from 0.1 to 1 MPa), olivine will
821 be mainly altered into hematite and Mg(Fe)-rich phyllosilicates. These iddingsitic-type
822 assemblages may clog most of the rock flow paths, resulting in a strong decrease in
823 permeability in a few days. Some carbonates can form in these conditions, but they are mainly
824 composed of calcium and iron despite the initial Mg-rich system (Fo₉₀). This denotes less
825 favorable conditions of crystallization for Mg- than for Ca- and Fe-carbonates.

826 Closer to the CO₂ input (i.e. $pCO_2 = 10$ MPa), olivine will be more efficiently altered.
827 This causes the formation of abundant etch-pits on the olivine surfaces and a larger amount of
828 poorly crystallized Fe(Mg)-rich phyllosilicates depleting the percolating fluids in Si and Fe
829 relative to Mg. In addition to these hydrous phases, magnesite precipitates as dense clusters in
830 the large pores. The carbonation rate of olivine can be 3 to 11 times higher at a pCO_2 of 10
831 MPa than when pCO_2 is 10 to 100 times lower, respectively. Both carbonated and hydrous
832 minerals induce apparently little changes in porosity but a strong decrease in permeability,
833 attesting to negative feedback effects of the olivine alteration products on the fluid flow.

834 Despite the differences in secondary mineralogy between the low and high pCO_2
835 experiments, all samples contain reduced carbon that may indicate a competition for reduction
836 and carbonation processes; both participating to the mineral sequestration of CO₂. Carbon
837 formation suggests reducing conditions probably caused by the oxidation of ferrous iron into
838 ferric iron. For the specific boundary condition of the experiments, carbon deposits are limited
839 to the pores located at the inlet in relation to the low production of hematite and the pH
840 gradient in the samples. Nevertheless, one can speculate that the formation of carbon can be a
841 significant mechanism of CO₂ sequestration in olivine-dominated basements.

842 For industrial application, long lasting injection is required. Accordingly, the objective
843 should be to prevent as best as possible precipitation in the vicinity of the well and to favor
844 mineralization as far as possible from the injection well. When investigating the injection of a
845 reactive fluid from a well, the most important feature is that seepage velocity decreases
846 linearly to quadratically as the distance to injection increases and therefore the apparent (or

847 dynamic) water/rock ratio decreases rapidly. Consequently, the most important feature for
848 optimizing injection is to inject at the largest flow rate as possible in order to locate
849 mineralization as far as possible from the injection well and thus mitigate permeability
850 reduction effects. From this perspective, one can speculate from the permeability (Fig. 2) and
851 CO₂ trapping (Fig. 10) curves that the medium pCO_2 value (1 MPa) would be the most
852 favorable option.

853

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861 suggestions and Rajdeep Dasgupta for editorial handling

862

863

864 **Table captions**

865

866 Table 1. Experimental setup and sample characteristics for the three experiments.

867

868 Table 2. Concentrations of major elements (Si, Mg, Fe and Ca, in ppm) measured in the inlet
869 fluid by ICP-MS.

870

871 Table 3. Bulk rock analyses. Hydrogen and carbon contents recalculated as H₂O and CO₂
872 contents respectively in the initial powder and the percolated olivine cores SC2-M and SC3-H
873 (analytical blanks subtracted).

874

875 Table 4. Mass balance calculations. Estimates of dissolved olivine and precipitated secondary
876 minerals relative to the initial samples mass, and corresponding changes in rock porosity.

877

878 **Figure captions**

879

880 Figure 1. Diagram of the ICARE-RFTS3 experimental device (Geosciences Montpellier).

881

882 Figure 2. Samples permeability k (in 10^{-15} m²) as a function of time (in hours) during
883 experiments SC1-L ($pCO_2 = 0.1$ MPa; $CO_2 = 6.26$ mmol.L⁻¹), SC2-M ($pCO_2 = 1$ MPa; $CO_2 =$
884 62.6 mmol.L⁻¹) and SC3-H ($pCO_2 = 10$ MPa; $CO_2 = 659.7$ mmol.L⁻¹). Symbols in inset.

885

886 Figure 3. (a) Si, (b) Mg, (c) Fe and (d) Ca outlet fluid concentrations (in ppm) versus the
887 elapsed time of the experiments (in hours). Dotted lines correspond to the inlet fluid
888 composition. Symbols in inset.

889

890 Figure 4. Binocular microscope photography of the olivine aggregates (a) before and (b,c,d)
891 after the percolation experiments: (b) sample SC1-L ($pCO_2 = 0.1$ MPa; $CO_2 = 6.26$ mmol.L⁻¹)
892 ¹), (c) sample SC2-M ($pCO_2 = 1$ MPa; $CO_2 = 62.6$ mmol.L⁻¹) and (d) sample SC3-H ($pCO_2 =$
893 10 MPa; $CO_2 = 659.7$ mmol.L⁻¹). White arrows denote the fluid flow direction during the
894 experiments. The white square indicates the location of the SEM image displayed in Figure 8.

895

896 Figure 5. SEM images of the samples after the experiments (a,b) SC1-L ($pCO_2 = 0.1$ MPa;
897 $CO_2 = 6.26$ mmol.L⁻¹), (c) SC2-M ($pCO_2 = 1$ MPa; $CO_2 = 62.6$ mmol.L⁻¹) and (d,e,f) SC3-H
898 ($pCO_2 = 10$ MPa; $CO_2 = 659.7$ mmol.L⁻¹). Reacted samples are mainly composed of olivine.
899 (a,b,c) Formation of amorphous Mg(Fe)-rich phyllosilicates (phyl) associated with
900 micrograins of silica, calcite and siderite. (d) Precipitation of poorly crystallized Fe(Mg)-rich
901 phyllosilicates forming a loose network of curled fibers. (e) Strong dissolution of olivine
902 evidenced by the development of conical-shaped etch-pits. (f) Sample SC3-H is also
903 characterized by the formation of dense clusters of magnesite (mgn) in large pores located
904 near dissolved olivine grains.

