1 **Revision 2**

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3 **Title:**

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5 **Aluminum speeds up the hydrothermal alteration of olivine**

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28   **Abstract**

29

30   The reactivity of ultramafic rocks under hydrothermal conditions controls chemical

31   fluxes at the interface between the internal and external reservoirs of silicate planets. On

32   Earth, hydration of ultramafic rocks is ubiquitous and operates from deep subduction

33   zones to shallow lithospheric environments where it considerably affects the physical

34   and chemical properties of rocks and can interact with the biosphere. This process also

35   has key emerging societal implications, such as the production of hydrogen as a source

36   of carbon-free energy. To date, the chemical model systems used to reproduce olivine

37   hydrothermal alteration lead to the formation of serpentine with sluggish reaction rates.

38   Here, we use in situ diamond anvil cell experiments and show that the presence of

39   aluminum in hydrothermal fluids increases the rate of olivine serpentinization by one to

40   two orders of magnitude. Aluminum increases the solubility of olivine and enhances the

41   precipitation of aluminous serpentine. After two days, olivine crystals were fully

42   transformed to aluminous serpentine under conditions typical of natural hydrothermal

43   environments, i.e., 200°C and 300°C, 200 MPa. This result motivates a re-evaluation of

44   the natural rates of olivine serpentinization and of olivine hydrolysis in general in a wide

45   range of settings. This discovery also opens the potential of the serpentinization reaction

46   for industrial scale production of hydrogen at economically feasible timescales and

47   temperature.

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49   **Keywords**: olivine, hydrothermal, serpentinization, aluminium

50   **1) Introduction**

51

52   The hydrothermal alteration of olivine is a widespread process that occurs in many

53   geological settings wherever warm aqueous fluids react with ultramafic mantle rocks or

54   olivine-rich magmatic rocks (e.g. wherlite, troctolites, gabbros). Most of the time, olivine

55   is transformed into the hydrous sheet silicate serpentine, plus variable amounts of iron

56   oxides and magnesium hydroxides as illustrated by the olivine serpentinization

57   reaction:

58   $(Mg_{0.9}Fe_{0.1})_2SiO_4 + 1.37\ H_2O \rightarrow 0.5\ Mg_3Si_2O_5(OH)_4 + 0.3\ Mg(OH)_2 + 0.067\ Fe_3O_4 + 0.07\ H_2$ (Eq1)

59   olivine (Fo$_{90}$)   Mg-serpentine   brucite   magnetite

60   If the system chemistry differs from that locally imposed by olivine, the hydrated

61   product minerals can differ. A silica input from either dissolving neighbouring minerals

62   or the hydrothermal fluid would inhibit brucite formation, and even lead to talc

63   precipitation for higher Si activity. Chlorite and tremolite may also form at olivine-

64   plagioclase contact within olivine-rich magmatic rocks. Talc-chlorite-tremolite-

65   serpentine is actually observed within oceanic detachment faults as a result of Si-Al-Ca

66   metasomatism by fluid arising from distant mafic units (Boschi et al. 2006; Jons et al.

67   2010).

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69   The hydrothermal alteration of olivine (e.g. Eq1) presents several fundamental and

70   societal implications. It alters the physical, mechanical and chemical properties of

71   ultramafic rocks and it is accompanied by a redox reaction producing hydrogen coupled

72   to reduction of water and oxidation of olivine ferrous component. The ferric iron is

73   integrated into iron oxides and/or into the hydrous phase. Indeed, chlorite and

74   serpentine can both incorporate important amounts of ferric iron in their structure (e.g.

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75   O'Hanley and Dyar 1993; Muñoz et al. 2006; Andreani et al. 2013). Hydrogen, resulting

76   from serpentine and/or chlorite formation, has been identified within fluids venting at

77   ultramafic-hosted hydrothermal sites along mid-ocean ridges (Charlou et al. 2002;

78   Seyfried et al. 2011) as well as in experiments performed in large-volume reactor (Allen

79   and Seyfried 2003; Seyfried et al. 2007; Marcaillou et al. 2011). Production of abiotic H_2

80   is also thermodynamically predicted using reaction path modelling (Klein et al. 2009). It

81   provides a source of metabolic energy for deep chemoautotrophic ecosystems and could

82   also act as an industrial-scale energy source. In the presence of CO_2, the availability of

83   molecular hydrogen also controls the balance between CO_2-mineralisation and abiotic

84   CO_2-reduction, including Fischer Tropsch-type reactions (McCollom and Seewald 2007;

85   Proskurowski et al. 2008). Ultramafic-hosted hydrothermal systems have thus been

86   proposed as a site for the emergence of the earliest ecosystems (Martin et al. 2008), as

87   well as for CO_2 storage and remediation both at industrial and geological time scales

88   (Kelemen and Matter 2008; Nakamura and Kato 2004; Andreani et al. 2009).

89   Serpentinized or metasomatized ultramafic rocks are common in the oceanic

90   lithosphere particularly along slow and ultra-slow spreading ridges (Cannat, 1993), in

91   subduction zones within and above the downgoing slab (Peacock 1990; Reynard et al.

92   2007), along active continental faults (Andreani et al. 2005; Solum et al. 2006) and

93   within Archean supracrustal terranes (Blais and Auvray 1990; Arndt et al. 2008). In

94   extraterrestrial environments, serpentines have been identified in meteorites (Tomeoka

95   and Tanimura 2000), and on the surface of Mars together with chlorite (Ehlmann et al.

96   2010). The presence of serpentine has also been hypothesized in the core of icy satellites

97   like Titan (Choukroun et al. 2010).

