



HAL
open science

Reactive transport experiments of coupled carbonation and serpentization in a natural serpentinite. Implication for hydrogen production and carbon geological storage

Florian Osselin, Michel Pichavant, Rémi Champallier, M. Ulrich, Hugues Raimbourg

► To cite this version:

Florian Osselin, Michel Pichavant, Rémi Champallier, M. Ulrich, Hugues Raimbourg. Reactive transport experiments of coupled carbonation and serpentization in a natural serpentinite. Implication for hydrogen production and carbon geological storage. *Geochimica et Cosmochimica Acta*, 2022, 318, pp.165 - 189. 10.1016/j.gca.2021.11.039 . insu-03470095

HAL Id: insu-03470095

<https://insu.hal.science/insu-03470095>

Submitted on 8 Dec 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Journal Pre-proofs

Reactive transport experiments of coupled carbonation and serpentinization in a natural serpentinite. Implication for hydrogen production and carbon geological storage

F. Osselin, M. Pichavant, R. Champallier, M. Ulrich, H. Raimbourg

PII: S0016-7037(21)00694-3
DOI: <https://doi.org/10.1016/j.gca.2021.11.039>
Reference: GCA 12473

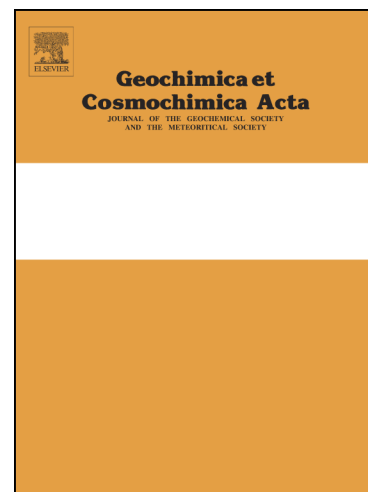
To appear in: *Geochimica et Cosmochimica Acta*

Received Date: 26 February 2021
Accepted Date: 30 November 2021

Please cite this article as: Osselin, F., Pichavant, M., Champallier, R., Ulrich, M., Raimbourg, H., Reactive transport experiments of coupled carbonation and serpentinization in a natural serpentinite. Implication for hydrogen production and carbon geological storage, *Geochimica et Cosmochimica Acta* (2021), doi: <https://doi.org/10.1016/j.gca.2021.11.039>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2021 Published by Elsevier Ltd.



Reactive transport experiments of coupled carbonation and serpentization in a natural serpentinite. Implication for hydrogen production and carbon geological storage

F. Osselin^{a,*}, M. Pichavant^a, R. Champallier^a, M. Ulrich^b, H. Raimbourg^a

^aInstitut des Sciences de la Terre d'Orléans, Université d'Orléans/CNRS/BRGM UMR7327, 1A Rue de la Ferrollerie, 45100, Orléans, France

^bUniversité de Strasbourg, CNRS, Institut Terre et Environnement de Strasbourg, UMR7063, 5 Rue Descartes, Strasbourg, F-67084, France

1 Abstract

2 Serpentization and carbonation of ultramafic formations is a ubiquitous phenomenon, which deeply
3 influences the biogeochemical cycles of water, hydrogen, carbon... while supporting the particular bio-
4 sphere around the oceanic hydrothermal vents. Carbonation of peridotites and other mafic and ultramafic
5 rocks is also a hot topic in the current energy landscape as the engineered sequestration of mineral CO₂
6 in these formations could help reduce the atmospheric emissions and cope with climate change. In this
7 study, we present two reactive percolation experiments performed on a natural serpentinite dredged from
8 the ultraslow South-West Indian Oceanic Ridge. The serpentinite cores (length 3-4 cm and dia. 5.6 mm)
9 were subjected for about 10 days to the continuous injection of a NaHCO₃-saturated brine at respectively
10 160°C and 280°C. Petrographic and petrophysical results as well as outlet fluid compositions were com-
11 pared to numerical batch simulations performed with the PHREEQC open software allowing to reconstruct
12 the mineralogical evolution of both cores. The most striking observation is the fast and dramatic decrease of
13 the permeability for both experiments principally due to the precipitation of carbonates. On the contrary,
14 serpentine was found to be less impacting as it precipitates in low-flow zones, out of the main percolation
15 paths. In total, about 5.6% of the total injected CO₂ was retained in the core, at 280°C. In the same time,
16 hydrogen was consistently produced with a total recovered H₂ corresponding to 0.8% of the maximum H₂
17 possible. The global behavior of the cores is interpreted as the result from an interplay between interacting
18 spatio-temporal lengthscales controlled by the Damköhler number.

19 1. Introduction

20 In the context of global warming and climate change, the development and implementation of Car-
21 bon Capture and Storage (CCS) technologies appears as an unavoidable mid-term solution. In particular,

*Corresponding author

Email address: florian.osselin@cnrs-orleans.fr (F. Osselin)

22 the sequestration of CO₂ in solid form through carbon mineralization combines the advantages of deep
23 geological storage with an increased safety compared with classical deep saline aquifer storage. Indeed,
24 even in the presence of an open pathway to the surface, no leakage is possible since the carbon dioxide is
25 completely mineralized (Seifritz, 1990; Kelemen and Matter, 2008). Among the different options, mafic to
26 ultramafic formations, rich in divalent cations (Mg, Fe, Ca) are probably the most attractive (Oelkers et al.,
27 2008) as basalts, peridotites and serpentinites are known to quickly react with carbon-rich fluids (Gadikota
28 et al., 2020), precipitating carbonates, storing the CO₂ safely over geological times (Mcgrail et al., 2006;
29 Kelemen et al., 2018). Interestingly, these mineralization reactions are also naturally occurring in a variety
30 of settings – e.g. as surface and near surface carbonation of ophiolites (Boschi et al., 2009; Kelemen et al.,
31 2011; Beinlich et al., 2012), or as higher temperature alteration as evidenced by the carbonate chimneys at
32 hydrothermal vents or by the formation of liswanite (i.e. quartz+carbonates) originating from the complete
33 carbonation of ultramafic lithologies (Hansen et al., 2005; Ulrich et al., 2014; Tominaga et al., 2017). Target
34 formations are for example the ophiolitic complex in Oman which could, according to Kelemen and Matter
35 (2008), store up to 77 trillion tons of CO₂, or basaltic formations in Iceland which have been the target for
36 the first pilot scale injection of carbon dioxide with great success by the CarbFix project team (Gíslason
37 et al., 2018).

38 Additionally, natural carbonation of mafic and ultramafic rocks is always tightly linked to serpentiniza-
39 tion processes themselves (Klein et al., 2013; McCollom et al., 2020), a specific set of reactions transforming
40 the minerals of anhydrous mantle peridotites into hydrated and less dense phyllosilicates – serpentine, talc
41 or clay minerals (sepiolite, saponite...) – through the influence of percolating seawater (Cannat et al.,
42 2010). One of the byproducts of these reactions is molecular hydrogen H₂ (McCollom and Bach, 2009). En-
43 gineered carbonation of mafic and ultramafic rocks could then also potentially be coupled with hydrogen
44 H₂ production, an economically inescapable component in the energy transition, but whose production
45 means are currently tightly linked to fossil fuel usages (International Energy Agency, 2019). The concomi-
46 tant industrial production of H₂ and carbon dioxide sequestration in ultramafic settings is a young field
47 of investigation (e.g. (Wang et al., 2019)) but whose results could be particularly interesting both for the
48 energy transition but also for the global understanding of the deep geochemical cycles (Escartín et al., 1997;
49 Gaillardet et al., 1999; Früh-Green et al., 2004; Paulick et al., 2006).

50 While batch experiments and reaction path studies of both carbonation and serpentinization of ultra-
51 mafic rocks are well described in the literature (Neubeck et al., 2011; Klein and Garrido, 2011; Malvoisin
52 et al., 2012; Grozeva et al., 2017; Miller et al., 2017; McCollom et al., 2020), percolation studies featur-
53 ing solid cores, in which a reactive solution is being injected at a constant flow rate or constant pressure
54 drop, are more scarce. This lack of experiments is regrettable because, while batch experiments help delve
55 into the complex geochemical interactions during the reaction, only reactive percolation experiments al-

low the observation of the coupling between hydrodynamics and chemistry, and its potential relationship with reaction-induced fracturing (Jamtveit et al., 2000; Ulven et al., 2014; Rudge et al., 2010; Evans et al., 2018). This so-called THMC behavior (Thermo-Hydro-Mechano-Chemical) is what actually controls the final assemblage of the altered lithology and not only the stability fields of the considered minerals.

In most of the reactive percolation experiments – (Peuble et al., 2015a,b, 2018, 2019) for carbonation and (Godard et al., 2013; Escario et al., 2018) for serpentinization on sintered olivine; Luhmann et al. (2017b) with the serpentinization of intact dunite at 150°C and 200°C; Tutolo et al. (2018) on the silicification of brucite; or Farough et al. (2016) on the serpentinization of fractured ultramafic cores at 260°C – the permeability is presenting a sharp drop during the experiment with usually a complete clogging after several days of injection. This loss of permeability is generally associated with the precipitation of neoformed minerals in the percolation paths and is tightly linked to the coupling between hydrodynamics and chemical kinetics.

In this study, we present two original experiments on a natural partially-serpentinized peridotite subjected to the injection of a carbonated fluid at 160°C and 280°C. Compared to the current literature on the topic, these experiments present two original novelties. First, the starting material is a natural partially serpentinized peridotite containing olivine, clino- and orthopyroxenes as well as serpentine and aragonite, contrary to the ideal sintered olivine or even dunite used in the literature. This type of rock is representative of most deep ocean ultramafic formations (e.g. at ultraslow spreading ridges (Dick, 1989)) and is thus better suited for in-situ carbonation and hydrogen production studies. Secondly, the second experiment was performed at 280°C, a common temperature of this kind of alterations (Menzel et al., 2018), but which had not been investigated before. The goal of these experiments was to track the evolution of the petrophysical and geochemical characteristics of the cores and assess their potential for carbon dioxide sequestration and hydrogen generation, as well as analyze the complex reactive transport couplings of these reactions.

2. Materials and Methods

2.1. Starting materials and characterization

2.1.1. Petrology

Three different thin sections were extracted from the initial serpentinite and analyzed with optical microscopy, SEM imaging coupled with EDS analyses, Electron Microprobe, Raman spectroscopy, as well as optical cathodoluminescence and micro-X-rays fluorescence (μ XRF). Modal composition was obtained from point counting (0.5mm \times 1 mm steps), including the 5 main identified phases: olivine, ortho- and clinopyroxenes, serpentine, aragonite and spinel. Magnetite was not included in the point counting due to the small size of the crystals. Similarly, aragonite was difficult to quantify due to the thinness of the veinlet network. In order to obtain the most accurate mineral proportions in the starting material, the composition

90 from point counting was compared with a composition calculated from the whole rock analysis (SARM -
91 Service d'Analyses des Roches et des Minéraux, Nancy – see Supplementary information for details of
92 the analytical procedures), combined with mineral formula calculated from EPMA measurements on the
93 phases of interest (see Supplementary information). The calculated composition only differs from the point
94 counting composition by a small decrease in clinopyroxene content (from 13 to 11%wt), an increase in
95 olivine (from 9.4 to 13%wt) and a small adjustment in aragonite, spinel and magnetite, but remains overall
96 very close.

97 2.1.2. *Petrophysical properties*

98 In order to characterize the petrophysical characteristics of the starting rock, Mercury Intrusion Porosime-
99 try (MIP) and BET analysis were performed on several cored samples. MIP was performed with an Auto-
100 Pore IV 9500 apparatus from Micromeritics while BET analysis was performed on a Quantachrome Nova
101 apparatus. Pre-experiment permeabilities were also measured for the two cores at room temperatures and
102 at working pressures (i.e. 100 bar of outlet pressure for the 160°C experiment and 200 bar for the 280°C
103 experiment – confinement pressure was set at least 70 bars above the injection pressure). The measurement
104 consisted in setting a pressure difference (ΔP) between the inlet and outlet and measuring the steady-state
105 flow rate. In order to improve the reliability of the measurements, a total of 4 ($\Delta P, Q$) pairs were performed
106 for each core and the permeability was retrieved from the slope of the linear regression (Osselin et al.,
107 2015b) using Darcy's law – $Q/A = (\kappa/\eta)(\Delta P/l)$ with Q the measured flow rate, A the cross section of the
108 core, η the viscosity of the fluid at the considered pressure and temperature, ΔP the imposed pressure
109 difference and l the length of the core. Since these pre-measurements were performed at room tempera-
110 ture, no chemical reaction was expected to occur. Results yielded a value of approximately 2.10^{-15}m^2
111 (2mD) for the core used for the experiment at 160°C and 4.10^{-15}m^2 (4mD) for the core used for the ex-
112 periment at 280°C. These values appear rather high compared to classic seafloor serpentinites (Reynard,
113 2013; Hatakeyama et al., 2017), but are consistent with some modeled permeability values obtained on
114 Oman serpentinitized peridotites (Dewandel et al., 2004; Katayama et al., 2020). The reason for these high
115 permeabilities is the presence of a large proportion of open fractures in the cores.

116 2.2. *Reactive percolation experiments*

117 The experiments started from cores (\varnothing 5.6 mm, lengths 4.1 cm for the experiments at 280°C and 3.9 cm
118 for the experiment at 160°C) drilled from a serpentinite block dredged from the South-West Indian Ocean
119 ridge (Rouméjon et al., 2014). The injected solution was prepared in advance as 2wt% NaCl and 5wt%
120 NaHCO_3 (i.e. $\approx 0.34\text{M NaCl} + 0.6\text{M NaHCO}_3$) with Sodium Chloride from Alfa Aesar (99+% purity) and
121 Sodium bicarbonate from SigmaUltra (99.5% purity). Room temperature pH was around 8.

122 The two reactive percolation experiments (one at 160°C denoted as LTE - Low Temperature Experiment
123 and the other at 280°C denoted as HTE - High Temperature Experiment) used a home-made permeameter

124 represented on Figure 1. It consists in a large volume (1 liter) autoclave connected to a piston-pump (PMHP
125 100-500, TOP Industry) controlling the confining pressure using deionized water as the confining fluid.
126 The core itself is inserted in a gold tube working as a jacket which transmits the confining pressure. At
127 both ends of the core, two stainless steel plugs are added to connect with the inlet and outlet capillaries
128 using Swagelok tube fittings as represented in the inset of Figure 1. The conical shape of the plugs allows
129 for an even distribution of the flow at the inlet and outlet. The sample is connected to two more pumps
130 controlling the inlet and outlet pressure. The autoclave is heated externally by a cylindrical oven controlled
131 with an Eurotherm regulator. Experimental temperature is measured inside the vessel next to the core
132 using an internal sheathed type K thermocouple and is known with an uncertainty $< 10^{\circ}\text{C}$. Temperatures
133 fluctuations during the experiments were limited to $1\text{-}2^{\circ}\text{C}$.

134 The system works at temperatures up to 400°C and confining pressures up to 500 bar. In this study, the
135 outlet pressure was set at 100 bar for LTE and 200 bar for HTE. Confining pressure was set 70 bar above
136 the inlet pressure. As clogging during the experiments occurs fast, we decided to control the injection by
137 imposing a constant pressure difference between the inlet and the outlet of the core in order to avoid an
138 uncontrolled increase of pressure in the case of complete clogging. The pressure difference was initially
139 set at 2 bars and was gradually increased during the experiment following the decrease of permeability
140 to maintain a flow rate around 0.5-0.6 ml/hr. Resulting flow rate as well as inlet/outlet pressures and
141 temperature were recorded with a frequency of 1 data point per second for the whole duration of the
142 experiment using an interfacing with the software Eurotherms iTools. The time-dependent permeability is
143 then calculated from Darcy's law as the ratio between the imposed pressure difference between inlet and
144 outlet and the corresponding measured flow rate. Viscosities were calculated from the IAPWS-97 equation
145 as 2.10^{-4} Pa.s at 160°C and 1.10^{-5} Pa.s at 280°C

146 2.2.1. *Geochemical relevance of experimental conditions*

147 The main purpose of the experiments is to study the coupling between physico-chemical processes (ad-
148 vection vs geochemical kinetics) at the core scale, and the experimental conditions (P,T,x) were chosen to
149 obtain the best compromise between reality and reasonable experimental time frames. The NaHCO_3 -rich
150 fluid used in the experiments is similar to the fluid compositions used in numerous studies of the carbon-
151 ation of ultramafic rocks (e.g. O'Connor et al. (2005); Chizmeshya et al. (2007); Andreani et al. (2009);
152 Hövelmann et al. (2011); Peuble et al. (2015a); Gadikota et al. (2020)). It presents however one fundamen-
153 tal difference with the cited studies, as the fluid in the presented experiments was not equilibrated with an
154 elevated partial pressure of CO_2 as is usually the case. This equilibration increases significantly the DIC
155 and decreases the pH which has for effect to increase the amount of potential carbonate precipitation but in
156 the same time increases also carbonate solubility. The higher pH in the presented experiments, in contrast,
157 accelerates the precipitation of carbonates but the relatively smaller amount of DIC limits the total amount

158 precipitated. However, this is partially balanced with the presence of aragonite in the starting material.

159 While NaHCO_3 -rich fluid compositions are recognized as favoring rapid carbonation of ultramafic min-
160 erals (Gadikota et al., 2014), they are not directly comparable with fluids in natural settings or in engineered
161 systems due to the significantly higher alkalinity and its strong effect on carbonate precipitation (Tutolo
162 et al., 2021). Indeed, while fluids related to serpentinization and carbonation of ultramafic rocks usually
163 present elevated pH (Cipolli et al., 2004; Chavagnac et al., 2013), their alkalinity and DIC remain gen-
164 erally around 1 mM, two to three orders of magnitude than the alkalinity in the presented experiments
165 and experiments in the literature. Similarly, fluids in engineered systems do not contain NaHCO_3 and are
166 only equilibrated with elevated CO_2 partial pressure (Kelemen et al., 2011). This difference in alkalinity
167 will favor a more intense carbonate precipitation in our experiments (and the experiments in the litera-
168 ture) than in a system without NaHCO_3 buffering. Nonetheless, even if not directly related to natural
169 fluids, the chosen fluid composition is considered adequate to reproduce alteration features from natural
170 serpentinization/carbonation reactions (Gadikota et al., 2014; Lafay et al., 2018), while allowing for shorter
171 experimental duration. It also provides a more straightforward comparison with the literature.

172 In terms of temperature conditions, the two chosen temperatures – 160°C and 280°C– correspond re-
173 spectively to a value close to the optimum for ultramafic mineral carbonation (O'Connor et al., 2005) and
174 close to the optimum of the serpentinization reaction (Martin and Fyfe, 1970; Kelemen and Matter, 2008;
175 Marcaillou et al., 2011; Malvoisin et al., 2012).