905

906 Figure 6. Raman analyses performed in the inlet area (< 5 mm) of the three percolated
907 samples. Raman spectra of forsterite, hematite, lizardite and iddingsite are from Cnopnras et
908 al. (1991), De Faria et al. (1997), Auzende et al. (2004), and Kuebler et al. (2003),
909 respectively.

910

911 Figure 7. Raman spectrum of the percolated sample SC3-H ($pCO_2 = 10$ MPa; $CO_2 = 659.7$
912 mmol.L⁻¹). The standard spectrum of magnesite is shown for comparison (Rividi et al., 2010).

913

914 Figure 8. (a, b) SEM images showing organic carbon in pores located at the inlet (< 5 mm). in
915 sample SC2-M ($pCO_2 = 1$ MPa; $CO_2 = 62.6$ mmol.L⁻¹). (c) Raman spectrum obtained on the
916 corresponding area with the typical D and G bands of reduced carbon at respective values of
917 1310 and 1560 cm⁻¹ (Galvez et al., 2013).

918
919 Figure 9. Room temperature Mössbauer spectra performed on (a) the initial bulk rock and the
920 reacted powders of (b) sample SC1-L ($pCO_2 = 0.1$ MPa; $CO_2 = 6.26$ mmol.L⁻¹), (c) sample
921 SC2-M ($pCO_2 = 1$ MPa; $CO_2 = 62.6$ mmol.L⁻¹) and (d) sample SC3-H ($pCO_2 = 10$ MPa; CO_2
922 = 659.7 mmol.L⁻¹). The experimental data are represented with circles, the fitted components
923 with dotted light and dark grey lines. Symbols in inset.

924
925 Figure 10: Mass (a) of dissolved olivine and (b) CO₂ trapped as carbon and carbonates
926 normalized to the initial samples mass. CO₂ contents deduced from geochemical analyses are
927 also reported. (c) Changes in porosity induced by the alteration of olivine into carbonates
928 (siderite or calcite in samples SC1-L and SC2-M; magnesite in sample SC3-H) and hydrous
929 phases (brucite or lizardite in samples SC1-L and SC2-M; goethite or lizardite in sample SC3-
930 H) in relation to the initial samples porosity. See text for details. Symbols in inset.

931
932 Figure 11: pH-pE stability diagram of (a, b, c) iron and (d, e, f) carbon phases . Calculations
933 are made at 185 °C under the CO₂ concentration conditions of (a, d) experiment SC1-L (CO_2
934 = 6.26 mmol.L⁻¹), (b, e) experiment SC2-M ($CO_2 = 62.6$ mmol.L⁻¹) and (c, f) experiment
935 SC3-H ($CO_2 = 659.7$ mmol.L⁻¹) using the JCHESS geochemical code (Van Der Lee and De
936 Windt, 2001). Crosses represent the initial pE and pH conditions of the fluid in each
937 experiment according to the calculations made with the PhreeqC geochemical code (Parkhurst
938 and Appelo, 2013). Initial pE values were calculated assuming an electric potential of -0.3 for
939 a Volvic® water at 25 °C and 0.1 MPa (Lorne et al., 1999). Abbreviations: mgt: magnetite;
940 Fe-phyll: Fe-rich phyllosilicates, sid: siderite.

941
942
943 **References**

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Experimental conditions (T = 185°C)			
Experiments	SC1-L	SC2-M	SC3-H
Duration of experiments (hours)	92.88	156.36	333.34
Total pressure (MPa)	25.0	25.0	20.0
CO ₂ partial pressure (MPa)	0.1	1.0	10.0
CO ₂ (mmol.L ⁻¹)	6.26	62.6	659.7
Initial magnetic susceptibility (10 ⁻⁸ m ³ .Kg ⁻¹)	16.9	17.6	19.2
Final magnetic susceptibility (10 ⁻⁸ m ³ .Kg ⁻¹)	16.9	17.4	21.8
Initial porosity (%)	10.96	11.30	10.57
Initial permeability (10 ⁻¹⁵ m ²)	1.876	1.561	4.589
Final permeability (10 ⁻¹⁵ m ²)	0.075	0.019	0.005

Table 1
Peuble et al., 2018

ICP-MS data	Det. Limit	Injected fluid
Si (ppm)	0.815	14.95
Mg	0.001	8.73
Fe	0.005	0.01
Ca	0.012	12.1

Table 2
Peuble et al., 2018

Bulk rock analyses (wt.%)	Initial olivine powder	SC2-M	SC3-H
H ₂ O	0.04	0.08	n.a.
CO ₂ inorganic	< 0.05	0.10	1.31
CO ₂ organic*	< 0.05	0.17	0.04
CO ₂ total	< 0.05	0.27	1.35

*Note. n.a.: not analyzed ; *organic carbon recalculated as CO₂*

Mass balance calculations		SC1-L	SC2-M	SC3-H
Mass Variation.	Dissolved olivine	-0.48	-3.69	-4.31
	Hydrous phases	0.40	3.15	0.50
	Carbonates	0.08	0.58	3.12
	Carbon	0.01	0.10	0.01
	Total	0.01	0.14	-0.68
$\Delta m/m_0$ in %	H ₂ O	0.18	1.44	0.10
	CO ₂ inorganic	0.03	0.22	1.61
	CO ₂ organic*	0.04	0.38	0.05
	CO ₂ total	0.07	0.60	1.66
Porosity changes. ϕ/ϕ_0	Calcite & Brucite	0.99	0.88	-
	Calcite & Serpentine	0.99	0.91	-
	Siderite & Brucite	0.99	0.89	-
	Siderite & Serpentine	0.99	0.93	-
	Magnesite & Goethite	-	-	1.05
	Magnesite & Serpentine	-	-	1.03