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99   Despite the ubiquity of fully to partially altered olivine in nature, the thermochemical

100   conditions and kinetics of this combined hydration and redox reaction are not yet well

101   established. Serpentine as a result of olivine hydration is widespread. The stability field

102   of serpentine in the MgO-SiO$_2$-H$_2$O (MSH) system extends up to a maximum temperature

103   of 730°C at 2.1 GPa, i.e., the invariant point of the dehydration curve of antigorite. At

104   lower pressure (< 1 GPa) the stability field of serpentine is enlarged toward high

105   temperature as a function of Al content in the MgO-Al$_2$O$_3$-SiO$_2$-H$_2$O (MASH) system

106   (O'Hanley 1996). Serpentinization is active at T < 150°C near ridge axes (Proskurowski

107   et al. 2006), and is suspected at even lower temperature within ophiolites (Barnes and

108   O'Neil 1978). Experimental studies have reproduced the serpentinization reaction of

109   olivine, pyroxene or bulk peridotite at temperatures between 188 and 560°C, and

110   pressures from 20 to 300 MPa (e.g. Allen and Seyfried 2003; Seyfried et al. 2007;

111   Marcaillou et al. 2011, McCollom and Seewald 2007; Martin and Fyfe 1970; Wegner and

112   Ernst 1983; Luquot et al. 2010). These experiments were performed in either pure

113   water or an aqueous fluid closer to seawater composition. They have mostly focused on

114   the chemical evolution of the fluid phase or on the rate of gas or organic compound

115   production. Serpentinization rates were measured in four of these studies only and were

116   found to be very low (Martin and Fyfe 1970; Wegner and Ernst 1983; Luquot et al. 2010;

117   Marcaillou et al. 2011). None of the above-mentioned experiments has used an aqueous

118   fluid with a seawater-modified chemistry, as expected in open natural settings, e.g. after

119   it has interacted with magmatic units or sediments. Although aluminumaluminum is one

120   of the common elements associated with the metasomatism of ultramafic rocks (e.g.

121   Boschi et al. 2006; Jons et al. 2010), its role in the hydrolysis of olivine has only been

122   investigated at low pH (2 < pH < 5) and low T conditions, T=65° (Chen and Brantley

123   2000). This is probably due to the fact that aluminum is often considered as an immobile

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124 element because of the very low solubility of aluminous minerals in pure water.

125 Nevertheless, several studies of metamorphic rocks describing ubiquitous Al-bearing

126 mineralization in veins have highlighted the mobility of Al within fluids (e.g. Kerrick

127 1990). Experimental works have also shown that the presence of Si or Na in solution

128 leads to the formation of Si-Al or Na-Al complexes respectively, for pH >4 to 5 (Diakonov

129 et al. 1996; Manning 2006). This complexation considerably enhances the solubility of

130 alumino-silicates and the mobility of aluminum in metamorphic or metasomatic fluids

131 despite current thoughts on the low solubility of corundum in pure water (Manning

132 2007). Moreover, abundant aluminum supply exceeding provision by pyroxenes in

133 ultramafic rocks is expected in fluids released from the dehydration of metapelites in

134 subduction zones as well as during the hydrothermal alteration of gabbros at mid-ocean

135 ridges. Aluminum was also abundant in primitive environments of both the Earth and

136 Mars, stored in either Al-rich minerals like plagioclase or Al-enriched ultramafic lavas

137 like Munro-type or other high Al_2O_3/TiO_2 komatiites (Arndt et al. 2008).

138 In order to investigate the influence of Al on the hydrothermal alteration of olivine in

139 those contexts, we have performed a series of experiments using a low-pressure

140 diamond anvil cell (lp-DAC, Supporting Figure S1 and Oger et al. 2005) under P-T

141 conditions representative of lower crust while following the reaction progress in situ by

142 optical imaging and by confocal Raman spectroscopy.

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144 **2) Methods**

145 Temperature in the low-pressure diamond anvil cell (lp-DAC, Supporting Figure S1) was

146 monitored with a thermocouple in contact with the gasket. Aluminum was introduced

147 either as a gel of aluminum hydroxide formed by reaction of $AlCl_3$ with water and

148 sodium hydroxide for experiments run at 200°C (pH set at 7, at 25°C), or as Al_2O_3 ruby

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149   microspheres for experiments run at 300°C (pH measured at 25°C = 6.8). The most

150   appropriate source of aluminum has been used for the two different temperatures in

151   order to always ensure an excess of aluminum in the fluid and keep similar cations in the

152   initial fluid for all experiments. Indeed, the reactivity and dissolution kinetics of Al_2O_3 in

153   a 0.5 m NaCl aqueous fluid was tested separately in a temperature-step experiment,

154   which showed an almost instantaneous dissolution of Al_2O_3 microspheres at a

155   temperature above 280°C only. Therefore, another source of Al, minimizing chemical

156   changes, has thus been chosen for the 200°C experiments. Al_2O_3 ruby microspheres also

157   allowed pressure measurement and pressure cell calibration. Pressure was set and

158   maintained constant throughout experiments by having a tight control of the gas

159   membrane pressure of the lp-DAC. The sample was sealed with a Ni-gasket lined with

160   gold to prevent reaction between the sample chamber and the gasket. Dimensions of the

161   reacting cell are 380 μm in diameter and 300 μm thickness (Figure S1).

162   The progress of reaction was monitored by optical microscopy and confocal Raman

163   microspectrometry using a Horiba Jobin-Yvon LabRAM HR800 Raman spectrometer at

164   the ENS (Lyon, France) using green laser at 514 cm^{-1} with a beam size of ~3 μm.

165   X-Ray Diffraction (XRD) spectra have been acquired under an angle-dispersive mode

166   using a monochromatic radiation (33 keV, λ=0.3738 Å), focused into a spot of 8x8 μm in

167   size.