176 2.2.2. Fluid and Mineral analysis

177 During HTE, for time intervals of roughly 24 hours at the beginning and less frequently thereafter, the
178 outlet pump was emptied and the outlet fluid was sampled for chemical analysis. Samples were immedi-
179 ately filtered on a $0.45\mu\text{m}$ nylon filter, stored in a fridge at 4°C and quickly analyzed, without any acid-
180 ification. No water analysis was performed for LTE. Cation analysis was performed at CETRAHE (Ionic
181 chromatography on a Dionex ICS 1100) while anion analysis was performed on site on a Ionic Chromatog-
182 raphy with a Dionex Ionpac AS11-HS column, and DIC (Dissolved Inorganic Carbon) was analyzed with a
183 Shimadzu TOC-L series. Dissolved hydrogen was also analyzed by gaz chromatography (see Supplemen-
184 tary materials 1 for the sampling and analytical protocol).

185 After the end the experiment, the core was retrieved and cut axially in half. A polished section of each
186 half-core was prepared for SEM examination coupled with EDS analyses, cathodoluminescence, Raman
187 spectroscopy, micro-X-rays fluorescence and microprobe analyses.

188 2.3. Numerical simulations with PHREEQC

189 In order to analyze the chemical evolution during the experiments, numerical simulations of equivalent
190 batch experiments were performed with PHREEQC (Appelo, 2015) and the Thermoddem database (Blanc
191 et al., 2012) under LTE and HTE pressure and temperature conditions (resp. 160°C, 100 bar and 280°C,

192 200 bar). The simulations were run as 1 kg of starting material to which was added at each step 1 pore
193 volume of the inlet solution (2% NaCl, 5% NaHCO₃ as in the actual experiments) considering a porosity of
194 10%. After equilibration, the solution is replaced by another pore volume of fresh solution until a total of
195 5000 pore volumes has been injected. This procedure simulates the continuous injection of the solution in
196 the core considering infinitely fast chemical reactions.

197 The starting material composition used for the simulations is the rescaled composition from Table 1
198 without the spinel phase. Indeed this phase appears mostly undisturbed after the experiments and its ad-
199 dition in the simulations would result in unnecessary complexity. All the starting minerals are considered
200 as pure phases of fixed composition as determined by EPMA (Supplementary information 3) and are only
201 allowed to dissolve. Their thermodynamic properties were calculated using the thermodynamic properties
202 of their end-member components and assuming ideal mixing behavior. The Thermoddem database does
203 not incorporate a description of the influence of Al on the thermodynamic properties of pyroxenes and, so,
204 the presence of Al in the proxenes was not taken into account.

205 For the precipitation, two kinds of product phases were considered, (1) solid solutions (assumed to be-
206 have ideally), such as neofomed serpentine, carbonates... and (2) pure phases such as quartz or hematite
207 (see Supplementary Information 2 for the complete list). In order to describe Fe(III) incorporation in
208 the serpentine solid solution, we used the data for cronstedtite-7Å (Fe₂Fe₂SiO₅(OH)₄) from the CarbFix
209 database (Voigt et al., 2018) instead of the Thermoddem database where Al is present. The Al substitution
210 in serpentine is instead modeled using data for amesite, Mg₂Al(AlSiO₅)(OH)₄, the Al-bearing serpentine
211 end-member. This phase, which is structurally closer to lizardite, is preferred to kaolinite, which was used
212 in some previous modelling (Klein and McCollom, 2013; Malvoisin, 2015).

213 A few other phases such as some amphiboles (edenite, riebeckite...) and sodic pyroxenes (aegirine)
214 were supersaturated in some of the simulations. However, these phases were not detected in the experi-
215 ments and are not included as potential product phases. In preliminary simulations, hydrated magnesium
216 carbonates (hydromagnesite and nesquehonite since there is no data for dypingite) were considered as sta-
217 ble phases. However, nesquehonite, regularly the predominant phase at high temperatures, is supposed
218 to dehydrate beyond 100-150°C (Morgan et al., 2015). Therefore, both hydromagnesite (which is never
219 stable in the simulations) and nesquehonite were subsequently removed from the potential list of stable
220 solids. Saponite and vermiculite are the only clay minerals considered in the simulations. For simplicity,
221 pure Na end-members are considered in the simulations despite their large compositional variability, and
222 also because of the large Na activity in the initial solution. For Fe-oxides, magnetite and hematite and, for
223 silica, quartz were considered as potentially saturating phases. For the carbon species, reduction of CO₂ to
224 CH₄ by H₂ was assumed not to occur. Indeed, this reaction is not observed in most experiments from the
225 literature, being considered as kinetically inhibited (McCollom and Seewald, 2001). However, reduction

226 of carbon dioxide into organic acids or even in some cases to solid carbon has been sometimes reported
227 (McCollom and Seewald, 2003; Andreani and Ménez, 2019; Peuble et al., 2019). Nevertheless, given that
228 definitive information is lacking on reaction paths and thermodynamical constants, such reactions were
229 not considered, even if the saturation index of graphite was tracked in the different simulations.

230 3. Results

231 3.1. Initial serpentinite

232 3.1.1. Petrography

233 The starting material is a partially serpentinized lherzolite containing olivine, ortho- and clinopyrox-
234 enes and serpentine as major minerals plus several minor phases (aragonite, magnetite and spinel). The
235 sample shows classic features of serpentinization on which carbonation events are superimposed (carbon-
236 ates are identified as aragonite on XRD diffractograms and Raman spectra). It comprises two parts, both
237 rich in olivine, which alternate at the cm scale and are best distinguished by their contrasted colors, re-
238 spectively green and brown to dark orange (Fig. 2). The green zones contain carbonates only as large veins
239 (mm to cm-scale), and are made up of relictual olivine in a serpentine mesh (Fig 3a). Oxides (magnetite) are
240 abundant, generally of small size and they are typically found partially rimming olivine crystals in the void
241 at the interface with the surrounding serpentine matrix (Fig 3b). Other occurrences of oxides are found as
242 small nodules embedded in the serpentine matrix ($\approx 10\mu\text{m}$) or in larger veins, a few μm wide and about
243 $100\mu\text{m}$ long, visibly filling already existing cracks in the serpentine matrix. Green areas are also visibly
244 porous as microfractures and sometimes mm-sized fractures develop in the serpentine matrix.

245 In contrast, the brown to dark orange zones are associated with more pervasive carbonates and a much
246 smaller quantity of Fe oxides (Fig. 3c,d). The latter occur embedded in the serpentine matrix ($\approx 1\mu\text{m}$) or
247 in carbonate-rich areas. Carbonates in the brown to dark orange zone appear to have cemented most of
248 the porosity visible in the green zone. A complete cementation of the space between olivine and matrix is
249 observed (Fig. 3d) as well as the occurrence of numerous thin veinlets connecting olivine relicts, probably
250 originating from fracturing events with olivine acting as hard spots around which stresses accumulated.
251 Carbonation of the protolith postdates serpentinization, with veins of carbonate (aragonite) crossing and
252 overprinting veins and serpentine structures. In particular, the large vein in Figure 3e, is the result of
253 the filling of a large fracture which appeared after most of the serpentinization occurred since alteration
254 features can be matched from both sides of the vein. The center of this large vein appears white under the
255 microscope and is analyzed as pure CaCO_3 aragonite with EDS and Raman spectroscopy, while the borders
256 present a rusty color visible with naked eye and under the microscope. These borders appear to consist
257 in an intimate mixture of Mg and Ca-carbonates and small oxides. Aragonite under cathodoluminescence
258 offers a color palette from yellow to green through light orange, but with overall little luminescence (Fig.

259 4a,b). The silicate background is significantly less luminescent with a dark pink shade, where only cpx can
 260 be discerned due to their lighter pink color.

261 In both zones, olivines present a clear hierarchical pattern – a pattern resulting from the successive frac-
 262 turing of the initial mineral into smaller domains (Iyer et al., 2008) – due to the fracturing of the olivine
 263 core and the replacement along the fractures (e.g. Røyne et al. (2008); Jamtveit et al. (2009); Kelemen
 264 and Hirth (2012); Røyne and Jamtveit (2015); Malvoisin et al. (2017)). Dissolution features are common
 265 but not ubiquitous and some olivine/serpentine interfaces appear quite smooth while etch pits and saw-
 266 toothed interfaces can be observed on other occasions (regularly observed in natural or experimental set-
 267 tings (Plümper et al., 2012; Klein et al., 2015; Lisabeth et al., 2017b)). Pyroxenes show different levels of
 268 replacement. As a general rule, clinopyroxenes appear less altered than orthopyroxenes. The least afflicted
 269 clinopyroxenes present light alterations along the cleavage (with serpentine as the replacing phase) and
 270 which progress orthogonally to it as observed on Figures 3e and f. At more advanced levels of replacement,
 271 the symmetry with respect to the cleavage planes is lost and clinopyroxenes start breaking into smaller
 272 independent fragments. Replacement can also occur along fractures not necessarily following the cleavage
 273 planes (Fig. 3f). As a result, some clinopyroxenes seem to be replaced without any visible pattern while
 274 some more intact crystals present a lamellar structure as in Figure 3e. Orthopyroxenes present a different
 275 pattern of alteration with little to no replacement along the cleavage and an alteration progressing mostly
 276 from fractures running through the mineral (Fig. 3f). Finally, the thin sections reveal some occurrences
 277 of Cr-spinel with different degrees of alteration, and some very rare occurrences of iron sulfide (probably
 278 pyrite) which occur as large (20 μ m to 100 μ m diameter) blobs.

279 From the EPMA results, two types of serpentine can be distinguished in both zones. An Al-poor serpen-
 280 tine ($Mg\# = MgO / (MgO + FeO) \approx 90$, $Al_2O_3 \approx 0.2wt\%$), is identified as lizardite by Raman spectroscopy and
 281 makes up the mesh texture surrounding the olivine relicts and originates from olivine serpentinization.
 282 The other type of serpentine is also identified as lizardite but contains a higher Al content (Al_2O_3 5-6wt%,
 283 $Mg\# \approx 88$) substituting for Si and is linked to the replacement of pyroxenes (bastite). On some rare occa-
 284 sions, veins of chrysotile can be observed which seem to have formed between the main serpentinization
 285 event and the carbonation event. The rest of the ultramafic minerals are forsteritic olivine Fo_{90} , enstatitic
 286 orthopyroxene (En_{89}) and clinopyroxene Di_{91} ($Di = X_{Diopside} / (X_{Diopside} + X_{Hedengergite})$).

287 3.1.2. Petrophysical properties

288 The mercury intrusion porosimetry distribution (Fig. 5) is centered around two classes of pores, with
 289 one class consisting of submicronic porosity (visible on SEM images both as the space between olivine and
 290 serpentine as well as the microfractures in the serpentine matrix) and the other consisting in larger pores
 291 with sizes from around 60 μ m and higher, most likely larger fractures. A smaller third class of pores with
 292 sizes between 5-10 μ m is also visible but it represents only a small fraction of the pore volume. This class of

293 pores is however rather important because it regroups a dense and connected network of small fractures,
 294 some of them partially filled by carbonates forming the so-called veinlets. In average, porosity of the cores
 295 is around 10%. BET measurements provide a specific surface area of around 10-12 m²/g which is divided
 296 into ≈ 7 m²/g for the micropores (< 2 nm) and 3-5 m²/g for bigger pores. Mercury intrusion porosimetry
 297 can as well provide an estimate of the specific surface area with $1.9 \cdot 10^{-4}$ m²/g for pores between 871 μ m
 298 and 62 μ m, $3.3 \cdot 10^{-3}$ m²/g for pores between 62 μ m and 1 μ m, and finally 2.3 m²/g for pores below 1 μ m.
 299 Since MIP does not consider pores below 6 nm, the rest of the specific surface area belongs to pores smaller
 300 than 6 nm which is consistent with BET results.

301 3.2. Numerical simulations

302 The equilibrium assemblage as a function of the injected pore volume (PV) is represented on Figure 6.
 303 Results are similar to previous numerical simulations of such systems (e.g. (Bruni et al., 2002; Klein and
 304 Garrido, 2011; Paukert et al., 2012; de Obeso and Kelemen, 2020) on EQ3/6 (Wolery, 1992)), and show that
 305 a serpentine/carbonate/clay assemblage coexists until 250PV at both 160°C and 280°C. Further injection
 306 of the carbonate solution at 160°C leads to a small talc window between 250 and 500PV before the silica
 307 becomes incorporated into quartz while the rest of the divalent cations get included in the carbonate phase.
 308 The assemblage at 280°C follows the same pattern with a slightly larger talc window. However beyond
 309 3600PV quartz disappears, the silica getting incorporated into the clay phase (saponite). This relative
 310 importance of the clay fraction in the mineral assemblage is due to the high amount of aluminum in the
 311 primary minerals (pyroxenes). The Al content could potentially be even higher if the spinel phase which
 312 was not considered in the simulation was also reacting. Interestingly, the initial serpentine (Mg#=0.9) is
 313 stable for a large range of injected PV for both temperatures while a neoformed, more iron-rich serpentine
 314 (Mg# \approx 0.6-0.7) is also found to be stable (Figs. 6a and 6b). At 160°C within the quartz/carbonate domain, a
 315 very small amount (<1%mol) of serpentine is still present as pure amesite Mg₂Al(AlSiO₅)(OH₄) following
 316 the release of Al from pyroxene dissolution and the absence of other Al-bearing phases. Some amphiboles
 317 are also expected to form at the beginning of the injection (PV<25) as well as chlorite, while brucite is
 318 never stable due to the high amount of pyroxenes and thus the high silica activity. In terms of iron oxides,
 319 the simulations at 280°C suggests an increasing precipitation of magnetite during the whole process. At
 320 160°C magnetite also occurs for most of the simulation albeit in smaller amounts. However, at 160°C,
 321 hematite replaces magnetite beyond 400PV while hematite only appears in HTE after 1700PV. Finally, the
 322 composition of the carbonate phase evolves from almost pure calcite at the beginning of the injection (from
 323 the recrystallization of aragonite) to a more complex solid solution incorporating Fe and Mg for increasing
 324 degrees of alteration. Aragonite is never stable in the simulations.

325 3.3. Reactive percolation experiments

326 A summary of the settings for both experiments is reported on Table 2.

3.3.1. Permeability evolution

The evolution of permeability for both experiments is shown on Figure 7. A global decrease is observed throughout the two experiments until cores became virtually impermeable. The decrease is in both cases linear on a log-plot (i.e. $\kappa/\kappa_0 = \exp(-t/\tau)$ with κ_0 the initial permeability, t the time and τ the characteristic time of decay). This exponential decrease of permeability over time is common in the description of fractured porous media subjected to dissolution-precipitation and fracture filling. Such behavior was for example described for granite under hydrothermal conditions (Morrow et al., 2001). Here, the decrease is made of a single step for LTE (characteristic time of 140 hours) and of two steps for HTE with a characteristic time of 92 hours during the first 5 days and of 37 hours thereafter. At the very beginning of LTE, the permeability shows a quick drop from 2 mD to 1mD, followed by a slight increase back to 1.5 mD before decreasing steadily. It is hard to assess if this behavior is an artifact due to the stabilization of the flow rate or if it is a consequence of some chemical or physical (fracture closing) mechanism.

3.3.2. 160°C experiment (LTE)

For this experiment, no fluid was sampled and so no information on hydrogen generation is available. Below, we concentrate on the mineralogical transformations resulting from fluid percolation. The reacted core was recovered in two pieces, the longest comprising almost the whole core, and the smallest, a few mm long, corresponding to the top end (fluid outlet). The presence of a nearly continuous layer of large ($\approx 20\mu\text{m}$) euhedral carbonate crystals at the broken end of the larger piece (Fig. 8d) suggests that breaking did not occur during recovery but rather occurred initially during mounting of the core in its Au jacket. These carbonate crystals have a high Mg content (up to 30wt% MgO).

The recovered core presents a distinct color from the initial green/brown protolith (Fig. 8 left), appearing light brown, and even yellowish. Pyroxenes retain their green/dark green color and, so, they stand out the most clearly, while the other phases (serpentine matrix+olivine relicts) were modified. Microscopic examination shows that the olivine relicts did not significantly change in number and shape compared to the initial protolith. However, while both green and brown to orange olivine-bearing zones were initially present, the reacted core is more homogeneously colored. Carbonate layers (identified as aragonite by Raman spectroscopy) are found around most olivine relicts and aragonite veinlets connect the olivine crystals (Fig. 8b). In other words, the textural attributes specific of the brown to orange part in the protolith have developed and extended in the reacted core. Pyroxenes seem more altered presenting visible dissolution features, such as ubiquitous saw-tooth patterns as well as networks of microfractures originating from etch-pits (Fig. 8c). However, these features are difficult to attribute to the experiments with certainty because of the initial heterogeneity of the starting protolith.

In general, aragonite veins appear yellow to orange under cathodoluminescence, with some greener and redder areas in a very similar fashion to the original protolith. Interestingly, the Raman spectra of

361 aragonite display some variability suggesting small compositional variations consistent with the color dif-
362 ferences seen in cathodoluminescence as well as μ XRF, which shows a Mg enrichment towards the border
363 of the veins probably due to the higher Mg activity next to the serpentine. The largest vein, which crosscuts
364 the whole core (Fig. 8a) presents on the walls the same rusty color as the large veins in the initial protolith
365 (Fig. 3e). This rusty zone is again composed of an intimate mixture of Ca- and Mg-carbonates and iron
366 oxides. Since the carbonate phase is almost exclusively aragonite, it is difficult to assess if any additional
367 aragonite precipitation took place during this experiment. In particular, the strong similarities between
368 cathodoluminescence images of the starting material and the LTE core (Figs. 4a,b,c) suggest that little to no
369 precipitation occurred and the overall aragonite amount did not drastically change. Nevertheless, the Mg
370 enrichment towards the veins walls could be the sign of extra precipitation of Mg-richer aragonite during
371 the experiment.

372 3.3.3. 280°C experiment (HTE)

373 The core after 10 days presents a striking brick-red color, in which both ortho- and clinopyroxenes
374 appear clearly reacted, along cleavage planes as well as new fractures (e.g. Fig. 9e). The color is attributed
375 to the presence of Fe(III) minerals, mainly hematite since pure cronstedtite, the Fe(III)-bearing end-member
376 of the serpentine family, is black (Hybler et al., 2016). However, no hematite crystals could be detected
377 by SEM suggesting that they only occur as very small crystallites. This alteration is very similar to the
378 formation of iddingsite, a mixture of smectite and Fe(III)-oxides (hematite or goethite) observed in similar
379 conditions (Peuble et al., 2019). However, EPMA measurements give a chemical composition closer to
380 serpentine than actual iddingsite, where depletion of Mg leads to high Fe/Mg (Delvigne et al., 1979). The
381 brick-red coloring is not homogeneous in the whole sample and a gradient from fully brick-red to pink
382 and even gray can be noted. SEM imaging reveal that this color gradient is directly linked to the presence
383 in variable amounts of residual olivines. Zones with the strongest red color completely lack olivine and
384 only consist of serpentine matrix plus carbonate veinlets (Fig. 9d, bottom), indicative of a high degree of
385 alteration. Conversely, the least colored zones contain olivines (the lighter the color, the more the olivine
386 relicts) and in particular the area next to the inlet. This part of the sample appears to have been barely
387 modified during the experiment and it shows features strikingly similar to green zones described in the
388 starting serpentinite. Yet, the pre-existing magnetite rim (Fig. 3c) is now found included in the serpentine
389 matrix at some distance away from olivine suggesting a volume reduction of the olivine cores (Fig. 9c).