Note: (-) loss & (+) gain ; *organic carbon recalculated as CO₂

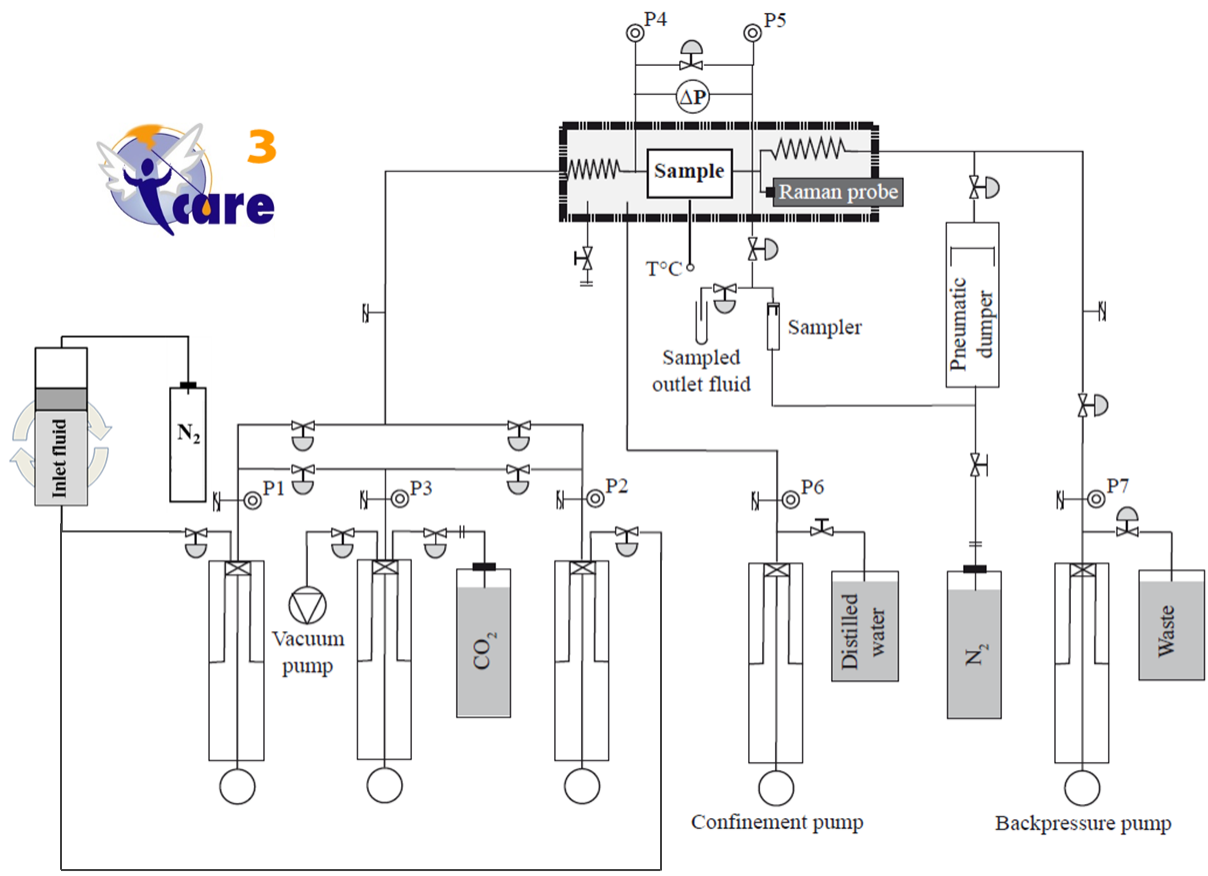


Figure 1. Peuble et al. 2018

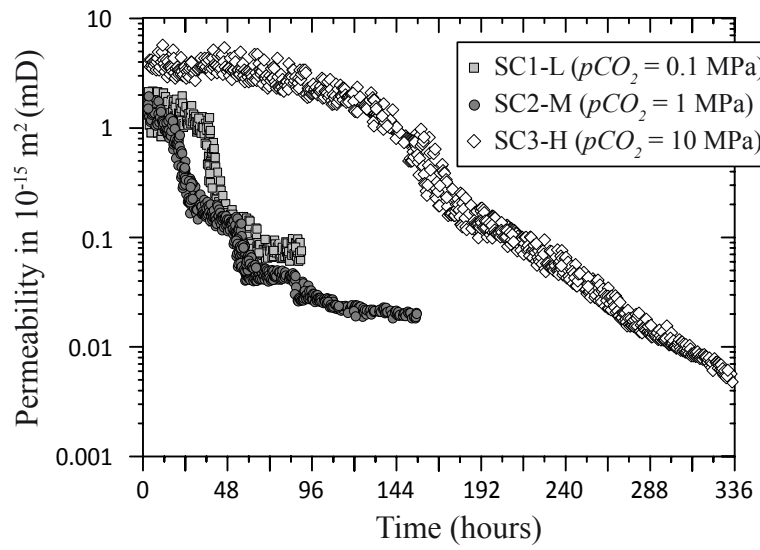