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169   **3) Experimental results**

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171   Experiments were run for 4.5 to 7.5 days with two olivine (Ol) grains reacted in saline

172   water (0.5 mol NaCl /kg) at 200°C and 300°C, and P=200 ±30 MPa. To ensure an excess

173   of Al in the fluid under the experimental conditions, aluminum was introduced either as

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174   a gel of aluminum hydroxide for experiments at 200°C, or as Al_2O_3 ruby microspheres

175   for experiments at 300°C. The importance of nucleation in the kinetics of olivine

176   serpentinization has also been tested by adding lizardite (Mg-serpentine) nuclei in a

177   subset of experimental runs. Table 1 summarizes the experimental conditions and main

178   results of the experiments reported hereafter.

179

180   Aluminum-free experiments N°1 and N°2 do not show any visible reaction progress

181   even after one-week duration, whereas reaction starts rapidly when Al is added to the

182   system in experiments N°3 and N°4 at 300°C and in experiments N°5 and N°6 at 200°C.

183   The first grains of reaction products appear on olivine within 2 hours (Table 1) in the

184   absence of lizardite nuclei and the reaction goes to completion in 2 days. The

185   progressive coating of initially transparent olivine and Al_2O_3 microspheres by brown

186   crystals is illustrated in Figure 1. Figure 2 shows the corresponding evolution of the

187   Raman spectra of olivine with time. It indicates the total disappearance of olivine after

188   t=47h, that is confirmed by the XRD characterization of final reaction products (Figure

189   3C). The softness of the material noticed during its extraction from the lp-DAC also

190   confirms the absence of any relict of olivine crystal in the core of the aggregate and the

191   completion of the reaction. Figure 3A and 3B show the ghost olivine grain fully replaced

192   by micrometric grains of a sheet silicate enriched in aluminum as evidenced by EDS-SEM

193   analyses. X-Ray Diffraction shows that this silicate belongs to the serpentine group of

194   minerals (Figure 3C). It was identified as the Al-rich serpentine amesite by Raman

195   spectroscopy (Figure 2) in all the Al-bearing experiments void of lizardite nuclei (Exp.

196   N°3a, 3b, 5, and 6). Serpentine is the only reaction product observed. Magnetite or

197   brucite predicted by equation 1 for a pure MSH system have not been detected. The

198   serpentine grains are enriched in iron and accommodate the iron released from olivine.

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199   The very fast precipitation of Al-rich serpentine may inhibit magnetite nucleation here.

200   However, this does not rule out the H_2 production since serpentines classically

201   incorporate non negligible amount of ferric iron in their structure that contributes to H_2

202   production (e.g. O'Hanley and Dyar 1993; Marcaillou et al. 2011; Andreani et al. 2013).

203   Unfortunately, H_2 could not be detected in situ since expected concentrations in the fluid

204   are below detection limit by Raman spectroscopy. Indirect estimation of H_2 by

205   quantifying the ferric iron in microscopic serpentine using synchrotron-based X-ray

206   absorption was beyond the scope of this work. When lizardite nuclei are added to the

207   starting materials at 300°C (Exp. N° 4), new serpentine grains formed after 1.5 days

208   (Supporting Figure S2) with a chemical composition and Raman spectra close to that of

209   the lizardite nuclei. The reaction, however, did not go to completion during the duration

210   of the experiment. We documented a fast partial transformation of olivine into

211   serpentine visible over 3 days and the reaction stopped or slowed down to a rate that

212   precluded further observation. The latter experiment illustrates the importance of

213   removing Al from the fluid or from the reactive interface in order to continue the

214   reaction. Experiment N°3b includes a first temperature step at 250°C for 3 days followed

215   by a second and final step of 300°C for 6 days. The latter experiment confirms that the

216   Al_2O_3 microspheres do not dissolve at 250°C and that, as a consequence, the

217   serpentinization reaction fails to start. Optical observations demonstrate that the onset

218   of serpentinization is correlated with the dissolution of Al_2O_3 microspheres at 300°C and

219   that the first grains of serpentine appear simultaneously on the surface of both olivine

220   grains and Al_2O_3 microspheres (Figure 1B). This supports the critical role of dissolved Al

221   to speed up both the dissolution kinetics of olivine and the nucleation and growth of Al-

222   rich serpentine. It also demonstrates that olivine dissolution is the limiting parameter of

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223   the serpentinization reaction and that olivine solubility is considerably enhanced by the

224   presence of dissolved Al in the fluid.

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226   **4) Mutually enhanced dissolution of olivine and alumina**

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228   Since Al is not a major component of olivine, it was not expected to directly control

229   olivine's solubility. At 300°C, 86 bars in aqueous solution, Salvi et al. (1998) nevertheless

230   found that $Al(OH)_3(H_3SiO_4)^-$ is the dominant aluminous silica species at pH <2 and pH >

231   4.5. They also observed that the formation of Al-Si complexes increases the solubility of

232   some aluminosilicates or oxide minerals such as kaolinite or boehmite, similar to that

233   was observed at higher P-T conditions (Manning, 2007). Under the conditions of the

234   present experiments, the best pH estimate is 6 at T = 300°C (CHESS code (Van der Lee et

235   al. 2002)). Thus, dissolved Al in our experiments should be complexed to the Si released

236   by dissolving olivine (Salvi et al. 1998). This may be responsible for the observed

237   increase in olivine solubility in our Al-bearing experiments and the fast serpentine

238   precipitation. Such a mutually enhanced dissolution of olivine and alumina leads to the

239   precipitation of amesite under the present experimental conditions (Figure 3) but may

240   also lead to the formation of other Al-rich hydrated silicate, like chlorite for instance,

241   under slightly different chemical conditions. When lizardite is initially present in the

242   system (Exp. N°4), aluminum still accelerates olivine dissolution. Serpentine growth

243   starts on olivine as well as on available lizardite nuclei which leads to a more magnesian

244   chemical composition of the newly formed serpentine. This slows down the reaction

245   since the Al released by the alumina microspheres is less efficiently removed from the

246   solution by serpentine precipitation. Thus, the equilibrium solubility of alumina under

247   those conditions is more rapidly reached. This effect certainly does not apply to open

248   natural systems where local chemical gradients and fluid renewal at mineral interface

249   are expected to refresh the fluid and thus remove excess Al from the reacting zone.

