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1 **Pressure-temperature estimates of the lizardite/antigorite transition**  
2 **in high pressure serpentinites.**

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19

20 **Abstract**

21           Serpentine minerals in natural samples are dominated by lizardite and antigorite. In  
22 spite of numerous petrological experiments, the stability fields of these species remain poorly  
23 constrained. This paper presents the petrological observations and the Raman spectroscopy  
24 and XRD analyses of natural serpentinites from the Alpine paleo-accretionary wedge.  
25 Serpentine varieties are identified from a range of metamorphic pressure and temperature  
26 conditions from sub-greenschist ( $P < 4$  kbar,  $T \sim 200$ - $300^{\circ}\text{C}$ ) to eclogite facies conditions ( $P$   
27  $> 20$  kbar,  $T > 460^{\circ}\text{C}$ ) along a subduction geothermal gradient. We used the observed mineral  
28 assemblage in natural serpentinite along with the  $T_{\text{max}}$  estimated by Raman spectroscopy of  
29 the carbonaceous matter of the associated metasediments to constrain the temperature of the  
30 lizardite to antigorite transition at high pressures. We show that below  $300^{\circ}\text{C}$ , lizardite and  
31 locally chrysotile are the dominant species in the mesh texture. Between  $320$  and  $390^{\circ}\text{C}$ ,  
32 lizardite is progressively replaced by antigorite at the grain boundaries through dissolution-  
33 precipitation processes in the presence of  $\text{SiO}_2$  enriched fluids and through a solid-state  
34 transition in the cores of the lizardite mesh. Above  $390^{\circ}\text{C}$ , under high-grade blueschist to  
35 eclogite facies conditions, antigorite is the sole stable serpentine mineral until the onset of  
36 secondary olivine crystallization at  $460^{\circ}\text{C}$ .

37 **Keywords:** Serpentinite; Raman spectroscopy; lizardite/antigorite transition; western Alps

## 38 1. Introduction

39           Serpentine minerals are phyllosilicates that contain up to 13 wt% water and that form  
40 during the hydration of basic to ultrabasic rocks. Hydration commonly takes place in ocean  
41 spreading context, thus documenting the chemical exchanges between the oceans and solid  
42 Earth (Alt and Shanks, 2003). Serpentinites are also common in blueschist to eclogite facies  
43 terranes of oceanic or mantle wedge origin (Hattori and Guillot, 2007). Due to serpentinites'  
44 low-variance metamorphic assemblage, it is generally difficult to evaluate the P-T conditions  
45 to which they were subjected (e.g., Evans, 2004), but the associated metamorphic rocks  
46 permit approximations of the conditions. It is therefore important to accurately and rapidly  
47 characterize these common serpentine minerals. Serpentine minerals, which have simplified  
48 structure formulae  $(\text{Mg, Fe}^{2+})_3 \text{Si}_2\text{O}_5(\text{OH})_4$ , are made of superposed 1:1 alternating tetrahedral  
49 and octahedral sheets. The different spatial arrangements of these layers result in three main  
50 serpentine minerals, i.e., lizardite, chrysotile and antigorite. The sheets form flat layers in  
51 lizardite, rolls in chrysotile and curved modulated structures in antigorite (e.g., Wicks and  
52 O'Hanley, 1988). Serpentinites in high-grade metamorphic terranes indicate that antigorite is  
53 the predominant species (Scambelluri et al., 1995; Trommsdorff et al., 1998; Auzende et al.,  
54 2002; 2006; Li et al., 2004; Groppo and Compagnoni, 2007; Padron-Navarta et al., 2008;  
55 Guillot et al., 2009). Moreover, experimental studies confirm that antigorite is the stable  
56 serpentine mineral under high-pressure conditions (Ulmer and Trommsdorff, 1995; Wunder  
57 and Schreyer, 1997; Bromiley and Pawley, 2003; Perrillat et al., 2005; Komabayashi et al.,  
58 2005; Reynard and Wunder, 2006; Padron-Navarta et al., 2010). Lizardite and chrysotile are  
59 the main varieties that are present in low-grade serpentinites from the oceanic lithosphere and  
60 from low-grade metamorphic ophiolites (Evans, 2004; Andréani et al., 2007). However, the  
61 transition from low-grade to high-grade serpentine minerals is poorly constrained.  
62 Thermodynamic data predict that above 300°C, the antigorite + brucite assemblage is more  
63 stable than lizardite, and chrysotile is absent (Evans, 2004). Moreover, the antigorite + brucite  
64 assemblage is often observed in natural samples, while the chrysotile + brucite assemblage is  
65 particularly abundant in retrogressed serpentinites (Baronnet and Belluso, 2002). Thus, further  
66 petrological investigations of natural serpentinite samples, where the P-T conditions are well-  
67 constrained, are required to refine the relative stability of each variety of serpentine over a  
68 wide range of metamorphic conditions. To definitively identify serpentine varieties,  
69 transmission electron microscopy (TEM) is usually required (Mellini et al., 1995; Auzende et  
70 al., 2002; Boudier et al., 2010). Indeed, serpentine grains are only a few microns in size and

71 can display various habitus, which makes optical identification inaccurate. Vibrational Raman  
72 spectroscopy is also a powerful method for processing large numbers of complex samples,  
73 and numerous studies have been devoted to its use in serpentine characterization (Lewis et al.,  
74 1996; Bard et al., 1997; Kloprogge et al., 1999; Rinaudo et al., 2003; Auzende et al., 2004;  
75 Groppo et al., 2006). In particular, the region of the OH stretching vibrational modes can be  
76 conveniently used to discriminate among the different varieties of serpentine (Auzende et al.,  
77 2004). The OH stretching modes in the high wavenumber range (approximately  $3500\text{ cm}^{-1}$ ) of  
78 the different serpentines are tentatively described in terms of the curvature of the layers, with  
79 potential applications for structural characterization by Raman spectroscopy. Raman  
80 spectroscopy permits the characterization of the phases at a micrometer scale of bulk samples  
81 or thin sections. To assess the reliability of Raman spectroscopy for identification purposes,  
82 we apply it to serpentines in a series of low to high pressure metamorphic serpentinite  
83 samples from the western Alps for which TEM characterization have been independently  
84 performed (Auzende et al., 2006). The serpentinites are also characterized by XRD in order to  
85 decipher the bulk serpentinite mineralogy.