390 Near the inlet, a wide (≈ 0.5 mm) carbonate vein wraps the untransformed olivine-rich zone. It shows the
391 same characteristics (in particular the rust colored border with porous texture and presence of Fe oxides
392 and Mg-rich carbonates) as aragonite veins found both in the LTE and in the starting serpentinite (Fig. 9a
393 and b). This vein marks the infilling of a large fracture visibly open and empty in the starting core. The rest
394 of the carbonates occur throughout the sample as a very dense network of veins and veinlets developed par-

395 allel to the flow direction and identified as calcite with Raman spectroscopy. Cathodoluminescence shows
396 that the network of calcite is significantly denser than the aragonite network of the starting material and
397 presents a very homogeneous and extremely bright red color, which contrasts with the less luminous color
398 gradients of the aragonite veins in the LTE and the initial serpentinite (Fig. 4). The only parts appearing
399 dark in cathodoluminescence are the relicts of pyroxenes. There is an inverse correlation between the den-
400 sity of the veinlets network and the presence of olivine, with the redder zones containing numerous small
401 veinlets while the less altered zones present either few veinlets or just a large vein cutting across (left and
402 right area of Fig.9d). As highlighted by the μ XRF imaging, the calcite network is only distributed within
403 fractures and veins and appears aligned with the flow direction. On the contrary, serpentine, does not show
404 any preferential orientation. Finally, spot analysis with electron microprobe (see supplementary data) did
405 not allow to identify unambiguously the neoformed serpentine, as all serpentine compositions which were
406 analyzed on HTE did not statistically deviate from the serpentine composition in the starting material.

407 Five aliquots of outlet fluid were sampled at different and increasing time intervals over the entire
408 experiment and analyzed for major cations and anions as well as for dissolved hydrogen. The data yield
409 the average concentrations of the effluent between two sampling events. Additionally the outlet solution is
410 being diluted when reaching the pump as the outlet pump is refilled with some deionized water after each
411 sampling. Data were rescaled by this dilution factor to obtain the actual outlet concentrations. Results
412 are presented in table 3, with the first number the measured concentration and the second, the rescaled
413 concentration.

414 Chloride concentration is mostly conserved during the experiment. The small variations observed could
415 possibly reflect the precipitation of halite, of which a few crystals were detected on SEM, as well as iowaite
416 $\text{Mg}_6\text{Fe}_2^{3+}(\text{OH})_{16}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ even if this mineral was not observed. Outlet Na and DIC concentrations ap-
417 pear systematically lower than the injected amount, suggesting some uptake by the core. Magnesium and
418 calcium show very similar evolution with concentrations below detection in the middle of the experiment
419 and two spikes, one at the very beginning and the other at the very end of the experiment. We note that
420 the inlet solution contains some Ca (0.39 mg/L) from imperfectly exchanged deionized water. This small
421 Ca background concentration actually facilitates mass balance comparisons. In particular, the absence of
422 detection of Ca in the outlet fluid following the early spike stresses that this element has been completely
423 trapped in the core. The dissolved hydrogen follows a trend similar to Ca and Mg with a first spike at 100
424 $\mu\text{mol}/\text{kgw}$ on the first day, followed by steady concentrations of around 30-50 $\mu\text{mol}/\text{kgw}$ in the following
425 days and finally a strong increase up to 162 $\mu\text{mol}/\text{kgw}$ in the last days.

426 The large uptake of DIC is supported by the very dense calcite network visible in Figure 9. It is also
427 possible that part of the injected DIC was reduced to organic molecules or even graphite, however no
428 evidence of this reaction was found. In parallel, the core has also taken up an unexpected amount of sodium

429 (5.6 mmol) which could not be related to any visible mineral. We can easily rule out any precipitation
430 of sodium-bearing mineral in the tubing or in the pump, as the only mineral which could precipitate is
431 halite and the uptake of chloride is two orders of magnitude smaller (0.2 mmol). A combination of three
432 options remain to explain the sodium behavior: clay precipitation, Na-bearing carbonate precipitation
433 or Na-adsorption. The first option is supported by PHREEQC simulations with clay phase composed of
434 saponite and vermiculite. However, the maximum quantity of Na mineralized in the simulations is around
435 1.5 mmol at an injected pore volume of 200 which is of the same order of magnitude but appears insufficient
436 to explain the Na uptake. The other option is the precipitation of Na-bearing carbonates, such as the rare
437 mineral eitelite ($\text{Na}_2\text{Mg}(\text{CO}_3)_2$). Finally the last possibility is the adsorption of Na on serpentine. It is
438 however difficult to assess the relative importance of these phenomena with certainty.

439 4. Discussion

440 4.1. Mineralogical evolution and pore size distribution

441 Despite very similar experimental conditions, except for the experimental temperature, HTE and LTE
442 present fundamentally different mineralogical and petrophysical behaviors. Indeed, the LTE presents little
443 evolution from the starting material, with relicts olivine and pyroxenes embedded in a serpentine matrix
444 through which run veins and veinlets of aragonite. Yet, despite the absence of obvious modifications from
445 the starting material mineralogy, the fast decrease in permeability of LTE is still evidence of a precipitation
446 leading to the clogging of the permeability, either from the serpentinization of olivine and pyroxenes, or
447 from the precipitation of extra aragonite in the open porosity (such as the Mg-enriched aragonite at the
448 interface between serpentine matrix and aragonite veins). The HTE presents on the contrary, not only a
449 complete replacement of the aragonite network by calcite, but also a significant increase in the number
450 and density of calcite veins throughout the core. The permeability decrease is significantly faster and is
451 consistent with the densification of the calcite network. Since the starting material was initially relatively
452 altered, it is quite difficult to quantify the alteration of the silicate minerals, but the strong alteration fea-
453 tures (olivine-free zones on Figure 9d, or heavily altered cpx 9e), which have no equivalent on the starting
454 material, suggest nevertheless that silicates were deeply altered during the experiment. The chemical
455 modification of the mineral assemblage of HTE is also evidenced from chemical analysis of the outlet fluid
456 with a leaching of Mg and Ca from the dissolution of the starting minerals, a production of hydrogen
457 through Fe oxidation, and an uptake of CO_2 feeding the calcite precipitation.

458 In the literature, the reactivity of ultramafic minerals to carbon-rich fluids has been extensively studied
459 both in natural environments (Hansen et al., 2005; Boschi et al., 2009; Beinlich et al., 2012; Chavagnac
460 et al., 2013; Falk and Kelemen, 2015; Miller et al., 2016; Tominaga et al., 2017; Menzel et al., 2018; May-
461 hew et al., 2018; de Obeso and Kelemen, 2018, 2020; Picazo et al., 2020; Ellison et al., 2021) and in batch
462 experiments (McCullom and Seewald, 2001; O'Connor et al., 2005; Chizmeshya et al., 2007; Neubeck et al.,

2011; Hövelmann et al., 2012; Gadikota et al., 2014; Lacinska et al., 2017; Grozeva et al., 2017; Miller et al., 2017; Lisabeth et al., 2017a,b; Gadikota et al., 2020; McCollom et al., 2020). The transformation of ultramafic rocks subjected to the percolation of carbon-rich fluids is usually described as a gradual evolution towards first a serpentine/carbonate assemblage at low degrees of alteration, then to a talc/carbonate assemblage (soapstone) following the increase of the Si/Mg ratio of the fluid due to the continuous dissolution of the silicate minerals and the uptake of Mg by the precipitating carbonates (Beinlich et al., 2012). At higher degrees of alteration, the further increase in Si/Mg ratio of the fluid leads to a final assemblage quartz/carbonate called listvenite, where all the silica from the primary minerals is taken up by the quartz phase, while the divalent cations are incorporated in the carbonate phase (Falk and Kelemen, 2015). This succession, which can occur without any other input than the CO₂ content of the infiltrating fluid (Menzel et al., 2018), is observable in numerous natural settings (Hansen et al., 2005; Beinlich et al., 2010; Power et al., 2013; Falk and Kelemen, 2015; Menzel et al., 2018) and in some experiments (e.g. Andreani et al. (2009); Peuble et al. (2015a)), and is perfectly consistent with our numerical results (Fig. 6). It is however not universal and some phases (e.g. talc) may be omitted depending on the percolating fluid composition and its velocity (Hinsken et al., 2017).

The final composition of both LTE and HTE – i.e. mostly serpentine + CaCO₃ (aragonite for LTE and calcite for HTE), relictual pyroxenes and olivine, iron oxides, absence of talc, quartz, or clay minerals – is characteristic of low alteration levels and corresponds to an injected pore volume up to 250 in the simulations (Fig. 6). However, the total injected pore volume of the experiments is actually one order of magnitude larger. PHREEQC simulations are indeed performed at equilibrium thus considering an infinite reaction rate at each step, or an infinitely slow flow rate (a case coined transport-limited as the extent of reaction does not depend on the reaction kinetics but is only limited by the capacity of the system to transport chemical species to and from the reactive surfaces). In the presented experiments, the actual behavior corresponds to an intermediate case with different and finite reaction rates for each mineral reaction. As a result, the system requires more fluid to achieve the same degree of alteration as the simulations, since the percolating fluid does not have enough time to fully react before exiting the core, limiting effectively the actual input in terms of dissolved CO₂. This relationship between chemical reaction and mass transfer by advection is scaled by the Damköhler number, $Da = \frac{k}{vc}$, with k the intrinsic reaction rate in mol.m⁻².s⁻¹, v the fluid velocity (from Darcy's law) and c the solubility in pure water of the considered mineral (Osselin et al., 2016, 2019). Large Da correspond to situations where the reaction occurs more rapidly than advection, either because of very fast kinetics or very slow flow rates similarly to PHREEQC simulations. This leads to a system at chemical equilibrium for every point in space and time. On the contrary, small Da correspond to situations where the reaction is much slower than the fluid velocity and the system remains permanently out of equilibrium (reaction-limited regime).

497 Since Da depends on both the intrinsic kinetics of the considered mineral as well as the fluid velocity,
 498 we can identify in our experiments three different zones with three different behaviors, following the three
 499 classes of pores identified by Mercury Intrusion Porosimetry (i.e. $>62\mu\text{m}$, $[1-62]\mu\text{m}$ and $<1\mu\text{m}$).

- 500 • **Large veins** In the larger veins, which correspond to the larger pore network (Zone 1 on Figure 11),
 501 dissolution of the primary minerals will be homogeneous over the whole length of the system and
 502 can be considered as far-from-equilibrium since these zones concentrate the largest flow. The system
 503 will be reaction-limited ($Da \ll 1$) as the quantity dissolved per unit time is only linked to the intrinsic
 504 dissolution rate of each mineral and their reactive surface area. For slow precipitating minerals (i.e.
 505 serpentine), precipitation will occur far from the inlet and most of the solutes will actually exit the
 506 system without any actual precipitation (net mass loss as confirmed by the Mg leaching on HTE).
 507 On the other hand, fast precipitating minerals (i.e. calcite and potentially hematite) will still be able
 508 to precipitate in these fractures (the only minerals with $Da \gg 1$, see Supplementary Information).
 509 The fact that some Ca is still leached from the core (albeit in smaller quantities than Mg) shows
 510 that despite the very fast kinetics of calcite precipitation, the conversion of aragonite to calcite is not
 511 complete.
- 512 • **Small veinlets** For the second class of pores (Zone 2 on Figure 11), on the contrary, the fluid velocity is
 513 significantly lower leading to a mixed- to transport-limited regime (i.e. $Da \gg 1$ for all minerals except
 514 cpx and magnesite) and a more localized reactivity. This means that the dissolution and precipitation
 515 of minerals will rather occur locally as an interface controlled process (Ruiz-Agudo et al., 2014),
 516 close to equilibrium, with the neoformed minerals precipitating at the same location than dissolution
 517 occurred. This situation can lead to the pseudomorphic mineral replacement by the synchronization
 518 of the reaction fronts (Putnis, 2009; Kondratiuk et al., 2017). Moreover, because of the limited flow,
 519 overall little CO_2 is brought to these areas meaning that little carbonation actually occurs, and only
 520 in the largest veinlets.
- 521 • **Small pores and fractures ($<1\mu\text{m}$)** For the third class of pores ($<1\mu\text{m}$), the velocity is almost neg-
 522 ligible and the solute transport is exclusively controlled by diffusion. This leads to a full transport-
 523 limited regime and thus very slow reaction rates. Similarly to the small veinlets, due to the extremely
 524 small flow rate, no CO_2 is able to reach these zones and so no carbonation occurs, allowing only
 525 serpentization reactions to take place.

526 At the core size, an interesting example of the relationship between kinetics and pore network can be
 527 observed on Figure 9d, highlighting the fundamental importance of diffusion and advection. The top part
 528 of the image presents a large vein cutting through an olivine-rich area, while the bottom part presents
 529 smaller veins and almost no olivine remaining. In the top part, the velocity in the vein is large and the ratio

530 between advection and diffusion (Péclet number) is much larger than 1, implying an advection-dominated
531 regime, while the rest of the surrounding matrix is diffusion-dominated. Since there is no advection in
532 the matrix the replacement reaction progresses very slowly, while dissolution/precipitation occurs more
533 rapidly in the large vein due to the fast advection. On the other hand, for the bottom part of the image, the
534 alteration is much more homogeneous as numerous fractures and veinlets percolate through the serpentine
535 matrix. The density of these veinlets allows for a faster elimination of the reaction products as well as an
536 increased input of dissolved CO_2 , accelerating olivine dissolution, consistent with the complete absence of
537 olivine relicts in this area. This type of observation can be extended to the whole core: wherever there is
538 an extended network of small veins, the system is strongly altered, while large veins seem to traverse the
539 system without much interactions. Another prime example of this behavior is the inlet of HTE, with the
540 very large vein of carbonate right next to a zone which was barely modified. During the experiment little
541 to no fluid at all flowed in this particular zone and thus little to no CO_2 because all the fluid was funneled
542 in the larger fracture. As a result, only pure serpentinization occurred leading to the clear "green"-type
543 textural features.

544 4.1.1. Carbonates precipitation

545 Aragonite presents the fastest dissolution kinetics of all the primary minerals at both temperatures.
546 In the absence of any other chemical reaction, this would mean that the solution percolating through the
547 sample will get quickly saturated and dissolution would occur only next to the inlet with a dissolution front
548 progressing in the sample following the depletion of aragonite ($Da \gg 1$). However, dissolution of aragonite
549 is coupled with the precipitation of calcite, which is more thermodynamically stable at both temperatures
550 and is just as fast to react as aragonite. As a result, as soon as supersaturation is generated by aragonite
551 dissolution, calcite should immediately precipitate. The consequence is that aragonite will never be at
552 equilibrium with the fluid and will keep dissolving as long as calcite is able to precipitate.

553 In HTE, aragonite is completely replaced as expected by a very chemically-homogeneous calcite, over
554 the whole length of the core. However, in LTE aragonite remains preserved and no calcite was identified by
555 Raman spectroscopy. Since thermodynamics predicts the total replacement of aragonite by calcite for both
556 LTE and HTE, this means that calcite precipitation was slowed or even inhibited, preventing the further
557 dissolution of aragonite. This inhibition can be explained by the effect of dissolved Mg on calcite precipi-
558 tation kinetics. Indeed, calcite precipitation is known to be strongly slowed down or even inhibited in the
559 presence of magnesium ions (Zhang and Dawe, 2000). This is one of the alleged reasons for the existence
560 of aragonite in marine serpentinites out of its usual high pressure domain of stability (Bonatti et al., 1980).
561 Thus calcite precipitation could have been slowed enough in the LTE to explain its absence, leading to an
562 aragonite-saturated solution in the whole core due to its fast dissolution kinetics. The consequence is that
563 the carbonate network was untouched in most of the core, with only the inlet being subjected to aragonite

564 dissolution. Interestingly, the carbonate veins next to the inlet appear extinct under cathodoluminescence
565 suggesting an evolution of the composition from the rest of the core and potentially corroborating the hy-
566 pothesis. In this context, the complete replacement of aragonite by calcite in HTE could be explained by a
567 less effective suppression of calcite precipitation by Mg^{2+} at a higher temperature, although calcite precip-
568 itation is probably still slower than in the absence of Mg since a small amount of Ca was still able to exit
569 the core.

570 Similarly, the complete absence of magnesite can be explained by the slower kinetics of magnesite pre-
571 cipitation compared to calcite and serpentine respectively. Magnesite is known to have very slow precip-
572 itation kinetics (Saldi et al., 2012) and considering the large difference in precipitation kinetics between
573 calcite and magnesite, dissolved inorganic carbon will be preferentially incorporated in calcite rather than
574 in magnesite, inhibiting the precipitation of the latter (Hövelmann et al., 2011). This is consistent with ex-
575 perimental (Andreani et al., 2009; Peuble et al., 2015b; Grozeva et al., 2017) and natural observations (Noël
576 et al., 2018; de Obeso and Kelemen, 2018) where calcite is the main carbonate phase if Ca is present, and
577 magnesite is virtually absent, except in low flow zones where the fluid resides long enough for magnesite to
578 precipitate ($Da \gg 1$ due to smaller v). In some cases, this kinetic effect leads to first the precipitation of cal-
579 cite followed by a progressive recrystallization of Mg-enriched calcite towards the dolomite end-member
580 if the fluid contains enough dissolved Mg (Grozeva et al., 2017). This is consistent with the detection of
581 Mg-enriched carbonates at the rim of the large veins (also observed in nature by de Obeso and Kelemen
582 (2018)), or with the large Mg-rich crystals from Figure 8b which appeared due to the exceptional slowing
583 of the fluid in this large artificial fracture.

584 Under our experimental conditions, serpentine also precipitates faster than magnesite and so the com-
585 petition for Mg should also favor the latter. The complete absence of magnesite is then due the kinetically
586 favored precipitation of calcite in high DIC zones and of serpentine in high silica zones. Magnesite or Mg-
587 rich carbonate solid solution (even potentially dolomite) is however expected to occur at higher degrees of
588 alteration as highlighted by PHREEQC simulations since the continuous supply of DIC forces the dissolu-
589 tion of serpentine and the release of Mg, leading to the progressive incorporation of Mg in the carbonate
590 solid solution.

591 4.1.2. Iron oxides

592 Numerical simulations predicts the precipitation of hematite after 1700PV at 280°C which is consistent
593 with the brick-red coloring of the core. This precipitation of hematite, which has already been observed in
594 similar situations (e.g. Godard et al. (2013)), can be explained by a combined action of hydrogen removal by
595 the continuous flow of solution and the constant input of dissolved oxygen from the injected fresh solution
596 (a calculated concentration of 0.226 mmol/kgw). The same simulation without dissolved oxygen produces
597 only magnetite even at the highest injected pore volumes consistent with natural serpentinization, where

598 magnetite is found almost exclusively and hematite is very rare due to the anoxic nature of serpentinizing
599 fluids. In contrast however, hematite is also predicted in the simulations at 160°C but does not seem to
600 have precipitated in the experiment. This discrepancy is easily explained by the fact that the simulations
601 predict hematite when all the primary minerals are altered and the system reaches the quartz/carbonate
602 assemblage, which is not the case since the alteration in LTE corresponds rather to an injected pore volume
603 of 250 or less due to the finite reaction kinetics.