250   The results of experiments N°3a, 3b, 5 and 6 are compared in Figure 4 to those of the Al-

251   free experiment N°1 and to previously published serpentinization rates of olivine

252   (Martin and Fyfe 1970; Wegner and Ernst 1983; Luquot et al. 2010) and of peridotite

253   (Marcaillou et al. 2011). Assuming a linear conversion rate of olivine into serpentine, we

254   obtain a mean serpentinisation rate of 49 % per day in the present study. This is c.a. 7 to

255   50 times higher than the rates reported under very similar conditions (3.7 - 7.5 % per

256   day (Martin and Fyfe 1970); 1 - 3 %/day (Wegner and Ernst 1983)). It is also 30 to 50

257   times higher than the rates of 1-2 % /day reported for peridotite at lower pressure (P =

258   30 MPa) with a smaller grain size of 1 μm (Marcaillou et al. 2011). The latter work also

259   shows that after 77% of serpentinization the conversion rate decreases down to 0.3

260   %/day and approaches that reported at 200°C, 20 MPa during dynamic percolation

261   experiments which was of 0.2-0.4%/day (Luquot et al. 2010); i.e. two orders of

262   magnitude lower than those in the Al-bearing experiment reported here.

263

264   **5) Implications**

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266   In natural open systems where a sustained H_2O flow allows hydration reactions, the rate

267   of olivine alteration may be increased at any time depending on the inlet fluid flux and

268   its Al content. Indeed, Al is always present in variable amount in serpentine minerals

269   ranging from 1 to 27 wt. % of Al_2O_3 (O'Hanley 1996; Beard et al. 2009), and it is a major

270   component of chlorite. Consequently our experimental results suggest that the

271   hydrothermal alteration of olivine is probably much faster in natural settings where

272   peridotites are intimately associated with Al-suppliers such as the common magmatic

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273   bodies in slow-spreading oceanic crust (Cannat 1993). This is actually well illustrated at

274   oceanic detachments where fault material results from peridotite-gabbro metasomatism

275   and where active hydrothermal fields are observed (McCaig et al. 2007). The

276   composition of fluids released at these hydrothermal vents is enriched in H_2, CH_4 and

277   complex organic compounds and is mainly controlled by serpentinization at depth. The

278   local abundance of Al issued from magmatic rocks certainly affects the fluxes of products

279   released during serpentinization, and in consequence the development of the ecosystem

280   associated with these hydrothermal fields (Schrenk et al. 2004). The effect of joined

281   alteration of olivine and Al-bearing mineral, like plagioclase, on H_2 production in a

282   natural system has indeed been described by Seyfried et al. (2011), based on the

283   chemistry of the fluids that escape the Rainbow hydrothermal field (36°N, Mid-Atlantic

284   Ridge).

285

286   The effect of Al on lower crust and upper mantle metamorphism and metasomatism is

287   expected to be even stronger at high pressure in subduction zones where those

288   reactions control the rheology and physical properties of the subducting plate and

289   mantle wedge (Peacock and Hyndman 1999; Reynard et al. 2007). Indeed, the solubility

290   of Al related to the stability of Na-Si-Al complexes in solution is greater at high pressure

291   (Manning 2007), and may exceed the solubility of Mg or Fe in fluids equilibrated with

292   mafic and felsic bulk compositions (Manning 2006).

293

294   Whatever the setting, the rate of metamorphic reaction is also a key parameter for

295   determining the contribution of reaction-enhanced processes at the micrometer-scale,

296   such as reaction-driven cracking, that can affect, in turn, macroscopic rock properties

297   like permeability (Jamveit et al. 2008; Rudge et al. 2010). Reaction-driven cracking has

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298   been proposed as an important positive feedback of the olivine hydration reaction that

299   creates permeability for fluid supply and increases the reactive surface area (Kelemen

300   and Hirth 2012). A well documented example is the case of fractured plagioclase grains

301   between serpentinized or chloritized olivine crystals in troctolites or olivine gabbros,

302   respectively. The present results suggest that the presence of Al in solution should, at

303   least locally, increase the contribution of reaction-induced cracking during retrograde

304   metamorphism of olivine-rich rocks.

305

306   The present results also provide a way to accelerate serpentinization reactions towards

307   an economically feasible time-scale for industrial H_2 production and/or CO_2 remediation

308   through the production of carbon compounds with a higher added value like CH_4 and

309   hydrocarbons. In comparison with available technologies for H_2 production that mainly

310   rely on fossil fuels (> 90% of H_2 production by steam reforming and < 1% via

311   electrolysis), olivine serpentinization is a carbon-free process. Energy minimization is

312   also obtained here by the exothermic character of the serpentinization reaction and by

313   lowering the temperature of the reaction to 200°C, as long as Al is available in solution.

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315   **6) Acknowledgments**

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502   **Figure legends**

503

504   **Figure 1 : Optical images of the reaction progress in the lp-DAC.** Development with

505   time (A to D) of aluminous serpentine at the expense of olivine and Al_2O_3 microspheres

506   during experiment N°3a (Table1).

507

508   **Figure 2** : **Monitoring reaction progress on the olivine grain with Raman**

509   **spectroscopy.** Example of reaction N°3a. Confocal Raman spectroscopy allows scanning

510   the olivine grain in depth. The time steps are those illustrated on Figure 1. The final

511   product of the reaction at t=47h is identified as amesite by comparison to the reference

512   spectrum from RUFF database. Olivine is the only mineral detected at t=0 and 2h. Then

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513   Raman modes characteristic of amesite (arrows) are observed with relict olivine at

514   t=16h. Olivine is fully replaced by amesite at t=47h.