Figure 2. Peuble et al. 2018

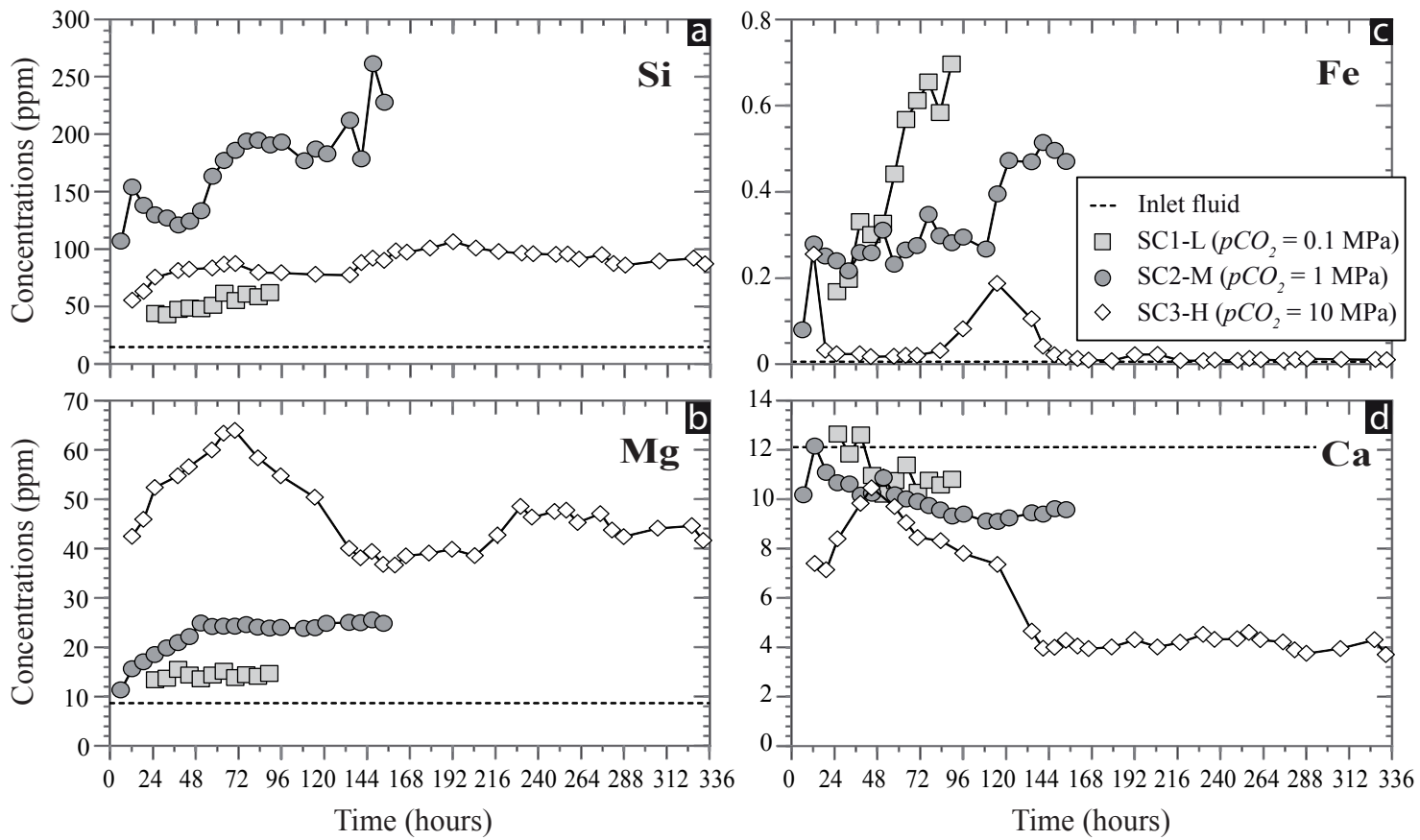


Figure 3. Peuble et al. 2018

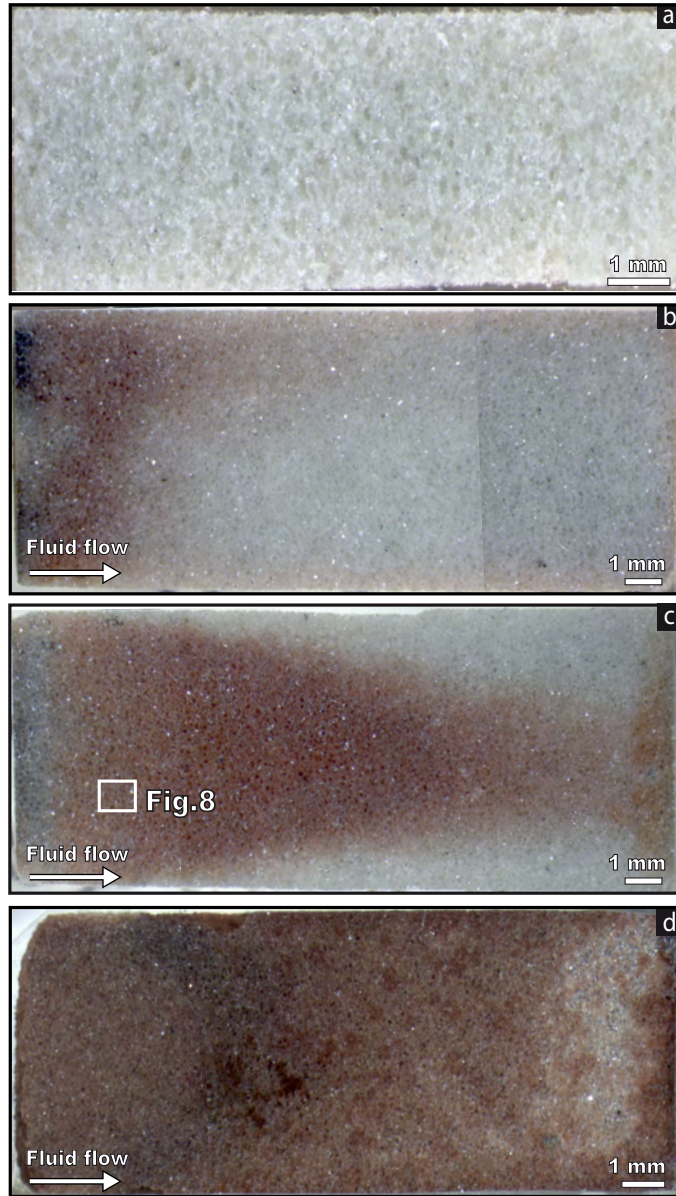