## 86 **2. Geological setting**

87 Alpine evolution along the Eurasia-Africa boundary was initially dominated by plate  
88 divergence, which induced Mesozoic rifting and oceanic opening. Since Cretaceous time, the  
89 plate convergence has resulted in subduction and collision (Rosenbaum and Lister, 2005;  
90 Dumont et al., 2012). This study focuses on the Piedmont zone of the southwestern Alps (Figs  
91 1a and 1b), which is composed of the association of units that originated in the distal  
92 European margin and from the nearby oceanic domain (Lemoine et al., 1986) and that were  
93 juxtaposed during the subduction and collision in Late Cretaceous to Tertiary times (Tricart,  
94 1984). The Piedmont zone includes different levels of the paleo-subduction zone, preserving  
95 the low thermal gradient ( $5\text{--}8\text{ }^{\circ}\text{C}/\text{km}$ ) associated with the subduction dynamics; moreover, it  
96 is partially overprinted by Alpine metamorphism conditions (Schwartz et al., 2001, 2007,  
97 Agard et al., 2002). At the top of the nappe pile, the Chenaillet massif corresponds to an  
98 obducted portion of the Tethyan oceanic lithosphere. This unit rests upon the Queyras  
99 Schistes lustrés (Fig. 1c), which represents a fossiliferous sedimentary accretionary wedge  
100 developed under blueschist facies conditions during the late Cretaceous–early Eocene  
101 subduction of the Tethyan Ocean (Schwartz, 2000; Tricart and Schwartz, 2006; Schwartz et  
102 al., 2009), as previously indicated by structural observations further to the north in the same  
103 Piedmont zone (Agard et al., 2001; Ganne et al., 2005). This domain derived from Mesozoic

104 oceanic sediments that were primarily composed of metamorphic marls, clays, and limestones  
105 (calcschists). These sediments were strongly deformed and metamorphosed during alpine  
106 subduction, and they outcrop today as foliated and polydeformed calcschists enclosing  
107 boudinaged meter- to kilometer-sized Jurassic ophiolites (Tricart and Lemoine, 1986;  
108 Lagabrielle and Polino, 1988). The P-T conditions increase towards the east, from low  
109 temperature-blueschist facies conditions (LT-blueschist) in western Queyras to the transitional  
110 conditions between high-temperature blueschist (HT-blueschist) and eclogite facies in eastern  
111 Queyras (Agard et al., 2001; Tricart and Schwartz, 2006; Schwartz et al., 2009). This  
112 blueschist domain is structurally above the Monviso eclogitic ophiolite. In this massif, the  
113 metasedimentary component is very small (< 20 vol.%) relative to the voluminous oceanic  
114 lithosphere (Schwartz et al., 2001). The serpentinite bodies are located along detachments and  
115 constitute a large volume of the eastern boundary of the massif (Schwartz et al., 2001,  
116 Angiboust et al., 2012). The Monviso ophiolite corresponds to the subduction channel  
117 (Guillot et al., 2009).

### 118 **3. Sampling strategy**

119 The Chenaillet-Queyras-Monviso transect is a unique natural laboratory for observing  
120 mineral changes in serpentinite along an increasing metamorphism gradient. However, there  
121 are no directly applicable thermal calibrations in serpentinites; therefore, we propose to  
122 estimate the thermal conditions by applying the method of Raman spectroscopy of  
123 carbonaceous material (RSCM) to the metasediments associated with the serpentinites to  
124 obtain the  $T_{\max}$  experienced by the serpentinites. A thermal transect is realized, according to  
125 25 metasediment samples from the Chenaillet to the Monviso (Fig. 1a, Table 1). These  
126 sediments are Cretaceous calcschists derived from foraminifera oozes (Deville et al., 1992).  
127 The lithology of each sample is not homogeneous due to the variation in carbonate-clay  
128 proportions. Moreover, the carbonate contents result both from biogenic production (pelagic  
129 foraminifera) and from detrital input (calciturbidites). The samples are strongly deformed, and  
130 the main schistosity is dominated by phengite, quartz, calcite and oxides. Glaucofane and  
131 pseudomorphs of lawsonite and zoisite are also present. Along this thermal transect, 7  
132 serpentinites have been studied (Fig. 1a). The serpentinite samples were taken from the cores  
133 of hecto-metric serpentinite bodies; these bodies were embedded in the metasediments from  
134 which the metasediment samples were acquired. These serpentinites escaped alpine  
135 deformations and preserved the oceanic mesh textures. Sample ICH2 comes from the  
136 ophiolitic Chenaillet massif. This sample records a low degree of metamorphic conditions,

137 with sea-floor metamorphism (Mével et al., 1978) overprinted by sub-greenschist facies  
138 conditions ( $P < 4$  kbar;  $T \sim 200$ - $300^{\circ}\text{C}$ ; Goffé et al., 2004) related to alpine metamorphism.  
139 Sample CR02 comes from the Cristillan massif at the western boundary of the Schistes lutrés  
140 complex in the LT-blueschist domain (Fig. 1). Two samples come from the medium-  
141 temperature blueschist domain (MT-blueschist) of the Schistes lutrés complex: RQ23 from  
142 the Rocca Nera massif and RQ16 from the Eychassier massif. Samples BB01 (Bric Bouchet  
143 massif) and RQ01 (Traversette massif) come from the HT-blueschist domain of the Schistes  
144 lutrés complex. The final sample, Vi01, comes from the Monviso eclogitic ophiolite.