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516   **Figure 3 : SEM and XRD characterization of the serpentine grains at the end of**

517   **reaction.** Example of Exp. N°3a. A) SEM image of the serpentine grains formed at the

518   expense of olivine. B) Zoom in of serpentine grains with EDS-SEM analysis of their mean

519   composition. C) XRD spectra of the serpentine grains with identification of the

520   characteristic peaks of serpentine minerals. No other phases are detected.

521

522   **Figure 4 : Comparison of the present results with serpentinization rates available**

523   **in the litterature.** Results of experiments N°1, 3a, 3b, 5, 6, realized with olivine grain

524   size ~100-150 μm, are plotted in comparison with the available data on serpentinization

525   rate of olivine or peridotite obtained under similar P-T conditions and grain size, i.e. 60-

526   80 μm (Martin and Fyfe 1970) and 105-150 μm (Wegner and Ernst 1983). Available

527   results obtained at lower P conditions (Luquot et al. 2010) and smaller grain sizes ~ 1

528   μm (Marcaillou et al. 2011) are also reported.

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538   **Table 1 : Experimental conditions and main results**

Solid reactants 0.5 m NaCl in deionized H_2O pH_{init} (25°C)= 7 reacted at **T=300°C**, P=200 MPa	Duration (hours)	First serpentine grain (hours from start)	Reaction completion at the end
N°1 : Ol	168	No reaction observed	No
N°2 : Ol + Liz	182	No reaction observed	No
N°3 **a :** Ol + Al_2O_3 **b*** : Ol + Al_2O_3	119 144	2 (± 0.25) 2 (±0.25)	Yes, completion at 48h (± 8) 65h (± 8)
N°4 : Ol + Al_2O_3 + Liz	112	38 (±3)	No, reaction stopped or slowed down at t = 70h (±5)
Solid reactants 0.5 m NaCl in deionized H_2O pH_{init}(25°C)= 7 reacted at **T=200°C**, P=200 MPa			
N°5 : Ol + $Al(OH)_3$ gel	70	1.5 (± 0.25)	Yes, completion at 45h (± 4)
N°6 : Ol + $Al(OH)_3$ gel	50	1 (± 0.25)	Yes, completion at 37h (± 6)

539   *Experiment N°3b includes a first temperature step at 250°C for 3 days, that is not reported in the table, followed by a second and
540   final step at 300°C for 6 days, reported in the table. No reaction was observed at 250°C since Al_2O_3 microspheres did not dissolve.

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544   **Figures**

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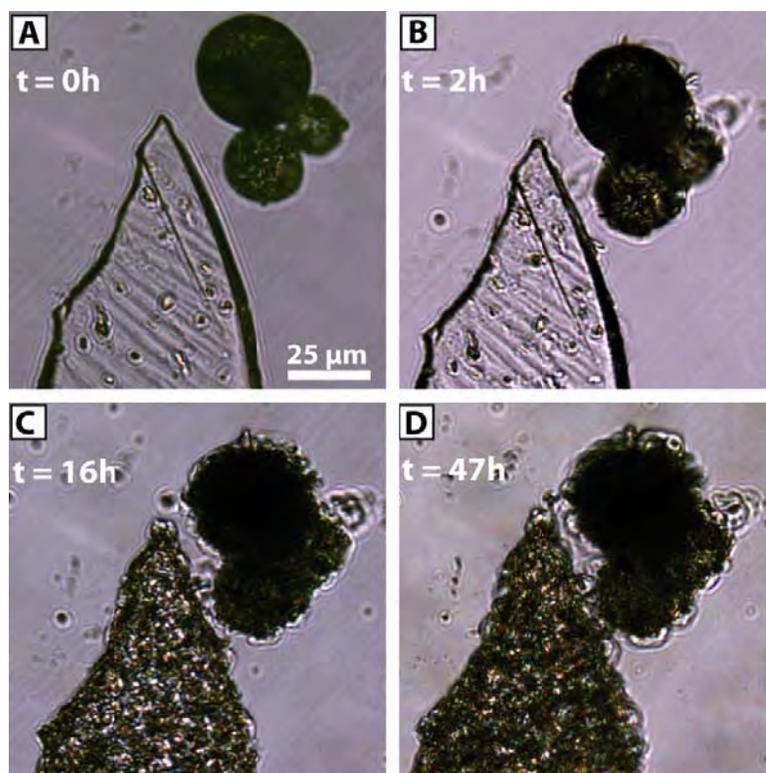
Figure 1

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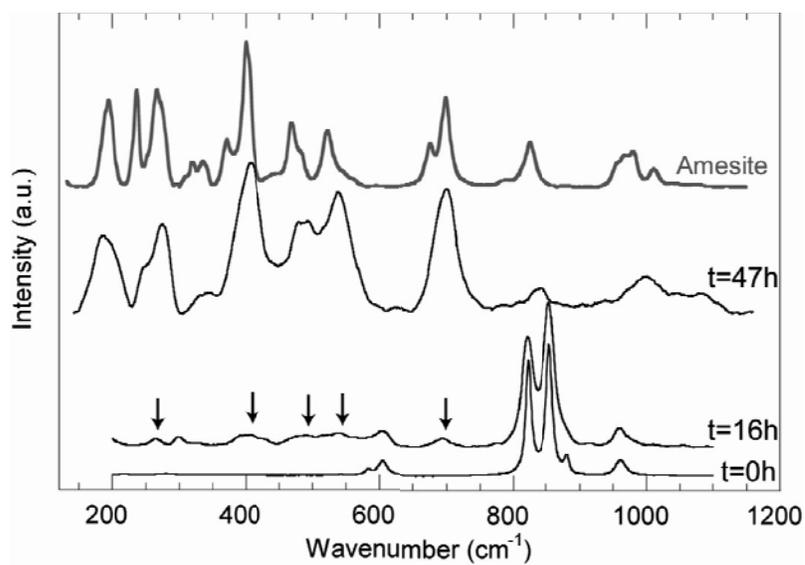
Figure 2