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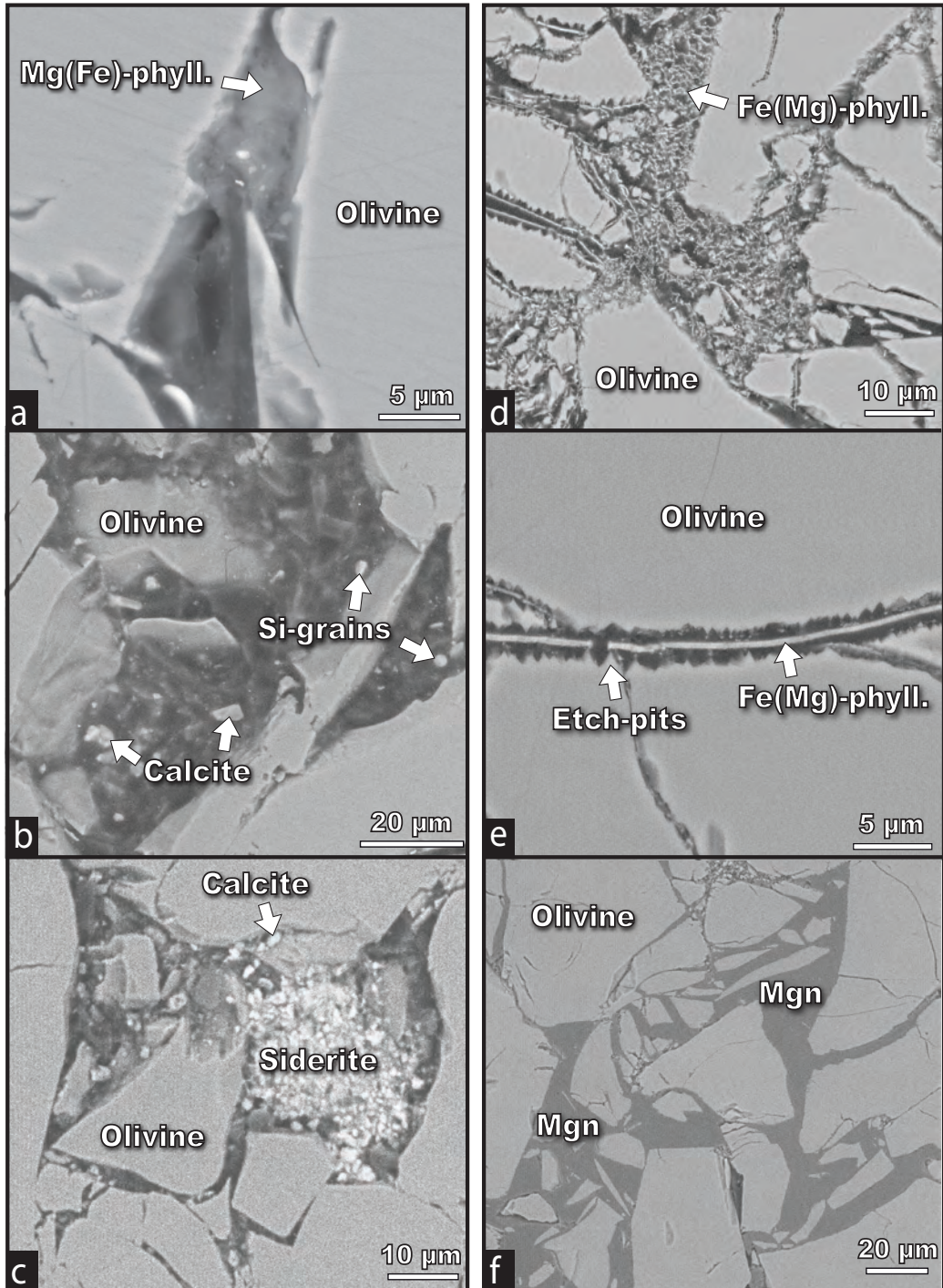


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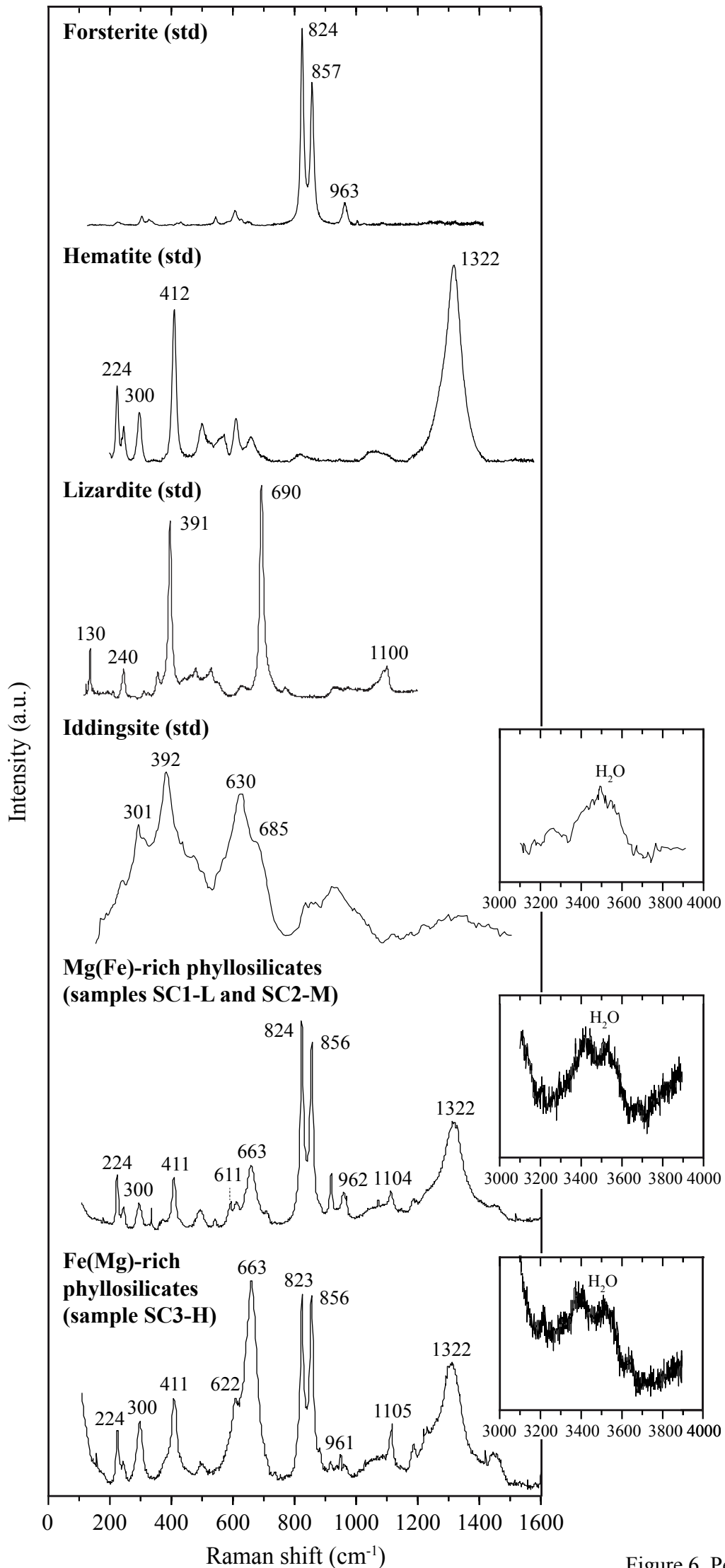