604 4.2. Permeability evolution and comparison with the literature

605 In order to interpret our permeability data, results from similar experiments in the literature are re-
606 ported in Table 4. The first 4 rows correspond to carbonation experiments while the next three are pure
607 serpentinization for comparison. In contrast with the other experiments in the Table, experiments of Lisa-
608 beth et al. (2017b) were proceeded under hydrostatic conditions and no flow rate conditions were imposed.
609 Carbonation experiments, even with strongly varying experimental conditions, report consistent values of
610 the characteristic decay time of 111, 60, 35 for experiments at respectively 150°C, 160°C and 180°C (Lis-
611 abeth et al. (2017b), this study and Peuble et al. (2015b)). Increasing temperature seems to accelerate the
612 decrease of permeability. Interestingly, both this study at 280°C and the slower flow rate in (Peuble et al.,
613 2015b) report an induction period of a few days with slower permeability decrease and similar decay time
614 (respectively 40 and 35 hours) before accelerating to respectively 16 and 2.5 hours. On the contrary, pure
615 serpentinization experiments report a much slower permeability decay rate with values ranging from 900
616 to 4500 hours, to the exception of Lisabeth et al. (2017b) with a decay rate of only 361 hours.

617 The difference stems from the difference in precipitation kinetics between silicate (serpentine) and car-
618 bonates. In particular, for higher flow rates, the slower serpentine precipitation leads to a non isochemical
619 behavior with most of the dissolved serpentine exiting the system instead of precipitating (Mg leaching).
620 The stark decrease in characteristic time from the experiment of Godard et al. (2013) when the flow rate
621 is decreased suggests an increase of precipitation and thus a faster decrease in permeability. We recal-
622 culated the Damköhler number in their experiment and obtained values of 10^{-5} for olivine and 10^{-4} for
623 serpentine (the change of flow rate does not modify the order of magnitude) confirming a reaction-limited
624 behavior but seemingly at odds with the author's interpretation of fast kinetics and a transport-limited
625 regime. However, similarly to our experiments, it is possible that some zones of lower flow rate can have a
626 more transport-limited regime impacting strongly the overall behavior. For these zones to appear, it would
627 require a decrease of the Darcy velocity of 4 orders of magnitude or pores 10 times smaller (from the cal-
628 culation of hydraulic resistance, considering similar surface areas), which are very likely to exist in their
629 system. These observation are perfectly supplemented by the evolution of permeability in the experiment
630 of Lisabeth et al. (2017b) who evidence a much faster decay rate, of the same order of magnitude of Godard
631 et al. (2013) after the change of flow rate. Since these experiments were made without imposing a flow rate,

632 the reaction occurs isochemically and the clogging of the permeability occurs thus faster.

633 Additionally, during serpentinization, the largest amount of precipitation occurs in the smallest pores
634 where the velocity is reduced enough to be closer to equilibrium. Since the hydraulic conductivity of these
635 pores is already very small, their clogging does not impact heavily the permeability. It is only when the
636 quantity of precipitates becomes significant in the larger pores that the overall permeability is reduced
637 which explains the very slow clogging time in these experiments. Interestingly, the characteristic time in
638 our experiments, for serpentine precipitation (defined as $\tau = c/(k \times s_R)$, with s_R the reactive surface area)
639 is around 5700 hours for serpentinization in the larger class of pores at 160°C. This value is of the same
640 order of magnitude than the permeability decay time for serpentinization-only experiments showing thus
641 clearly the control of serpentine precipitation on the evolution of permeability (similarly to Godard et al.
642 (2013) conclusions) and thus the reaction-limited characteristics of the experiments.

643 On the other hand, carbonation experiments present a much faster decay rate because of the much faster
644 kinetics associated with carbonate precipitation. Since carbonate precipitation can occur in a broader class
645 of pores (and in particular in the large main percolation paths), permeability is more heavily and more
646 rapidly impacted. The characteristic time for the precipitation of magnesite in our experiments is around
647 20 hours, similar to values reported for the carbonation of sintered olivine, showing again the control of
648 the precipitating mineral on the permeability decay in case of reaction-limited experiments (as described
649 by Peuble et al. (2015b)). Yet, permeability in HTE decays much slower than the characteristic time of
650 aragonite to calcite transformation (of the order of the millisecond) or even the precipitation of extra cal-
651 cite. This is because for HTE, the aragonite/calcite replacement is not reaction-limited (because of the fast
652 kinetics) but transport-limited. The control on the permeability decay is then a coupling between time of
653 residence of the fluid and replacement kinetics. Interestingly, for LTE, where the aragonite/calcite replace-
654 ment is not expected to happen to a large extent, the decay time is still much faster than serpentinization
655 suggesting that some extra carbonate precipitation occurred to some extent, through the precipitation of
656 the co-injected Na^+ , Ca^{2+} and DIC and the presence of Mg^{2+} from silicate dissolution.

657 The literature often considers that precipitation of carbonates is less impactful on the permeability
658 because of the small volume change associated compared with silicate precipitation (e.g. Beinlich et al.
659 (2012)). Our experiments suggest the contrary as the decay of permeability is more consistent with carbon-
660 ate precipitation than silicates. It is actually a well-known phenomenon that a small variation of porosity
661 can lead to dramatic drop in permeability (Muller et al., 2009) if precipitation occurs in 'strategic' locations,
662 and even if the associated volume change is small.

663 4.3. Hydrogen production and CO_2 sequestration

664 Hydrogen production in mid-ocean ridge is a fundamental process in the seawater cycle through the
665 oceanic crust as well as an important component in the deep-sea biome and ecosystem. However, estima-

tion of the global H₂ output from the mid-ocean ridges is incredibly challenging as the output does not only depend on the raw quantities of water and peridotite but also on the coupling between transport and reactivity. The numerical simulations in this article, based on a fully transport-limited regime, reproduce quite accurately the hydrogen concentrations however it significantly overestimates the total amount produced with an expected 280 mmol compared to the total of 10 μmol measured during the experiment. While the measurement of hydrogen is probably underestimated because of losses in the outlet pump as well as during the sampling the large difference is once again due to kinetics reasons as the slower dissolution in the experiments lead to a slower release of Fe²⁺ in solution and thus a slower H₂ production rate. The other reason for the lower production of hydrogen is the potential reduction of DIC suggested by the large discrepancy between input and output CO₂ during HTE. Carbon dioxide can either be reduced to solid carbonaceous matter (Sforna et al., 2018) or organic acids (McCollom and Seewald, 2003). However, neither of these hypothesis could be confirmed as no carbonaceous matter was detected in the cores, and no measurement of dissolved organics was proceeded in the fluid samples. One could expect that the total H₂ could get closer to the expected amount the longer the experiment lasts, but the complete clogging of the system from carbonate precipitation prevented to test this hypothesis. In the end, the total yield before clogging of HTE was only 0.8% for hydrogen production if taking into account all the Fe²⁺ in the initial core.

Studies on oceanic serpentinization and H₂ production usually invoke reaction-induced fracturing to explain sustained permeability despite the large unfavorable volume change between peridotite minerals and serpentine (Jamtveit et al., 2000; Iyer et al., 2008; Kelemen and Hirth, 2012; Zhu et al., 2016; Malvoisin et al., 2017; Xing et al., 2018). In our experiments as well as in numerous experiments in the literature (e.g. (Hövelmann et al., 2012; van Noort et al., 2017) as well as the literature cited in Table 2) only clogging occurs and no positive feedback is observed. For reaction-induced fracturing to occur, a substantial supersaturation has to be built as the force pushing minerals to precipitate should overcome the mechanical resistance of the surrounding matrix (Scherer, 1999; Coussy, 2006; Kelemen and Hirth, 2012; Osselin et al., 2013, 2015a). In the presented experiments, calcite precipitation occurs very rapidly and no high supersaturation is allowed to build-up leading to small crystallization forces and *in fine* little to no fracturation. Our experiments suggest then that in the case of rapid precipitation, carbonation is a self-limiting process which, if happening in parallel with serpentinization might strongly hinder hydrogen production by clogging the permeability and preventing deep fluid infiltration. However, one needs to keep in mind that the injected solution in our experiments is DIC-rich and with a pH favoring rapid precipitation of carbonates. More acidic or less alkaline fluids would lead to a slower precipitation of carbonates and thus to a smaller impact on the permeability. Moreover, in the case where precipitation of calcite is slowed down or even blocked (e.g. low temperature), or in the case of rapid, local, changes of P, T conditions (faster than the pre-

700 cipitation kinetics), high local supersaturation can occur, leading to the generation of crystallization forces
701 and ultimately fracturation. The fact that the carbonation of natural sites (e.g. Lost City (Kelley et al.,
702 2005), or Oman (Kelemen and Matter, 2008; Mervine et al., 2014)) has been ongoing for tens to hundreds
703 of thousands of years, suggests that clogging is not systematic and that some positive feedbacks must be at
704 play (Kelemen et al., 2019, 2020).

705 This permeability impairment due to carbonate precipitation poses a huge threat on the viability of
706 carbon sequestration techniques relying on the reactivity of ultramafic rocks, using leached Mg and Ca as
707 counter-cations for the precipitation of carbonates. Our experiments, despite being performed with much
708 higher alkalinity than potential engineered processes and not equilibrated with an elevated partial pressure
709 of CO_2 , show that substrates containing significant amounts of natural carbonates is a potential liability
710 as the fast reprecipitation of these carbonates depending on the thermodynamic disequilibrium induced
711 by the percolating fluid might lead to a fast and deadly drop in injectivity. In the same vein, substrates
712 with a high content in clinopyroxenes might not be ideal either due to the fast precipitation of Ca-bearing
713 carbonates. This is however balanced by the extremely slow dissolution kinetics of cpx in these conditions.
714 The paradoxical conclusion is that in order to get the best long-term yield in terms of hydrogen production
715 and CO_2 sequestration, it is better to slow down the kinetics of carbonate precipitation so that they do not
716 precipitate in the main percolation paths, but rather in the smaller pore network, similarly to serpentine,
717 where they would not have such a dramatic impact on permeability.

718 5. Conclusion

719 We presented in this article two experiments of reactive percolation of a NaHCO_3 -rich brine at 160°C
720 and 280°C in natural serpentinite cores in order to study the dynamic competition between serpentiniza-
721 tion and carbonation of ultramafic formations. During the 10 to 14 days of the experiments, the perme-
722 ability of the cores dropped by several orders of magnitude, while the final yields at 280°C were 5.6% for
723 CO_2 sequestration (quantity of CO_2 stored over quantity injected) and 0.8% for H_2 production calculated
724 from the total Fe content in the initial core.

725 The reason for the dramatic permeability drop was identified as the precipitation of carbonates in the
726 main percolation path, precipitation made possible by their fast reaction kinetics compared to the flow rate
727 ($\text{Da} \gg 1$). In contrast, precipitation of silicate minerals (serpentine) was found to be less impactful since
728 they preferentially precipitates in low-flow zones due to their slow reaction kinetics. This discrepancy
729 between high-flow zones and low-flow zones is directly linked to the pore size distribution of the starting
730 protolith and justifies the use of natural cores for these kind of studies.

731 The control on the mineralogical assemblage by the relative kinetics of precipitation of the secondary
732 phases and their relationship with advection, makes comparisons of natural samples with static batch ex-
733 periments and numerical simulations complicated and potentially misleading. For example, such compar-

734 isons could lead to the underestimation of the quantity of fluid which percolated through the considered
735 formation. This was for example the case in our experiments where the mineral assemblage was represen-
736 tative of an injected pore volume of 250 or less while the actual quantity of fluid injected in the cores was
737 about ten times larger.

738 In conclusion, results from the experiments highlight the importance of quantitatively analyzing the
739 spatio-temporal lengthscales associated with the different chemical reactions occurring in the considered
740 system and their relationship with the pore size distribution. These lengthscales are directly linked to
741 the Damköhler number and to the type of reaction regime (transport-limited vs reaction-limited) allowing
742 the interpretation of the final results in terms of a dynamic interplay between dissolution and precipita-
743 tion, controlled by the local flow rate and the local pore geometry. In particular, the complex pore size
744 distribution in natural rocks leads to very different behavior even for a homogeneous mineralogy.

745 6. Acknowledgements

746 We would like to thank P. Penhoud for XRD and cathodoluminescence data. This research was sup-
747 ported by the LABEX Voltaire (ANR-10-LABX-100-01) and EQUIPEX PLANET (ANR-11-EQPX-0036). We
748 would also like to thank B. Tutolo, P. Kelemen, G. Pokrovski, and an anonymous reviewer for their com-
749 ments and suggestions on the manuscript.

750 References

- 751 Andreani M., Luquot L., Gouze P., Godard M., Hois E. and Gibert B. (2009) Experimental Study of
752 Carbon Sequestration Reactions Controlled by the Percolation of CO₂-Rich Brine through Peridotites.
753 *Environmental Science & Technology*, **43**(4), 1226–1231. doi:10.1021/es8018429.
- 754 Andreani M. and Ménez B. (2019) New perspectives on abiotic organic synthesis and processing during
755 hydrothermal alteration of the oceanic lithosphere. In B. Orcutt, I. Daniel and R. Dasgupta, editors, *Deep*
756 *Carbon: Past to Present*. pages 447–479.
- 757 Appelo C.A. (2015) Principles, caveats and improvements in databases for calculating hydrogeochemical
758 reactions in saline waters from 0 to 200°C and 1 to 1000atm. *Applied Geochemistry*, **55**, 62–71. doi:
759 10.1016/j.apgeochem.2014.11.007.
- 760 Beinlich A., Austrheim H., Glodny J., Erambert M. and Andersen T.B. (2010) CO₂ sequestration and ex-
761 treme Mg depletion in serpentinized peridotite clasts from the Devonian Solund basin, SW-Norway.
762 *Geochimica et Cosmochimica Acta*, **74**(24), 6935–6964. doi:10.1016/j.gca.2010.07.027.
- 763 Beinlich A., Plümpner O., Hövelmann J., Austrheim H. and Jamtveit B. (2012) Massive serpentinite carbon-
764 ation at Linnajavri, N-Norway. *Terra Nova*, **24**(6), 446–455. doi:10.1111/j.1365-3121.2012.01083.x.

- 765 Blanc P., Lassin A., Piantone P., Azaroual M., Jacquemet N., Fabbri A. and Gaucher E.C. (2012) Thermod-
766 dem: A geochemical database focused on low temperature water/rock interactions and waste materials.
767 *Applied Geochemistry*, **27**(10), 2107–2116. doi:10.1016/j.apgeochem.2012.06.002.
- 768 Bonatti E., Lawrence J.R., Hamlyn P.R. and Breger D. (1980) Aragonite from deep sea ultramafic rocks.
769 *Geochimica et Cosmochimica Acta*, **44**(8), 1207–1214. doi:10.1016/0016-7037(80)90074-5.
- 770 Boschi C., Dini A., Dallai L., Ruggieri G. and Gianelli G. (2009) Enhanced CO₂-mineral sequestration by
771 cyclic hydraulic fracturing and Si-rich fluid infiltration into serpentinites at Malenetrata (Tuscany, Italy).
772 *Chemical Geology*, **265**(1-2), 209–226. doi:10.1016/j.chemgeo.2009.03.016.
- 773 Bruni J., Canepa M., Chiodini G., Cioni R., Cipolli F., Longinelli A., Marini L., Ottonello G. and Vetusch
774 Zuccolini M. (2002) Irreversible water-rock mass transfer accompanying the generation of the neutral,
775 Mg-HCO₃ and high-pH, Ca-OC spring waters of the Genova province, Italy. *Applied Geochemistry*, **17**(4),
776 455–474. doi:10.1016/S0883-2927(01)00113-5.
- 777 Cannat M., Fontaine F. and Escartín J. (2010) Serpentinization and associated hydrogen and methane fluxes
778 at slow spreading ridges. pages 241–264. doi:10.1029/2008GM000760.
- 779 Chavagnac V., Ceuleneer G., Monnin C., Lansac B., Hoareau G. and Boulart C. (2013) Mineralogical assem-
780 blages forming at hyperalkaline warm springs hosted on ultramafic rocks: A case study of Oman and
781 Ligurian ophiolites. *Geochemistry, Geophysics, Geosystems*, **14**(7), 2474–2495. doi:10.1002/ggge.20146.
- 782 Chizmeshya A.V.G., McKelvy M.J., Squires K., Carpenter R.W. and Bearat H. (2007) A Novel Approach
783 to Mineral Carbonation: Enhancing Carbonation While Avoiding Mineral Pretreatment Process Cost.
784 Technical report, Arizon State University. doi:10.2172/924162.
- 785 Cipolli F., Gambardella B., Marini L., Ottonello G. and Zuccolini M.V. (2004) Geochemistry of high-
786 pH waters from serpentinites of the Gruppo di Voltri (Genova, Italy) and reaction path model-
787 ing of CO₂sequestration in serpentinite aquifers. *Applied Geochemistry*, **19**(5), 787–802. doi:
788 10.1016/j.apgeochem.2003.10.007.
- 789 Coussy O. (2006) Deformation and stress from in-pore drying-induced crystallization of salt. *Journal of the*
790 *Mechanics and Physics of Solids*, **54**(8), 1517–1547. doi:10.1016/j.jmps.2006.03.002.
- 791 Delvigne J., Bisdorn E.B.A., Sleeman J. and Stoops G. (1979) Olivines, their Pseudomorphs and Secondary
792 Products.
- 793 Dewandel B., Lachassagne P. and Qatan A. (2004) Spatial measurements of stream baseflow, a relevant
794 method for aquifer characterization and permeability evaluation. Application to a hard-rock aquifer, the
795 Oman ophiolite. *Hydrological Processes*, **18**(17), 3391–3400. doi:10.1002/hyp.1502.