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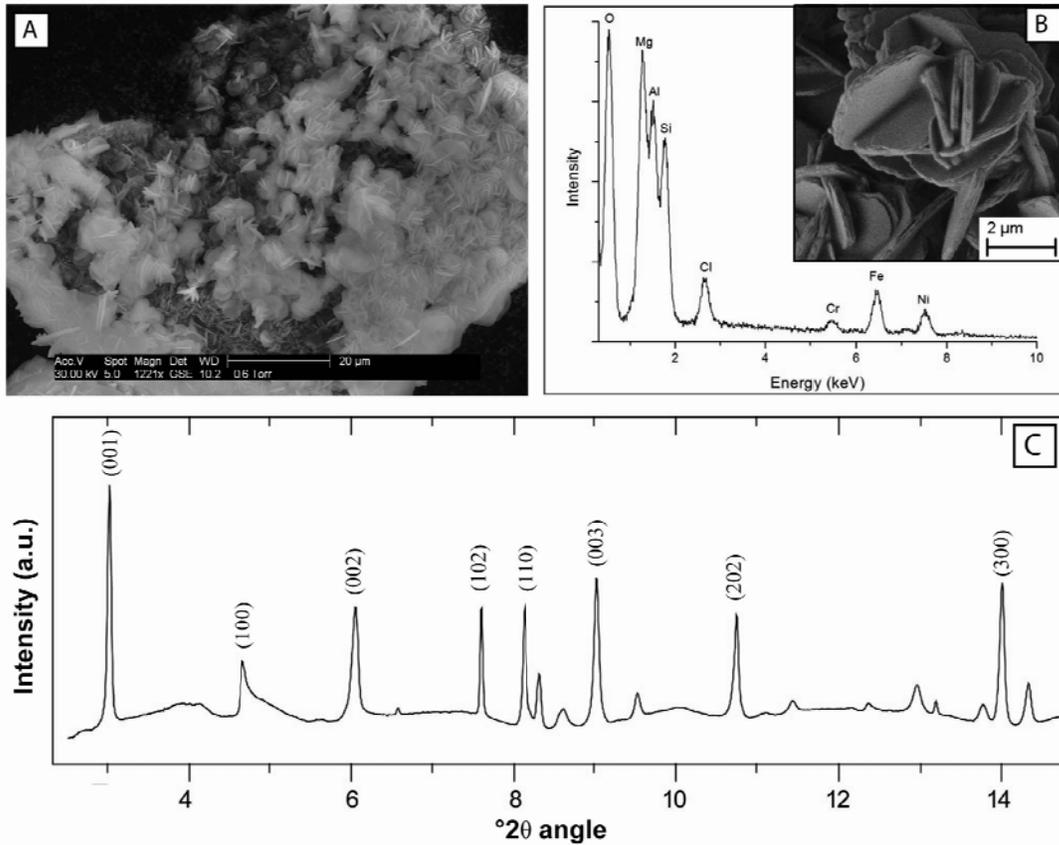
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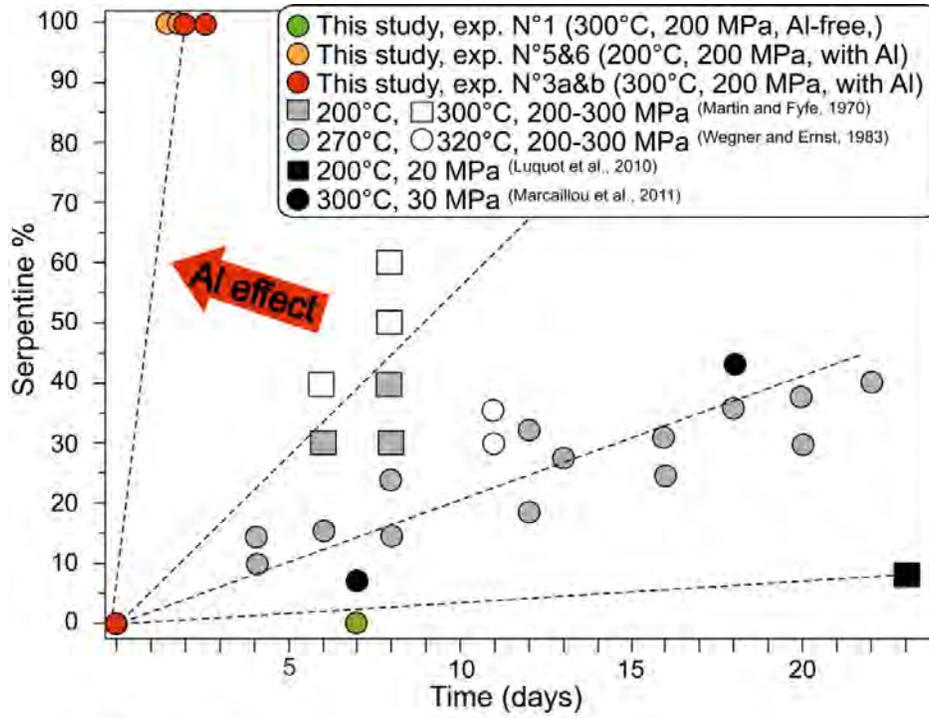
Figure4

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567   **SUPPORTING INFORMATION**