Figure 6. Peuble et al. 2018

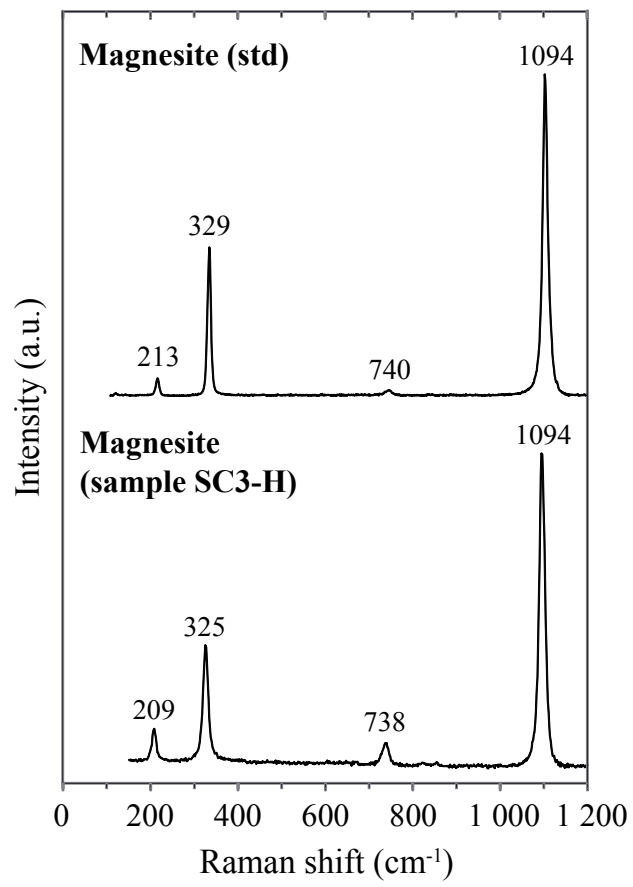


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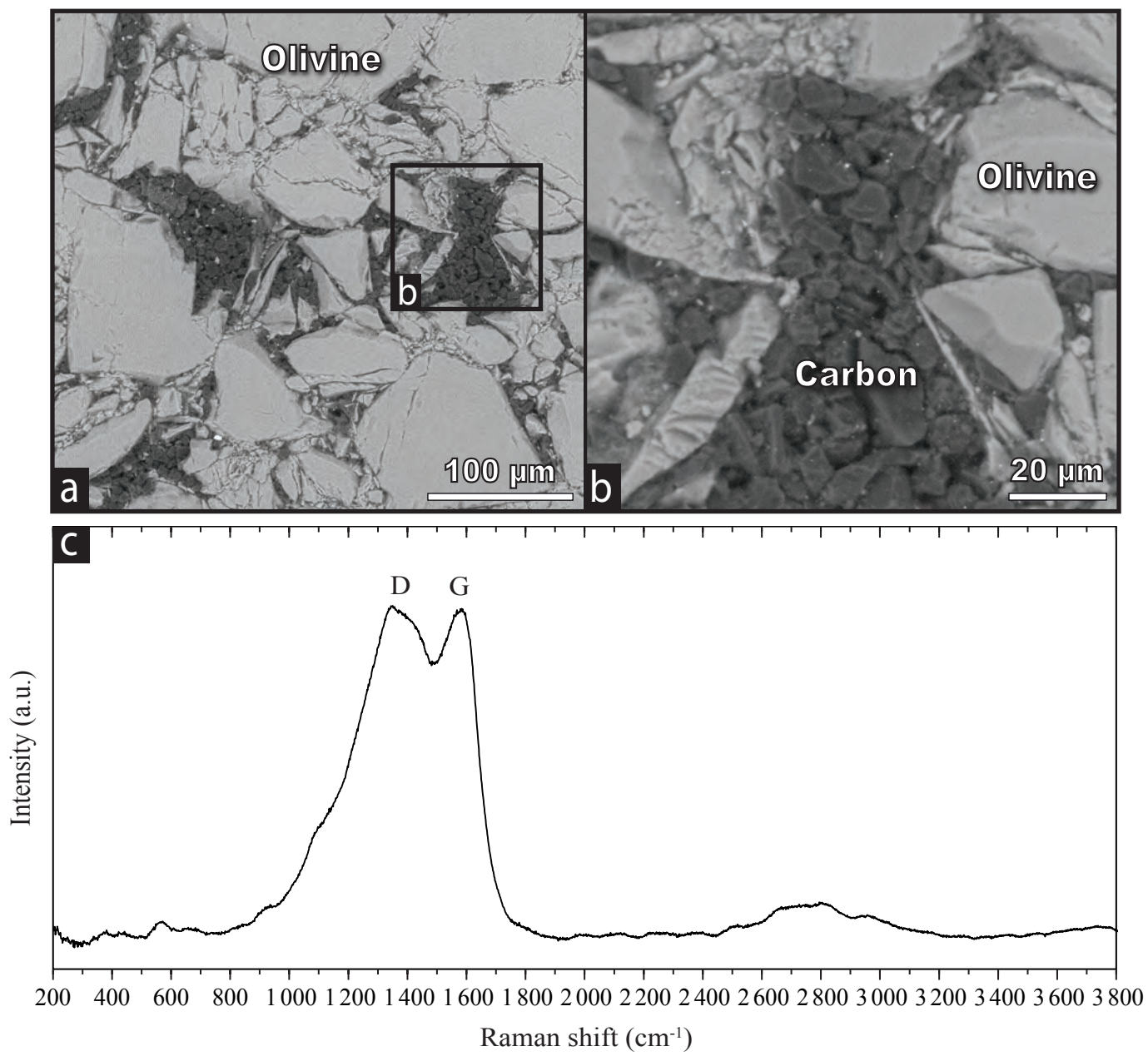