- 796 Dick H.J. (1989) Abyssal peridotites, very slow spreading ridges and ocean ridge magmatism. *Geological*
797 *Society Special Publication*, **42(42)**, 71–105. doi:10.1144/GSL.SP.1989.042.01.06.
- 798 Ellison E.T., Templeton A.S., Zeigler S.D., Mayhew L.E., Kelemen P.B. and Matter J.M. (2021) Low-
799 Temperature Hydrogen Formation During Aqueous Alteration of Serpentinized Peridotite in the Samail
800 Ophiolite. *Journal of Geophysical Research: Solid Earth*, **126(6)**, 1–25. doi:10.1029/2021JB021981.
- 801 Escario S., Godard M., Gouze P. and Leprovost R. (2018) Experimental study of the effects of so-
802 lute transport on reaction paths during incipient serpentinization. *Lithos*, **323**, 191–207. doi:
803 10.1016/j.lithos.2018.09.020.
- 804 Escartín J., Hirth G. and Evans B. (1997) Effects of serpentinization on the lithospheric strength and the
805 style of normal faulting at slow-spreading ridges. *Earth and Planetary Science Letters*, **151(3-4)**, 181–189.
806 doi:10.1016/S0012-821X(97)81847-X.
- 807 Evans O., Spiegelman M. and Kelemen P.B. (2018) A Poroelastic Model of Serpentinization: Exploring the
808 Interplay Between Rheology, Surface Energy, Reaction, and Fluid Flow. *Journal of Geophysical Research:*
809 *Solid Earth*, **123(10)**, 8653–8675. doi:10.1029/2017JB015214.
- 810 Falk E.S. and Kelemen P.B. (2015) Geochemistry and petrology of listvenite in the Samail ophiolite, Sul-
811 tanate of Oman: Complete carbonation of peridotite during ophiolite emplacement. *Geochimica et Cos-*
812 *mochimica Acta*, **160**, 70–90. doi:10.1016/j.gca.2015.03.014.
- 813 Farough A., Moore D.E., Lockner D.A. and Lowell R.P. (2016) Evolution of fracture permeability of ultra-
814 mafic rocks undergoing serpentinization at hydrothermal conditions: An experimental study. *Geochem-*
815 *istry, Geophysics, Geosystems*, **17(1)**, 44–55. doi:10.1002/2015GC005973.
- 816 Früh-Green G.L., Connolly J.A., Plas A., Kelley D.S. and Grobety B. (2004) Serpentinization of oceanic
817 peridotites: Implications for geochemical cycles and biological activity. *Geophysical Monograph Series*,
818 **144(November 2014)**, 119–136. doi:10.1029/144GM08.
- 819 Gadikota G., Matter J., Kelemen P., Brady P.V. and Park A.H.A. (2020) Elucidating the differences in the
820 carbon mineralization behaviors of calcium and magnesium bearing alumino-silicates and magnesium
821 silicates for CO₂ storage. *Fuel*, **277(March)**, 117900. doi:10.1016/j.fuel.2020.117900.
- 822 Gadikota G., Matter J., Kelemen P. and Park A.H.A. (2014) Chemical and morphological changes during
823 olivine carbonation for CO₂ storage in the presence of NaCl and NaHCO₃. *Physical Chemistry Chemical*
824 *Physics*, **16(10)**, 4679–4693. doi:10.1039/c3cp54903h.

- 825 Gaillardet J., Dupré B., Louvat P. and Allège C.J. (1999) Global silicate weathering and CO₂ consumption
826 rates deduced from the chemistry of large rivers. *Chemical Geology*, **159(1-4)**, 3–30. doi:10.1016/S0009-
827 2541(99)00031-5.
- 828 Gíslason S.R., Sigurdardóttir H., Aradóttir E.S. and Oelkers E.H. (2018) A brief history of Carb-
829 Fix: Challenges and victories of the project's pilot phase. In *Energy Procedia*, volume 146. doi:
830 10.1016/j.egypro.2018.07.014.
- 831 Godard M., Luquot L., Andreani M. and Gouze P. (2013) Incipient hydration of mantle lithosphere at
832 ridges: A reactive-percolation experiment. *Earth and Planetary Science Letters*, **371-372**, 92–102. doi:
833 10.1016/j.epsl.2013.03.052.
- 834 Grozeva N.G., Klein F., Seewald J.S. and Sylva S.P. (2017) Experimental study of carbonate formation in
835 oceanic peridotite. *Geochimica et Cosmochimica Acta*, **199**, 264–286. doi:10.1016/j.gca.2016.10.052.
- 836 Hansen L.D., Dipple G.M., Gordon T.M. and Kellett D.A. (2005) Carbonated serpentinite (listwanite) at
837 Atlin, British Columbia: A geological analogue to carbon dioxide sequestration. *Canadian Mineralogist*,
838 **43(1)**, 225–239. doi:10.2113/gscanmin.43.1.225.
- 839 Hatakeyama K., Katayama I., Hirauchi K.I. and Michibayashi K. (2017) Mantle hydration along outer-rise
840 faults inferred from serpentinite permeability. *Scientific Reports*, **7(1)**, 1–8. doi:10.1038/s41598-017-
841 14309-9.
- 842 Hinsken T., Bröcker M., Strauss H. and Bulle F. (2017) Geochemical, isotopic and geochronological char-
843 acterization of listvenite from the Upper Unit on Tinos, Cyclades, Greece. *Lithos*, **282-283**, 281–297.
844 doi:10.1016/j.lithos.2017.02.019.
- 845 Hövelmann J., Austrheim H., Beinlich A. and Anne Munz I. (2011) Experimental study of the carbonation of
846 partially serpentinitized and weathered peridotites. *Geochimica et Cosmochimica Acta*, **75(22)**, 6760–6779.
847 doi:10.1016/j.gca.2011.08.032.
- 848 Hövelmann J., Austrheim H. and Jamtveit B. (2012) Microstructure and porosity evolution dur-
849 ing experimental carbonation of a natural peridotite. *Chemical Geology*, **334**, 254–265. doi:
850 10.1016/j.chemgeo.2012.10.025.
- 851 Hybler J., Sejkora J. and Venclík V. (2016) Polytypism of cronstedtite from Pohled, Czech Republic. *Euro-
852 pean Journal of Mineralogy*, **28(4)**, 765–775. doi:10.1127/ejm/2016/0028-2532.
- 853 International Energy Agency (2019) The Future of Hydrogen. Technical report, International Energy
854 Agency.

- 855 Iyer K., Jamtveit B., Mathiesen J., Malthe-Sørenssen A. and Feder J. (2008) Reaction-assisted hierarchi-
856 cal fracturing during serpentinization. *Earth and Planetary Science Letters*, **267(3-4)**, 503–516. doi:
857 10.1016/j.epsl.2007.11.060.
- 858 Jamtveit B., Austrheim H. and Malthe-Sørenssen A. (2000) Accelerated hydration of the Earth's deep crust
859 induced by stress perturbations. *Nature*, **408(6808)**, 75–78. doi:10.1038/35040537.
- 860 Jamtveit B., Putnis C.V. and Malthe-Sørenssen A. (2009) Reaction induced fracturing during replacement
861 processes. *Contributions to Mineralogy and Petrology*, **157(1)**, 127–133. doi:10.1007/s00410-008-0324-y.
- 862 Katayama I., Abe N., Hatakeyama K., Akamatsu Y., Okazaki K., Ulven O.I., Hong G., Zhu W., Cordonnier
863 B., Michibayashi K., Godard M. and Kelemen P. (2020) Permeability Profiles Across the Crust-Mantle
864 Sections in the Oman Drilling Project Inferred From Dry and Wet Resistivity Data. *Journal of Geophysical*
865 *Research: Solid Earth*, **125(8)**, 1–9. doi:10.1029/2019JB018698.
- 866 Kelemen P., Aines R., Bennett E., Benson S., Carter E., Coggon J., de Obeso J., Evans O., Gadikota G., Dipple
867 G., Godard M., Harris M., Higgins J., Johnson K., Kourim F., Lafay R., Lambart S., Manning C., Matter
868 J., Michibayashi K., Morishita T., Noël J., Okazaki K., Renforth P., Robinson B., Savage H., Skarbek R.,
869 Spiegelman M., Takazawa E., Teagle D., Urai J. and Wilcox J. (2018) In situ carbon mineralization in
870 ultramafic rocks: Natural processes and possible engineered methods. *Energy Procedia*, **146(August)**,
871 92–102. doi:10.1016/j.egypro.2018.07.013.
- 872 Kelemen P., Benson S.M., Pilorgé H., Psarras P. and Wilcox J. (2019) An Overview of the Status and Chal-
873 lenges of CO₂ Storage in Minerals and Geological Formations. *Frontiers in Climate*, **1(November)**, 1–20.
874 doi:10.3389/fclim.2019.00009.
- 875 Kelemen P.B. and Hirth G. (2012) Reaction-driven cracking during retrograde metamorphism:
876 Olivine hydration and carbonation. *Earth and Planetary Science Letters*, **345-348**, 81–89. doi:
877 10.1016/j.epsl.2012.06.018.
- 878 Kelemen P.B., Matter J., Streit E.E., Rudge J.F., Curry W.B. and Blusztajn J. (2011) Rates and Mechanisms
879 of Mineral Carbonation in Peridotite: Natural Processes and Recipes for Enhanced, in situ CO₂ Capture
880 and Storage. *Annual Review of Earth and Planetary Sciences*, **39(1)**, 545–576. doi:10.1146/annurev-earth-
881 092010-152509.
- 882 Kelemen P.B. and Matter J.M. (2008) In situ carbonation of peridotite for CO₂ storage. *Proceedings of the*
883 *National Academy of Sciences*, **105(45)**, 17295–17300. doi:10.1073/pnas.0805794105.
- 884 Kelemen P.B., McQueen N., Wilcox J., Renforth P., Dipple G. and Vankeuren A.P. (2020) Engineered carbon

- 885 mineralization in ultramafic rocks for CO₂ removal from air: Review and new insights. *Chemical Geology*,
886 **550(May)**, 119628. doi:10.1016/j.chemgeo.2020.119628.
- 887 Kelley D.S., Karson J.A., Früh-Green G.L., Yoerger D.R., Shank, Timothy M., Butterfield D.A., Hayes J.M.,
888 Schrenk M.O., Olson E.J., Proskurowski G., Jakuba M., Bradley A., Larson B., Ludwig K., Glickson D.,
889 Kate B., Bradley A.S., Brazlton W.J., Roe K.K., Elend M.J., Delacour A., Bernasconi S., Lilley M.D., Baross
890 J.A., Summons R.E. and Sylva S.P. (2005) A Serpentinite-Hosted Ecosystem: The Lost City Hydrothermal
891 Field. *Science*, **307(5714)**, 1428–1434. doi:10.1126/science.1102556.
- 892 Klein F., Bach W. and McCollom T.M. (2013) Compositional controls on hydrogen generation during ser-
893 pentinization of ultramafic rocks. *Lithos*, **178**, 55–69. doi:10.1016/j.lithos.2013.03.008.
- 894 Klein F. and Garrido C.J. (2011) Thermodynamic constraints on mineral carbonation of serpentinized peri-
895 dotite. *Lithos*, **126(3-4)**, 147–160. doi:10.1016/j.lithos.2011.07.020.
- 896 Klein F., Grozeva N.G., Seewald J.S., McCollom T.M., Humphris S.E., Moskowitz B., Berquó T.S. and Kahl
897 W.A. (2015) Fluids in the Crust. Experimental constraints on fluid-rock reactions during incipient ser-
898 pentinization of harzburgite. *American Mineralogist*, **100(4)**. doi:10.2138/am-2015-5112.
- 899 Klein F. and McCollom T.M. (2013) From serpentinization to carbonation: New insights from a CO₂ injec-
900 tion experiment. *Earth and Planetary Science Letters*, **379(31)**, 137–145. doi:10.1016/j.epsl.2013.08.017.
- 901 Kondratiuk P., Tredak H., Upadhyay V., Ladd A.J. and Szymczak P. (2017) Instabilities and finger formation
902 in replacement fronts driven by an oversaturated solution. *Journal of Geophysical Research: Solid Earth*,
903 **122(8)**, 5972–5991. doi:10.1002/2017JB014169.
- 904 Lacinska A.M., Styles M.T., Bateman K., Hall M. and Brown P.D. (2017) An Experimental Study of the
905 Carbonation of Serpentinite and Partially Serpentinised Peridotites. *Frontiers in Earth Science*, **5**. doi:
906 10.3389/feart.2017.00037.
- 907 Lafay R., Montes-Hernandez G., Renard F. and Vonlanthen P. (2018) Intracrystalline Reaction-Induced
908 Cracking in Olivine Evidenced by Hydration and Carbonation Experiments. *Minerals*, **8(9)**, 412. doi:
909 10.3390/min8090412.
- 910 Lisabeth H., Zhu W., Xing T. and De Andrade V. (2017a) Dissolution-Assisted Pattern Formation During
911 Olivine Carbonation. *Geophysical Research Letters*, **44(19)**, 9622–9631. doi:10.1002/2017GL074393.
- 912 Lisabeth H.P., Zhu W., Kelemen P.B. and Ilgen A. (2017b) Experimental evidence for chemo-mechanical
913 coupling during carbon mineralization in ultramafic rocks. *Earth and Planetary Science Letters*, **474**, 355–
914 367. doi:10.1016/j.epsl.2017.06.045.

- 915 Luhmann A.J., Tutolo B.M., Bagley B.C., Mildner D.F., Scheuermann P.P., Feinberg J.M., Ignatyev K.
916 and Seyfried W.E. (2017a) Chemical and physical changes during seawater flow through intact dunite
917 cores: An experimental study at 150–200 °C. *Geochimica et Cosmochimica Acta*, **214**, 86–114. doi:
918 10.1016/j.gca.2017.07.020.
- 919 Luhmann A.J., Tutolo B.M., Bagley B.C., Mildner D.F.R., Seyfried W.E. and Saar M.O. (2017b) Permeability,
920 porosity, and mineral surface area changes in basalt cores induced by reactive transport of CO₂-rich
921 brine. *Water Resources Research*, **53**(3), 1908–1927. doi:10.1002/2016WR019216.
- 922 Malvoisin B. (2015) Mass transfer in the oceanic lithosphere: Serpentinization is not isochemical. *Earth and*
923 *Planetary Science Letters*, **430**, 75–85. doi:10.1016/j.epsl.2015.07.043.
- 924 Malvoisin B., Brantut N. and Kaczmarek M.A. (2017) Control of serpentinisation rate by reaction-induced
925 cracking. *Earth and Planetary Science Letters*, **476**, 143–152. doi:10.1016/j.epsl.2017.07.042.
- 926 Malvoisin B., Brunet F., Carlut J., Rouméjon S. and Cannat M. (2012) Serpentinization of oceanic peri-
927 dotites: 2. Kinetics and processes of San Carlos olivine hydrothermal alteration. *Journal of Geophysical*
928 *Research: Solid Earth*, **117**(4). doi:10.1029/2011JB008842.
- 929 Marcaillou C., Muñoz M., Vidal O., Parra T. and Harfouche M. (2011) Mineralogical evidence for H₂ de-
930 gassing during serpentinization at 300°C/300bar. *Earth and Planetary Science Letters*, **303**(3–4), 281–290.
931 doi:10.1016/j.epsl.2011.01.006.
- 932 Martin B. and Fyfe W. (1970) Some experimental and theoretical observations on the kinetics of hydra-
933 tion reactions with particular reference to serpentinization. *Chemical Geology*, **6**(9), 185–202. doi:
934 10.1016/0009-2541(70)90018-5.
- 935 Mayhew L.E., Ellison E.T., Miller H.M., Kelemen P.B. and Templeton A.S. (2018) Iron transformations
936 during low temperature alteration of variably serpentinized rocks from the Samail ophiolite, Oman.
937 *Geochimica et Cosmochimica Acta*, **222**, 704–728. doi:10.1016/j.gca.2017.11.023.
- 938 McCollom T.M. and Bach W. (2009) Thermodynamic constraints on hydrogen generation during
939 serpentinization of ultramafic rocks. *Geochimica et Cosmochimica Acta*, **73**(3), 856–875. doi:
940 10.1016/j.gca.2008.10.032.
- 941 McCollom T.M., Klein F., Moskowitz B., Berquó T.S., Bach W. and Templeton A.S. (2020) Hydrogen gen-
942 eration and iron partitioning during experimental serpentinization of an olivine–pyroxene mixture.
943 *Geochimica et Cosmochimica Acta*, **282**, 55–75. doi:10.1016/j.gca.2020.05.016.

- 944 McCollom T.M. and Seewald J.S. (2001) A reassessment of the potential for reduction of dissolved CO₂ to
945 hydrocarbons during serpentinization of olivine. *Geochimica et Cosmochimica Acta*, **65(21)**, 3769–3778.
946 doi:10.1016/S0016-7037(01)00655-X.
- 947 McCollom T.M. and Seewald J.S. (2003) Experimental constraints on the hydrothermal reactivity of organic
948 acids and acid anions: I. Formic acid and formate. *Geochimica et Cosmochimica Acta*, **67(19)**, 3625–3644.
949 doi:10.1016/S0016-7037(03)00136-4.
- 950 Mcgrail B.P., Schaef H.T., Ho A.M., Chien Y.j., Dooley J.J. and Davidson C.L. (2006) Potential for carbon
951 dioxide sequestration in flood basalts. **111(August)**, 1–13. doi:10.1029/2005JB004169.
- 952 Menzel M.D., Garrido C.J., López Sánchez-Vizcaíno V., Marchesi C., Hidas K., Escayola M.P. and Delgado
953 Huertas A. (2018) Carbonation of mantle peridotite by CO₂-rich fluids: the formation of listvenites in
954 the Advocate ophiolite complex (Newfoundland, Canada). *Lithos*, **323**. doi:10.1016/j.lithos.2018.06.001.
- 955 Mervine E.M., Humphris S.E., Sims K.W., Kelemen P.B. and Jenkins W.J. (2014) Carbonation rates of peri-
956 dotite in the Samail Ophiolite, Sultanate of Oman, constrained through ¹⁴C dating and stable isotopes.
957 *Geochimica et Cosmochimica Acta*, **126**, 371–397. doi:10.1016/j.gca.2013.11.007.
- 958 Miller H.M., Matter J.M., Kelemen P., Ellison E.T., Conrad M.E., Fierer N., Ruchala T., Tominaga M.
959 and Templeton A.S. (2016) Modern water/rock reactions in Oman hyperalkaline peridotite aquifers
960 and implications for microbial habitability. *Geochimica et Cosmochimica Acta*, **179**, 217–241. doi:
961 10.1016/j.gca.2016.01.033.
- 962 Miller H.M., Mayhew L.E., Ellison E.T., Kelemen P., Kubo M. and Templeton A.S. (2017) Low temperature
963 hydrogen production during experimental hydration of partially-serpentinized dunite. *Geochimica et*
964 *Cosmochimica Acta*, **209**, 161–183. doi:10.1016/j.gca.2017.04.022.
- 965 Morgan B., Wilson S.A., Madsen I.C., Gozukara Y.M. and Habsuda J. (2015) Increased thermal stabil-
966 ity of nesquehonite (MgCO₃ · 3H₂O) in the presence of humidity and CO₂: Implications for
967 low-temperature CO₂ storage. *International Journal of Greenhouse Gas Control*, **39**, 366–376. doi:
968 10.1016/j.ijggc.2015.05.033.
- 969 Morrow C.A., Moore D.E. and Lockner D.A. (2001) Permeability reduction in granite under hydrothermal
970 conditions the granite decreased with time t , following the exponential relation portional to temperature
971 and ranged between between Figure 1. Cylindrical sample configurations for permeability tests. *Journal*
972 *of Geophysical Research*, **106(Table 1)**, 30,551–30,560.
- 973 Muller N., Qi R., Mackie E., Pruess K. and Blunt M.J. (2009) CO₂ injection impairment due to halite pre-
974 cipitation. *Energy Procedia*, **1(1)**, 3507–3514. doi:10.1016/j.egypro.2009.02.143.