#### 145 **4. Temperature estimates from Raman spectroscopy of carbonaceous** 146 **material (RSCM)**

##### 147 4.1. Analytical conditions

148 Raman spectroscopy on carbonaceous material (RSCM) is based on the quantitative  
149 degree of graphitization of the organic material during regional metamorphic processes. The  
150 graphitization phenomenon corresponds to the solid-state transformation of organic matter  
151 into carbonaceous material. The structure of carbonaceous matter is not sensitive to the  
152 retrograde history related to the exhumation of metamorphic rocks. The progressive  
153 graphitization process can be used to estimate the peak temperature ( $T_{\text{max}}$ ) reached by a given  
154 sample (Beysac et al., 2002, 2003). The degree of graphitization appears to be independent  
155 of the metamorphic pressure, although a minimum pressure is required for the graphitization  
156 process to take place (Quirico et al., 2009). This thermometer is based on the quantification of  
157 the degree of ordering of the carbonaceous material, using the R2 area ratio between the G,  
158 D1 and D2 bands ( $R2 = D1/[G+D1+D2]$ ) extracted from the Raman spectra (Beysac et al.,  
159 2002). The R2 ratio is linearly correlated with the  $T_{\text{max}}$  of the metamorphic cycle ( $T_{\text{max}}(^{\circ}\text{C}) =$   
160  $-445 \times R2 + 641$ ). This correlation may be used as a thermometer with an intrinsic error  
161 calibration of  $50^{\circ}\text{C}$  due to the petrological data used for calibration and a relative accuracy of  
162 approximately  $15^{\circ}\text{C}$  (Beysac et al., 2007).

163 Raman spectroscopy was performed at the ENS-Lyon using a Horiba Jobin-Yvon  
164 LabRam HR800 apparatus. The excitation was realized by an argon laser with a wavelength  
165 of 514 nm. An Olympus<sup>TM</sup> BX30 open microscope equipped with a  $\times 100$  objective lens was  
166 coupled to the spectrometer to focus the laser beam onto an area that was  $1 \mu\text{m}$  in diameter.  
167 The backscatter of the Raman signal was collected. The acquisition duration was

168 approximately 120 s distributed over two accumulating cycles, with a laser power of  
169 approximately 700  $\mu$ W at the sample surface. The signal was dispersed using a 1800  
170 lines/mm grating. The Raman spectrometer was calibrated with a silicon standard. For each  
171 sample, 11 to 13 spectra were recorded (noted 'n' in Table 1). The baseline correction, peak  
172 position, and band width were determined using the Peakfit© software.

#### 173 4.2. $T_{\max}$ results

174 From west to east, the Raman spectra show a decrease of the D1 peak area associated  
175 with a decrease in the width of the G band, resulting in a decrease of the R2 ratio (Fig. 1b).  
176 This trend in the R2 ratio is compatible with a  $T_{\max}$  increase in the metamorphic samples  
177 (Beysac et al., 2007; Lanari et al., 2012). The  $T_{\max}$  estimates by RSCM thermometry range  
178 from  $330 \pm 20^\circ\text{C}$  to  $520 \pm 20^\circ\text{C}$  (Table 1). The projection of the estimated  $T_{\max}$  along a WSW  
179 to ENE profile (XX' in Fig. 1c) shows a progressive increase of  $T_{\max}$ . This increase in  
180 temperature is compatible with the metamorphic gradient already proposed by Tricart and  
181 Schwartz (2004) in the studied area. The temperature increase from west to east is also  
182 consistent with the increase in pressure along a low-temperature subduction-related  
183 geothermal gradient (Goffé et al., 2004; Lardeaux et al., 2006, Angiboust et al., 2012). This  
184 relationship allows us to associate a pressure maximum with the  $T_{\max}$  estimated by RSCM.  
185 The sub-greenschist facies domain of the Chenaillet massif corresponds to a P-T range of  $P < 4$   
186 kbar and  $T \sim 200\text{-}300^\circ\text{C}$ . The LT-blueschist domain corresponds to P-T conditions of  $P = 9\text{-}$   
187  $11$  kbar and  $320 < T < 360^\circ\text{C}$ ; the MT-blueschist domain indicates P-T conditions of  $10\text{-}12$   
188 kbar and  $340\text{-}390^\circ\text{C}$ ; the HT-blueschist domain corresponds to P-T conditions of  $12 < P < 15$   
189 kbar and  $380 < T < 470^\circ\text{C}$ ; and the eclogitic domain indicates conditions of  $20 < P < 26$  kbar  
190 and  $480 < T < 520^\circ\text{C}$ .

## 191 5. XRD serpentinites characterization

### 192 5.1. Experimental conditions

193 The  $< 2$  mm fraction of the serpentinite samples was powdered using a McCrone  
194 micronizing mill and washed with  $\text{H}_2\text{O}$ . The resulting slurry was centrifuged and freeze-dried  
195 before being prepared as a randomly oriented mount. The XRD patterns were recorded with a  
196 Bruker D5000 powder diffractometer equipped with a SolX Si(Li) solid state detector from  
197 Baltic Scientific Instruments using  $\text{CuK}\alpha$  1+2 radiation. The intensities were recorded at



198 0.04° 2-theta step intervals from 5 to 90° (5 s counting time per step) for bulk serpentinite  
199 mineralogy determination. The XRD detection level was approximately one percent (< 1%).