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569   **Figures**
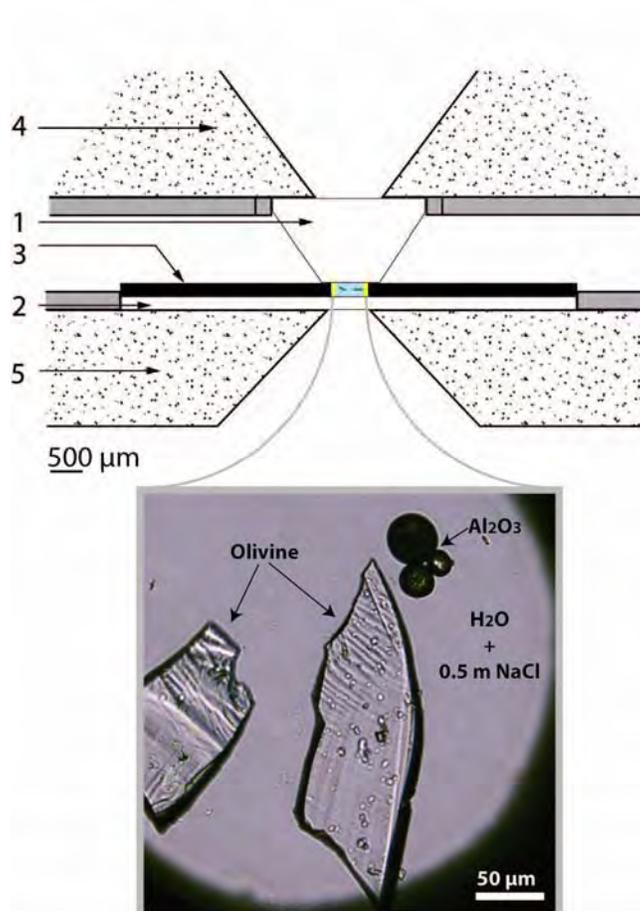
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571   **Supporting Figure S1. Scheme of the low-pressure diamond anvil cell**. (1) diamond

572   anvil, (2) diamond window, (3) Ni sample gasket lined with gold (inner diameter = 380

573   μm ; thickness = 300 μm), (4, 5) tungsten carbide seats. The experimental volume

574   (coloured in blue) is filled with reactants as illustrated by the optical image experiment

575   load N°3a at t=0. For mode details on the lp-DAC, see Oger et al. (2005).

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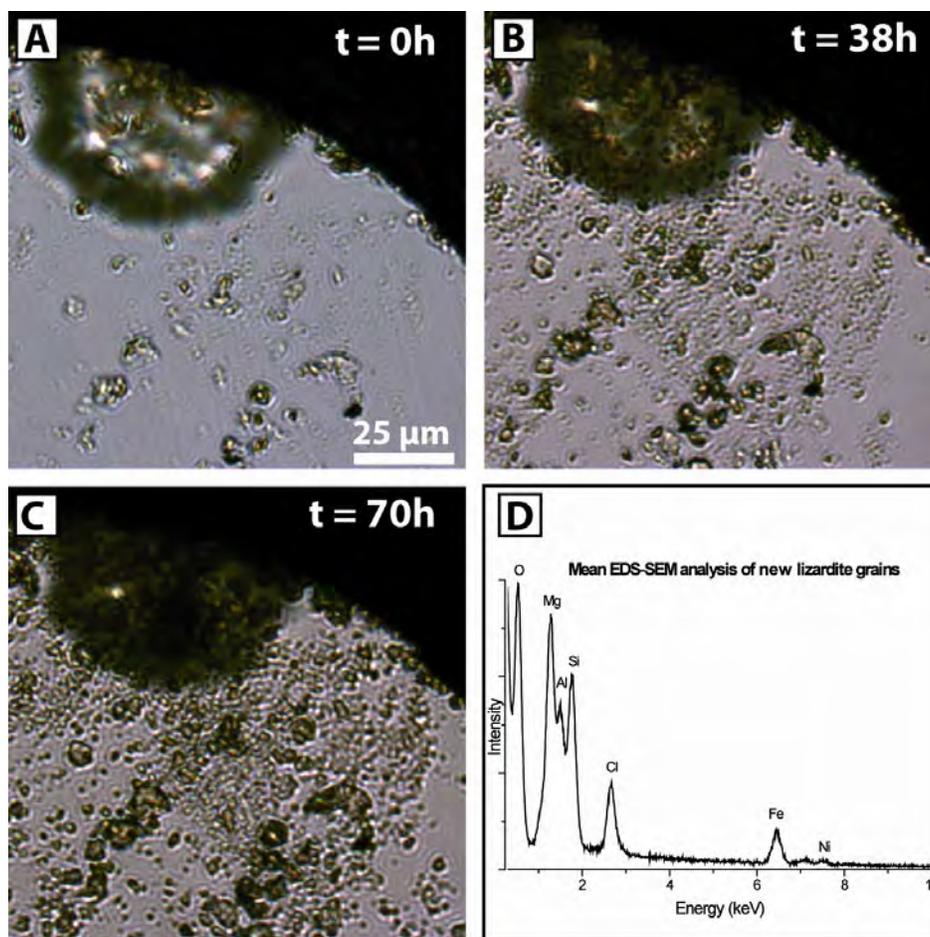
577

578 **Supporting Figure S2 : Optical images of the reacting cell**. Development with time of

579 serpentine at the expense of olivine and on inital lizardite nuclei during experiment N°4

580 (Table1).

