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Protracted hydrothermal alteration recorded at the microscale in the Chenaillet ophicarbonates (Western Alps): Insights from *in situ* $\delta^{18}O$ thermometry in serpentine, carbonate and magnetite

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Abstract

The study of serpentinites and ophicarbonates from ophiolitic terrains provides a three-dimensional perspective on the hydration and carbonation processes affecting modern oceanic lithosphere. The Chenaillet ophiolite (western Alps) is interpreted as a fragment of an oceanic core complex that resembles a modern slow spreading center, and it was weakly affected by Alpine metamorphism. Ophicarbonates from the Chenaillet ophiolite were targeted in this study for *in situ* analysis by Secondary Ion Mass Spectrometry (SIMS) of oxygen and carbon isotopes in serpentine, calcite, dolomite and magnetite. The high spatial resolution of SIMS allowed us to target different serpentine, carbonate and magnetite generations intergrown at scales ≤ 50 μm, and reveal systematic zoning in $\delta^{18}O$ with a range of 5.8‰ in serpentine (from 3.0 to 8.8‰, V-SMOW), 21.2‰ in carbonate (9.4 to 30.6‰), and 5.6‰ in magnetite (–5.0 to –10.6‰). Coupled analysis of oxygen isotopes in seven different touching-pairs of co-crystallized serpentine+carbonate and serpentine+magnetite provides independent constraints on both the temperatures and $\delta^{18}O_{(water)}$ values during serpentinization and carbonation responsible for the formation of the Chenaillet ophicarbonates. The new stable isotope data and thermometric estimates can be directly linked to textural and petrographic observations. These new results identify at least four different stages of hydrothermal alteration in the Chenaillet ophicarbonates: (1) peridotite hydration during seafloor exhumation at temperatures down to 200-130 °C and water $\delta^{18}O$ values varying from 5 to 2‰, as documented by serpentine+magnetite in mesh textures; (2) carbonation during exhumation near the seafloor at temperatures as low as 10 °C assuming water $\delta^{18}O$ values of –1‰, as documented by the highest oxygen isotope ratios in texturally older calcite; (3)

serpentinization and carbonation at temperatures up to 240 °C and water $\delta^{18}O$ values of 2-3‰, as documented by serpentine+magnetite in veins crosscutting mesh textures (T = 192±66 °C, $\delta^{18}O_{(water)}$ = 2±1‰, 2 standard deviation), serpentine+magnetite (T = 182±32 °C, $\delta^{18}O_{(water)}$ = 2±1‰) and serpentine+dolomite (T = 243±79 °C, $\delta^{18}O_{(water)}$ = 3±2‰) in recrystallized hourglass domains within serpentinite clasts, serpentine+dolomite (T = 229±50 °C, $\delta^{18}O_{(water)}$ = 3±1‰) and serpentine+calcite (T = 208±40 °C, $\delta^{18}O_{(water)}$ = 2±1‰) within the fine-grained calcite matrix surrounding serpentinite clasts; (4) late stage carbonation at temperatures down to 70-40 °C assuming water $\delta^{18}O$ values of 3 to –1‰, as documented by the highest oxygen isotope ratios in a large calcite vein crosscutting both serpentinite clasts and fine-grained carbonate matrix. We suggest that the textural and isotopic observations are consistent with a protracted serpentinization and carbonation of the lithospheric mantle that started during progressive exhumation to the seafloor and continued due to interaction with hot and isotopically shifted seawater, which circulated at depth in the oceanic crust and was then discharged near the seafloor, similar to modern mid-ocean ridge venting systems.

1. INTRODUCTION

Serpentinization and carbonation of ultramafic rocks occur over a wide range of environments and physical-chemical conditions. The majority of modern serpentinites form at slow and ultraslow spreading ridges during mantle unroofing and exhumation at the seafloor at temperatures varying from 500 °C to <100 °C (e.g., Mével, 2003; Barnes et al., 2009; Boudier et al., 2010; Bach et al., 2011; Rouméjon et al., 2018). Carbonation reactions resulting in the formation of veins and ophicarbonates (i.e., carbonated ultramafic breccias resulting from repeated tectonic and/or hydraulic fracturing of serpentinites) are usually associated with late stages of low-temperature alteration near the seafloor (Bonatti et al., 1974; Mével, 2003; Früh-Green et al., 2004; Manatschal and Müntener, 2009). Serpentinization of the subcontinental mantle is also documented at ocean-continent transition (OCT) boundaries (e.g., Iberia-Newfoundland rifted margins) where seawater infiltration is favored by crustal thinning and tectonic activity (e.g., Boillot et al., 1989; Skelton and Valley, 2000; Manatschal and Müntener, 2009; Schwarzenbach et al., 2013; Alt et al., 2018; Picazo et al., 2019). In addition to passive margins, serpentinization and carbonation of peridotite also occur at active margins and on continental settings. Ultramafic rocks exposed in ophiolitic terrains can undergo further hydration and carbonation due to low-temperature (<50 °C) interaction with meteoric water (e.g., Barnes and O'Neil, 1969; Barnes et al., 1978; Neal and Stanger, 1985; Streit et al., 2012; Barnes et al., 2013; Falk et al., 2016).

The study of ophiolitic terrains is fundamental to unravel the magmatic, tectonic and hydrothermal evolution of ocean basins from rift-drift and seafloor spreading stages to subduction initiation and final closure (Dilek and Furnes, 2014). In fact,

ophiolites represent an analogue for present-day oceanic crust and preserve the only evidence for ocean basins older than ~170 Ma (Dilek and Furnes, 2014; Pearce, 2014). Ophiolites provide better access than the one-dimensional drill cores from modern oceanic crust, but they often record intense alteration during their passage from rift to subduction/collision zone to mountain belt (Pierce, 2014; Staudigel et al., 2014). Constraining *P-T* conditions and fluid sources of hydration and carbonation reactions in ultramafic rocks from ophiolitic terrains is also important for better characterizing the conditions that favor dissolution and precipitation of carbonate minerals in these lithologies, with implications for better estimating the potential for permanent storage of CO_2 in ultramafic rocks (Kelemen and Matter, 2008; Kelemen et al., 2011). It is also crucial for tracing the mobilization and fluxes of water, carbon and fluid-mobile elements among Earth's different reservoirs (e.g., Scambelluri et al., 2004; Alt et al., 2012; Collins et al., 2015) and the production of fluids enriched in hydrogen, methane and other hydrocarbons both at near-surface conditions (Kelley et al., 2005; Miller et al., 2016) and in subduction zones (Vitale Brovarone et al., 2017).

Oxygen isotopes have been extensively used as geothermometers and tracers to determine the temperatures and fluid sources during peridotite hydration and carbonation in various tectonic settings (e.g., Wenner and Taylor, 1971, 1973; Agrinier and Cannat, 1997; Früh-Green et al., 1990, 1996; Barnes et al., 2009; Lafay et al., 2017; Noël et al., 2018; Rouméjon et al., 2018; Scicchitano et al., 2018a,b, 2020). This method requires knowledge of mineral-fluid or mineral-mineral oxygen isotope fractionation factors and assumption that isotope equilibrium between co-precipitated minerals and fluids was achieved and preserved. Measured $\delta^{18}O$ values in co-precipitated minerals can, then, be combined with corresponding calibrations of oxygen isotope fractionations to independently calculate both the equilibrium

127 temperature and the oxygen isotope composition of the interacting fluid. Several
128 studies (e.g., Wenner and Taylor, 1971; O'Hanley and Offler, 1992; Früh-Green et al.,
129 1996; Alt and Shanks, 2006; Barnes et al., 2009) have estimated serpentinization
130 temperatures and fluid $\delta^{18}O$ values using the equilibrium oxygen isotope fractionation
131 between coexisting serpentine and magnetite previously separated from the rock.
132 Geothermometry in carbonated serpentinites has recently been achieved using
133 carbonate clumped isotope techniques that allow calculating equilibrium temperatures
134 independently of the isotopic composition of the fluids from which carbonate formed
135 (e.g., Streit et al., 2012; Falk and Kelemen, 2015; de Obeso and Kelemen, 2018).
136 Studies based on mineral separates and clumped isotope techniques represent a
137 fundamental achievement in our understanding of the temperatures at which
138 serpentinization and carbonation of ultramafic rocks occur. Nevertheless, they likely
139 represent average estimates and overlook the larger complexity of these reactions
140 recorded at the microscale by the occurrence of multiple serpentine and carbonate
141 generations. In fact, recent *in situ* oxygen isotope studies by Secondary Ion Mass
142 Spectrometry (SIMS) in serpentinites and carbonated serpentinites from different
143 tectonic settings have shown a significant variation in the oxygen isotope composition
144 of serpentine and carbonate minerals recorded at the microscale (Noël et al., 2018;
145 Rouméjon et al., 2018; Scicchitano et al., 2018a, 2020). The high spatial resolution of
146 SIMS techniques allows the analysis of oxygen isotopes to be measured along
147 detailed traverses through co-precipitated host rock and vein minerals that are in
148 textural equilibrium at scales ≤ 50 μm (Turnier et al., 2020). Consequently, it is a
149 powerful tool for obtaining independent estimates of serpentinization temperatures
150 and fluid $\delta^{18}O$ values framed in a petrological context in rocks that record multiple
151 stages of fluid-rock interactions (e.g., Scicchitano et al., 2018b, 2020) as well as for

testing the achievement of isotopic equilibrium during serpentinization processes (e.g., Lafay et al., 2019).

In this study we apply SIMS techniques in combination with new reference materials (Scicchitano et al., 2020) to analyze oxygen and carbon isotopes in serpentine, carbonate (calcite, dolomite) and magnetite in order to unravel the complex fluid-rock history recorded at the microscale in ophicarbonate samples from the Chenaillet ophiolite. The fine-grained textures observed in the investigated samples can only be targeted by SIMS, which requires the use of matrix-matched reference materials (Valley and Kita, 2009). The new analytical capabilities provide unique constraints on oceanic hydrothermal alteration recorded in the Chenaillet ophiolite that were not resolved by earlier studies based on conventional data. Furthermore, the ability to target mineral phases that are in textural equilibrium (e.g., serpentine-carbonate, serpentine-magnetite) allowed us to constrain independently both alteration temperatures and fluid sources.

2. GEOLOGICAL SETTING AND PREVIOUS STUDIES

The Chenaillet ophiolite in the Franco-Italian Alps (Fig. 1) is interpreted as a remnant of embryonic oceanic crust formed at the distal part of a Magma-Poor-Ocean Continent Transition (MP-OCT) margin (Manatschal and Müntener, 2009; Manatschal et al., 2011; Li et al., 2013; Lafay et al., 2017) resembling actual slow spreading centers (Lagabrielle and Cannat, 1990; Lagabrielle and Lemoine, 1997). It consists mainly of pillow lavas with Mid Ocean Ridge Basalt (MORB) geochemical signature superimposed on tectonically exhumed gabbros and serpentinized mantle rocks comparable to oceanic core complexes (OCC) exposed in modern slow- to

177 ultraslow-spreading ridges (Manatschal and Müntener, 2009; Manatschal et al., 2011;
178 Li et al., 2013; Lafay et al., 2017). Recent U–Pb zircon ages in the gabbros suggest
179 that the Piemont-Liguria oceanic domain formed between 158-166 Ma (Li et al.,
180 2013). No sheeted dike complex and post-rift sedimentary cover are observed in the
181 Chenaillet ophiolite; sediments occur locally and consist of reworked mafic and
182 ultramafic rocks covered by pelagic deposits, radiolarite and limestones (Lemoine et
183 al., 1983; Manatschal et al., 2011). In contrast to other ophiolitic terrains in the Alps,
184 the Chenaillet ophiolite escaped high-pressure metamorphism during the Late
185 Cretaceous to Eocene Alpine subduction and was only weakly overprinted by
186 subgreenschist to lower greenschist facies metamorphism during thrusting onto the
187 European margin (Mével et al., 1978; Goffé et al., 2004; Manatschal and Müntener,
188 2009; Manatschal et al., 2011). High- to low-temperature hydrothermal processes in
189 the Chenaillet ophiolite occurred in an oceanic setting prior to obduction and are
190 represented by mylonitized amphibole-bearing gabbros (Mével et al., 1978),
191 serpentinites and ophicarbonates (Manatschal and Müntener, 2009; Lafay et al.,
192 2017). Serpentinization of mantle rocks is pervasive and original silicate minerals
193 from the igneous stage are usually replaced by mesh and bastite textures typical of
194 seafloor alteration under static conditions (Andreani et al., 2007; Manatschal and
195 Müntener, 2009; Manatschal et al., 2011; Lafay et al., 2017). The pioneering work of
196 Lemoine et al. (1983) and Lagabrielle and Lemoine (1997) has been recently
197 reconsidered by Lafay et al. (2017) who provided a detailed petrological, geochemical
198 and stable isotope (O, C, H) study of ophicarbonates from the Chenaillet ophiolite.
199 These rocks consist of few tens of meter thick layers (Fig. 1b) of breccia found atop
200 massive serpentinites near the serpentinite-basalt transition. Ophicarbonate breccias
201 are made of slightly rounded serpentinite clasts cemented by a matrix of small (~12

μm in average) calcite grains (Lemoine et al., 1983; Lafay et al., 2017) (Fig. A.1). The diversity of microstructures (veins, replacement, matrix) allowed the authors to identify multiple events of carbonation following initial serpentinization of peridotites, which were attributed to a progressive cooling during exhumation of the mantle at the seafloor (Lafay et al., 2017). However, values of $\delta^{18}O$ in serpentine (3.3 to 5.1‰) and carbonates (11 to 16‰) could suggest that both serpentinization and carbonation occurred at higher temperatures (T = 155-190 °C and 110-180 °C, respectively) than seafloor alteration (Lafay et al., 2017). These temperature estimates should be reexamined. They were calculated assuming a constant unaltered seawater composition (Lafay et al., 2017) and homogenous mineral grains. However, the microstructures and chemical zoning suggest that the micro-drilling technique used to select serpentine and carbonate for stable isotope analyses has mixed different generations resulting in average compositions. In light of recent analytical developments allowing accurate *in situ* analysis of oxygen and carbon isotopes in serpentine, magnetite and carbonate by SIMS (Valley and Kita, 2009; Huberty et al.., 2010; Kita et al., 2011; Śliwiński et al., 2015a,b; Scicchitano et al., 2018a, 2020), a number of ophicarbonates studied by Lafay et al. (2017) were reanalyzed for stable isotope ratios (O, C) by SIMS to: (i) target the various serpentine and carbonate generations identified by Lafay et al. (2017) that could not be separated with micro-drilling techniques due to their fine-grained size, (ii) identify systematic isotopic zoning recorded at the microscale in both serpentine and carbonate, (iii) couple *in situ* analysis of oxygen isotopes in potentially co-crystallized minerals (serpentine-calcite, serpentine-dolomite, calcite-dolomite, serpentine-magnetite) to estimate the equilibrium temperature independently of the fluid composition. To the best of our knowledge, this study represents the first successful attempt to applying the

serpentine-magnetite geothermometer at the microscale and provides the first stable isotope data in dolomite in these samples that could not be targeted by previous studies due to its small grain size.