## 200 5.2. Results

201 The XRD results and the mineralogical assemblages are presented in Figure 2 and  
202 Table 2. All of the XRD lines of the samples are dominated by serpentine minerals  
203 (serpentine species > 90%) associated with magnetite (Fig. 2). Brucite is not observed;  
204 however, mineral species are not detected below a concentration of 1 wt%. The serpentinite  
205 sampled in the Chenaillet massif (ICH2) is composed of serpentine, magnetite, chlorite and  
206 rare magmatic clinopyroxene. The serpentinites sampled in the LT-blueschist (CR02) and  
207 MT-blueschist (RQ23 and RQ16) domains present mineralogical assemblages dominated by  
208 serpentine and minor magnetite. In Sample RQ16, chlorite is detected. The serpentinites from  
209 the HT-blueschist (BB01 and RQ01) and eclogitic (Vi01) domains are composed of  
210 serpentine, metamorphic olivine and magnetite. The mineral antigorite is detectable in the  
211 XRD spectrum of Sample BB01 (Fig. 2 and Table 2). The presence of olivine is related to the  
212 onset of antigorite destabilization during the dehydration reaction (Evans, 2004). This  
213 secondary olivine appears in Samples RQ01 and Vi01. In Sample Vi01, clinopyroxene and  
214 chlorite are detected, in accordance with the microscopic observations (Auzende et al., 2006).  
215 To precisely identify the varieties of serpentines, we used Raman spectroscopy coupled with  
216 microscopic observations.

## 217 6. Serpentine characterizations

### 218 6.1. Raman spectrometry

219 The different serpentine species have been characterized by Raman spectroscopy  
220 coupled with petrographic observations of polished thin-sections of serpentinites. The Raman  
221 signal was acquired over approximately 90 s in three accumulating cycles, with a laser output  
222 power on the sample surface adjusted between 10 and 20 mW. The spectral resolution was 1  
223  $\text{cm}^{-1}$  using 1800 lines/mm grating. A reproducibility of 1  $\text{cm}^{-1}$  was attained on successive  
224 spectra of a given mineral sample. The spectral regions from 150 to 1150  $\text{cm}^{-1}$  and from 3600  
225 to 3720  $\text{cm}^{-1}$  were investigated because they include the lattice vibrational modes and the OH  
226 stretching mode region that is characteristic of serpentine species, respectively (Rinaudo et al.,  
227 2003; Auzende et al., 2004; Groppo et al., 2006).

228 The bands detected in these spectral regions are indicative of the crystalline structure of the  
229 sample. For each spectra, the assignment of the band position and the full width at half  
230 maximum were determined using the Peakfit© software.

231 In the low wavenumber region, four main peaks (near 230, 390, 690 and 1100  $\text{cm}^{-1}$ )  
232 characterize the spectra of lizardite and chrysotile (Fig. 3a). Intense peaks specific to the  
233 antigorite spectrum occur at lower wavenumbers (226, 373, 680 and 1043  $\text{cm}^{-1}$ ) and are much  
234 broader than those corresponding to other serpentines (Fig. 3b). The differences between  
235 chrysotile and lizardite spectra, although small, can be clearly identified by the sharpness of  
236 the Raman lines. In particular, a single band at 1100  $\text{cm}^{-1}$  is observed in chrysotile, whereas  
237 several convoluted bands are observed between 1060 and 1100  $\text{cm}^{-1}$  in lizardite (Fig. 3a). In  
238 the high wavenumber region, the convoluted vibrational modes attributed to the OH stretching  
239 of serpentine are located between 3600 and 3720  $\text{cm}^{-1}$ . In chrysotile, the most intense band  
240 occurs at 3697  $\text{cm}^{-1}$ , with a distinct shoulder at 3690  $\text{cm}^{-1}$  and a weak band at 3648  $\text{cm}^{-1}$ .  
241 Lizardite has a markedly different spectrum (Fig. 3a): the most intense band occurs at a lower  
242 frequency (minimum at 3680  $\text{cm}^{-1}$ ) with a well-defined high frequency band at 3703  $\text{cm}^{-1}$ . In  
243 antigorite, the spectra are characterized by a broad band at 3670  $\text{cm}^{-1}$  and a sharp band at  
244 3700  $\text{cm}^{-1}$  (Fig. 3b). Mixed lizardite/antigorite spectra are also observed (Fig. 3c). In the low  
245 wavenumber region, the peak at 1043  $\text{cm}^{-1}$  is present (as in antigorite), but the peak at 373  $\text{cm}^{-1}$   
246 is shifted to  $\sim 380 \text{ cm}^{-1}$  (toward the classical  $\sim 390 \text{ cm}^{-1}$  peak of lizardite). In the high  
247 wavenumber region, the second “antigorite” peak at 3700  $\text{cm}^{-1}$  is still present, but the most  
248 intense peak is located between 3670  $\text{cm}^{-1}$  and 3680  $\text{cm}^{-1}$ , in an intermediate position between  
249 the most intense “antigorite” and “lizardite” peaks (Fig. 3c).

## 250 6.2. Petrology

251 The repartition of the serpentine species correlates with the  $T_{\text{max}}$  along the XX' profile  
252 (Fig. 1c). Lizardite dominates in the greenschist and LT-blueschist facies (from  $< 300^\circ\text{C}$  to  
253  $360^\circ\text{C}$ ), while antigorite progressively appears in the LT-blueschist facies. Antigorite  
254 becomes progressively dominant in the MT-blueschist facies ( $340\text{-}390^\circ\text{C}$ ), ultimately  
255 becoming the sole serpentine species in the HT-blueschist and eclogite facies ( $T > 380^\circ\text{C}$ ).  
256 Chrysotile is observed in all of the high pressure serpentinite samples, filling in the late cracks  
257 or micro-fractures related to the samples' final exhumation at the ductile/brittle transition. In  
258 the following paragraphs, we detail the mineralogy and texture of the serpentinites according

259 to the degree of metamorphism. The  $T_{\max}$  for each serpentinite sample refers to the  $T_{\max}$   
260 estimated from the associated metasediments.