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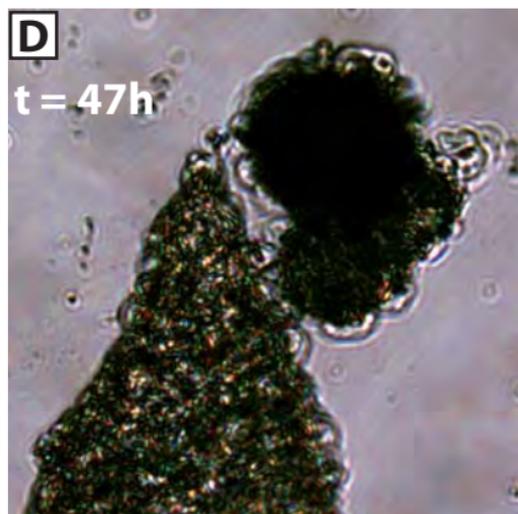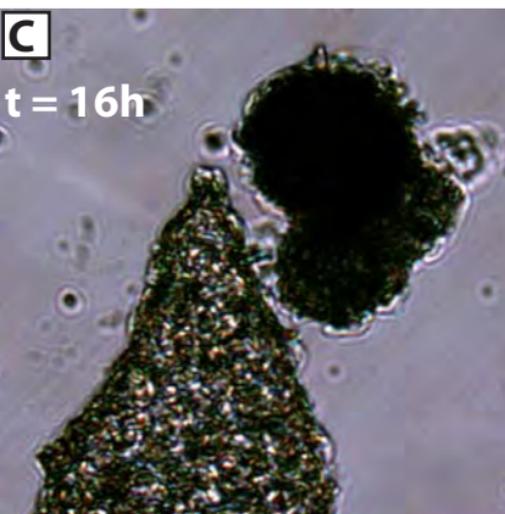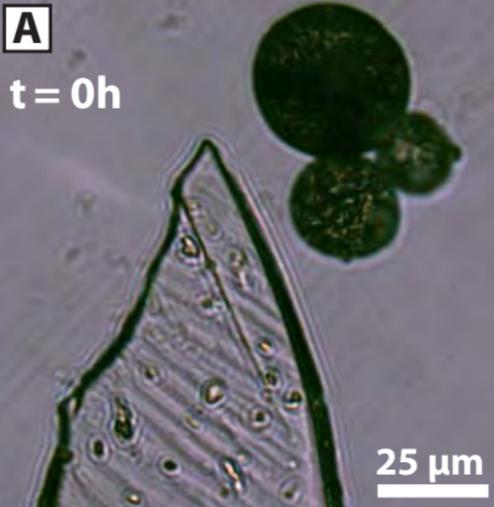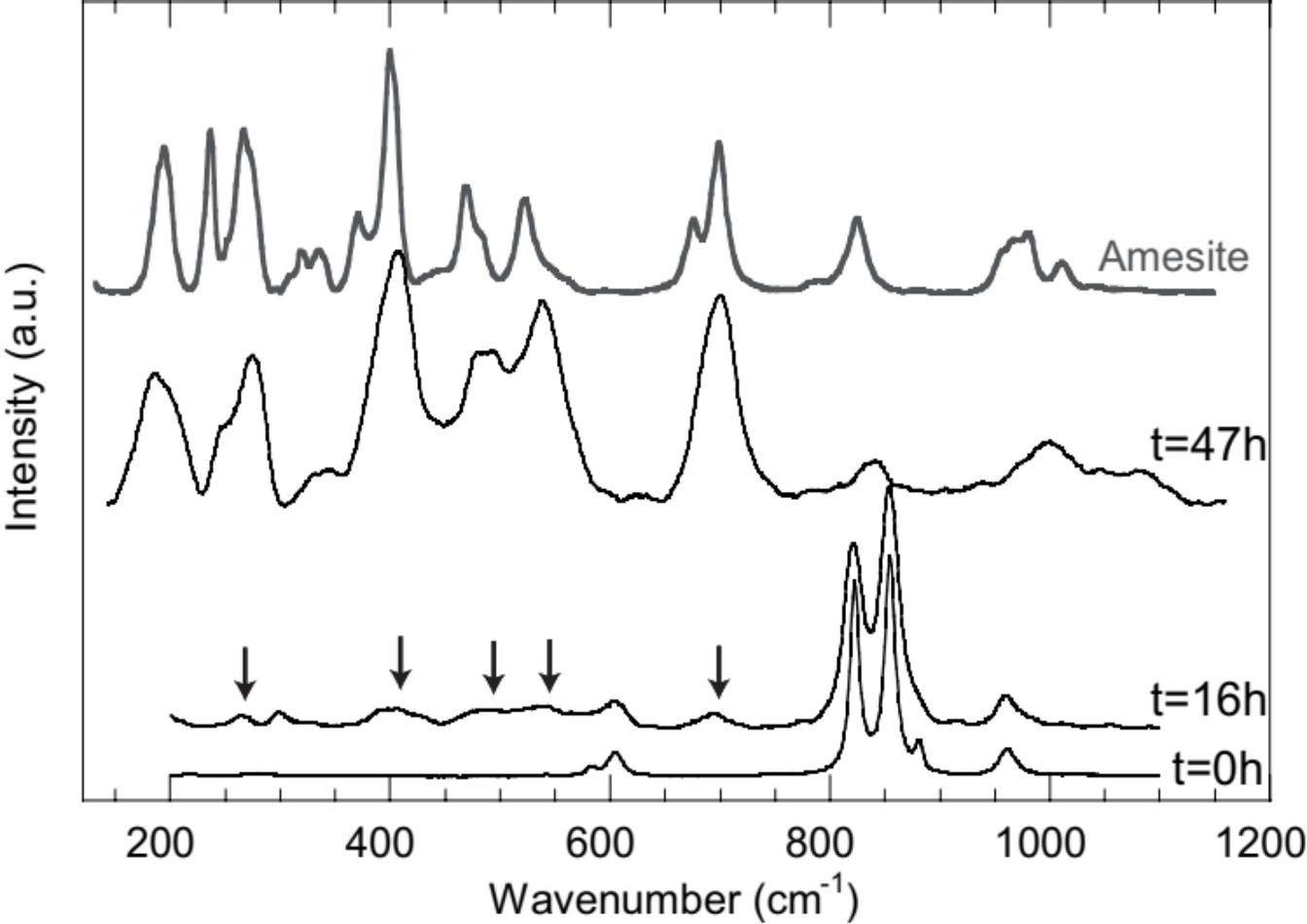
Figure 1

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Figure4