- 975 Neubeck A., Duc N.T., Bastviken D., Crill P. and Holm N.G. (2011) Formation of H₂ and CH₄ by weathering
976 of olivine at temperatures between 30 and 70°C. *Geochemical Transactions*, **12(1)**, 6. doi:10.1186/1467-
977 4866-12-6.
- 978 Noël J., Godard M., Oliot E., Martinez I., Williams M., Boudier F., Rodriguez O., Chaduteau C., Escario S.
979 and Gouze P. (2018) Evidence of polygenetic carbon trapping in the Oman Ophiolite: Petro-structural,
980 geochemical, and carbon and oxygen isotope study of the Wadi Dima harzburgite-hosted carbonates
981 (Wadi Tayin massif, Sultanate of Oman). *Lithos*, **323**, 218–237. doi:10.1016/j.lithos.2018.08.020.
- 982 van Noort R., Wolterbeek T., Drury M., Kandianis M. and Spiers C. (2017) The Force of Crystalliza-
983 tion and Fracture Propagation during In-Situ Carbonation of Peridotite. *Minerals*, **7(10)**, 190. doi:
984 10.3390/min7100190.
- 985 de Obeso J.C. and Kelemen P.B. (2018) Fluid rock interactions on residual mantle peridotites overlain by
986 shallow oceanic limestones: Insights from Wadi Fins, Sultanate of Oman. *Chemical Geology*, **498(Jan-**
987 **uary)**, 139–149. doi:10.1016/j.chemgeo.2018.09.022.
- 988 de Obeso J.C. and Kelemen P.B. (2020) Major element mobility during serpentinization, oxidation and
989 weathering of mantle peridotite at low temperatures. *Philosophical Transactions of the Royal Society A:*
990 *Mathematical, Physical and Engineering Sciences*, **378(2165)**. doi:10.1098/rsta.2018.0433.
- 991 O'Connor W., Dahlin D.C., Rush G., Gerdemann S.J., Penner L. and Nilsen D. (2005) Aqueous Mineral
992 Carbonation: Mineral Availability, Pretreatment, Reaction Parametrics, and Process Studies. *Doe/Arc-Tr-*
993 *04-002*, (**April**), 1–19. doi:10.13140/RG.2.2.23658.31684.
- 994 Oelkers E.H., Gislason S.R. and Matter J. (2008) Mineral carbonation of CO₂. *Elements*, **4(5)**, 333–337.
995 doi:10.2113/gselements.4.5.333.
- 996 Osselin F., Fabbri A., Fen-Chong T., Dangla P., Pereira J.M. and Lassin A. (2015a) Stress from NaCl crys-
997 tallisation by carbon dioxide injection in aquifers. *Environmental Geotechnics*, **2(5)**, 280–291. doi:
998 10.1680/envgeo.13.00057.
- 999 Osselin F., Fabbri A., Fen-Chong T., Pereira J.M., Lassin A. and Dangla P. (2015b) Experimental investigation
1000 of the influence of supercritical state on the relative permeability of Vosges sandstone. *Comptes Rendus -*
1001 *Mecanique*, **343(9)**. doi:10.1016/j.crme.2015.06.009.
- 1002 Osselin F., Fen-Chong T., Fabbri A., Lassin A., Pereira J.M. and Dangla P. (2013) Dependence on injection
1003 temperature and on aquifer's petrophysical properties of the local stress applying on the pore wall of a
1004 crystallized pore in the context of CO₂ storage in deep saline aquifers. *EPJ Applied Physics*,
1005 **64(2)**, 21101. doi:10.1051/epjap/2013120529.

- 1006 Osselin F, Kondratiuk P, Budek A., Cybulski O., Garstecki P. and Szymczak P. (2016) Microfluidic obser-
1007 vation of the onset of reactive infiltration instability in an analog fracture. *Geophysical Research Letters*,
1008 **43(13)**. doi:10.1002/2016GL069261.
- 1009 Osselin F, Kondratiuk P, Cybulski O., Garstecki P. and Szymczak P. (2019) Microfluidic measurement of
1010 the dissolution rate of gypsum in water using the reactive infiltration-instability. *E3S Web of Conferences*,
1011 **98**, 04010. doi:10.1051/e3sconf/20199804010.
- 1012 Paukert A.N., Matter J.M., Kelemen P.B., Shock E.L. and Havig J.R. (2012) Reaction path modeling of en-
1013 hanced in situ CO₂ mineralization for carbon sequestration in the peridotite of the Samail Ophiolite,
1014 Sultanate of Oman. *Chemical Geology*, **330-331**, 86–100. doi:10.1016/j.chemgeo.2012.08.013.
- 1015 Paulick H., Bach W., Godard M., De Hoog J.C., Suhr G. and Harvey J. (2006) Geochemistry of abyssal
1016 peridotites (Mid-Atlantic Ridge, 15°20'N, ODP Leg 209): Implications for fluid/rock interaction in slow
1017 spreading environments. *Chemical Geology*, **234(3-4)**, 179–210. doi:10.1016/j.chemgeo.2006.04.011.
- 1018 Peuble S., Andreani M., Godard M., Gouze P., Barou F., Van De Moortele B., Mainprice D. and Reynard
1019 B. (2015a) Carbonate mineralization in percolated olivine aggregates: Linking effects of crystallographic
1020 orientation and fluid flow. *American Mineralogist*, **100(2-3)**, 474–482. doi:10.2138/am-2015-4913.
- 1021 Peuble S., Andreani M., Gouze P., Pollet-Villard M., Reynard B. and Van de Moortele B. (2018) Multi-scale
1022 characterization of the incipient carbonation of peridotite. *Chemical Geology*, **476(May 2017)**, 150–160.
1023 doi:10.1016/j.chemgeo.2017.11.013.
- 1024 Peuble S., Godard M., Gouze P., Leprovost R., Martinez I. and Shilobreeva S. (2019) Control of CO₂ on flow
1025 and reaction paths in olivine-dominated basements: An experimental study. *Geochimica et Cosmochimica*
1026 *Acta*, **252**, 16–38. doi:10.1016/j.gca.2019.02.007.
- 1027 Peuble S., Godard M., Luquot L., Andreani M., Martinez I. and Gouze P. (2015b) CO₂ geological storage in
1028 olivine rich basaltic aquifers: New insights from reactive-percolation experiments. *Applied Geochemistry*,
1029 **52**, 174–190. doi:10.1016/j.apgeochem.2014.11.024.
- 1030 Picazo S., Malvoisin B., Baumgartner L. and Bouvier A.s. (2020) Low Temperature Serpentinite Replace-
1031 ment by Carbonates during Seawater Influx in the Newfoundland Margin. *Minerals*, **10(2)**, 184. doi:
1032 10.3390/min10020184.
- 1033 Plümper O., Røyne A., Magrasó A. and Jamtveit B. (2012) The interface-scale mechanism of reaction-
1034 induced fracturing during serpentinization. *Geology*, **40(12)**, 1103–1106. doi:10.1130/G33390.1.

- 1035 Power I.M., Harrison A.L., Dipple G.M., Wilson S.A., Kelemen P.B., Hitch M. and Southam G. (2013) Carbon
1036 Mineralization: From Natural Analogues to Engineered Systems. *Reviews in Mineralogy and Geochemistry*,
1037 **77(1)**, 305–360. doi:10.2138/rmg.2013.77.9.
- 1038 Putnis A. (2009) Mineral Replacement Reactions. *Reviews in Mineralogy and Geochemistry*, **70(1)**, 87–124.
1039 doi:10.2138/rmg.2009.70.3.
- 1040 Reynard B. (2013) Serpentine in active subduction zones. *Lithos*, **178**, 171–185. doi:
1041 10.1016/j.lithos.2012.10.012.
- 1042 Rouméjon S., Cannat M., Agrinier P., Godard M. and Andreani M. (2014) Serpentinization and fluid path-
1043 ways in tectonically exhumed peridotites from the southwest Indian ridge (62-65°E). *Journal of Petrology*,
1044 **56(4)**, 703–734. doi:10.1093/petrology/egv014.
- 1045 Røyne A. and Jamtveit B. (2015) Pore-Scale Controls on Reaction-Driven Fracturing. *Reviews in Mineralogy*
1046 *and Geochemistry*, **80(1)**, 25–44. doi:10.2138/rmg.2015.80.02.
- 1047 Røyne A., Jamtveit B., Mathiesen J. and Malthe-Sørensen A. (2008) Controls on rock weathering rates by
1048 reaction-induced hierarchical fracturing. *Earth and Planetary Science Letters*, **275(3-4)**, 364–369. doi:
1049 10.1016/j.epsl.2008.08.035.
- 1050 Rudge J.F., Kelemen P.B. and Spiegelman M. (2010) A simple model of reaction-induced cracking applied
1051 to serpentinization and carbonation of peridotite. *Earth and Planetary Science Letters*, **291(1-4)**, 215–227.
1052 doi:10.1016/j.epsl.2010.01.016.
- 1053 Ruiz-Agudo E., Putnis C.V. and Putnis A. (2014) Coupled dissolution and precipitation at mineral-fluid
1054 interfaces. doi:10.1016/j.chemgeo.2014.06.007.
- 1055 Saldi G.D., Schott J., Pokrovsky O.S., Gautier Q. and Oelkers E.H. (2012) An experimental study of mag-
1056 nesite precipitation rates at neutral to alkaline conditions and 100-200°C as a function of pH, aque-
1057 ous solution composition and chemical affinity. *Geochimica et Cosmochimica Acta*, **83**, 93–109. doi:
1058 10.1016/j.gca.2011.12.005.
- 1059 Scherer G.W. (1999) Crystallization in pores. *Cement and Concrete Research*, **29(29)**, 1347–1358.
- 1060 Seifritz W. (1990) CO₂ disposal by means of silicates. *Nature*, **345(6275)**, 486–486. doi:10.1038/345486b0.
- 1061 Sforza M.C., Brunelli D., Pisapia C., Pasini V., Malferrari D. and Ménez B. (2018) Abiotic formation of
1062 condensed carbonaceous matter in the hydrating oceanic crust. *Nature Communications*, **9(1)**. doi:
1063 10.1038/s41467-018-07385-6.

- 1064 Tominaga M., Beinlich A., Lima E.A., Tivey M.A., Hampton B.A., Weiss B. and Harigane Y. (2017) Multi-
1065 scale magnetic mapping of serpentinite carbonation. *Nature Communications*, **8**(1). doi:10.1038/s41467-
1066 017-01610-4.
- 1067 Tutolo B.M., Awolayo A. and Brown C. (2021) Alkalinity Generation Constraints on Basalt Carbonation for
1068 Carbon Dioxide Removal at the Gigaton-per-Year Scale. *Environmental Science and Technology*, **55**(17),
1069 11906–11915. doi:10.1021/acs.est.1c02733.
- 1070 Tutolo B.M., Luhmann A.J., Tosca N.J. and Seyfried W.E. (2018) Serpentinization as a reactive transport
1071 process: The brucite silicification reaction. *Earth and Planetary Science Letters*, **484**, 385–395. doi:
1072 10.1016/j.epsl.2017.12.029.
- 1073 Ulrich M., Muñoz M., Guillot S., Cathelineau M., Picard C., Quesnel B., Boulvais P. and Couteau C.
1074 (2014) Dissolution-precipitation processes governing the carbonation and silicification of the serpen-
1075 tinite sole of the New Caledonia ophiolite. *Contributions to Mineralogy and Petrology*, **167**(1), 1–19. doi:
1076 10.1007/s00410-013-0952-8.
- 1077 Ulven O.I., Jamtveit B. and Malthe-Sørenssen A. (2014) Reaction-driven fracturing of porous rock. *Journal*
1078 *of Geophysical Research: Solid Earth*, **119**(10), 7473–7486. doi:10.1002/2014JB011102.
- 1079 Voigt M., Marieni C., Clark D.E., Gislason S.R. and Oelkers E.H. (2018) Evaluation and refine-
1080 ment of thermodynamic databases for mineral carbonation. *Energy Procedia*, **146**, 81–91. doi:
1081 10.1016/j.egypro.2018.07.012.
- 1082 Wang J., Watanabe N., Okamoto A., Nakamura K. and Komai T. (2019) Pyroxene control of H₂ produc-
1083 tion and carbon storage during water-peridotite-CO₂ hydrothermal reactions. *International Journal of*
1084 *Hydrogen Energy*, **44**(49), 26835–26847. doi:10.1016/j.ijhydene.2019.08.161.
- 1085 Wolery T. (1992) EQ3/6, a software package for geochemical modeling of aqueous systems: Package
1086 overview and installation guide (Version 7.0). Technical report, Lawrence Livermore National Labo-
1087 ratory (LLNL), Livermore, CA (United States). doi:10.2172/138894.
- 1088 Xing T., Zhu W., Fusses F. and Lisabeth H. (2018) Generating porosity during olivine carbonation via
1089 dissolution channels and expansion cracks. *Solid Earth*, **9**(4), 879–896. doi:10.5194/se-9-879-2018.
- 1090 Zhang Y. and Dawe R.A. (2000) Influence of Mg²⁺ on the kinetics of calcite precipitation and calcite crystal
1091 morphology. *Chemical Geology*, **163**(1-4), 129–138. doi:10.1016/S0009-2541(99)00097-2.
- 1092 Zhu W., Fusses F., Lisabeth H., Xing T., Xiao X., De Andrade V. and Karato S.I. (2016) Experimental ev-
1093 idence of reaction-induced fracturing during olivine carbonation. *Geophysical Research Letters*, **43**(18),
1094 9535–9543. doi:10.1002/2016GL070834.

Table 1: Top table: Mass fractions of the different minerals calculated from point counting. Bottom table: measured and recalculated whole rock composition from the modal composition and the composition of the different phases as measured by EPMA. LOI = loss on ignition. Major elements quantified by IPC-OES. $Fe_2O_3T = FeO + Fe_2O_3$.

Mineral	Serpentine	Orthopyroxene	Clinopyroxene	Olivine	Aragonite	Spinel	Magnetite
Green Zone 1 (%wt)	49.6	15.6	10.0	9.2	13.4	2.1	-
Orange Zone 1 (%wt)	63.7	18.5	6.7	8.0	2.7	0.4	-
Orange Zone 2 (%wt)	52.9	20.8	16.7	7.0	0.9	1.7	-
Average (%wt)	50.2	19.7	12.9	9.4	5.9	1.9	-
Recalculated composition (%wt)	50	19	11	13	4.5	1	1.5

Whole Rock composition														
Oxide(%wt)	SiO ₂	Al ₂ O ₃	Fe ₂ O _{3T}	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	LOI	CO ₂	H ₂ O
Measured	41.41	3.07	8.29	4.74	0.11	33.31	5.03	0.15	< ld	0.091	< ld	7.69	1.88	6.38
Recalculated	41.8	3.08	8.32	-	-	33.4	5.05	-	-	-	-	-	1.89	6.41
Relative error (%)	-0.09	-0.22	-0.06	-	-	-0.13	-0.13	-	-	-	-	-	-0.01	-0.05

Table 2: Summary of the settings for the two percolation experiments

	LTE	HTE
Temperature (°C)	160	280
Duration (days)	14	10
Flow rate (ml/hr)	≈0.6	
Fluid composition	2%wt NaCl, 5%wt NaHCO ₃	
Core length (cm)	3.9	4.1
Core diameter (mm)	5.6	
Initial mineral composition	Ol, Opx, Cpx, Serp, Ara, Fe-ox, Spinel	
Identified neoformed Minerals	Ara(?), Serp, Mg-CaCO ₃	Serp, Cal, Hem

Table 3: Chemical analysis for samples from the reactive percolation experiment at 280°C. < ld = below detection limit.

Sample	Elapsed time days	Cl		DIC		Na		Ca		Mg		H ₂	
		mg/L	mol/L	mg/L	mol/L	mg/L	mol/L	mg/L	μmol/L	mg/L	μmol/L	μmol/kgw	μmol/kgw
Inlet solution	-	12,160	0.342	7,190	0.599	21,920	0.954	0.39	9.7	< ld	< ld	0	0
Sample 1	1	-	-	-	-	10,453	0.792	1.23	53.6	0.13	9.3	44	76
Sample 2	2	7,090	0.270	4,650	0.523	14,680	0.863	0.22	7.42	0.12	6.67	20	27
Sample 3	3	8,640	0.299	5,430	0.556	16,530	0.884	< ld	< ld	< ld	< ld	26	32
Sample 4	6	8,740	0.291	5,660	0.557	17,923	0.921	< ld	< ld	< ld	< ld	36	42
Sample 5	9	7,540	0.262	5,700	0.587	17,216	0.926	0.41	12.6	1.28	65.1	125	154

Table 4: Characteristic decay time for permeability evolution for reactive transport experiments of pure serpentinization and carbonation of ultramafic rocks from the literature.

Reference	flow rate ml/hr	Characteristic time hr	Temperature °C	Core	Solution
Peuble et al. (2015b)	0.1 1	35 then 2.5 after 1.5 day 17	180	sintered olivine	NaHCO ₃ buffered - pCO ₂ = 10MPa
Peuble et al. (2018)	12 then 6	80	160	sintered olivine	NaCl 1M, NaHCO ₃ 0.4M, pCO ₂ = 11MPa
Peuble et al. (2019)	0.5	160 then 40 after 5 days 35 80 then 40 after 1.5 days	185	sintered olivine	Volvic® + 10MPaCO ₂ Volvic® + 1MPaCO ₂ Volvic® + 0.1MPaCO ₂
Lisabeth et al. (2017b)	0	111	150	Thermally cracked Twin Sisters dunite	0.6M NaHCO ₃ , pCO ₂ =3.6MPa
Luhmann et al. (2017a)	0.01 0.01	950 920 (70 in the first days)	150 200	intact dunite	Artificial seawater
Godard et al. (2013)	0.2 then 0.06 after 8 days	4500 then 140	160	sintered olivine	Artificial seawater
Lisabeth et al. (2017b)	0	361	150	Thermally cracked Twin Sisters dunite	deionized water
This study	≈0.6	60 40 first 6 days, 16 after	160 280	natural serpentinite	2%wt NaCl, 5%wt NaHCO ₃ , no pCO ₂