261 Sample ICH2 ( $T < 300^{\circ}\text{C}$ ) is characterized by the development of a mesh texture underlined  
262 by magnetite, which suggests the classical reaction of olivine + water = serpentine (mesh) +  
263 magnetite  $\pm$  brucite (Figs 4a and 4a'). The Raman spectrometry shows that lizardite is the  
264 dominant serpentine species. Locally, the mesh is crosscut by secondary chrysotile veins.

265 Sample CR02 ( $T_{\max} = 340^{\circ}\text{C}$ ) shows a mesh texture consisting of lizardite surrounded by  
266 magnetite (Figs 4b and 4b'). Locally, secondary antigorite (representing less than 10% of the  
267 matrix) crystallized at the boundaries of relict brownish lizardite crystals. We assign the  
268 lizardite crystallization to the sea-floor metamorphism (oceanic serpentinization) and the  
269 antigorite crystallization to the LT-blueschist metamorphism.

270 Sample RQ23 ( $T_{\max} = 356^{\circ}\text{C}$ ) is equally composed of antigorite and relics of lizardite (Figs 4c  
271 and 4c'). The antigorite crystallized at the grain boundaries of the lizardite relics and as  
272 millimeter-sized antigorite patches with an interlocking texture. The lizardite relics present  
273 the typical mixed lizardite-antigorite Raman spectra, suggesting the partial mineral  
274 replacement of oceanic lizardite by metamorphic micrometric antigorite. Magnetite locally  
275 underlines the original mesh texture.

276 Sample RQ16 ( $T_{\max} = 373^{\circ}\text{C}$ ) shows the same mineral relationship as Sample RQ23, with  
277 some relics of lizardite that have a mixed character between antigorite and lizardite (Figs 4d  
278 and 4d'). The antigorite that developed at the grain boundaries enlarged and the blades of  
279 antigorite crystallized. In this sample, the proportion of magnetite decreased, but chlorite  
280 crystallized (Fig. 2), which suggests the development of chlorite at the expense of magnetite  
281 in the presence of aluminum.

282 Sample BB01 ( $T_{\max} = 402^{\circ}\text{C}$ ), coming from the HT-blueschist unit, is composed only of  
283 antigorite and a string of magnetite that underlies the previous oceanic mesh texture (Figs 5a  
284 and 5a'). The patches are composed of sub-millimetric interlocking blades of antigorite. The  
285 presence of antigorite is readily detectable in the XRD spectra (Fig. 2).

286 In Sample RQ01 ( $T_{\max} = 463^{\circ}\text{C}$ ), only antigorite serpentine is observed (Figs. 5b and 5b').  
287 The mesh, still underlined by magnetite and bastite (free of magnetite), remains preserved,  
288 which suggests a static crystallization of antigorite at the expense of oceanic lizardite. The  
289 olivine peak appears in the XRD spectra.

290 In Sample Vi01 ( $T_{\max} = 498^{\circ}\text{C}$ ), antigorite is again the sole serpentine species (Figs. 5c and  
291 5c'). Similar to Sample RQ01, the pseudomorphic texture (mesh and bastite) is preserved and  
292 underlined by magnetite, but antigorite blades of a few hundred microns have started to  
293 obliterate the mesh texture. In this sample, we observed olivine and chlorite signals in the  
294 XRD spectra (Fig. 2).

### 295 6.3. Electron microprobe

296 In addition, the major element concentrations of the serpentine species were acquired  
297 using a Cameca SX100 electron microprobe at the “Laboratoire Magma et Volcans”  
298 (Clermont Ferrand, France). The operating conditions were as follows: an accelerating voltage  
299 of 15 kV, a sample current of 15 nA and a counting time of 10 s/element, except for Ni (20 s).  
300 The standards used were albite (Na), forsterite (Mg), orthoclase (K), wollastonite (Ca and Si),  
301  $\text{MnTiO}_3$  (Ti and Mn),  $\text{Cr}_2\text{O}_3$  (Cr), fayalite (Fe), olivine (Ni), and synthetic  $\text{Al}_2\text{O}_3$  (Al).  
302 Representative analyses are reported in Table 3. Serpentine phases can contain over 13 wt%  
303 of water in their crystal structure. The volatile content is not always correlated with the degree  
304 of serpentinization because other phases (e.g., talc, brucite, chlorite, clay minerals) associated  
305 with serpentine minerals can influence this measurement. In the studied samples, the volatile  
306 content (100% – wt% major elements) varies from 12.54 to 15.67 wt% (Table 3). We did not  
307 observe any correlation between the volatile content in the serpentine minerals and the degree  
308 of metamorphism. However, we did observe a relationship between the homogenization of the  
309 serpentine composition and the degree of metamorphism (Fig. 6). When plotted on the  $\text{SiO}_2$   
310 vs.  $\text{Al}_2\text{O}_3$  field, the lower metamorphic samples are scattered, while the higher metamorphic  
311 samples are grouped closer to the end-member antigorite composition (Fig. 6), with 44 wt%  
312  $\text{SiO}_2$  and 1.03 wt%  $\text{Al}_2\text{O}_3$  (Deer et al., 1992). The samples with an intermediate degree of  
313 metamorphism, dominated by mixed lizardite/antigorite, fall between the lizardite and  
314 antigorite fields. It is also noticeable that the  $\text{Al}_2\text{O}_3$  content decreases and the  $\text{SiO}_2$  content  
315 increases with the degree of metamorphism (Fig. 6). This increase of  $\text{SiO}_2$  in serpentine is  
316 correlated with a slight increase of whole-rock  $\text{SiO}_2$  content, from ~39.4 wt% at grade 0 to  
317 ~40.5 wt% (Lafay et al., in press).

## 318 7. Discussion

### 319 7.1. Lizardite to antigorite transitions

320 The aim of this study is to develop a combined mineral investigation of serpentinites  
321 and compare the results with  $T_{\max}$  estimates from associated metasediments. This approach  
322 allows us to indirectly constrain the P-T conditions of the phase changes in natural  
323 serpentinites and to compare our results with previous experimental works. Moreover, most of  
324 the published results concerning the changes from lizardite/chrysotile to antigorite are  
325 acquired through experiments performed at intermediate pressures of approximately 6-7 kbar  
326 (e.g., O'Hanley (1996)); our samples allow us to characterize this transition at higher pressures  
327 (between 4 and 26 kbar) that are pertinent to the P-T conditions in subduction zones. Our  
328 study highlights the following important points:

329 1-The early serpentinization stage is related to the hydrothermalism of the oceanic lithosphere  
330 and generates lizardite-bearing mesh textures (Figs. 7a and 7b).

331 2-In the lowest-grade metamorphic units (sub-greenschist facies;  $P < 4$  kbar;  $T \sim 200$ - $300^{\circ}\text{C}$ ),  
332 antigorite is absent and lizardite is the dominant phase. Such observations are in agreement  
333 with previous experimental results (e.g., Evans, 2004).

334 3-In polymetamorphic weakly deformed domains, the oceanic mesh textures are preserved in  
335 all peak P-T conditions (Fig. 7b). At the initial stages, antigorite appears along the lizardite  
336 grain boundaries (Fig. 7c) and at more evolved stages overprints lizardite (Fig. 7d), preserving  
337 the initial textures (mesh and bastite). This observation argues against the commonly  
338 proposed idea that antigorite preferentially crystallizes within deformed domains (Miyashiro  
339 et al., 1969).

340 4-Antigorite crystallizes in two distinct crystallographic sites. Antigorite first appears in LT-  
341 blueschist at  $320^{\circ}\text{C}$  at the lizardite grain boundary, forming a network of veins (Fig. 7c).  
342 These veins grow with the degree of metamorphism, from  $\sim 20$   $\mu\text{m}$  up to  $150$   $\mu\text{m}$  (Fig. 7d) in  
343 the MT-blueschist facies (up to  $390^{\circ}\text{C}$ ). Such crystallization texture is typical of mineral  
344 replacement by dissolution-precipitation processes in the presence of a free fluid (Putnis,  
345 2009; Lafay et al., 2012).

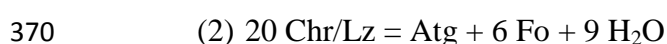
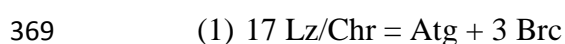
346 The second crystallographic site is where antigorite crystallizes in the cores of lizardite grains  
347 in MT-blueschist facies conditions (Fig. 7d). Raman spectrometry shows mixed  
348 lizardite/antigorite spectra, suggesting an intimate association of lizardite and antigorite at the  
349 micron-scale (Fig. 7a). This intimate mineral association suggests a solid-state transition (Eda  
350 et al., 2006). The solid-state crystallization of antigorite at the expense of lizardite is partial

351 between 340 and 380°C and complete above in HT-blueschist and eclogitic facies conditions  
352 (Figs. 7a and 7e).

## 353 7.2. Lizardite to antigorite reactions

354 In the literature, it is typically proposed that the thermal stability fields of antigorite  
355 and lizardite overlap between temperatures of 250 and 500°C, while chrysotile is metastable  
356 (e.g., Evans, 2004). We can refine the relative stability fields of lizardite and antigorite from  
357 our observations of high-pressure natural samples. It is well known that serpentinization is a  
358 complex process controlled by time- and site-dependent variables such as fluid/rock ratios,  
359 silica activity, oxygen fugacity and pH (Evans, 2004; Frost and Beards, 2007). Lizardite and  
360 antigorite are co-stable (or at least the lizardite is not completely destabilized) between 320  
361 and 390°C for pressures greater than 9 kbar (Fig. 7). It is noticeable that below 300°C and 4  
362 kbar, antigorite is not observed. This observation contradicts the phase diagram of O'Hanley  
363 (1996), in which antigorite appears at 250°C at low pressures, and suggests that antigorite  
364 crystallization is not only temperature dependent but also may be pressure dependent (Ulmer  
365 and Trommsdorff, 1995; Wunder and Schreyer, 1997).

366 Thermodynamic work on the serpentinite multisystem predicts the crystallization of antigorite  
367 (Atg) at the expense of chrysotile (Chr) or lizardite (Lz), according to the following reactions  
368 (Evans, 2004) with forsterite (Fo) and brucite (Brc):

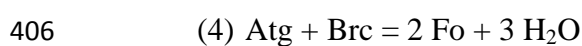


372 Reactions (1) and (2) are thermodynamically favorable for temperatures between 300 and  
373 400°C (Fig. 8), while at lower temperatures, the conversion of lizardite to antigorite is  
374 thermodynamically more efficient with a modest introduction in the serpentinite multisystem  
375 of SiO<sub>2</sub> (e.g., Evans, 2004). Brucite is not detected as a byproduct of antigorite; however, we  
376 can conclude that brucite is not present in the studied samples below the XRD concentrations  
377 (< 1 wt%), although brucite is detected in the Monviso serpentinites (Debret, pers. com.). The  
378 absence of brucite could be interpreted either as the result of a lower olivine hydration with  
379 respect to enstatite hydration (precluding the release of Mg necessary to the brucite  
380 crystallization) or as the consumption of brucite during prograde reactions. Metamorphic