3. PREPARATION OF GRAIN MOUNTS AND ANALYTICAL METHODS

Five ophicarbonate samples (RL3, RL6, RL7, RL9 and RL10) from the Chenaillet ophiolite previously characterized by Lafay et al. (2017) were prepared for oxygen and carbon isotope analysis by SIMS, as described in the Electronic Appendix A.

A Hitachi S3400 Variable Pressure (VP) Scanning Electron Microscope (SEM) at the Department of Geoscience (University of Wisconsin-Madison, UW-Madison) was operated at low (P = 30 Pa) and high vacuum in backscattered electron (BSE) mode to identify the different generations of serpentine, carbonate and magnetite in the Chenaillet ophicarbonates described by Lafay et al. (2017). Carbonate minerals were also imaged using a cathodoluminescence (CL) Gatan PanaCL/F system. Careful SEM imaging in BSE, secondary electron (SE) and CL modes was performed following each SIMS session to check the location and features of all SIMS pits. We rejected analyses where pits were located on fractures, mixed domains or other features that could alter isotope ratios. Prior to SEM analysis, mounts were coated with carbon or a thin layer of gold; to avoid affecting carbon isotope ratios during SIMS analysis in carbonates, no carbon coating was used on the corresponding mounts. The accelerating voltage and working distance were usually ~15 or 10 kV and ~10 or 15 mm for BSE and CL imaging, respectively.

Serpentine, calcite, dolomite and magnetite from the Chenaillet ophicarbonates were analyzed for major and minor element mineral chemistry using a CAMECA

252 SXFive Field Emission Electron Microprobe (EPMA) at the Department of
253 Geoscience (UW-Madison). Details of EPMA methods are given in the Electronic
254 Appendix A. Direct analysis of oxygen with EPMA was necessary for accurate
255 quantification of variable Fe oxidation in serpentine and magnetite and variable water
256 contents in serpentine. All serpentine analyses were normalized to 18 (O + OH)
257 according to the general formula $Mg_6Si_4O_{10}(OH)_8$. Approximate H_2O content (wt.%)
258 was calculated based on excess oxygen values measured by EPMA assuming total
259 iron as Fe^{2+} (Table A.1). Carbonate analyses were normalized to 6 O according to the
260 general formula $(Ca,Mg)_2(CO_3)_2$ (Table A.2). Magnetite analyses were normalized to
261 3 cations according to the general formula Fe_3O_4, and approximate Fe^{3+} and Fe^{2+}
262 contents were estimated by charge balance (Table A.3).
263 A CAMECA IMS-1280 large radius multicollector secondary ion mass
264 spectrometer at the WiscSIMS laboratory (UW-Madison) was used to perform *in situ*
265 oxygen and carbon isotope analyses of serpentine, carbonate and magnetite in the
266 Chenaillet ophicarbonates during seven analytical sessions (Tables A.1 to A.4).
267 Details on analytical settings are given in the Electronic Appendix A. We monitored
268 bias, drift and external precision during each analytical session by bracketing 10-20
269 unknown analyses with at least eight analyses of the reference material located in the
270 same grain mount. Matrix effects on bias due to variations in Mg/Fe ratios in
271 serpentine and dolomite-ankerite solid solutions, which are observed during oxygen
272 and carbon isotope analysis by SIMS (Śliwiński et al., 2015a,b; Scicchitano et al.,
273 2020), were monitored and quantified for each analytical session by constructing a
274 calibration curve using a suite of serpentine and carbonate reference materials (Table
275 A.4). These calibration curves were then used to correct $\delta^{18}O$ and $\delta^{13}C$ values
276 measured in serpentine and dolomite from the Chenaillet ophicarbonates. Orientation

277 effects in chrysotile were estimated by analyzing two different orientations of the
278 chrysotile C22908 reference material as described in Scicchitano et al. (2018a, 2020),
279 while orientation effects in magnetite were minimized using a special 3 kV protocol
280 (see Electronic Appendix A for details) and evaluated by analyzing ~30 grains with
281 different orientation of the magnetite M7-5830 reference material (Huberty et al.,
282 2010; Kita et al., 2011).
283
284 **4. RESULTS**
285
286 **4.1. Petrography and mineral chemistry**
287
288 For the purpose of this study, we summarize the main textures targeted for *in situ*
289 analysis by SIMS, which are essential for putting into petrological context the new
290 oxygen and carbon isotope data.
291
292 **4.1.1. Serpentine**
293
294 Serpentine is the main constituent of the serpentinite clasts where it forms either
295 mesh textures characterized by well-defined cores and rims (Fig. 2a-c) or hourglass
296 textures in which a distinction between mesh rim and mesh center is not possible (Fig.
297 2d). Raman spectroscopy showed that mesh cores consist of a mixture between
298 lizardite and chrysotile (hereafter referred to as "serpentine"), whereas mesh rims
299 consist of pure lizardite (Lafay et al., 2017). Magnetite (up to ~20 μm large) is often
300 observed around mesh cores in sample RL6 (Fig. 2b), while it is usually lacking or
301 very limited in mesh textures of other samples. It is occasionally possible to identify

302 an inner and outer mesh core both surrounded by magnetite (Fig. 2b). A complex
303 network of mesh veinlets (V-1) consisting of lizardite+magnetite follows original
304 (pristine silicate) grain boundaries (Fig. 2e-f), while larger lizardite+magnetite veins
305 250 μm in width (V-2) crosscut mesh and hourglass textures (Fig. 2g). In sample
306 RL6, lizardite+dolomite layers are observed within the carbonate matrix (Fig. 2j-k);
307 this serpentine generation is hereafter referred to as "matrix serpentine". Finally,
308 small chrysotile aggregates up to a few tens of μm large (Lafay et al., 2017) are
309 widespread in the carbonate matrix surrounding serpentinite clasts (Fig. 2k-l).
310 Mesh cores have higher Mg numbers [Mg# = 100 × Mg/(Mg+Fe), molar, with Fe
311 = Fe(total)] and silica contents relative to mesh rims in all samples (Fig. A.2). In
312 particular, mesh cores in samples RL6, RL7 and RL9 have Mg# ranging between 96
313 and 99 mole % and SiO_2 contents ranging between 40.6 and 43.4 wt.%, whereas mesh
314 rims have Mg# of 90 to 97 mole % and SiO_2 contents of 38.0 to 42.0 wt.% (Fig. A.2,
315 Table A.1). A similar trend between Mg# and silica is observed in mesh textures from
316 samples RL10 and RL3, which however show lower Mg# (91 to 95 mole % in mesh
317 cores, 85 to 95 mole % in mesh rims) and comparable SiO_2 contents (39.9 to 42.5
318 wt.% in mesh cores, 36.0 to 42.8 wt.% in mesh rims) relative to mesh serpentine in
319 the other three samples (Fig. A.2, Table A.1). The variability in alumina content is
320 lower in mesh serpentine from samples RL6, RL7 and RL9 (Al_2O_3 = 0.2-1.3 wt.%)
321 relative to mesh serpentine from samples RL10 and RL3 (Al_2O_3 = 0.1-4.3 wt.%) (Fig.
322 A.2, Table A.1). Serpentine in hourglass textures has a similar chemical composition
323 as serpentine in mesh rims (Fig. A.2, Table A.1). Lizardite in V-1 veins has similar
324 silica (SiO_2 = 41.2-43.1 wt.%) and alumina contents (Al_2O_3 = 0.1-0.6 wt.%) across
325 different samples, whereas Mg# decreases from sample RL9 (Mg# = 96-97) to
326 samples RL10 and RL3 (Mg# = 94-95) (Fig. A.2, Table A.1). Lizardite in V-2 veins

and “matrix serpentine” observed in sample RL6 have similar chemical compositions as those of mesh cores in the same sample (Fig. A.2, Table A.1). Chrysotile in the carbonate matrix surrounding serpentinite clasts is also characterized by higher Mg# in samples RL6, RL7 and RL9 (Mg# = 94-98) relative to samples RL10 and RL3 (Mg# = 88-95; Fig. A.2, Table A.1); in contrast, both silica and alumina contents are similar across different samples (SiO_2 = 39.5-44.2 wt.%, Al_2O_3 = 0.2-2.2 wt.%).

4.1.2. Carbonates within serpentinite clasts

Serpentine in mesh cores is often partially or completely replaced by calcite (hereafter referred to as C2, Lafay et al., 2017) and relict serpentine inclusions are frequently observed in calcite mesh (Fig. 2a-c). C2 calcite is sometimes connected to calcite veinlets ~10 μm in width (hereafter C1; Lafay et al., 2017); the largest C1 calcite veins (up to 500 μm in width) crosscut serpentine in mesh and hourglass textures as well as V-1 and V-2 lizardite+magnetite veins (Fig. 2h-i). Although C1 calcite veins are usually restricted to individual clasts and are often truncated at the edges of the clasts, they sometimes propagate into the surrounding carbonate matrix (Fig. A.1). SEM-CL imaging shows complex patchy zoning and resorption features in both C1 veins and C2 mesh suggesting multiple events of recrystallization (Fig. 3). As previously shown by Lafay et al. (2017), the edges of C1 calcite veins are sometimes delimited by distinct CL calcite rims (Fig. 3b-c).

In addition to calcite, subordinate dolomite is observed in some samples as (i) rims around C2 calcite mesh (Fig. 3e, 4a), (ii) borders along C1 veins at the boundary with serpentine (Fig. 3a, 4b), (iii) subhedral grains associated with “matrix serpentine” in sample RL6 (Fig. 2k, 4c) and (iv) veinlets in the C3 calcite matrix.

352 No significant variation is observed in the chemical composition of calcite in
353 different textures across different samples (Table A.2). FeO and MnO contents are
354 usually <0.5 wt.% with the exception of calcite in C2 mesh (FeO = 0.1-1.3 wt.%)
355 from sample RL6. In contrast, the MgO content in calcite from different textures has a
356 larger variability from 0.02 to 1.6 wt.% (Table A.2).
357 Dolomite has a similar chemical composition in all samples and textural locations
358 with FeO content varying from 0.1 to 1.2 wt.% and MnO content <0.3 wt.%; Fe# is
359 <3 mole %.
360
361 **4.1.3. Carbonates surrounding serpentinite clasts**
362
363 Serpentinite clasts are embedded in a calcite matrix (hereafter C3; Lafay et al.,
364 2017) that appears either "turbid", when intergrown with fine-grained chrysotile
365 aggregates as documented through Raman spectroscopy (Lafay et al., 2017), or
366 "clear", when no chrysotile is present (Fig. A.3). Clear calcite domains (hereafter
367 C1') in the C3 calcite matrix were interpreted by Lafay et al. (2017) as remnants of
368 C1 veins channeling fluids. Calcite veins ~100 μm in width (hereafter C3-veins)
369 sometimes crosscut the C3 calcite matrix but not the lizardite+dolomite layers (Fig.
370 2j). Finally, a large calcite vein ~5 mm in width (hereafter C4; Lafay et al., 2017)
371 crosscuts both C3 calcite matrix and serpentinite clasts in sample RL9 (Fig. A.1).
372 SEM-CL imaging shows that C1' clear calcite domains consist of large calcite grains
373 that sometimes exhibit a concentric (Fig. 5a-b) or oscillatory CL zoning (Fig. 5c)
374 truncated by the surrounding aggregates of fine-grained C3 calcite matrix; the latter
375 also shows a similar concentric CL zoning (Fig. 5a, d). Calcite grains in C1' are often
376 crosscut or bounded by later calcite veinlets (hereafter C1'-veins) (Fig. 5a, c). In

contrast, C3-veins do not exhibit complex CL zoning (Fig. 5d). In addition to calcite, dolomite was observed at the boundary between C4 vein and serpentinite clast in sample RL9 (Fig. 4d).

FeO and MnO contents are usually <0.5 wt.% with the exception of calcite in C3-veins (MnO = 0.1-0.7 wt.%) from sample RL6. In contrast, the MgO content in calcite from different textures has a larger variability from 0.03 to 1.9 wt.% (Table A.2). No significant variation is observed between different textures across different samples.

4.2. Oxygen and carbon isotopes by SIMS

4.2.1. Serpentine

In situ oxygen isotope analyses of serpentine were performed in two analytical sessions (S1 and S2; Table A.1). A suite of six (S1) to seven (S2) antigorite reference materials was analyzed at the beginning of each analytical session in order to build a calibration curve for the correction of polymorph-specific matrix effects due to Mg/Fe variations in the compositional range Mg# = 77.5-99.5 (Table S2 in Scicchitano et al., 2020). Lizardite (L3431) and chrysotile (C22908) reference materials (Scicchitano et al., 2018a, 2020) were also analyzed to correct for the bias relative to the normalizing antigorite reference material Al06-44A (Table S2 in Scicchitano et al., 2020). A bias of ~1‰ was measured between lizardite L3431 and antigorite Al06-44A in both analytical sessions. Orientation effects in chrysotile C22908 were ~1‰ in all analytical sessions, hence this is considered as a limitation on the accuracy of analyses done in this polymorph, but no orientation effects are detected for lizardite or

antigorite. Measured $\delta^{18}O$ values in serpentine from the Chenaillet ophicarbonates were corrected according to the method described in Scicchitano et al. (2020) and are reported relative to the V-SMOW scale (Table A.1).

The highest average $\delta^{18}O$ values are recorded in the core of mesh textures where oxygen isotope ratios vary between 4.4 and 8.5‰ with no distinction between calcite-free and calcite-bearing mesh cores (Fig. 6). Although mesh rims show a large variability in oxygen isotope ratios with $\delta^{18}O$ values varying from 4.5 to 8.8‰, their average $\delta^{18}O$ values are generally lower compared to mesh cores (Fig. 6). No correlation between $\delta^{18}O$ value and Mg# was observed in mesh textures. Lizardite in V-1 veins has an oxygen isotope composition varying from 3.5 to 6.4‰ with average $\delta^{18}O$ values lower relative to mesh rims (Fig. 6). Lizardite in V-2 veins crosscutting both V-1 veins and mesh textures has low $\delta^{18}O$ values of 3.2-4.2‰ (Fig. 6). Similar low oxygen isotope ratios relative to mesh cores are recorded in hourglass serpentine ($\delta^{18}O$ = 3.8-5.7‰), "matrix serpentine" ($\delta^{18}O$ = 3.1-5.4‰) and serpentine in the C4 calcite vein ($\delta^{18}O$ = 4.0-4.8‰) (Fig. 6). Chrysotile in the C3 calcite matrix has a large variability in $\delta^{18}O$ values from 3.0 to 5.7‰ (Fig. 6).

Overall, SIMS analyses allow identifying a larger variation in serpentine $\delta^{18}O$ values (from 3.0 to 8.8‰) relative to previous studies on powdered micro-drilled samples ($\delta^{18}O$ = 3.3-5.1‰; Lafay et al., 2017) as well as a systematic variation in $\delta^{18}O$ values between different serpentine generations.

4.2.2. Carbonate

In situ oxygen and carbon isotope analyses in carbonates were performed in four analytical sessions (S3 to S5 for O, S6 for C; Table A.2). Calcite UWC-3 (Kozdon et

al., 2009) was used as a working reference material. A suite of seven to ten carbonate reference materials was analyzed at the start of each session to calibrate matrix effects in samples with chemical composition along the dolomite-ankerite solid solution series (Table A.4). Measured $\delta^{18}O$ and $\delta^{13}C$ values in dolomite from the Chenaillet ophicarbonates were corrected according to the method described in Śliwiński et al. (2015a,b) and for the bias between dolomite UW6220 and calcite UWC-3 reference materials (Table A.2). Values of $\delta^{18}O$ and $\delta^{13}C$ are reported relative to the V-SMOW and V-PDB scales, respectively (Table A.2).

Values of $\delta^{18}O$ for calcite in C1 veins mostly range between 9.4 and 13.9‰ and occasionally up to 22.3‰ (Fig. 7). The highest $\delta^{18}O$ values are commonly observed at the edges of large C1 veins (Fig. 3b). Analyses performed across one of the largest C1 veins (Fig. 3c, A.4a) showed a nearly symmetric edge-to-edge oxygen isotope zoning up to ~3‰ with the lowest $\delta^{18}O$ values in the core of the vein (Fig. A.4). Values of $\delta^{13}C$ for C1 calcite veins vary between –0.6 and 2.4‰ but no systematic correlation is observed with textures (Fig. A.5). Calcite in C2 mesh textures shows the largest variability in oxygen isotope composition with $\delta^{18}O$ values ranging from 9.8 to 30.6‰ (Fig. 7), whereas $\delta^{13}C$ values vary between –2.6 and 1.9‰ (Fig. A.5). The highest $\delta^{18}O$ values in C2 calcite mesh are typically observed at the core of mesh textures, whereas the edges usually have lower $\delta^{18}O$ values (Fig. 3d-i). It is sometimes possible to observe resorption textures where calcite with low $\delta^{18}O$ values, similar to those measured in nearby C1 veinlets, replaces C2 calcite mesh cores with higher $\delta^{18}O$ values (Fig. 3f-i). Calcite in C1' textures also shows a large variability in oxygen and carbon isotopes similar to C2 calcite mesh with $\delta^{18}O$ and $\delta^{13}C$ values of 10.6 to 24.9‰ and –1.1 to 1.6‰, respectively (Fig. 7, A.5). Similar to calcite in C2 mesh textures, the highest $\delta^{18}O$ values in C1' textures are commonly observed in the cores

452 of large calcite grains (Fig. 5 and Electronic Appendix B). Late C1'-veins
453 crosscutting or bounding C1' calcite grains have low $\delta^{18}O$ values of 10.9 to 11.8‰
454 (Fig. 5c, 7 and Electronic Appendix B) and $\delta^{13}C$ values of –0.6 to 0.7‰ (Fig. A.5).
455 Similarly, calcite in the fine-grained C3 matrix and crosscutting C3-veins also have
456 low $\delta^{18}O$ values of 9.8-12.9‰ and 10.5-11.5‰, respectively (Fig. 5d, 7 and B.1 in
457 Electronic Appendix B); $\delta^{13}C$ values vary from –0.1 to 2.2‰ and –0.6 to 0.6‰,
458 respectively (Fig. A.5). Finally, calcite in the latest C4 vein has the highest average
459 oxygen isotope composition (average $\delta^{18}O$ = 21.1‰, Fig. 7) and carbon isotope
460 values similar to calcite in other textural locations ($\delta^{13}C$ = –0.7 to 1.7‰, Fig. A.5).
461 Dolomite associated with mesh textures in serpentinite clasts has $\delta^{18}O$ values of 10.7
462 to 14.1‰ (n = 20) that are comparable to the oxygen isotope composition of dolomite
463 bordering C1 calcite veins ($\delta^{18}O$ = 10.1-11.9‰, n = 9) and the C4 vein ($\delta^{18}O$ = 11.2-
464 12.5‰, n = 2) (Table A.2). Similar $\delta^{18}O$ values are also recorded in subhedral
465 dolomite associated with matrix serpentine in the layers at the boundary between
466 serpentinite clasts and C3 calcite matrix ($\delta^{18}O$ = 11.4-13.2‰, n = 5) (Table A.2).
467 SIMS analyses show a much larger variability (~21‰) in calcite $\delta^{18}O$ values
468 relative to ~6‰ variation described in Lafay et al. (2017). Additionally, the ability to
469 place SIMS data into a petrological context highlights that higher $\delta^{18}O$ values in
470 zoned C1 veins, C2 mesh and C1' calcite domains likely represent an older signature
471 that is progressively replaced by younger calcite generations with lower $\delta^{18}O$ values
472 (core of C1 veins, C1'-veins, C3 matrix and C3-veins). SEM-CL imaging linked to
473 oxygen isotope ratios also allowed distinguishing C1' domains from C1 open veins.
474 Values of $\delta^{18}O$ increase again in the latest C4 calcite vein (average $\delta^{18}O$ = 21.1‰)
475 crosscutting serpentinite clasts and C3 calcite matrix (average $\delta^{18}O$ = 11.1‰). Values
476 of $\delta^{13}C$ measured by SIMS vary by ~4.5‰ at most in C2 calcite mesh, similar to the

variation observed by Lafay et al. (2017). Nevertheless, SIMS analyses are generally higher relative to those reported in Lafay et al. (2017) (–2.6 to +2.4‰ vs. –5.2 to +0.4‰, respectively).

4.2.3. Magnetite

In situ oxygen isotope analyses in magnetite were performed in one analytical session (S7; Table A.3). The extent of crystal orientation effects in magnetite was determined by bracketing analyses of the M7-5830 magnetite reference material with eight analyses of the UWQ-1 quartz reference material (Kelly et al., 2007) (Table A.4). A grain-to-grain reproducibility of ~1‰ (2 standard deviations, 2SD) was obtained (using the low-kV protocol of Kita et al., 2011) in both M7-5830 and UWQ-1 (Table A.4); hence this represents the maximum precision achievable during oxygen isotope analyses of magnetite in this study. Magnetite analyses in the ophicarbonate samples from the Chenaillet ophiolite were bracketed with eight analyses in the UWC-3 calcite reference material (Kozdon et al., 2009) located in the same grain mounts in order to monitor bias, drift and external precision (Table A.3). Magnetite analyses were corrected for the bias between UWC-3 calcite and M7-5830 magnetite reference materials measured in different mounts, and they are reported relative to the V-SMOW scale (Tables A.3 and A.4).

Magnetite grains larger than ~10 μm located in different textures (mesh, V-1 and V-2 veins, hourglass serpentine) were targeted for SIMS oxygen isotopes analysis in samples RL6, RL3 and RL9 (Table A.3). Magnetite in mesh textures (Fig. 2b and A.6a) shows the largest variability in $\delta^{18}O$ values from –10.6 to –5.0‰ (n = 32). Magnetite in V-1 veins (Fig. 2f and A.6b) and V-2 veins (Fig. 2g and A.6c) has

oxygen isotope ratios varying from –8.5 to –7.3‰ (n = 3) and –7.7 to –10.6‰ (n = 2), respectively. Magnetite associated with hourglass serpentine (Fig. 2d and A.6d) has an oxygen isotope composition of –9.6 to –8.0‰ (n = 4).

5. DISCUSSION

5.1. Estimating alteration temperatures and water $\delta^{18}O$ values in co-crystallized mineral pairs

Based on textural observations, we identified seven pairs of minerals that appear to be in textural equilibrium along the metasomatic sequence and, therefore, assumed to have co-crystallized: (i) lizardite+magnetite in mesh textures with a single mesh core, V-1 veins (Fig. 2e, f), V-2 veins (Fig. 2g), and in the hourglass matrix (Fig. 2d); (ii) lizardite+dolomite in the layers at the boundary between serpentinite clast and carbonate matrix (Fig. 2k and 4c) as well as with hourglass serpentine (Fig. 4b, d); (iii) chrysotile+calcite in the C3 calcite matrix (Fig. 2l). Coupled oxygen isotope analysis by SIMS in these mineral pairs allows us to test whether isotopic equilibrium was achieved during hydration and carbonation reactions, in which case equilibrium temperatures and water $\delta^{18}O$ values are independently estimated.

5.1.1. Serpentine-magnetite

The majority of targeted serpentine-magnetite pairs (n = 17, Table 1) are in mesh textures (sample RL6) because of the larger (>10 μm) size of magnetite grains. Only a

limited number of analyses was possible in V-1 veins (n = 1), V-2 veins (n = 2) and hourglass matrix (n = 4) because of the small grain size of magnetite (Table 1).

A large uncertainty exists on the serpentine-water oxygen isotope fractionation because different calibrations (Wenner and Taylor, 1971; Savin and Lee, 1988; Früh-Green et al., 1996; Zheng, 1993; Saccocia et al., 2009) disagree by >4‰ and up to ~20‰ when extrapolated to temperatures <200 °C (see Fig. 10 and discussion in Scicchitano et al., 2020). In this study, the preferred calibrations for calculating the equilibrium temperature for each serpentine-magnetite pair are the serpentine-water oxygen isotope fractionation factors of Früh-Green et al. (1996) and the magnetite-water oxygen isotope fractionation factors of Bottinga and Javoy (1973). The same calibrations were then used to calculate the oxygen isotope composition of water in equilibrium with both serpentine and magnetite at each equilibrium temperature (Table 1 and Fig. 8). For mesh cores, equilibrium temperatures vary from 204 °C to 132 °C and $\delta^{18}O_{(water)}$ values decrease with temperature from 5.2 to 1.8‰ (Fig. 8). For serpentine-magnetite pairs in V-1 veins, V-2 veins and hourglass textures, equilibrium temperatures vary from 173 °C, 169-215 °C and 162-198 °C, respectively, while water $\delta^{18}O$ values vary between ~1 and 3‰ (Fig. 8).

For comparison, equilibrium temperatures and $\delta^{18}O_{(water)}$ values were also calculated using other calibrations. Estimates calculated by combining the serpentine-water oxygen isotope fractionation factors of Saccocia et al. (2009) with the magnetite-water oxygen isotope fractionation factors of Bottinga and Javoy (1973) differ by ~50 °C (from 261 to 191 °C) and ~1‰ (from ~4 to 0‰), respectively, relative to estimates derived from the calibration by Früh-Green et al. (1996) (Fig. 8 and Table 1). Temperatures calculated with the calibration of Saccocia et al. (2009) could be overestimated of up to 40 °C (at exchange fraction < 40%) due to a bias in

551 their serpentine-water calibration resulting from extrapolation of equilibrium
552 fractionation factors in three-exchange site systems using the methods described by
553 Northrop and Clayton (1966) or Zheng et al. (1994), which are valid for two-
554 exchange site systems (Agrinier and Javoy, 2016). Equilibrium temperatures
555 calculated by combining the serpentine-water and magnetite-water oxygen isotope
556 fractionation factors of Zheng (1991, 1993) as well as the serpentine-magnetite
557 calibration by Früh-Green et al. (1996; their Eq. 3) are ~50-70 °C lower than those
558 estimated using the serpentine-water and magnetite-water calibrations by Früh-Green
559 et al. (1996) and Bottinga and Javoy (1973) (Table A.5). Considering the maximum
560 uncertainties derived from the various calibration equations and $\delta^{18}O$ measurements,
561 we estimate a total uncertainty of ±80 °C on the calculated equilibrium temperatures.
562 The uncertainty on $\delta^{18}O_{(water)}$ values is estimated to be in the order of ±1‰.
563
564 **5.1.2. Serpentine-dolomite**
565
566 Lizardite and subhedral dolomite grains in the layers at the boundary between
567 serpentinite clast and carbonate matrix are relatively homogenous in oxygen isotopes
568 with average $\delta^{18}O$ values of 4.7±1.4‰ (2SD, n = 10) and 12.2±1.3‰ (2SD, n = 5),
569 respectively, suggesting that they are in isotopic equilibrium. Using the average $\delta^{18}O$
570 values measured by SIMS, we calculated an oxygen isotope fractionation ($\Delta^{18}O_{Dol\text{-}Srp}$)
571 of 7.5‰, which corresponds to an equilibrium temperature of 229 °C (Fig 9a). In
572 order to calculate the temperature at which serpentine and dolomite formed, we used
573 the empirical calibration of the serpentine-water oxygen isotope fractionation by
574 Früh-Green et al. (1996) and the calibration of the dolomite-water oxygen isotope
575 fractionation (experiments at T = 252-292 °C, Matthews and Katz, 1977).

576 Extrapolation of the experimental calibration by Saccocia et al. (2009) would result
577 in an unrealistically high equilibrium temperature (even if accounting for the bias
578 described by Agrinier and Javoy, 2016) given a maximum calculated $\Delta^{18}O_{Dol\text{-}Srp}$ of
579 5.6‰ is obtained assuming T = 500 °C, which is the maximum thermal stability of
580 serpentine in oceanic settings (e.g., Mével, 2003). Consequently, we consider
581 extrapolation of the empirical calibration by Früh-Green et al. (1996) more reliable.
582 At a temperature of 229 °C, serpentine and dolomite would be in equilibrium with a
583 fluid of 3.3‰ (Fig. 9b). Similar equilibrium temperature of 240 °C and water $\delta^{18}O$
584 value of 3.3‰ are calculated using the average oxygen isotope ratios measured in
585 hourglass serpentine and dolomite pairs (Table 2, Fig. 9). These estimates are within
586 uncertainty of those calculated for lizardite+magnetite pairs in hourglass textures.
587
588 **5.1.3. Serpentine-calcite**
589
590 Calcite in the fine-grained C3 matrix and the co-crystallized fine-grained chrysotile
591 have average $\delta^{18}O$ values of 11.1±1.2‰ (2SD, n = 57) and 3.9±1.4‰ (2SD, n = 22),
592 respectively, corresponding to a $\Delta^{18}O_{Cal\text{-}Srp}$ of 7.2‰ (Fig. 9a). Combining the
593 empirical calibration of the serpentine-water system by Früh-Green et al. (1996) with
594 the experimental calibration of the calcite-water oxygen isotope fractionation
595 (experiments at T = 0-500°C, O'Neil et al., 1969), yields an equilibrium temperature
596 of 208 °C and a $\delta^{18}O_{(water)}$ of 2.0‰ (Fig. 9). The calibration by O'Neil et al. (1969) is
597 in good agreement with experimental calibrations by Golyshev et al. (1981) and Kim
598 and O'Neil (1997). As for the dolomite-serpentine pair, the experimental calibration
599 by Saccocia et al. (2009) for the calcite-serpentine pair would result in unrealistically

high equilibrium temperature not consistent with seafloor serpentinization (T >500 °C).

5.2. Evolution model for the hydrothermal alteration in the Chenaillet ophiolite

In the following discussion, stable isotope data are combined with petrographic observations and well-documented geological context to reconstruct the main phases of fluid-rock interaction recorded in the Chenaillet ophicarbonates (Fig. 10, 11). Alteration temperatures and water oxygen isotope compositions estimated independently from mineral-mineral pairs (see above) are used as anchor points for the interpretations.

5.2.1. Exhumation to the seafloor: early serpentinization followed by low-*T* carbonation

Oxygen isotope values of serpentine increase from V-1 mesh veins ($\delta^{18}O$ = 3.5 to 6.4‰) to mesh cores ($\delta^{18}O$ = 4.4 to 8.5‰), with no distinction between carbonate-free and carbonate-bearing mesh textures (Fig. 6, 10). Additionally, serpentine in mesh textures associated with magnetite has similar oxygen isotope and chemical compositions as serpentine in magnetite-free mesh textures from the same sample. Hence, we assume that the formation of serpentine in different mesh cores (i.e., magnetite- and calcite-bearing versus magnetite- and calcite-free) is attributable to the same hydrothermal event. The physical-chemical conditions at which serpentine in V-1 mesh veins and mesh rims formed cannot be independently constrained, but it is likely that they record the earliest stages of alteration with V-1 veins acting as

625 conduicts that allowed progressive fluid percolation and pervasive replacement in
626 mesh cores. The variation in Mg# and Al_2O_3 observed in mesh textures from samples
627 RL6, RL7 and RL9 versus samples RL10 and RL3 (Fig. A.2) suggests formation of
628 serpentine after olivine versus pyroxene, respectively (e.g., Deschamps et al., 2013).
629 Because no relict pyroxene and olivine are observed in any of the investigated
630 samples, it is possible that serpentinization started at T>400 °C (favoring rapid
631 dissolution of orthopyroxene) and then proceeded at T<300 °C (favoring rapid
632 dissolution of olivine), as documented by experimental studies (e.g., Martin and Fyfe,
633 1970; Allen and Seyfried, 2003). The limited occurrence of antigorite, chlorite and
634 tremolite in the Chenaillet ophicarbonates (Lafay et al., 2017) is consistent, in fact,
635 with greenschist facies conditions (T = 300-500 °C). The abundant precipitation of
636 massive magnetites in mesh cores would explain the formation of serpentine with
637 higher Mg# in response to changes in the conditions of hydrothermal alteration. It
638 should be noted that the marked crystallization of magnetite in mesh cores could be a
639 consequence of the combined variation in fluid temperature and $\delta^{18}O$ composition,
640 water/rock ratio (W/R) and redox conditions (Klein et al., 2009, 2013).
641 In light of the above assumptions, the physical-chemical conditions at which the
642 serpentine-magnetite pairs in mesh textures formed (i.e., T = 204 to 132 °C and
643 $\delta^{18}O_{(water)}$ = 5 to 2‰) can be considered valid for serpentine in all mesh cores. It is
644 worth noting that the concomitance between cooling and decrease in water $\delta^{18}O$
645 values results in a net variation of magnetite and serpentine $\delta^{18}O$ values by ~5.5‰
646 and ~0.4‰, respectively (Fig. A.7); this is consistent with the variability in $\delta^{18}O$
647 values measured by SIMS in serpentine-magnetite pairs (Table 1). The decrease in
648 fluid $\delta^{18}O$ values during cooling is consistent with a progressive evolution from a
649 rock-dominated system during early stages of serpentinization (or low W/R), with

650 water $\delta^{18}O$ values similar to the oxygen isotopic composition of the upper mantle
651 ($\delta^{18}O_{mantle}$ = 5.5‰, $\delta^{18}O_{olivine}$ = 5.18±0.28‰; e.g., Mattey et al., 1994; Chazot et al.,
652 1997), to a fluid-dominated system during later stages of serpentinization (or high
653 W/R) and exhumation of the mantle near the seafloor. Calculated water $\delta^{18}O$ values of
654 ~2‰ agree well with $\delta^{18}O$ values of 1.2-1.5‰ (Logatchev hydrothermal field) and
655 2.2-2.4‰ (Nibelungen hydrothermal field) measured in hot (T = 192-365°C)
656 ultramafic-hosted vent fluids sampled along the Mid-Atlantic slow-spreading ridge
657 (e.g., Charlou et al., 2010 and references therein; Schmidt et al., 2011), which are
658 higher in $\delta^{18}O$ than present-day pure seawater (0‰) due to interaction with the
659 oceanic crust (e.g., Mével, 2003). Similar temperatures (T = 265-364°C) and $\delta^{18}O$
660 values (1.1-2.4‰) are also recorded in mafic-hosted vent fluids (e.g., Jean-Baptiste et
661 al., 1997).

662 Our new *in situ* data are overall in agreement with the original suggestion of Lafay
663 et al. (2017) who, in continuity with the tectonic models proposed by Manatschal et
664 al. (2011), proposed that exhumation of oceanic units occurred along detachment
665 faults favoring hydration and carbonation of mantle rocks (Fig. 12a). The authors
666 proposed that serpentinization initiated in a shallow seafloor environment at
667 conditions of at least 150 °C, with reactive fluids assumed to have $\delta^{18}O$ values of 0-
668 2‰. The new *in situ* data suggest comparable temperature estimates within
669 uncertainty, but independently constrain the composition and origin of the interacting
670 fluids as well as identify that early serpentinization was followed by early low-
671 temperature carbonation due to exposure of the mantle rocks on the paleo seafloor and
672 interaction with low-temperature seawater (Fig. 12a). This is documented by the
673 zonation in $\delta^{18}O$ values observed in some carbonate generations (Fig. 7, 10), with
674 texturally older calcite domains having high $\delta^{18}O$ values in zoned C2 calcite mesh

675 (18.0-30.6‰), at the edges of zoned C1 veins (18.7-22.3‰) and in the cores of zoned
676 C1' domains (18.2-24.9‰), which are comparable to those reported for marine
677 carbonates and metacarbonates from the Lago Nero unit (Lemoine et al., 1983). Such
678 carbonates likely formed at temperatures as low as 10 °C assuming interaction with
679 pure seawater in an ice-free world ($\delta^{18}O = -1‰$). Such low carbonation temperatures
680 relative to serpentinization are also consistent with the observation that calcite in
681 mesh textures is clearly replacing (hence postdating) serpentine.
682
683 **5.2.2. An active hydrothermal cell: coupled high-*T* carbonation and**
684 **serpentinization**
685
686 An overall decrease in oxygen isotope values with textural progression is recorded
687 by both serpentine and carbonate in all investigated samples (Fig. 6, 7, 10). In
688 particular, $\delta^{18}O$ values of serpentine in V-2 veins ($\delta^{18}O$ = 3.2-4.2‰) and hourglass
689 textures ($\delta^{18}O$ = 3.8-5.7‰) are ~3‰ lower on average relative to serpentine in mesh
690 cores (Fig. 6). Similarly, texturally younger calcite in zoned C2 mesh, C1 veins and
691 C1' domains has $\delta^{18}O$ values down to ~10‰ (Fig. 7, 10). Low oxygen isotope ratios
692 are also recorded in lizardite at the boundary between serpentinite clast and carbonate
693 matrix ($\delta^{18}O$ = 3.1-5.4‰), chrysotile intergrown with fine-grained C3 calcite ($\delta^{18}O$ =
694 3.0-5.7‰), C3 calcite matrix ($\delta^{18}O$ = 9.8-12.8‰), C3-veins ($\delta^{18}O$ = 10.7-11.4‰) and
695 C1'-veins ($\delta^{18}O$ = 10.9‰). Oxygen isotope thermometry from mineral pairs (see
696 above) suggests that such a drop in $\delta^{18}O$ values in both serpentine and carbonates is
697 consistent with a crystallization temperature of up to 240 °C and water $\delta^{18}O$ value of
698 2±1‰. The smooth oxygen isotope zoning in both C1 veins and C1' domains as well
699 as the similarity in fluid $\delta^{18}O$ compositions between early and late stages of

700 hydrothermal alteration point to a continuous process that likely occurred entirely in a
701 seafloor environmental setting. The pervasive carbonation textures often overprint
702 serpentinization ones, but we do not exclude that carbonation initiated while residual
703 anhydrous silicates were still present. The calculated oxygen isotope compositions of
704 water are consistent with isotopically shifted seawater rather than indicative of
705 interaction with meteoric water or metamorphic fluids in continental settings. Oxygen
706 isotope values measured in serpentine fall in the range of oceanic serpentinites
707 (Wenner and Taylor, 1973) and all values of $\delta^{13}C$ in carbonates (from –2.6 to +2.4‰)
708 suggest a seawater origin for carbon. It is worth noting that in a $\delta^{18}O$ versus $\delta^{13}C$ plot,
709 the carbonates from the Chenaillet ophiolite show a distinct horizontal trend parallel
710 to the $\delta^{18}O$ axis (Fig. A.5) suggesting that the fraction of CO_2 in the fluid was not
711 significant. Calcite can precipitate at a mole fraction of $CO_2/(CO_2 + H_2O)$ as low as
712 0.01, but in such case a high water/rock ratio is required for a significant carbonation.
713 Carbonate cements commonly form at low temperature from seawater (biogenic and
714 abiogenic) and freshwater (calcretes and speleothems). High-$\delta^{18}O$ carbonates are
715 assumed to form in equilibrium with very low-*T* seawater and our new thermometry
716 estimates suggest that low-$\delta^{18}O$ carbonates in the Chenaillet ophicarbonates formed at
717 high temperature. Consequently, both temperature and water $\delta^{18}O$ must have changed.
718 The flat trend can result from the dissolution and reprecipitation of pre-existing
719 carbonates that interacted with nearly pure water such that the $\delta^{13}C$ remained
720 constant. This agrees with observations of dissolution and reprecipitation textures in
721 the carbonates of the investigated samples.
722 Heating associated with burial during oceanic spreading is an unlikely scenario to
723 explain this high-*T* hydrothermal event due to the intense fracturing of the
724 ophicarbonates that points to active tectonics, accordingly to Lafay et al. (2017) who

725 also suggested that authigenic carbonation, partially replacing serpentinites and
726 achieving mantle minerals alteration, occurred under brittle conditions favored by the
727 likely fluid-dominated system and tectonic context. In fact, the authors hypothesized
728 that the composition of the fluid and the temperature conditions evolved in a
729 hydrothermal environment comparable to that observed in the vicinity of mid-ocean
730 hydrothermal vents, i.e. active tectonic and magmatic conditions. The occurrence of a
731 warmer (200-240 °C) stage of hydrothermal alteration due to interaction with evolved
732 seawater-derived fluids ($\delta^{18}O$ = 2-3‰) documented by the new *in situ* data could be
733 the result of burial by lavas causing reheating and channeling of upwelling
734 hydrothermal fluids along high-angle faults (Fig. 12b). Such a scenario would be
735 consistent with the tectonic models of Manatschal et al. (2011) for the Chenaillet
736 ophiolite suggesting that a first stage of mantle exhumation along a detachment fault
737 was followed by a stage of 'high-angle extrusion', when magma and fluids were
738 remobilized along high-angle faults acting also as feeder channels for the overlying
739 pillow basalts. A similar model of high-temperature hydrothermal discharge, driven
740 by mafic intrusions, along normal faults lying at high angle to an oceanic detachment
741 surface was proposed by Alt et al. (2018) in the northern Appenine ophiolites. The
742 authors documented an evolution of the fault system at the paleo-seafloor from talc
743 alteration and sulfide deposits, typical of high-temperature hydrothermal discharge (T
744 ≈ 350 °C), to carbonated serpentinites formed at T ≈ 100 °C (Alt et al., 2018).
745 Carbonates formed at temperatures as high as ~ 225 °C are observed also in the
746 serpentinite basement of the Lost City Hydrothermal Field in the Mid-Atlantic Ridge,
747 where they precipitate from warm hydrothermal fluids with high concentrations of
748 methane and hydrogen derived from serpentinization (Früh-Green et al., 2003).
749

5.2.3. Late stage veining

The youngest C4 calcite vein records a large variability in $\delta^{18}O$ values (12.3 to 23.9‰) and the highest average oxygen isotope composition among different carbonate generations (Fig. 7). No independent calculations of temperature and fluid oxygen isotope composition are possible due to the lack of mineral pairs. It is, therefore, necessary to assume that the variation in $\delta^{18}O$ values is due to a variation in temperature, fluid oxygen isotope composition or more likely a combination of both. Given the lowest $\delta^{18}O$ values are comparable to those measured in the "high-temperature" carbonates, it is plausible that formation of the C4 vein started in similar physical-chemical conditions and continued due to interaction with progressively cooler and low- $\delta^{18}O$ hydrothermal fluids (down to a minimum of ~40 °C, assuming $\delta^{18}O_{(water)}$ of –1‰) due to mixing with fresh seawater channeled along fractures at shallower depths. Such estimates are comparable, for instance, to the active vent fluids sampled at the Lost City Hydrothermal Field characterized by low temperature (T = 55-75 °C) and $\delta^{18}O$ values (0-0.1‰), and are interpreted to result from mixing between seawater and high-pH fluids derived from subsurface serpentinization reactions (Früh-Green et al., 2003). The evolutionary model suggested here for the hydrothermal alteration of the Chenaillet ophicarbonates is consistent with the overall observation that this ophiolitic terrain was only partly affected by low-grade metamorphism during obduction.

6. CONCLUSIONS

774 We performed *in situ* analysis by SIMS of oxygen and carbon isotopes in
775 serpentine, calcite, dolomite and magnetite from ophicarbonate samples from the
776 Chenaillet ophiolitic complex (western Alps). SIMS analysis revealed unprecedented
777 zoning in oxygen isotope ratios of serpentine (3.0 to 8.8‰), calcite (9.4 to 30.6‰)
778 and magnetite (–5.0 to –10.6‰) relative to previous studies, which relied on
779 conventional bulk analysis. To the best of our knowledge, we document the first
780 evidence of 'cold carbonates' (i.e., carbonates with $\delta^{18}O > 25‰$; e.g., Fig. 6 in Picazo
781 et al., 2020 and references therein) in Alpine ophiolites. The lack of such high oxygen
782 isotope signatures in other Alpine ophiolitic terrains could be due to the much larger
783 sampling scale of the bulk techniques that average $\delta^{18}O$ values of multiple mineral
784 generations. The high spatial resolution of SIMS allowed direct quantification of
785 oxygen isotope ratios in mineral pairs that are in textural equilibrium and are
786 interpreted to have co-crystallized. The relative oxygen isotope homogeneity of the
787 targeted mineral pairs is consistent with isotopic equilibrium allowing for the
788 independent calculation of equilibrium temperatures and water oxygen isotope values.
789 Considering that the temperature-pressure stabilities of serpentine minerals are not
790 well constrained, *in situ* stable isotope thermometry presents a powerful tool to
791 constrain the conditions at which alteration of ultramafic rocks occurs in various
792 tectonic settings. Additionally, numerical models by Klein and Garrido (2011) show
793 that temperature-dependent activity gradients of both aqueous carbon dioxide
794 (aCO_2,aq) and aqueous silica ($aSiO_2$,aq) determine the carbonation potential of
795 serpentinite. Independently constraining the formation temperature is therefore
796 essential to estimating $aSiO_{2(aq)}$, $aCO_{2(aq)}$, oxygen fugacity and pH, which in turn
797 would allow estimating the phase equilibria with implications for the monitoring of
798 reaction progress during CO_2 sequestration of ultramafic rocks (Klein and Garrido,

2011). Nevertheless, a major source of uncertainty on the calculation of alteration temperatures, particularly for the serpentine-water system, remains the large discrepancy between different calibrations of the oxygen isotope fractionation at $T <$ 200 °C, hence future studies should aim to improve such calibrations. The new dataset and thermometry estimates in the Chenaillet ophiolite are interpreted as indicative of a continuous hydrothermal alteration starting during uplift and exposure of the lithospheric mantle to the seafloor, subsequently followed by further carbonation and serpentinization induced by hot (up to 240 °C) and isotopically shifted ($\delta^{18}O$ ~2‰) seawater, and finally by channeling of and mixing with low-T and low-$\delta^{18}O$ seawater along fractures. This scenario is consistent with alteration occurring in long-lived hydrothermal systems controlled by tectonic activity where multiple metasomatic events can explain effective mantle hydration and carbonation over a few tens of thousands of years. Carbonation of ultramafic rocks in oceanic settings plays an important role for the global carbon cycle as abyssal peridotites and serpentinites might act as a sink for CO_2. Unraveling the complexity and sequence of reactions, temperatures and fluid compositions responsible for peridotite or serpentinite carbonation in oceanic and continental settings is important for correctly estimating rates of mineral carbonation and potential for CO_2 intake.

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1109
1110

FIGURE AND TABLE CAPTIONS

Fig. 1. (a) Tectonic map of the Piemont domain of the western Alps. (b). Geological map of the Chenaillet massif (star in Fig 1a, modified after Lafay et al., 2017) showing the location of the ophicarbonate outcrops and investigated samples.

Fig. 2. SEM-BSE images of representative textures observed in the Chenaillet ophicarbonates. (a) Serpentine mesh textures with and without C2 calcite partially replacing serpentine in mesh cores (sample RL6). (b) Complex mesh textures showing inner and outer cores surrounded by magnetite; inner cores are locally fully replaced by C2 calcite (sample RL6). (c) Mesh inner and outer cores completely replaced by C2 calcite (sample RL6). (d) Hourglass serpentine associated with magnetite (sample RL9). (e, f) Lizardite+magnetite veinlets (V-1) following original grain boundaries (samples RL3 and RL10). (g) Large lizardite+magnetite vein (V-2) crosscutting mesh textures (sample RL6). (h) C1 calcite vein crosscutting V-2 veins (sample RL6). (i) Textural link between C2 calcite in mesh textures and C1 calcite veins (sample RL10). (j, k) Lizardite+dolomite layers within the C3 calcite matrix containing a relict spinel (Spl); C3 calcite matrix is associated with small chrysotile grains (Ctl) and sometimes crosscut by calcite veins free of serpentine (C3-vein) (sample RL6). (l) Chrysotile grains in C3 calcite matrix (sample RL6). White and red circles are oxygen ($\delta^{18}O_{VSMOW}$, ‰) and carbon ($\delta^{13}C_{VPDB}$, ‰, in parentheses) isotope SIMS pits, respectively. Srp = serpentine, Ctl = chrysotile, Lz = lizardite, Cal = calcite, Dol = dolomite, Mag = magnetite, Spl = Cr-spinel.

Fig. 3. SEM-CL images showing representative CL features in (a-c) C1 calcite veins (samples RL9, RL3 and RL10) and (d-i) C2 calcite mesh (samples RL6, RL10 and RL9). C1 veins are sometimes rimmed by a distinct brighter (b) or darker (c) CL

1136 layer. C2 calcite mesh have marked euhedral (g, i) to anhedral (f, h) CL zonation.
1137 Resorption features are sometimes observed in C2 calcite mesh (f-i). White and red
1138 circles are locations of oxygen ($\delta^{18}O_{VSMOW}$, ‰) and carbon ($\delta^{13}C_{VPDB}$, ‰, in
1139 parentheses) isotope SIMS pits, respectively.

1140 **Fig. 4**. SEM-BSE images of representative dolomite textures in the Chenaillet
1141 ophicarbonates. Dolomite is observed as (a) rims around C2 calcite mesh (sample
1142 RL9), (b) borders along C1 calcite veins at the contact with serpentine (sample RL7),
1143 (c) subhedral grains in the lizardite layers at the boundary between serpentinite clasts
1144 and C3 calcite matrix (sample RL6), (d) borders between C4 calcite vein and
1145 serpentinite clast (sample RL9). White and red circles are oxygen ($\delta^{18}O_{VSMOW}$, ‰)
1146 and carbon ($\delta^{13}C_{VPDB}$, ‰, in parentheses) isotope SIMS pits, respectively.

1147 **Fig. 5**. SEM-CL images showing representative CL features in the carbonate matrix
1148 surrounding serpentinite clasts (samples RL6 and RL10). Domains with large calcite
1149 grains (C1') showing concentric (a-b) or oscillatory CL zoning (c) are surrounded by
1150 an aggregate of fine-grained calcite+chrysotile (a-b). (a, c) Large calcite grains in C1'
1151 domains are crosscut or bounded by calcite veinlets (C1'-veins). (d) Sharp contact
1152 between a calcite C3-vein and the surrounding fine-grained calcite matrix (C3). White
1153 and red circles in (c) and (d) are locations of oxygen ($\delta^{18}O_{VSMOW}$, ‰) and carbon
1154 ($\delta^{13}C_{VPDB}$, ‰, in parentheses) isotope SIMS pits, respectively. Dashed lines in (a) to
1155 (c) are locations of SIMS oxygen and carbon isotope traverses (see Electronic
1156 Appendix B).

1157 **Fig. 6**. Summary of oxygen isotope data in serpentine from the Chenaillet
1158 ophicarbonates measured by SIMS.

1159 **Fig. 7**. Summary of oxygen isotope data in carbonate from the Chenaillet
1160 ophicarbonates measured by SIMS.

1161 **Fig. 8**. Serpentine-magnetite thermometry. (a) Calculation of equilibrium
1162 temperatures for serpentine-magnetite pairs in different textures based on SIMS-
1163 measured mineral $\delta^{18}O$ values. (b) Calculation of water oxygen isotope values in
1164 equilibrium with both serpentine and magnetite in different textures based on
1165 calculated equilibrium temperatures. Solid and dashed lines are calculated equilibrium
1166 temperatures based on serpentine-water oxygen isotope fractionation factors by Früh-
1167 Green et al. (1996) and Saccocia et al. (2009), respectively. Magnetite-water oxygen
1168 isotope fractionation factors are after Bottinga and Javoy (1973).
1169 **Fig. 9**. Serpentine-carbonate thermometry. (a) Calculation of equilibrium
1170 temperatures for lizardite+dolomite and chrysotile+calcite pairs based on SIMS-
1171 measured mineral $\delta^{18}O$ values. (b) Calculation of water oxygen isotope values in
1172 equilibrium with serpentine, dolomite and calcite in each pair based on calculated
1173 equilibrium temperatures. Solid and dashed lines are calculated equilibrium
1174 temperatures for dolomite-serpentine (Matthews and Katz, 1977; Früh-Green et al.,
1175 1996) and calcite-serpentine (O'Neil et al., 1969; Früh-Green et al., 1996),
1176 respectively.
1177 **Fig. 10**. Summary of the different mineral generations and corresponding $\delta^{18}O$ values
1178 (‰). Formation is attributed to four stages of hydrothermal alteration in the Chenaillet
1179 ophicarbonates.
1180 **Fig. 11**. Schematic illustration showing the progression of textural and *T*- $\delta^{18}O_{(water)}$
1181 variations in the Chenaillet ophicarbonates. Ol = olivine, Opx = orthopyroxene, Cr-
1182 Spl = Cr-spinel, Srp_C = serpentine mesh core, Srp_R = serpentine mesh rim, Mag =
1183 magnetite, Lz = lizardite, Dol = dolomite, Ctl = chrysotile. $\delta^{18}O_W$ = oxygen isotope
1184 values of water.

Fig. 12. Simplified cross section showing the evolution of the hydrothermal system presented in this study in a seafloor tectonic setting (modified after Manatschal et al., 2011 and Lafay et al., 2017). Numbers correspond to the stages of alteration shown in Fig. 11.

Table 1. Serpentine-magnetite thermometry for ophicarbonates from the Chenaillet ophiolite.

Table 2. Serpentine-dolomite thermometry in hourglass textures for ophicarbonates from the Chenaillet ophiolite.

SUPPLEMENT FIGURE AND TABLE CAPTIONS

Fig. A.1. SEM-BSE maps of thin sections from the investigated samples from the Chenaillet ophiolite.

Fig. A.2. Diagrams showing the major and minor element chemical composition of serpentine in different textural locations in the various investigated samples. Cal = calcite, Srp = serpentine.

Fig. A.3. SEM-BSE images showing "turbid" calcite domains associated with chrysotile grains (C3) and "clear" calcite domains lacking chrysotile (C1') in the carbonate matrix surrounding serpentinite clasts (Chenaillet ophicarbonates).

Fig. A.4. (a) SIMS oxygen isotope edge-to-edge traverse across a large (~1 mm) C1 calcite vein shown in Fig. 3c. SEM-CL (b) and SEM-BSE (c) images in a different area of the same vein showing ~ 3‰ variation in $\delta^{18}O$ values. White and red circles are locations of oxygen ($\delta^{18}O_{VSMOW}$, ‰) and carbon ($\delta^{13}C_{VPDB}$, ‰, in parentheses) isotope SIMS pits, respectively.

Fig. A.5. Plot of $\delta^{18}O$ versus $\delta^{13}C$ in different calcite generations from the Chenaillet ophicarbonates.

Fig. A.6. BSE-SEM images of SIMS pits on magnetite from the Chenaillet ophicarbonates. (a) Mesh texture (sample RL6), (b) V-1 vein (sample RL3), (c) V-2 vein (sample RL6), and (d) hourglass texture (sample RL9). White areas are remnants of Au coating. White circles are locations of oxygen ($\delta^{18}O_{VSMOW}$, ‰) isotope SIMS pits.

Fig. A.7. Model showing the net variation in oxygen isotope ratios in both serpentine and magnetite as a function of a contemporary variation in temperature and water $\delta^{18}O$. Serpentine-water and magnetite-water oxygen isotope fractionation factors are after Früh-Green et al. (1996) and Bottinga and Javoy (1973), respectively.

Fig. A.8. Representative SEM-BSE images of SIMS pits in serpentine (a), calcite (b), dolomite (c) and magnetite (d).

Table A.1. Complete data table for oxygen isotope analyses by SIMS (A.1a) and corresponding EPMA (A.1b) in serpentine from the Chenaillet ophicarbonates.

Table A.2. Complete data table for oxygen (A.2a) and carbon (A.2b) isotope analyses by SIMS as well as representative EPMA (A.2c) in carbonate from the Chenaillet ophicarbonates.

Table A.3. Complete data table for oxygen isotope analyses in magnetite by SIMS (A.3a) and representative EPMA (A.3b) from the Chenaillet ophicarbonates.

Table A.4. Complete data table for oxygen (A.4a) and carbon (A.4b) isotope analyses by SIMS in carbonate and magnetite (A.4c) reference materials. Data on serpentine reference materials are published in Scicchitano et al. (2020) in supplementary Table S2 (sessions S6 and S8).

1235 **Table A.5**. Serpentine-magnetite thermometry for ophicarbonates from the Chenaillet

1236 ophiolite using different serpentine-magnetite calibrations.

1237 **Table 1**. Serpentine-magnetite thermometry for ophicarbonates from the Chenaillet ophiolite.

Analysis ID	Texture	$\delta^{18}O$ (‰) *serpentine*	$\delta^{18}O$ (‰) *magnetite*	$\Delta^{18}O$(Srp-Mag)	*T* (°C)* *calculated*	$\delta^{18}O_w$ (‰)* *calculated*	*T* (°C)** *calculated*	$\delta^{18}O_w$ (‰)** *calculated*
RL6-1-(Srp-18b/Mag-1)	mesh	6.6	-6.0	12.7	196	4.3	245	3.1
RL6-1-(Srp-18b/Mag-2)	mesh	6.6	-5.6	12.2	204	4.5	252	3.4
RL6-1-(Srp-20/Mag-3)	mesh	6.7	-5.7	12.5	199	4.5	248	3.4
RL6-1-(Srp-34/Mag-4)	mesh	6.6	-10.2	16.9	136	2.1	194	0.0
RL6-1-(Srp-24/Mag-5)	mesh	7.8	-6.3	14.2	172	4.7	225	3.2
RL6-1-(Srp-25/Mag-7)	mesh	7.4	-5.5	12.9	192	5.0	242	3.7
RL6-1-(Srp-27/Mag-8)	mesh	6.3	-9.8	16.3	144	2.2	201	0.3
RL6-1-(Srp-29/Mag-9)	mesh	6.8	-6.3	13.2	188	4.2	239	2.9
RL6-1-(Srp-41/Mag-17)	mesh	7.2	-5.1	12.3	202	5.1	250	3.9
RL6-1-(Srp-42/Mag-18)	mesh	7.4	-5.6	13.1	188	4.9	239	3.6
RL6-1-(Srp-50/Mag-19)	mesh	5.2	-9.6	15.0	161	1.8	216	0.1
RL6-1-(Srp-49/Mag-21)	mesh	6.9	-10.2	17.3	132	2.2	191	0.1
RL6-1-(Srp-49/Mag-22)	mesh	6.9	-9.5	16.5	141	2.6	198	0.6
RL6-2-(Srp-28/Mag-13)	mesh	7.4	-5.0	12.6	198	5.2	247	4.0
RL6-2-(Srp-27/Mag-14)	mesh	7.2	-7.6	14.9	162	3.7	217	2.1
RL6-2-(Srp-26/Mag-15)	mesh	7.5	-7.9	15.5	154	3.7	210	2.0
RL6-2-(Srp25/Mag-16)	mesh	7.4	-8.0	15.6	153	3.7	209	1.9
RL6-2-(Srp-13/Mag-5)	V-2 vein	4.1	-10.1	14.4	169	1.0	223	-0.6
RL6-2-(Srp-18/Mag-10)	V-2 vein	3.8	-7.7	11.6	215	2.0	261	1.1
RL3-(Srp-43/Mag-5)	V-1 vein	5.8	-8.2	14.1	173	2.8	226	1.3
RL9-(Srp-54/Mag-16)	hourglass Srp	5.2	-9.6	14.9	162	1.8	216	0.1
RL9-(Srp-58/Mag-18)	hourglass Srp	4.5	-8.4	13.1	190	2.0	240	0.7
RL9-(Srp-57/Mag-19)	hourglass Srp	4.6	-9.1	13.8	178	1.7	230	0.3
RL9-(Srp-56/Mag-20)	hourglass Srp	4.5	-8.0	12.5	198	2.3	247	1.1

* Srp-water after Früh-Green et al. (1996), ** Srp-water after Saccocia et al. (2009). Mag-water are after Bottinga and Javoy (1973). $\delta^{18}O_w$ = calculated oxygen isotope value of water in equilibrium with serpentine and magnetite.

1238

Table 2. Serpentine-dolomite thermometry in hourglass textures for ophicarbonates from the Chenaillet ophiolite.

Analysis ID	Texture	$\delta^{18}O$ (‰) *serpentine*	$\delta^{18}O$ (‰) *dolomite*	$\Delta^{18}O$(Dol-Srp)	*T* (°C) *calculated*	$\delta^{18}O_w$ (‰) *calculated*
RL9-1-(Srp-1/Dol-1)	hourglass	4.3	11.8	7.5	228	2.9
RL9-1-(Srp-4/Dol-2)	hourglass	4.4	11.7	7.3	235	3.1
RL9-1-(Srp-6/Dol-4)	hourglass	4.1	12.6	8.5	190	1.6
RL9-1-(Srp-10/Dol-5)	hourglass	4.3	12.0	7.6	220	2.7
RL9-1-(Srp-26/Dol-6)	hourglass	4.8	12.6	7.8	215	3.0
RL9-1-(Srp-29/Dol-10)	hourglass	4.3	12.2	7.9	213	2.5
RL9-1-(Srp-46/Dol-14)	hourglass	4.3	10.1	5.8	315	4.5
RL9-1-(Srp-51/Dol-15)	hourglass	4.3	12.5	8.2	200	2.1
RL9-1-(Srp-59/Dol-19)	hourglass	4.2	11.2	7.0	250	3.2
RL7-(Srp-4/Dol-4)	hourglass	4.6	10.9	6.3	285	4.3
RL7-(Srp-10/Dol-2)	hourglass	5.6	11.8	6.2	290	5.4
RL7-(Srp-9/Dol-1)	hourglass	5.0	11.6	6.6	270	4.4

Srp-water after Früh-Green et al. (1996), Dol-water after Matthews and Katz (1977). $\delta^{18}O_w$ = calculated oxygen isotope value of water in equilibrium with serpentine and dolomite.

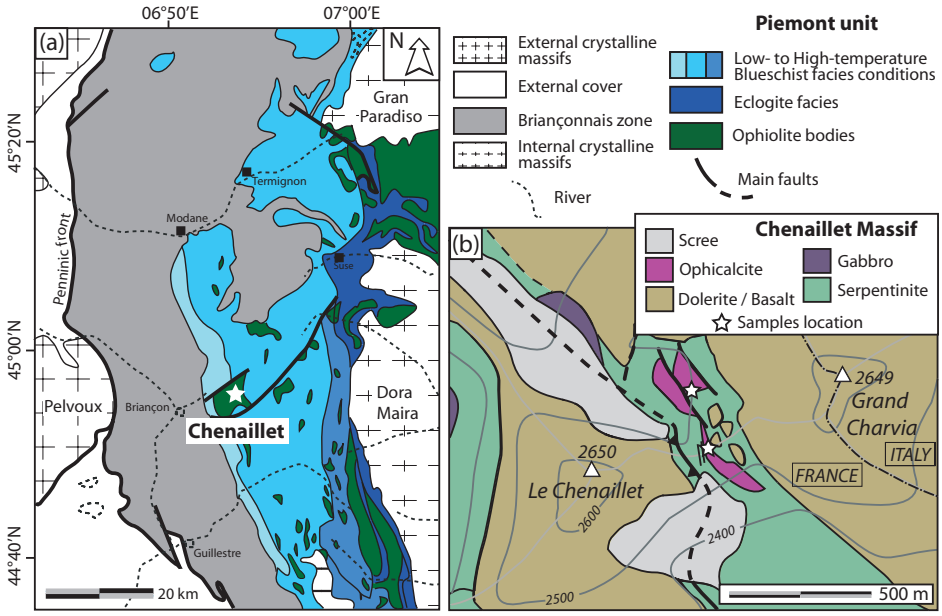
06°50'E
07°00'E
(a)
N
45°20'N
45°00'N
44°40'N
Gran
Paradiso
Termignon
Modane
Penninic front
Suse
Pelvoux
Briançon
Chenaillet
Dora
Maira
Guillestre
20 km
External crystalline massifs
External cover
Briançonnais zone
Internal crystalline massifs
River
Piemont unit
Low- to High-temperature Blueschist facies conditions
Eclogite facies
Ophiolite bodies
Main faults
(b)
Chenaillet Massif
Scree
Ophicalcite
Dolerite / Basalt
Gabbro
Serpentinite
Samples location
2649
Grand
Charvia
ITALY
FRANCE
2650
Le Chenaillet
2600
2400
2500
500 m

Figure 1

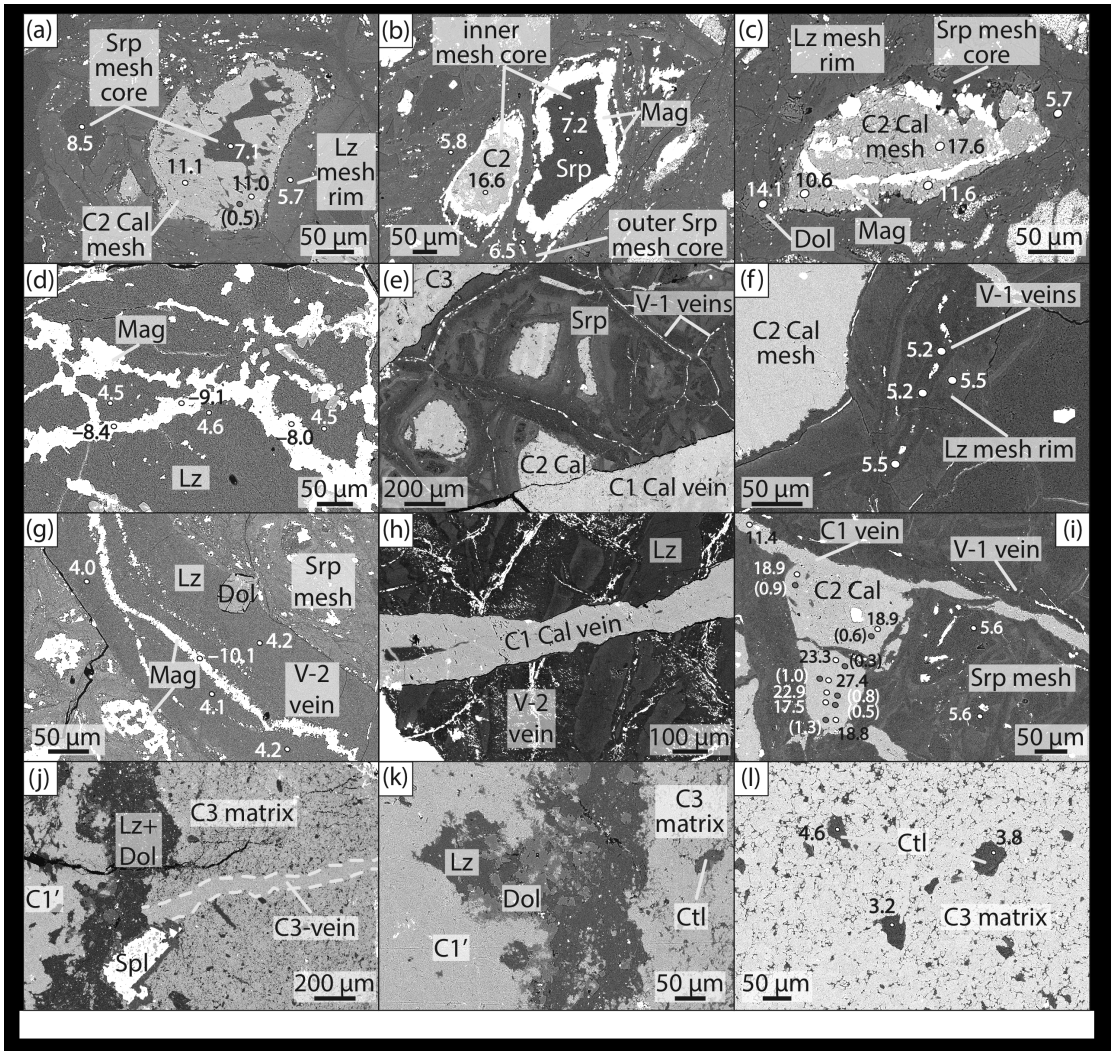
(a)
Srp mesh core
8.5
7.1
11.1
11.0
5.7
Lz mesh rim
(0.5)
C2 Cal mesh
50 µm
(b)
inner mesh core
Mag
7.2
5.8
C2
16.6
Srp
50 µm
6.5
outer Srp mesh core
(c)
Lz mesh rim
Srp mesh core
5.7
C2 Cal mesh
17.6
14.1
10.6
11.6
Dol
Mag
50 µm
(d)
Mag
4.5
9.1
8.4
4.6
4.5
8.0
Lz
50 µm
(e)
C3
V-1 veins
Srp
C2 Cal
200 µm
C1 Cal vein
(f)
V-1 veins
C2 Cal mesh
5.2
5.5
5.2
Lz mesh rim
5.5
50 µm
(g)
4.0
Lz
Dol
Srp mesh
4.2
10.1
Mag
4.1
V-2 vein
50 µm
4.2
(h)
Lz
C1 Cal vein
V-2 vein
100 µm
(i)
11.4
C1 vein
V-1 vein
18.9
(0.9)
C2 Cal
18.9
(0.6)
5.6
23.3
(0.3)
(1.0)
27.4
Srp mesh
22.9
(0.8)
17.5
(0.5)
5.6
(1.3)
18.8
50 µm
(j)
C3 matrix
Lz+ Dol
C1′
C3-vein
Spl
200 µm
(k)
C3 matrix
Lz
Dol
Ctl
C1′
50 µm
(l)
4.6
Ctl
3.8
3.2
C3 matrix
50 µm

Figure 2

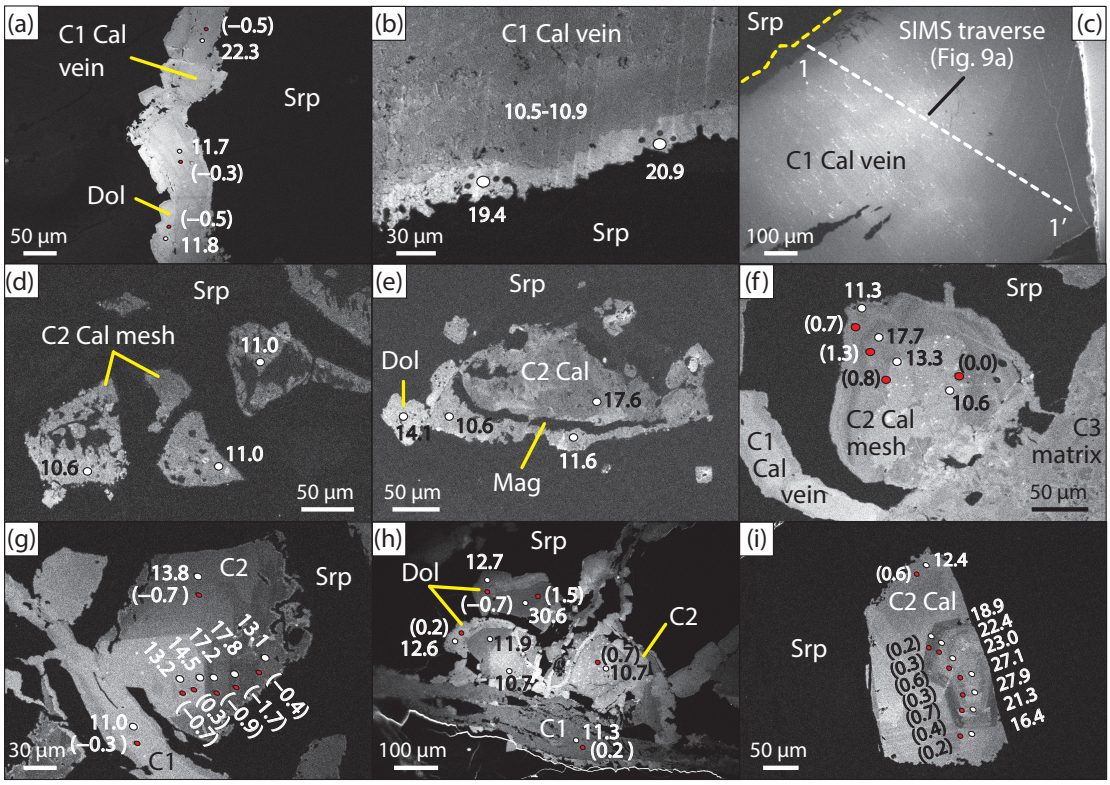
(a)
C1 Cal vein
(–0.5)
22.3
Srp
11.7
(–0.3)
Dol
(–0.5)
11.8
50 µm
(b)
C1 Cal vein
10.5-10.9
20.9
19.4
Srp
30 µm
Srp
SIMS traverse (Fig. 9a)
(c)
1
C1 Cal vein
1′
100 µm
(d)
Srp
C2 Cal mesh
11.0
11.0
10.6
50 µm
(e)
Srp
Dol
C2 Cal
17.6
14.1
10.6
11.6
Mag
50 µm
(f)
11.3
Srp
(0.7)
17.7
(1.3)
13.3
(0.0)
(0.8)
10.6
C2 Cal mesh
C3 matrix
C1 Cal vein
50 µm
(g)
13.8
(–0.7)
C2
Srp
13.1
17.8
17.2
14.5
13.2
(–0.4)
(–1.7)
(–0.9)
(0.3)
(–0.7)
11.0
(–0.3)
C1
30 µm
(h)
Srp
Dol
12.7
(–0.7)
(1.5)
30.6
(0.2)
12.6
11.9
C2
(0.7)
10.7
10.7
C1
11.3
(0.2)
100 µm
(i)
12.4
(0.6)
C2 Cal
18.9
22.4
23.0
27.1
27.9
21.3
16.4
Srp
(0.2)
(0.3)
(0.6)
(0.3)
(0.7)
(0.4)
(0.2)
50 µm

Figure 3

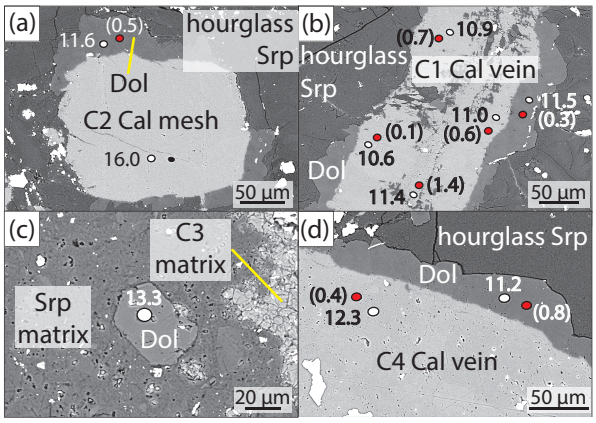
(a)
11.6
(0.5)
hourglass Srp
Dol
C2 Cal mesh
16.0
50 µm
(b)
(0.7)
10.9
hourglass Srp
C1 Cal vein
11.5
(0.3)
11.0
(0.6)
(0.1)
10.6
Dol
11.4
(1.4)
50 µm
(c)
C3 matrix
Srp matrix
13.3
Dol
20 µm
(d)
hourglass Srp
Dol
11.2
(0.8)
(0.4)
12.3
C4 Cal vein
50 µm

Figure 4

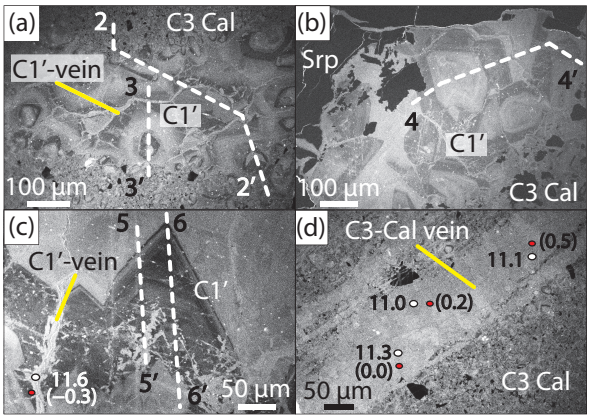
(a)
2
C3 Cal
C1′-vein
3
C1′
100 µm
3′
2′
(b)
Srp
4′
4
C1′
100 µm
C3 Cal
(c)
5
6
C1′-vein
C1′
11.6
(–0.3)
5′
6′
50 µm
(d)
C3-Cal vein
(0.5)
11.1
11.0
(0.2)
11.3
(0.0)
50 µm
C3 Cal

Figure 5

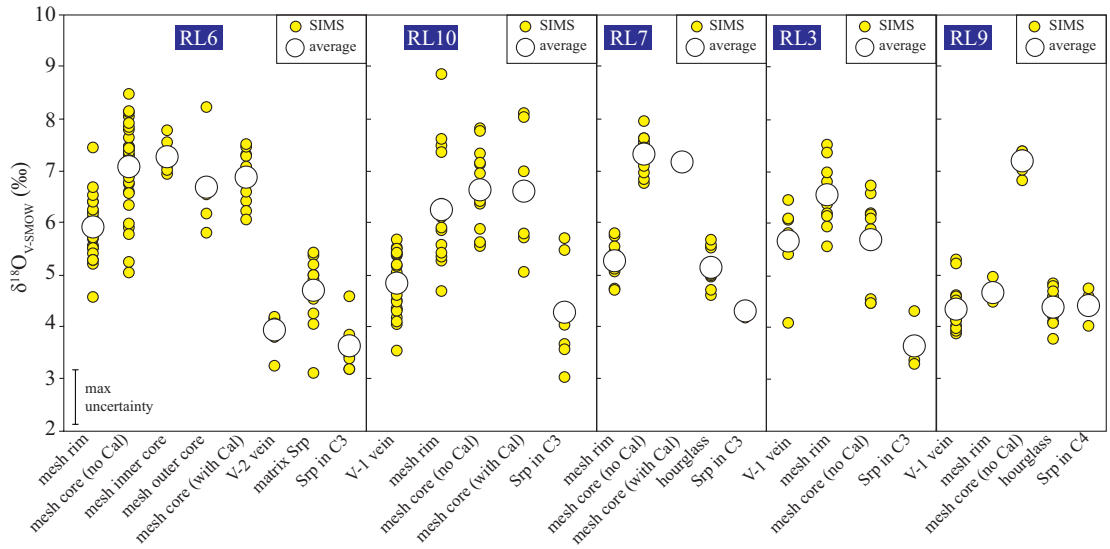
RL6
RL10
RL7
RL3
RL9
SIMS
average
max
uncertainty
δ18OV-SMOW (‰)
mesh rim
mesh core (no Cal)
mesh inner core
mesh outer core
mesh core (with Cal)
V-2 vein
matrix Srp
Srp in C3
V-1 vein
hourglass
Srp in C4

Figure 6

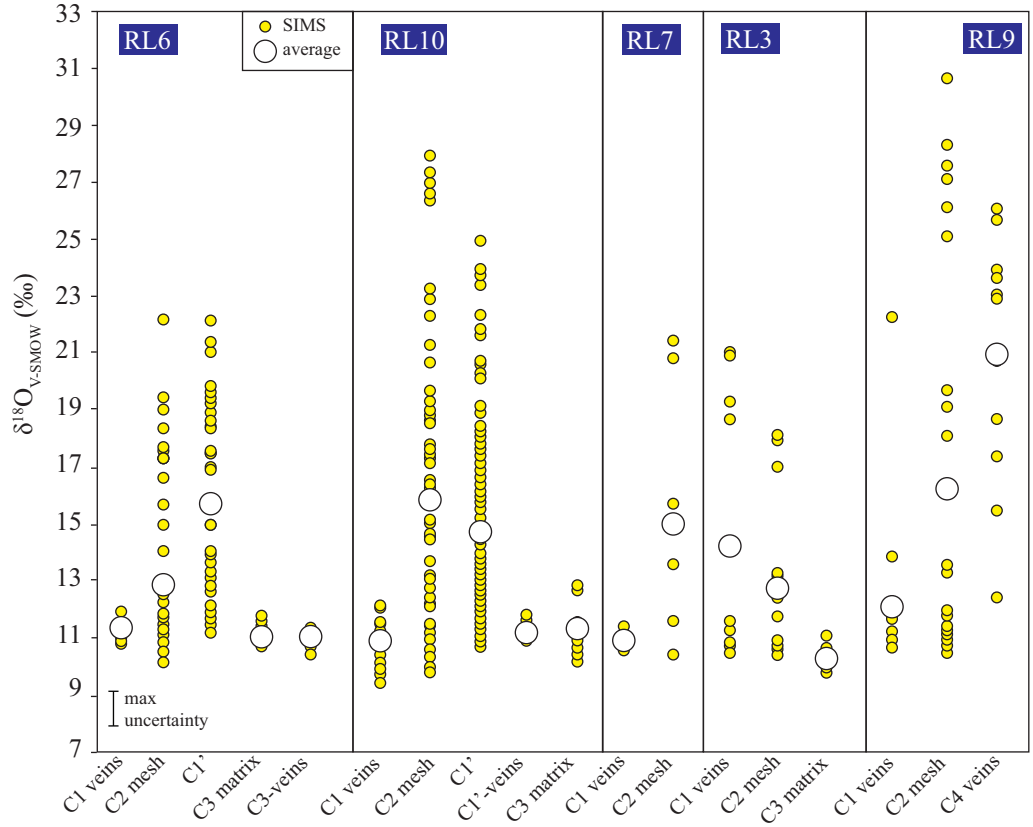
RL6
SIMS
average
RL10
RL7
RL3
RL9
$\delta^{18}O_{V\text{-}SMOW}$ (‰)
max
uncertainty
C1 veins
C2 mesh
C1'
C3 matrix
C3-veins
C1 veins
C2 mesh
C1'
C1'-veins
C3 matrix
C1 veins
C2 mesh
C1 veins
C2 mesh
C3 matrix
C1 veins
C2 mesh
C4 veins

Figure 7

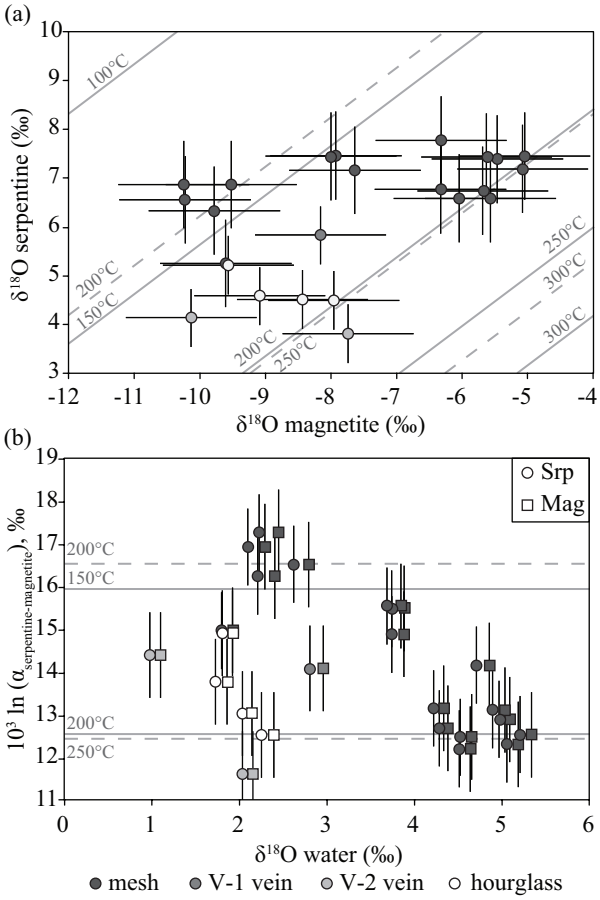
(a)
δ18O serpentine (‰)
δ18O magnetite (‰)
100°C
200°C
150°C
200°C
250°C
250°C
300°C
300°C
(b)
10³ ln (αserpentine-magnetite), ‰
δ18O water (‰)
Srp
Mag
200°C
150°C
200°C
250°C
mesh
V-1 vein
V-2 vein
hourglass

Figure 8

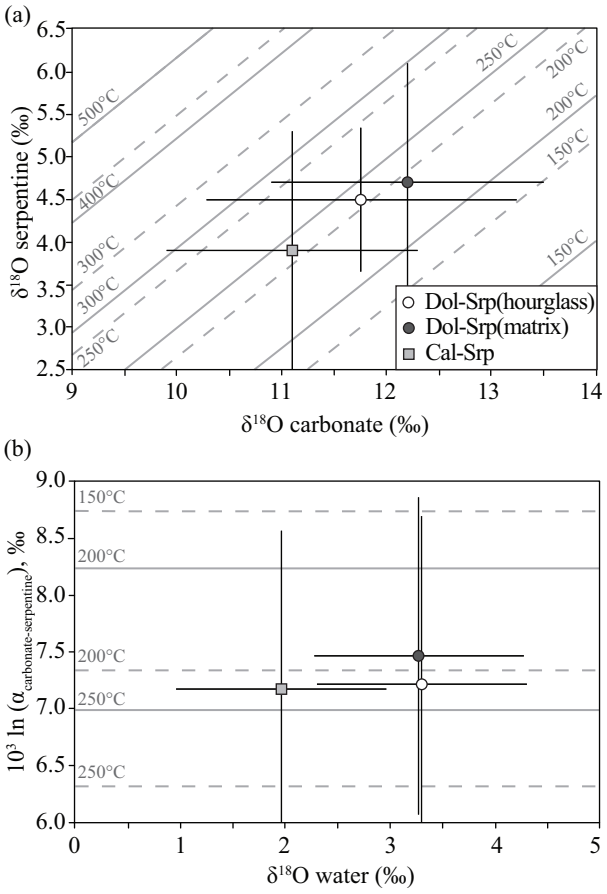
(a)
δ18O serpentine (‰)
δ18O carbonate (‰)
500°C
400°C
300°C
300°C
250°C
250°C
200°C
200°C
150°C
150°C
Dol-Srp(hourglass)
Dol-Srp(matrix)
Cal-Srp
(b)
10³ ln (αcarbonate-serpentine), ‰
δ18O water (‰)
150°C
200°C
200°C
250°C
250°C

Figure 9

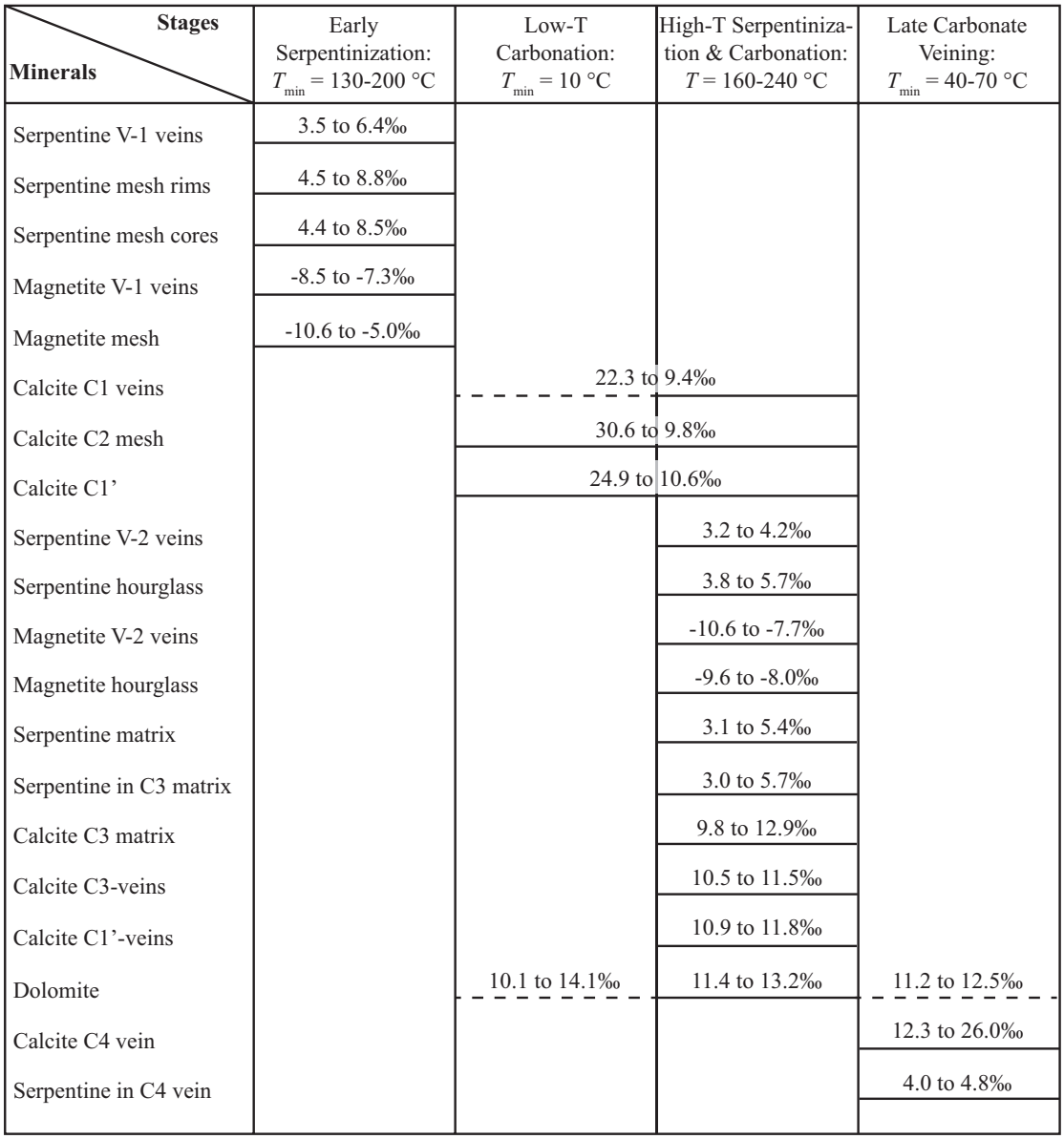
Stages
Minerals
Early Serpentinization: T_{min} = 130-200 °C
Low-T Carbonation: T_{min} = 10 °C
High-T Serpentiniza-tion & Carbonation: T = 160-240 °C
Late Carbonate Veining: T_{min} = 40-70 °C
Serpentine V-1 veins
3.5 to 6.4‰
Serpentine mesh rims
4.5 to 8.8‰
Serpentine mesh cores
4.4 to 8.5‰
Magnetite V-1 veins
-8.5 to -7.3‰
Magnetite mesh
-10.6 to -5.0‰
Calcite C1 veins
22.3 to 9.4‰
Calcite C2 mesh
30.6 to 9.8‰
Calcite C1'
24.9 to 10.6‰
Serpentine V-2 veins
3.2 to 4.2‰
Serpentine hourglass
3.8 to 5.7‰
Magnetite V-2 veins
-10.6 to -7.7‰
Magnetite hourglass
-9.6 to -8.0‰
Serpentine matrix
3.1 to 5.4‰
Serpentine in C3 matrix
3.0 to 5.7‰
Calcite C3 matrix
9.8 to 12.9‰
Calcite C3-veins
10.5 to 11.5‰
Calcite C1'-veins
10.9 to 11.8‰
Dolomite
10.1 to 14.1‰
11.4 to 13.2‰
11.2 to 12.5‰
Calcite C4 vein
12.3 to 26.0‰
Serpentine in C4 vein
4.0 to 4.8‰

Figure 10

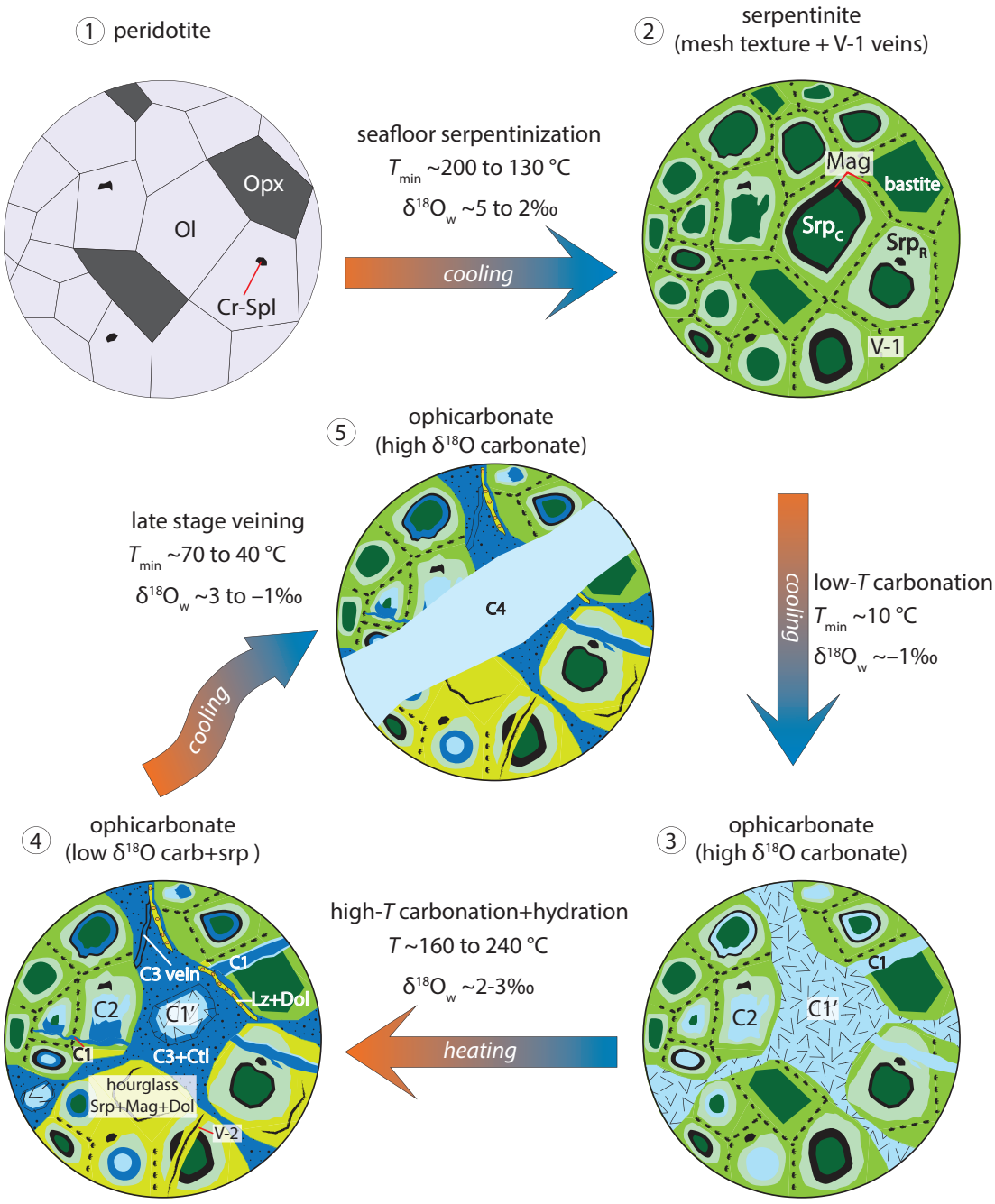
1 peridotite
Opx
Ol
Cr-Spl
seafloor serpentinization
T_{min} ~200 to 130 °C
$\delta^{18}O_w$ ~5 to 2‰
cooling
2 serpentinite
(mesh texture + V-1 veins)
Mag
bastite
Srp_C
Srp_R
V-1
5 ophicarbonate
(high $\delta^{18}O$ carbonate)
C4
late stage veining
T_{min} ~70 to 40 °C
$\delta^{18}O_w$ ~3 to −1‰
cooling
cooling
low-T carbonation
T_{min} ~10 °C
$\delta^{18}O_w$ ~−1‰
4 ophicarbonate
(low $\delta^{18}O$ carb+srp)
C3 vein
C1
Lz+Dol
C2
C1′
C1
C3+Ctl
hourglass
Srp+Mag+Dol
V-2
high-T carbonation+hydration
T ~160 to 240 °C
$\delta^{18}O_w$ ~2-3‰
heating
3 ophicarbonate
(high $\delta^{18}O$ carbonate)
C1
C2
C1′

Figure 11

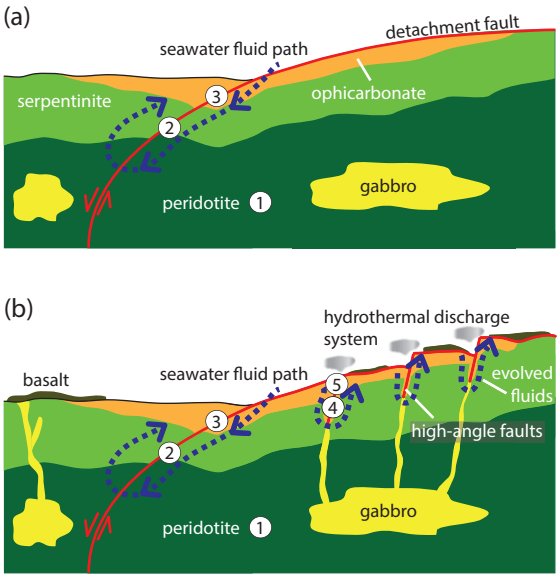
(a)
detachment fault
seawater fluid path
serpentinite
ophicarbonate
3
2
peridotite 1
gabbro
(b)
hydrothermal discharge system
basalt
seawater fluid path
5
4
3
evolved fluids
high-angle faults
2
peridotite 1
gabbro

Figure 12