Figure 8. Peuble et al. 2018

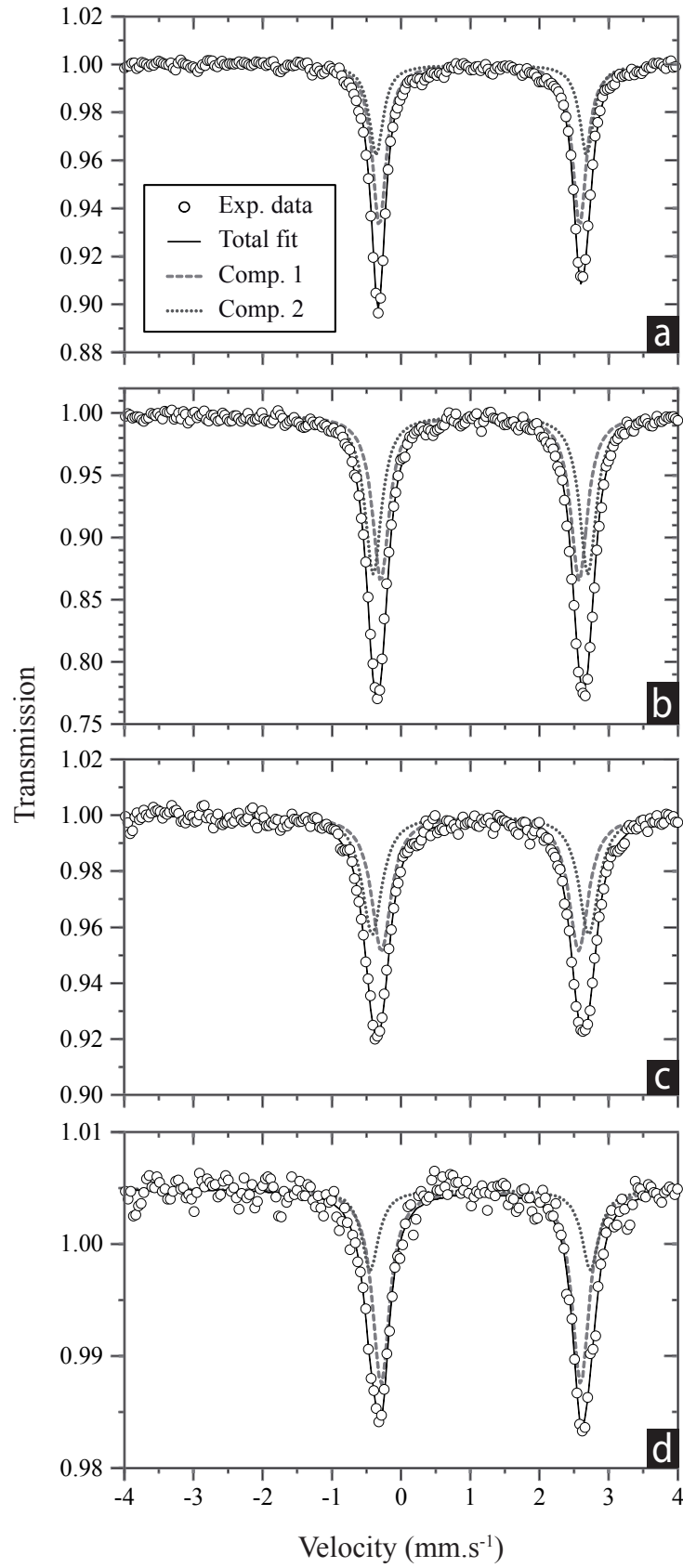


Figure 9. Peuble et al. 2018

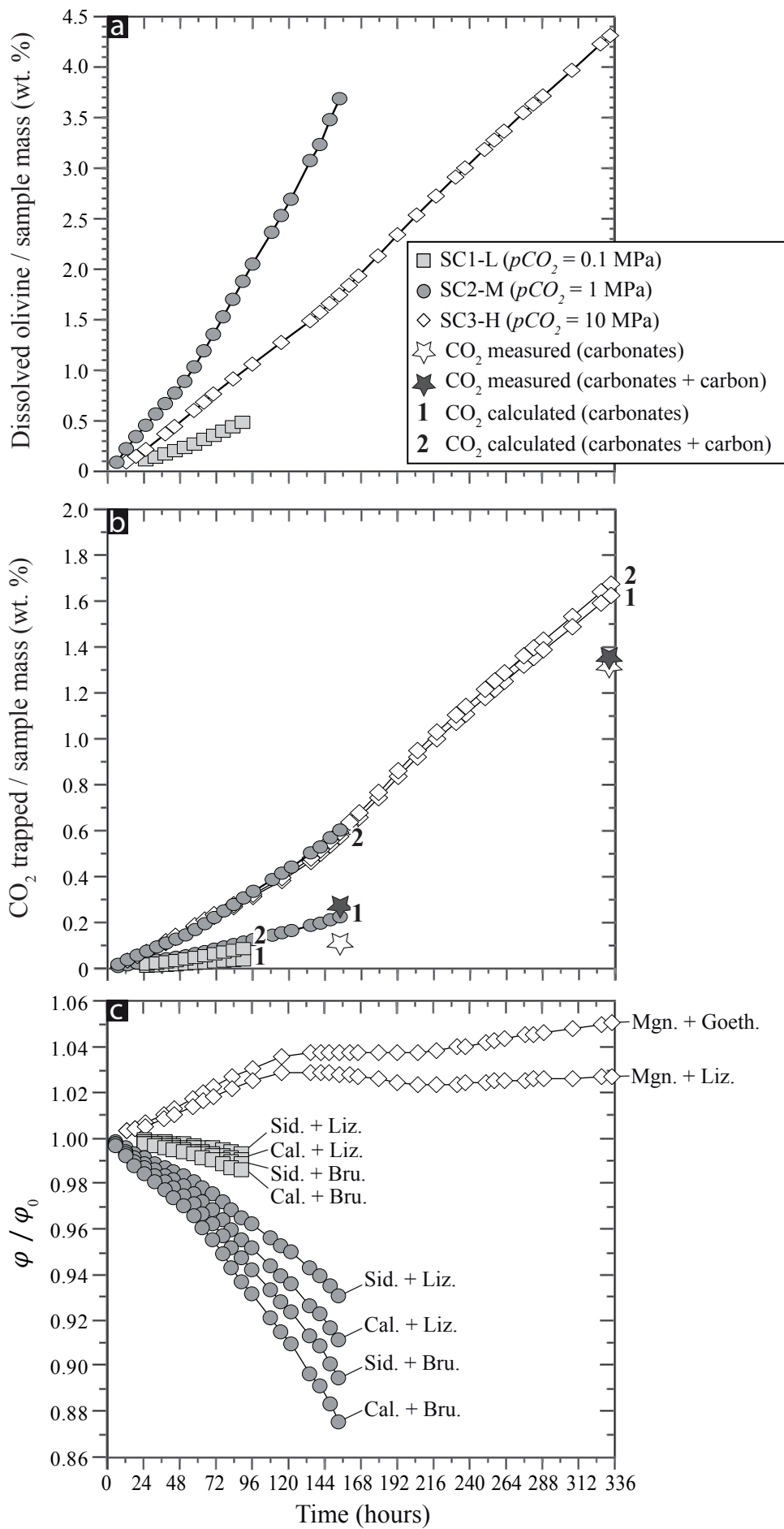


Figure 10. Peuble et al. 2018

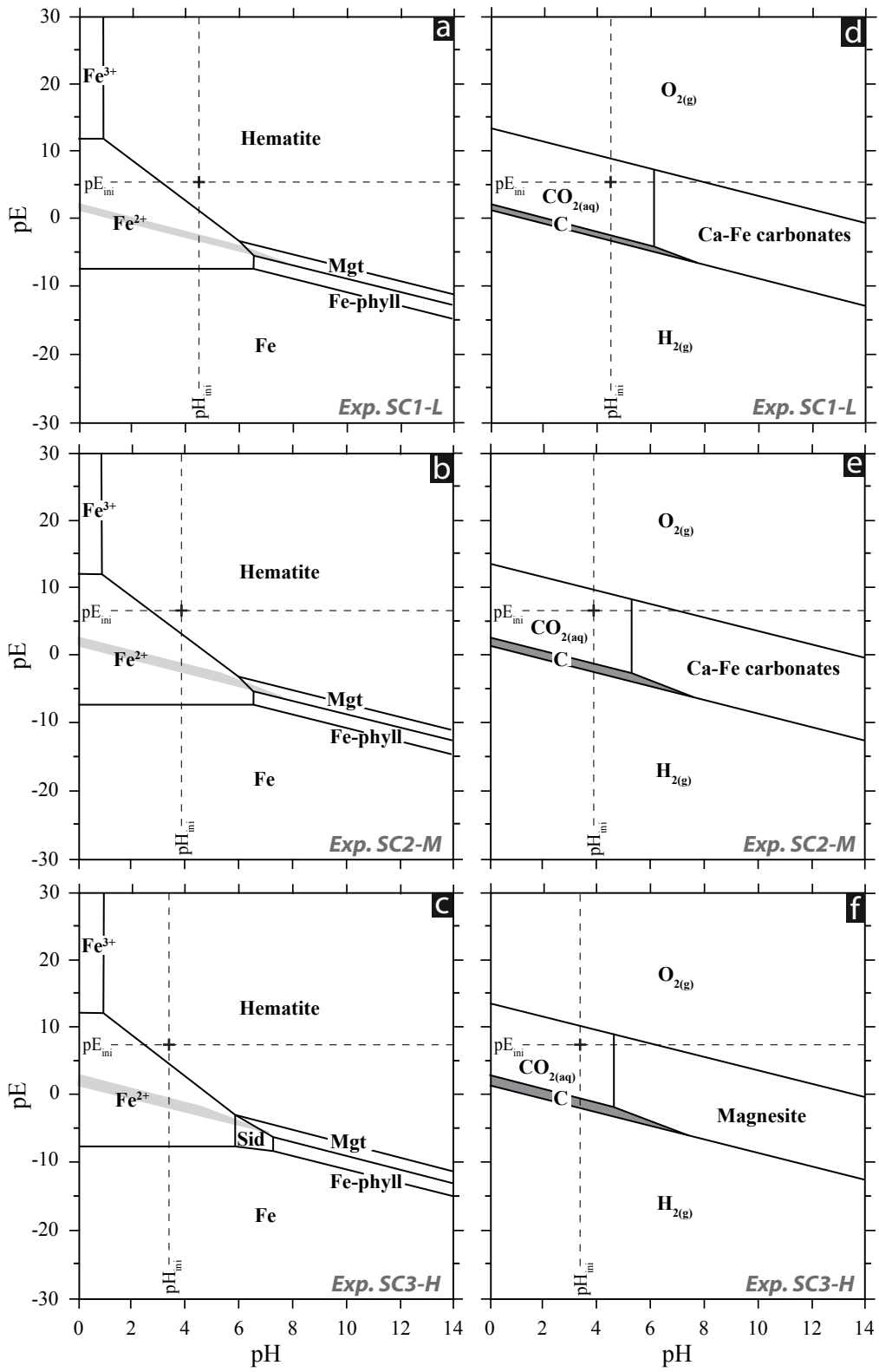


Figure 11. Peuble et al. 2018