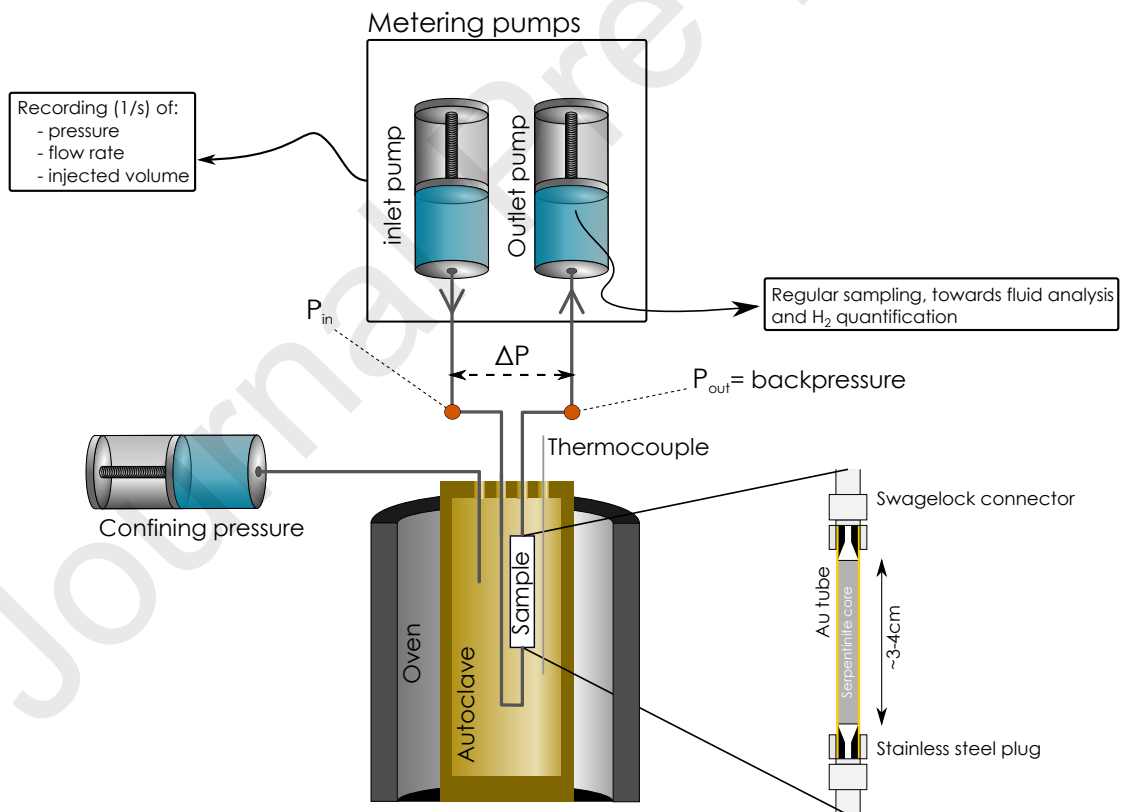


Figure 1: Schematics of the permeameter

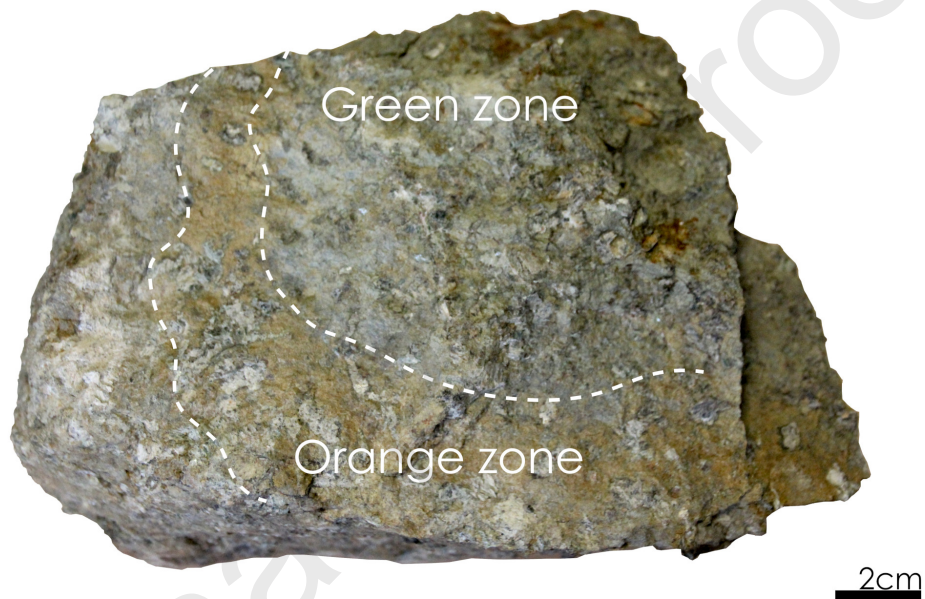


Figure 2: Macroscopic view of the initial serpentinite. The green zone is characterized by serpentinization features with little to no carbonates, while the orange brown zone is characterized by pervasive carbonation.

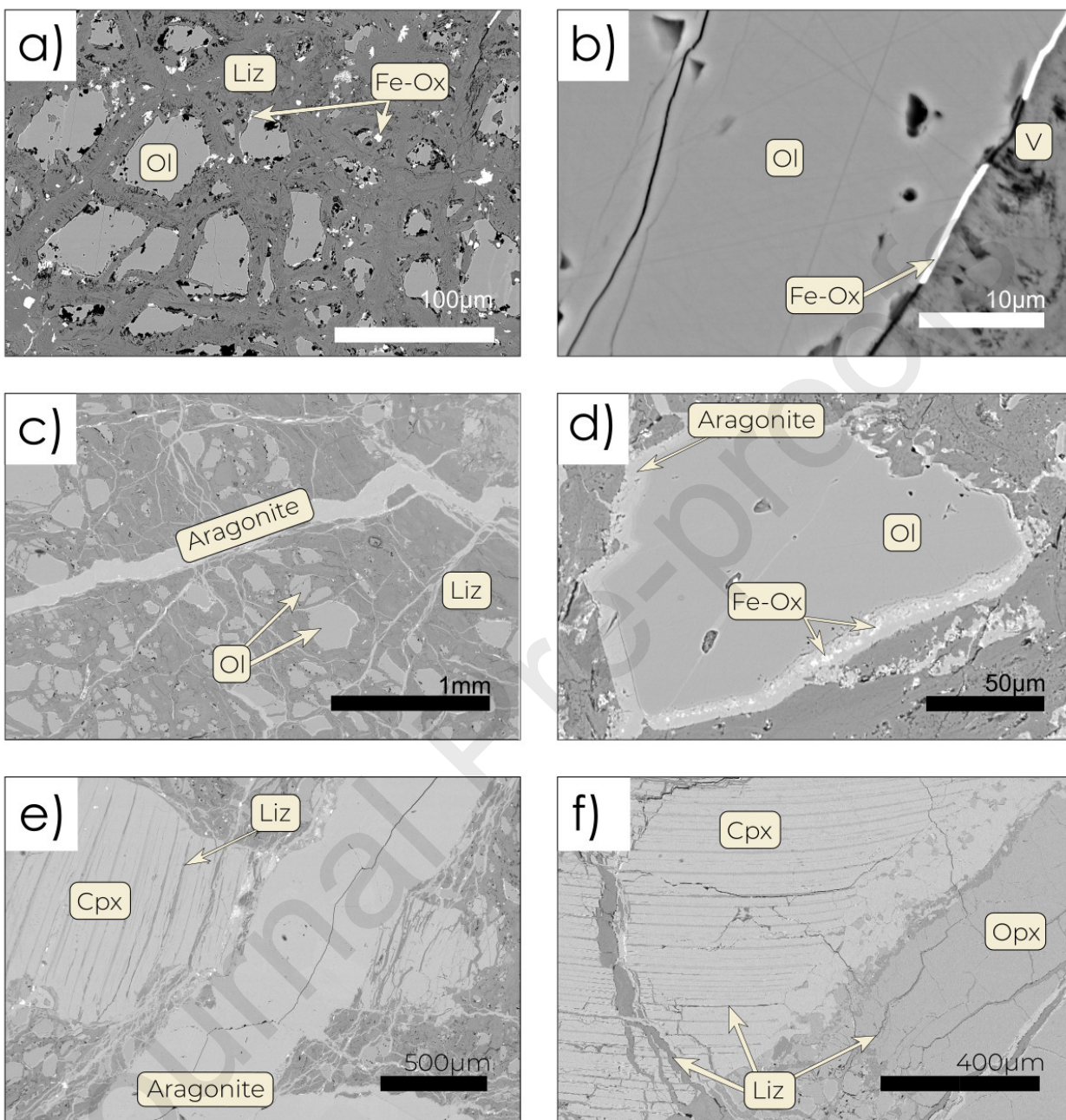


Figure 3: SEM images of characteristic textural features in the starting serpentinite. a) View of the green zone showing the olivine relicts and the serpentine matrix with large Fe-oxides. b) enlarged view of a) showing the olivine-matrix interface with small locally distributed Fe-oxides. Notice the void at the interface. c) Image of the brown orange zone showing different generations of carbonate-filled veins crosscutting the matrix. d) enlarged view of c) showing the continuous carbonate layer with Fe-oxide inclusions around the olivine. e) large aragonite vein (≈ 1 mm) cutting through an altered clinopyroxene. The alteration follows the cleavages and is made of serpentine (bastite). f) clinopyroxene (left with alteration along the cleavage and some fractures, and orthopyroxene (right) showing comparatively little alteration and only along fractures. Notice the contrast in alteration textures between, in the green zone (a, b), the thin and discontinuous iron oxide rim around the olivine, and, in the brown orange zone (c, d) the continuous layer of carbonate.

Cpx=clinopyroxene, Ol=Olivine, Serp=serpentine, Fe-Ox=Iron oxides and V=void

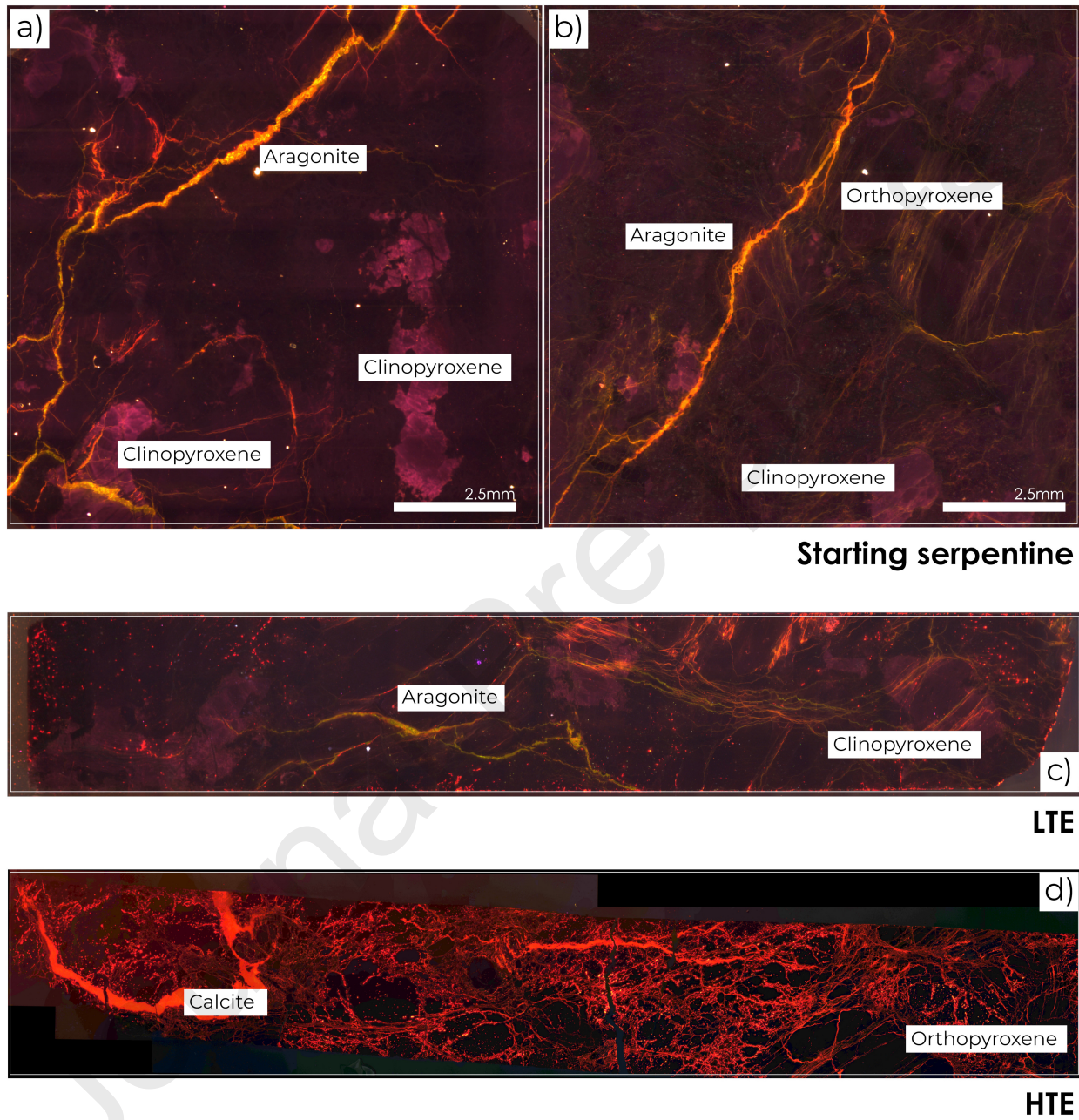


Figure 4: Cathodoluminescence images from the starting material (a and b), LTE (c) and HTE (d). Note the stark contrast between a,b,c versus d. In the starting material as well as LTE, aragonite is visible as a loose network, appearing yellow to green and presenting little luminescence. In the contrary, calcite on HTE is very luminescent with a very dense network of red and bright luminescence.

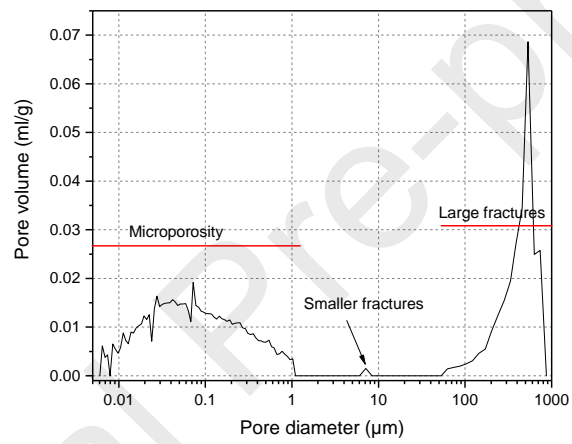


Figure 5: Pore size distribution in the starting serpentinite

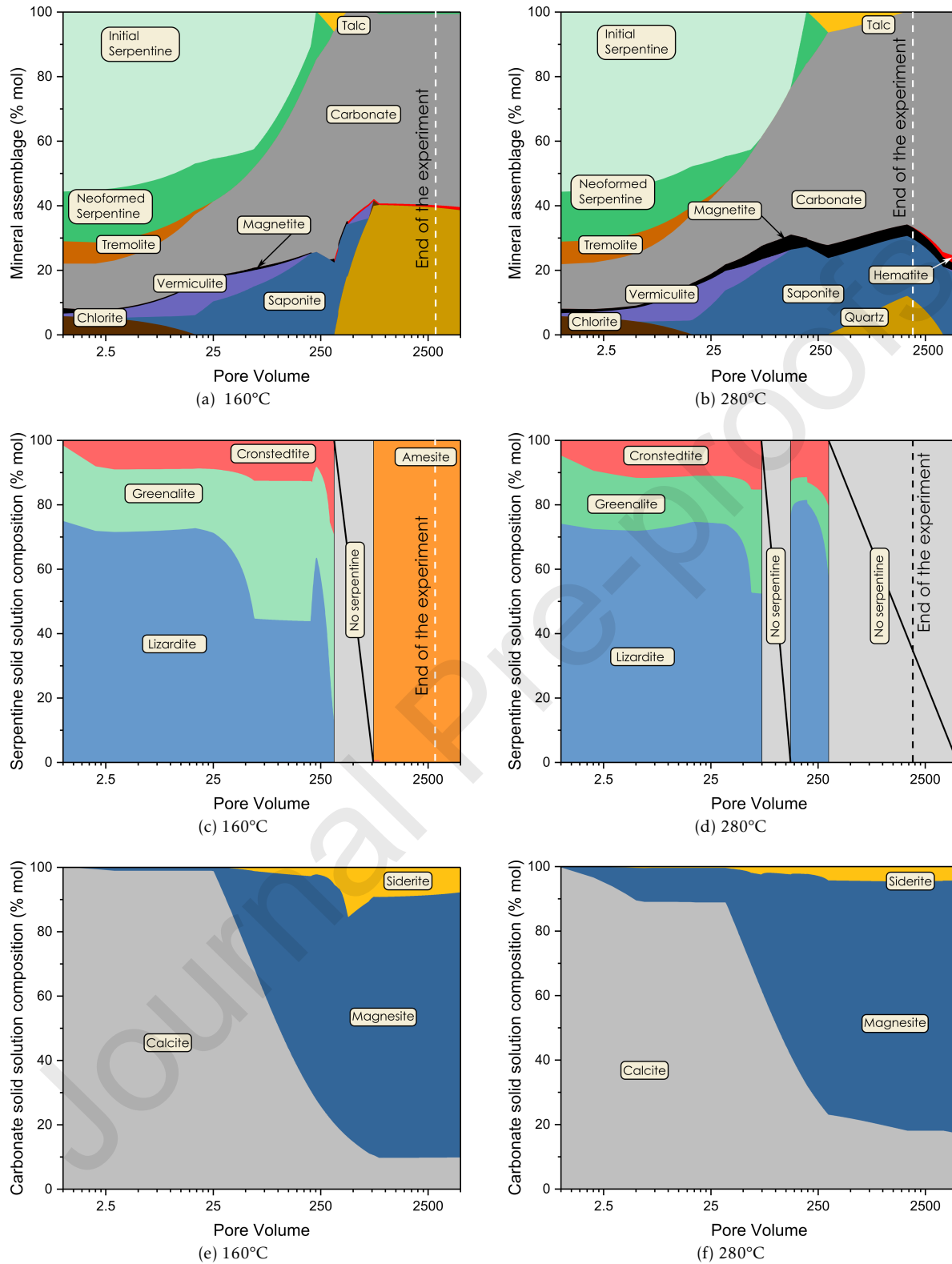


Figure 6: Thermodynamic modeling of fluid-rock interactions with PHREEQC. 6a and 6b: evolution of the mineral assemblage with the W/R ratio at 160°C and 280°C respectively. 6c and 6d: evolution of the modal proportion of the precipitated serpentine phase. 6e and 6f: evolution of the modal proportion of the carbonate phase. The dashed line corresponds to the end of the experiments. One pore volume corresponds to W/R ratio=0.04 considering a 10% porosity

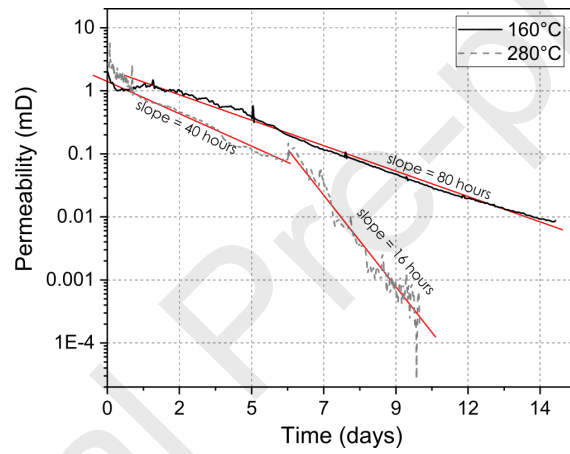


Figure 7: Variation of the permeability as a function of time for the two reactive percolation experiments