381 olivine is rare and observed in the studied samples at temperatures higher than 460°C. Thus,  
382 Reactions (1) and (2) cannot explain the crystallization of antigorite at low temperatures (<  
383 330°C according to Evans (2004)). In contrast, we clearly observe the direct crystallization of  
384 veins of antigorite at the expense of lizardite starting at 320°C in the presence of  
385 metasediments. Moreover, we observe a general enrichment in SiO<sub>2</sub> throughout the antigorite  
386 (Fig. 6) that is correlated with a whole-rock SiO<sub>2</sub> enrichment along the metamorphic gradient  
387 (Lafay et al., in press). This finding suggests the onset of antigorite crystallization at 320°C,  
388 assisted by SiO<sub>2</sub>-rich fluids, according to Reaction (3), by dissolution-precipitation processes  
389 (Fig. 8). Rüpke et al. (2004) have shown that above a depth of 50 km (T < 300°C), oceanic  
390 sediments release almost 50% of their initial water content. This fluid is enriched in volatile  
391 elements and silica and potentially hydrated the mantle wedge (e.g., Bebout and Barton, 1989;  
392 Bebout et al., 1999). Fluid exchange between the subducted oceanic sediments and our  
393 serpentinite samples is clearly demonstrated by the enrichment of volatile elements,  
394 particularly in the antigorite (Lafay et al., in press). Thus, the most favorable circumstances  
395 for silicification are waters that are equilibrated with sedimentary rocks in the Alpine wedge  
396 and that percolated into the serpentinites, as observed in the Catalina Schist in California  
397 (Bebout and Barton, 1989, Bebout et al., 2004).

398 As already discussed, we also observed the solid-state transformation of lizardite into  
399 antigorite, suggesting the progression of Reaction (1) between 340 and 380°C. In the natural  
400 samples presented here, this reaction occurred at slightly higher temperatures than were  
401 predicted by thermodynamic calculations (260-310°C at 10 kbar, Evans, 2004).

402 At a minimum temperature of 460°C, secondary olivine crystallized (Fig. 2), which suggests  
403 the onset of antigorite destabilization. This is compatible with a decrease of the whole-rock  
404 L.O.I from 13 wt% to < 12 wt% (Lafay et al., in press). According to Evans (2004), it  
405 corresponds to the reaction:



407 In the natural samples studied, this reaction occurred at  $\geq 460^\circ\text{C}$  and  $P > 12 \text{ kbar}$ , as  
408 predicted by thermodynamic calculations (Evans, 2004). However, this reaction involves  
409 brucite, which we did not detect in the samples. Thus, we propose that the brucite produced  
410 by Reaction (1) at lower temperatures is completely consumed by Reaction (4) along the  
411 subduction gradient (Fig. 8).

## 412 **8. Conclusion**

413 Raman spectroscopy and XRD are efficient methods for identifying different species  
414 of serpentine because serpentine optical identification is difficult. In addition, various  
415 serpentine species are often interpenetrated, and Raman micro-spectrometry proves to be a  
416 useful micro-characterization tool for resolving structural differences at the scale of the  
417 various grain generations. The application of these methods to samples from the Alps shows  
418 that lizardite is preserved under sub-greenschist facies conditions in oceanic environment and  
419 ophiolites. Antigorite progressively replaces lizardite under LT- to MT-blueschist facies  
420 conditions (320-390°C) and is the sole serpentine phase under HT-blueschist to eclogites  
421 facies conditions (> 380°C). Our study shows several generations of serpentine in sea-floor  
422 and metamorphic processes. Below 320°C, lizardite and chrysotile are the only stable  
423 serpentine species. Between 320°C and 390°C, lizardite and antigorite coexist and antigorite  
424 develops at the expense of lizardite through two processes. Antigorite first appears at the  
425 lizardite grain boundaries through dissolution-precipitation processes in the presence of SiO<sub>2</sub>.  
426 We propose that this fluid comes from the local dehydration of the surrounding  
427 metasediments in subduction environments. Antigorite also crystallizes in the cores of the  
428 lizardite mesh through solid-state transitions at slightly higher temperatures, between 340°C  
429 and 380°C. This transition is characterized by mixed lizardite/antigorite Raman spectra.  
430 Above 390°C and 12 kbar, lizardite is absent and antigorite is the only stable serpentine  
431 species. Above 460°C, antigorite begins to destabilize into olivine. We did not detect  
432 brucite in any of the studied samples, although this mineral is theoretically involved in the  
433 transition from lizardite to antigorite. We propose that the brucite produced at low  
434 temperatures is consumed at higher temperatures and remains a transition phase. This process  
435 would explain why brucite is rarely observed in natural samples in oceanic and subduction  
436 environments worldwide.

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619

620 **Figure captions**

621 Fig. 1. (a) Tectonic sketch map of the southwestern Alps, and  $T_{\max}$  results of metasediments  
622 obtained by the RSCM method. Seven serpentinites were sampled along the paleo-subduction  
623 zone from sub-greenschist (Chenaillet) to eclogitic (Monviso) facies conditions. (b)  
624 Characteristic evolution of Raman spectra from selected metasediments. Positions of the  
625 graphite G band and D1, D2, D3 defect bands are indicated. For each spectrum, the value of  
626 the mean R2 ratio ( $R2=D1/[G+D1+D2]$  peak area ratio) is given (see Table 1). (c)  $T_{\max}$  results  
627 projected onto a WSW – ENE cross section (XX').

628

629 Fig. 2. XRD patterns of serpentinites. The mineralogy is dominated by a magnetite and  
630 serpentine assemblage. The antigorite peaks (black star) and olivine (Ol) appear in samples  
631 RQ01 and Vi01. The presence of olivine is due to the onset of antigorite destabilization into  
632 olivine.

633

634 Fig. 3. Raman spectra acquired from different varieties of serpentine from the study area in  
635 low frequency ( $150-1150\text{ cm}^{-1}$ ) and OH stretching ( $3600\text{ to }3720\text{ cm}^{-1}$ ) ranges. The  
636 characteristic bands of antigorite ( $373, 1043, 3670\text{ and }3700\text{ cm}^{-1}$ ) and lizardite ( $390, 3680,$   
637  $3703\text{ cm}^{-1}$ ) are indicated in grey. (a) Raman spectra of lizardite and chrysotile. (b) Raman  
638 spectra of antigorite related to the  $T_{\max}$ . (c) Raman spectra of mixed lizardite/antigorite  
639 serpentine.

640

641 Fig. 4. Photomicrographs of characteristic textures of serpentinite from the study area: Atg,  
642 antigorite; lz, lizardite; Chr, chrysotile; Mag, magnetite; x, polarized light; x', crossed-  
643 polarized light. The  $T_{\max}$  obtained from the associated metasediments is also indicated.

644 (a-a'). Sample ICH2 (Chenaillet massif). Mesh texture developed from olivine is observed in  
645 locations where lizardite is the only developed serpentine species. At the top of the image,  
646 secondary veins infilled by chrysotile cross-cut the mesh texture.

647 (b-b'). Sample CR02 comes from the low-temperature blueschist domain (Cristillan massif).  
648 The sample is dominated by mesh texture underlined by lizardite. Secondary antigorite  
649 crystallized at the boundary of the lizardite minerals. In the antigorite zone, relics of lizardite  
650 (brownish minerals) are still present.

651 (c-c'). Sample RQ23 comes from medium-temperature blueschist domain (Rocca Bianca  
652 massif). The sample is equally dominated by lizardite and antigorite. In the lizardite-dominant  
653 zone (greenish color), the mesh texture is partly preserved; however, antigorite developed at  
654 the expense of lizardite at the grain boundaries. Antigorite minerals with interlocked  
655 microstructures also form millimeter-sized patches that are free of lizardite relics.

656 (d-d'). Sample RQ16 comes from the intermediate-temperature blueschist domain (Refuge du  
657 Viso). The sample is dominated by antigorite minerals, which are developed in a dense  
658 network of veins at the expense of lizardite preserved in mesh texture.

659

660 Fig. 5. Photomicrographs of characteristic textures of serpentine species from the western  
661 Alps: Atg, antigorite; Lz, lizardite; Chr, chrysotile; Mag, magnetite; x, polarized light; x',  
662 crossed-polarized light. The  $T_{\max}$  obtain on the associated metasediments is also indicated.

663 (a-a'). Sample BB01 comes from the high-temperature blueschist domain (Bric Bouchet  
664 massif). This sample is dominated by antigorite. The magnetite underlines the early mesh  
665 structure.

666 (b-b'). Sample RQ01 comes from the high-temperature blueschist domain (Traversette  
667 massif). In this sample, only antigorite is observed. Mesh and bastite textures are well  
668 preserved, suggesting a static crystallization of antigorite, most likely at the expense of early  
669 lizardite produced during ocean floor metamorphism.

670 (c-c'). Sample Vi01 comes from Monviso eclogitic ophiolite. The antigorite is the only  
671 serpentinite species that preserves the mesh texture underlined by magnetite.

672

673 Fig. 6. Microprobe analyses (in weight %) of serpentinite samples plotted in an  $\text{Al}_2\text{O}_3$  versus  
674  $\text{SiO}_2$  diagram (cf Table 3). The arrow indicates the metamorphic trend from sub-greenschist  
675 to eclogitic metamorphic facies conditions. The antigoritization processes in the serpentinites  
676 are characterized by a chemical homogenization associated with the increase in the  
677 metamorphic conditions.

678

679 Fig. 7. Idealized sketch determined from natural serpentinites that shows the evolution of the  
680 antigoritization processes under a HP metamorphic gradient. (a) Characteristic Raman spectra  
681 of serpentine species from the study area. The bands of antigorite (373, 1043, 3670 and 3700  
682  $\text{cm}^{-1}$ ) are indicated in grey. (b) In sub-greenschist conditions, only lizardite is present. (c) In  
683 LT-blueschist, antigorite appears along the lizardite grain boundaries via a dissolution-  
684 precipitation process. (d) In MT-blueschist, the antigorite becomes the major phase. The veins  
685 of antigorite at the lizardite grain boundaries widen and the cores of lizardite show a mixed  
686 lizardite/ antigorite Raman spectra related to the onset of the solid-state transition. (e) In HT-  
687 blueschist, antigorite becomes the sole serpentine variety. Antigorite develops infra-  
688 millimetric blades superimposed over the original mesh texture.

689

690 Fig. 8. Phase diagram of antigorite and lizardite (after Evans, 2004): Lz, lizardite; Atg,  
691 antigorite; Chr, chrysotile; Fo, forsterite; Tlc, talc; Brc, brucite. Reactions (1) and (3)  
692 correspond to the onset of the reactions while (1') and (3') correspond to the end of these



693 reactions with the complete consumption of lizardite. Metamorphic facies are from Spear  
694 (1993). The natural stability field domain of coexisting lizardite and antigorite is restricted to  
695 a temperature range between ~320 and 390°C. At 390°C and above, the lizardite is entirely  
696 replaced by antigorite. Above 460°C, Reaction (4) results in the onset of crystallization of  
697 olivine. Between 320 and 390°C, the antigorite develops though Reaction (3) in the presence  
698 of SiO<sub>2</sub>-rich fluids by dissolution-precipitation processes. Between 340 and 380°C, Reaction  
699 (2) is also observed in the core of lizardite antigorite by solid-state transformation.

700

701 Table 1. RSCM results with longitude (Long.) and latitude (Lat.) in decimal degrees  
702 (WGS84), number of Raman spectra (n), R2 ratio (mean and standard deviation) and T<sub>max</sub>  
703 (mean and 1-σ uncertainty).

704

705 Table 2. Mineral assemblage of the studied serpentinites as detected by XRD, with (+ + +)  
706 major phase, (+) minor phase (<10%), and (-) absent or below detection limit (<1%). Facies  
707 metamorphic conditions and T<sub>max</sub> are also given. The black star indicates the presence of  
708 antigorite.

709

710 Table 3. Representative microprobe analyses of serpentine minerals from alpine serpentinites.  
711 All values are in wt% (b.d.l. = below detection limit; n.d. = not determined).