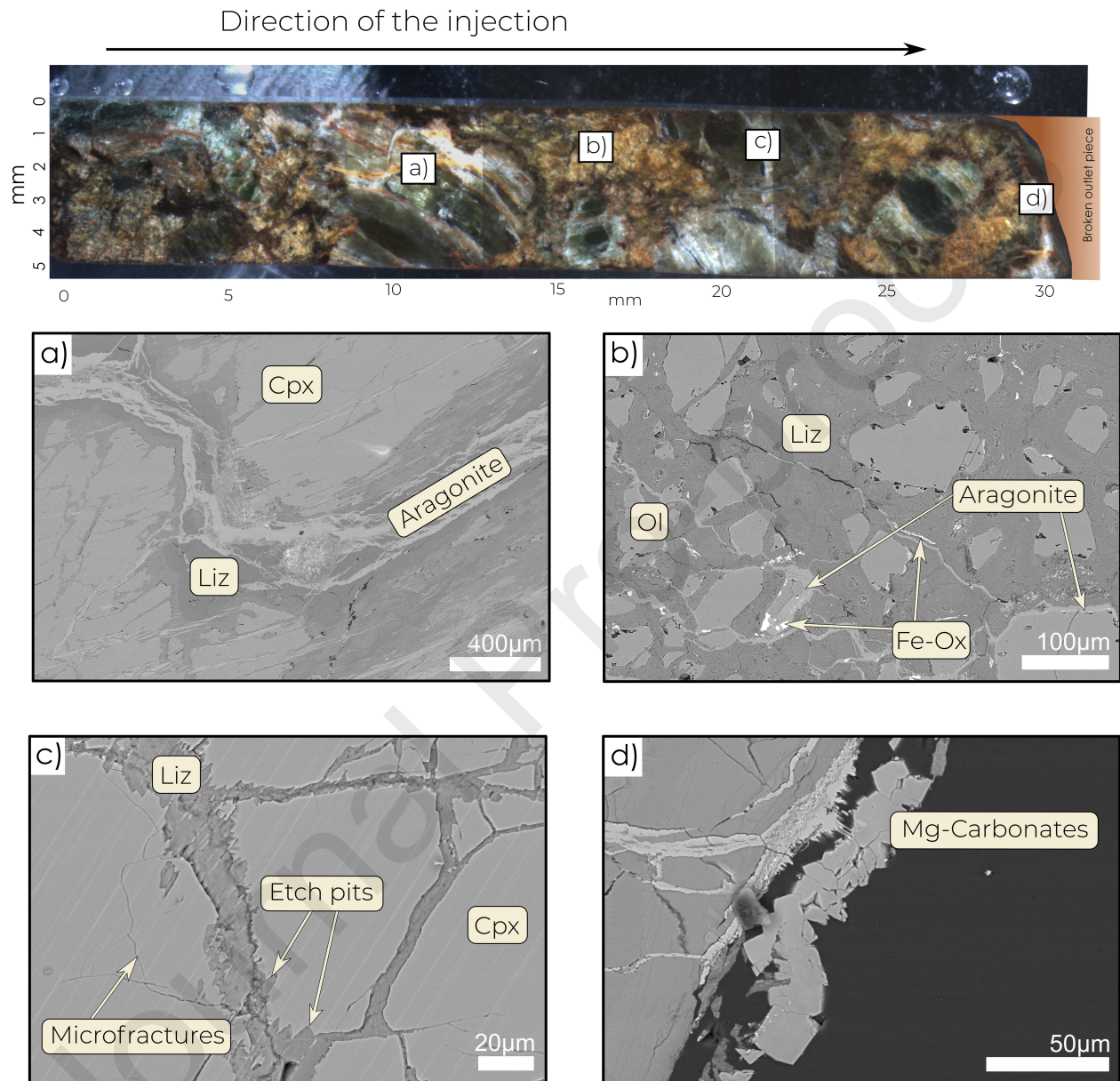


Figure 8: Different views of the main part of the core reacted at 160°C. The optical view highlights the yellowish serpentine matrix and the green to dark green pyroxenes (top). SEM images a) to d) represent respectively a large carbonate vein (aragonite) through a cpx, an olivine-rich zone with carbonate rimming and veinlets, an altered clinopyroxene with microfractures originating from etch pits and probably linked to reaction-induced fracturing, and finally Mg-rich carbonates at the broken end. Due to the little alteration of the core, it is difficult to assess if these features were originally in the starting core or are a consequence of the experiment.

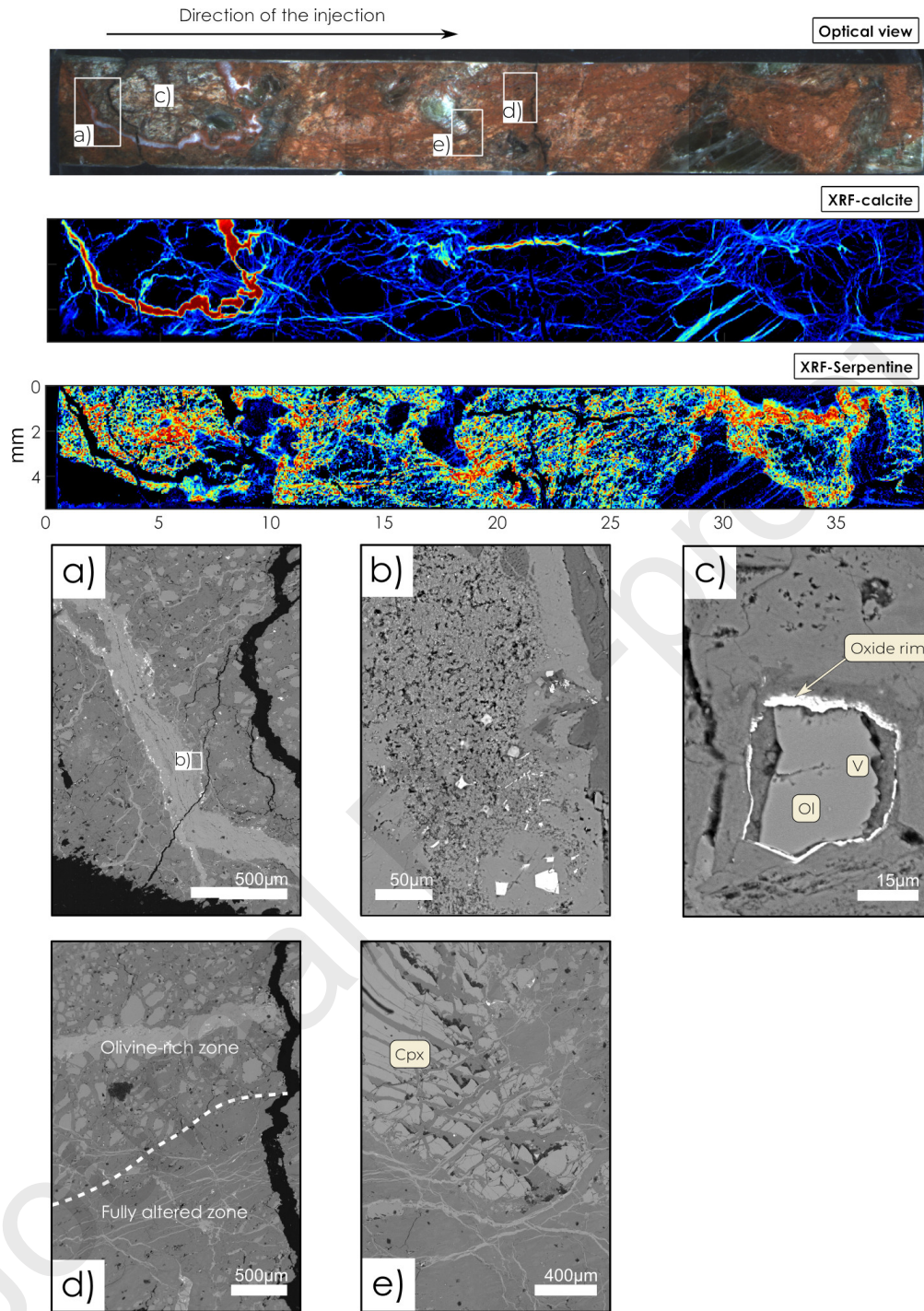


Figure 9: Different views of the main part of the core reacted at 280°C. The optical view highlights the brick-red serpentine matrix and the green to dark green pyroxenes (top panel). The two μ XRF panels show the difference between the calcite phase associated with oriented veins and the serpentine more broadly located and without any preferential orientation. Images a) and b) represent the wide calcite vein next to the inlet. Image c) pictures a relict olivine of the olivine-rich zone near the inlet with the magnetite rim. Image d) shows the juxtaposition of a fully altered zone (left) with thin veinlets and no olivines, and a less altered zone with relict olivine and a large vein. The velocity of the flow in the large vein explains the lack of lateral alteration. Finally image e) depicts a heavily altered clinopyroxene with alteration along the cleavage and fractures associated with reduced carbon (zoom shown in image f).

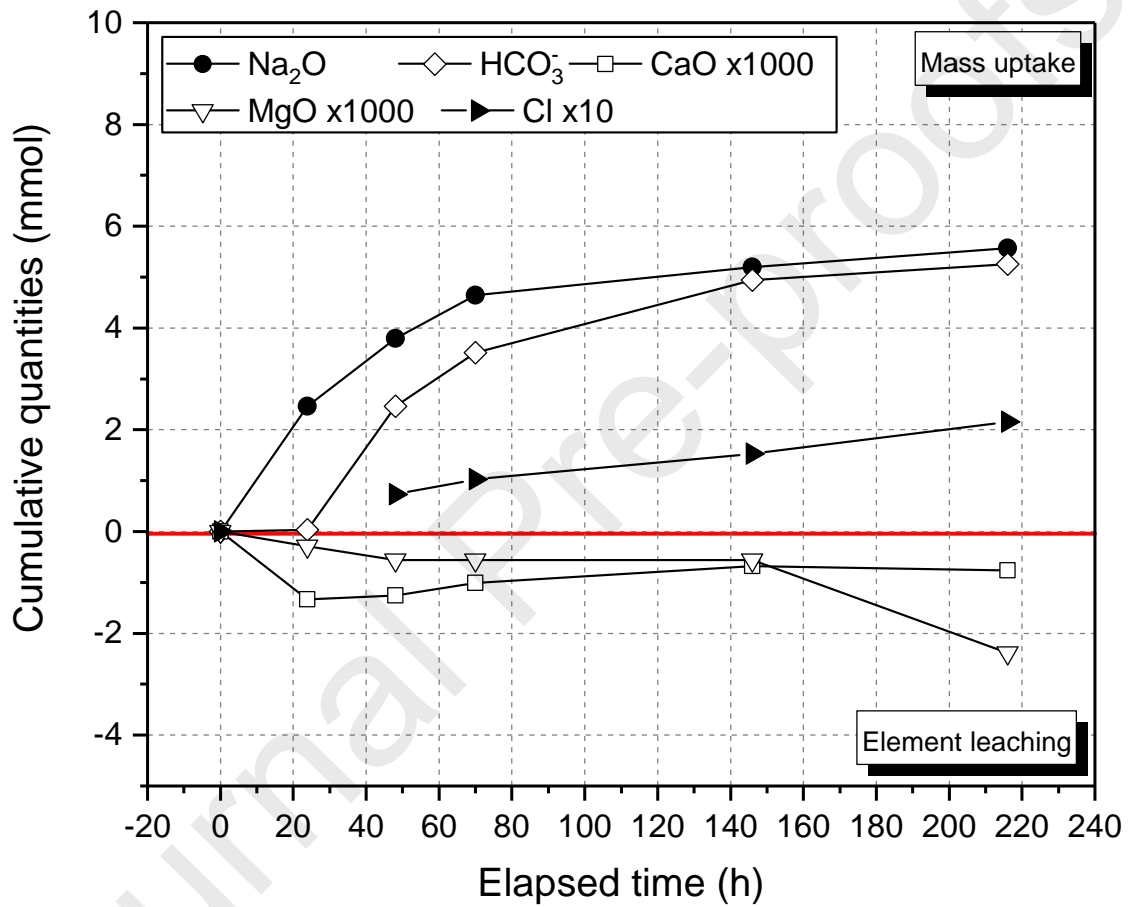


Figure 10: Cumulative mass balance for the measured oxides for HTE

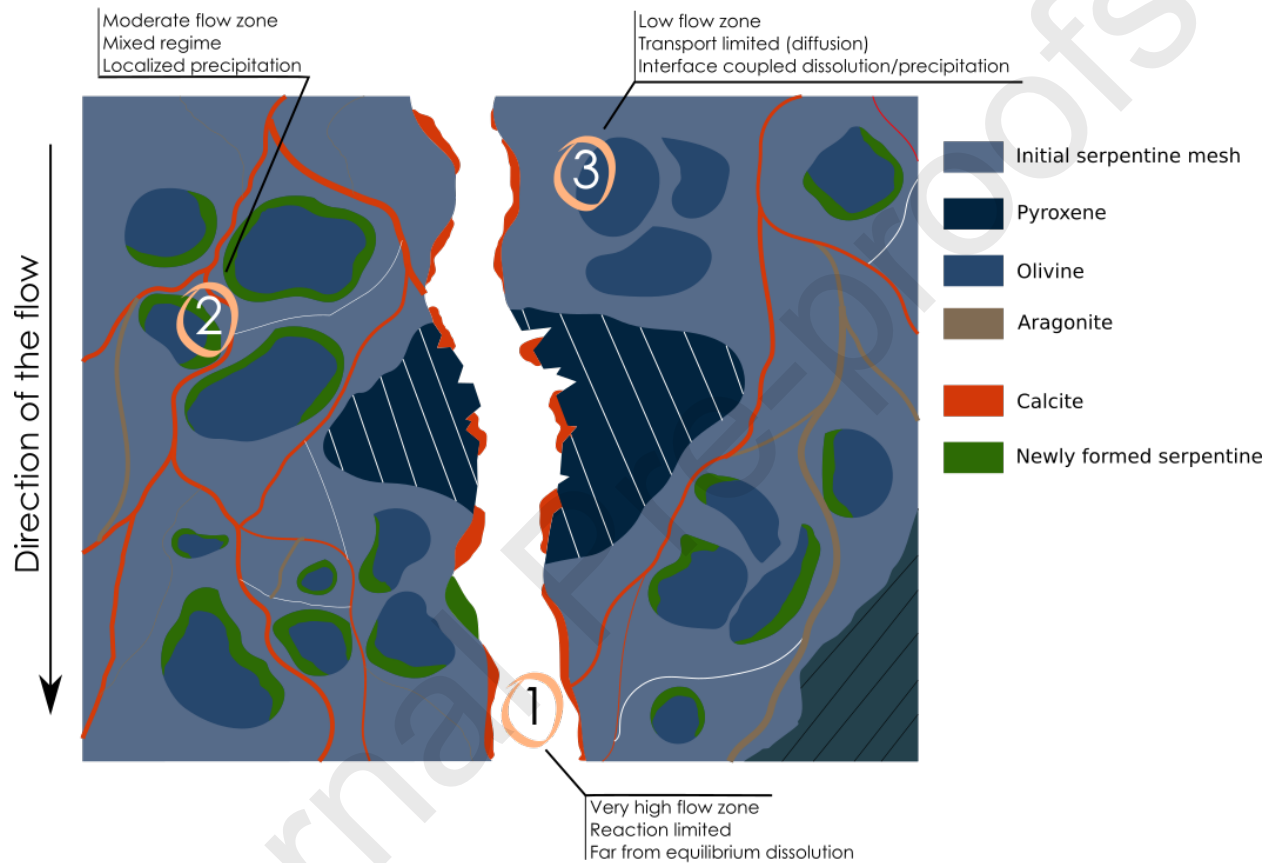


Figure 11: Schematics summarizing the overall behavior during the reactive percolation experiments at 280°C. The behavior can be divided into three main zones, with the larger fractures seeing most of the flow, the smaller fracture network seeing an intermediate flow rate while the porous serpentine matrix sees little to no flow. This has consequences on the location of the dissolution and precipitation of the different minerals.

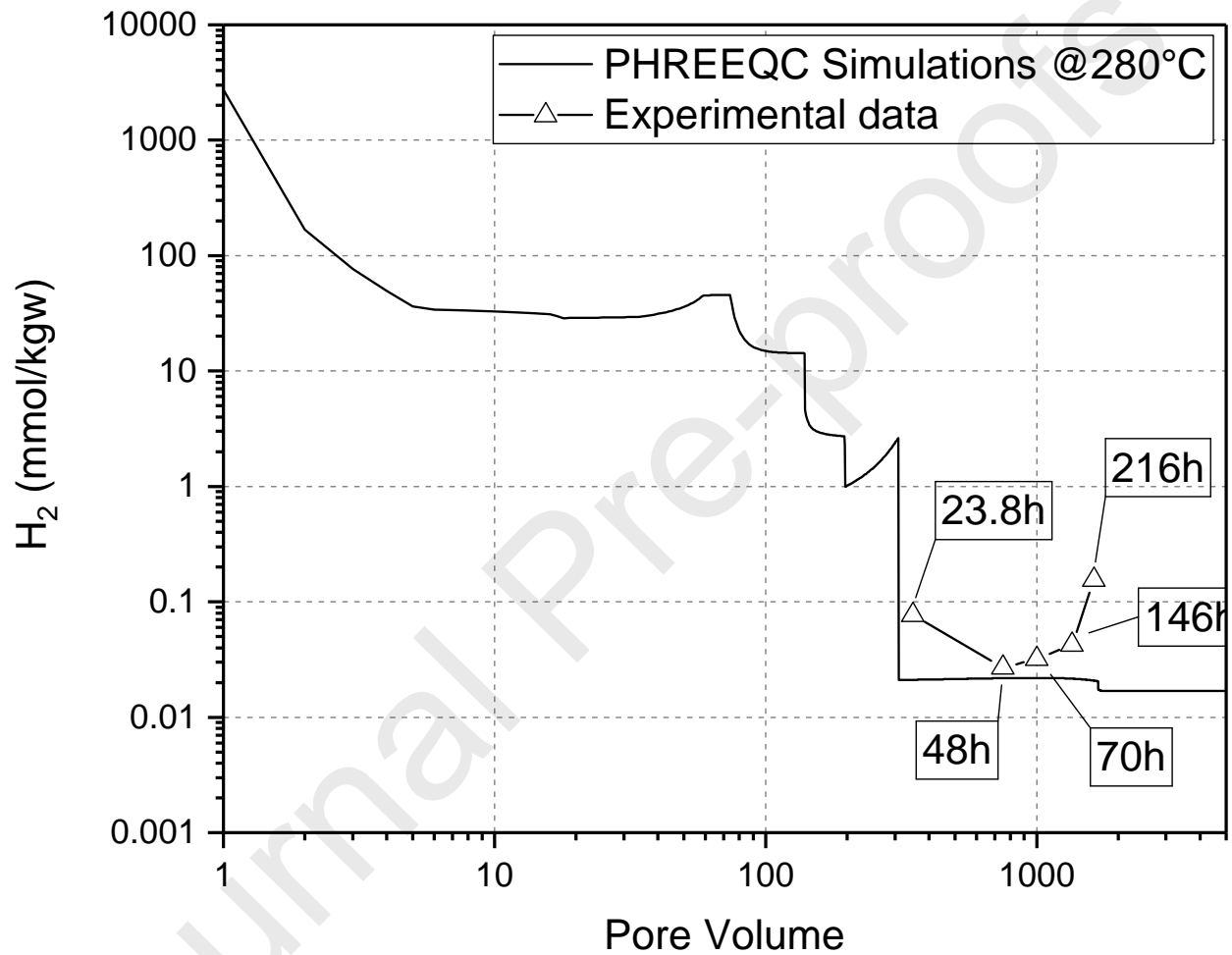


Figure 12: Comparison between experiment (HTE - symbols) and simulations (solid line) in terms of H₂ concentration. Labels on the experimental data points correspond to the time of sampling

Declaration of interests

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: