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### ► To cite this version:

Marc Ulrich, Manuel Munoz, Philippe Boulvais, Michel Cathelineau, Dominique Cluzel, et al.. Serpentinization of New Caledonia peridotites: from depth to (sub-)surface. Contributions to Mineralogy and Petrology, 2020, 75 (9), pp.91. 10.1007/s00410-020-01713-0 . insu-02890835

**HAL Id: insu-02890835**

**<https://insu.hal.science/insu-02890835>**

Submitted on 7 Jul 2020

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# Serpentinization of New Caledonia peridotites: from depth to (sub-)surface

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*Keywords: Serpentinization, New Caledonia ophiolite, subduction, obduction, serpentine  
geochemistry, meteoric fluid circulation.*

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## ABSTRACT

Serpentinization processes occur at geological settings notably during oceanic subduction and obduction, where mantle rocks interact with water. Different types of serpentine minerals form according to temperature and pressure conditions, and potentially chemical exchanges. Therefore, the characterization of serpentine minerals, and the possible occurrence of multiple serpentine generations in mantle rocks provide essential constraints on the conditions of fluid-rock interactions in the mantle. The serpentinite sole of the Peridotite Nappe of New Caledonia (Southwest Pacific) is the result of several superimposed serpentinisation events. The latter were discriminated using mineralogical and geochemical approaches and modeling.

Lizardite represents more than 80% of the entire serpentine content of the ophiolite. It is crosscut by several veins of other serpentine species in the serpentinite sole. The relative chronology appears as follows: lizardite 1 → lizardite 2 → antigorite → chrysotile → polygonal serpentine. The transition from primary/magmatic minerals to lizardite 1 is almost isochemical. Then, the development of lizardite 2 yields an enrichment in fluid-mobile elements such as Cs, Rb, Ba, U and light rare-earth elements and an apparent increase of the  $Fe^{3+}/Fe_T$  ratio. The modeling of  $\delta^{18}O$  values (1.9‰ to 13.9‰) and  $\delta D$  values (88‰ to 106‰) of all serpentine species through Monte-Carlo simulations show that New Caledonia serpentines were mainly formed in equilibrium with fluids released by the dehydration of altered oceanic crust (AOC) during subduction between 250°C and 350°C. AOC-derived fluids are not the unique source of fluids since a low temperature (100-150°C) meteoric component is also predicted by the models. Thus, serpentine acts as a tape-recorder of fluid-rock interactions into the mantle from depth to (sub-)surface.

## INTRODUCTION

Serpentinization is a hydrothermal alteration process that leads to upper mantle hydration. Serpentine minerals are ubiquitous in ultramafic rocks from various geological settings and their crucial role in tectonic and chemical processes has been widely documented over the past two decades: In divergent environments, which include ultraslow and slow-spreading centers and mantle-exhuming passive margins, serpentine occurs mainly along fractures and detachment faults, weakening the upper mantle, promoting strain localization and resulting in the exhumation of serpentinized peridotites at the seafloor (Andréani et al. 2014; 2007; Cannat et al. 1995; Chenin et al. 2017; Delacour et al. 2008; Gillard et al. 2019; Guillot et al. 2015; Mével 2003; Picazo et al. 2012). Such tectonic processes involve significant mass transfer between the mantle and oceanic reservoirs (Alt and Shanks III 2003; Iyer et al. 2008; Kodolanyi et al. 2012; Pinto et al. 2016; Rouméjon et al. 2015; Schwarzenbach et al. 2015). Also, the rheology of serpentinized rocks strongly influences deformation and seismicity in the forearc and controls geodynamics of the subduction zone

66 (Hyndman and Peacock 2003; Peacock and Hyndman 1999; Stern 2002). Here again, serpentine is  
67 assumed to be one of the most efficient ways to recycle water and fluid-mobile elements (FME) into  
68 the deeper mantle (Debret et al. 2013; Deschamps et al. 2012; 2011; Klein et al. 2017; Poli and  
69 Schmidt 2002; Rüpke et al. 2004; Savov et al. 2005; Scambelluri et al. 2004). Thus, the uppermost  
70 part of the oceanic lithosphere is hydrothermally altered before entering subduction zones. Then, the  
71 dehydration of the subducting slab favors the formation of forearc serpentine, which hosts a large  
72 amount of water (up to ~13 wt.%). The circulation of such an amount of aqueous fluids may, in turn,  
73 transport fluid-mobile elements (FME) deep into the mantle down to ~150 km (Ulmer and  
74 Trommsdorff 1995; Wunder et al. 2001). At temperature above ~650°C, serpentine is no longer stable  
75 and aqueous fluids are liberated by serpentine breakdown, triggering mantle wedge melting that gives  
76 rise to arc volcanism (Hattori and Guillot 2003; Iwamori 1998; Reynard 2013; Schmidt and Poli 1998;  
77 Ulmer and Trommsdorff 1995; 1999). Therefore, studying serpentinite is fundamental in the aim of  
78 addressing questions about plate tectonics and global geochemical cycles.

79 When convergence results in the closure of ocean basins, slices of the forearc mantle may be  
80 obducted. Serpentinite then acts as a lubricant, facilitating the ophiolite emplacement and subsequent  
81 exhumation of the high pressure rocks (Agard et al. 2016; Guillot et al. 2009; 2000; Schwartz et al.  
82 2001). However, the conditions of fluid-rock interactions and serpentine formation, as well as the  
83 nature and source of serpentinizing fluids, are mostly unconstrained.

84 In New Caledonia (NC), large ultramafic massifs form an extensive and well-exposed ophiolite  
85 obducted during the Late Eocene, termed Peridotite Nappe (Figure 1; Avias 1967). Peridotites  
86 recorded various degrees of serpentinization, and the base of the Peridotite Nappe is made of a thick  
87 serpentinite sole characterized by multiple generations of serpentine veins, the origin of which  
88 remains unclear (Frost et al. 2013; Gautier et al. 2016; Mothersole et al. 2017; Quesnel et al. 2016b;  
89 Ulrich et al. 2014). In this paper, the source and nature of the fluids involved in the serpentinization  
90 are therefore unraveled thanks to new petrological, mineralogical and geochemical data as well as  
91 geochemical modeling.

## 92 93 **GEOLOGICAL SETTINGS**

94 New Caledonia is an island of the SW Pacific, ~1300 km to the east of Australia, which forms  
95 the northernmost part of the Norfolk Ridge, an elongated slice of thinned and largely submarine  
96 continental crust, rifted from the Gondwana margin during the Late Cretaceous. The Peridotite  
97 Nappe tectonically overlies a patchwork of pre-Oligocene terranes and covers at present about one-  
98 third of the island. The main unit is located in the south of the island, so-called Massif du Sud, and  
99 several tectonic klippen are spread along the West coast (**Figure 1**). All these units result from the  
100 evolution of a marginal basin that opened to the east of the Norfolk Ridge during the Campanian-

101 Paleocene (90 Ma—55 Ma; Cluzel et al. 2001). This basin was inverted at 56 Ma by northeastward-  
102 subduction (Cluzel et al. 2012a) and the upper plate of the system (the Loyalty Basin) was obducted  
103 at ca. 34 Ma (Cluzel et al. 1998) when the Norfolk ridge entered the trench and jammed the Eocene  
104 subduction. Harzburgites and dunites formed in a supra-subduction zone environment are  
105 predominant, while lherzolites, inherited from the initial marginal basin are also found in the  
106 northernmost massifs (Pirard et al. 2013; Secchiari et al. 2016; 2019; Ulrich et al. 2010). The  
107 Peridotite Nappe bears a lateritic regolith (up to 100 m thick) that contains ~10% of the world Ni  
108 reserves (McRae 2018). The Peridotite nappe overlies the Poya Terrane, which corresponds to a  
109 large composite allochthon formed of two sub-units: i) tectonic slices of massive and pillow basalt  
110 (Poya Terrane Basalts) of dominant MORB affinity and abyssal argillites of Campanian to Early  
111 Eocene age (Aitchison et al. 1995), derived from the upper oceanic crust of the South Loyalty Basin  
112 (Cluzel et al. 1997; Eissen et al. 1998) and accreted in the fore-arc region of the Loyalty Arc (Cluzel  
113 et al. 2001), and ii) Coniacian-Santonian distal turbidites (Kone Facies) accumulated on the ancient  
114 passive margin of the Norfolk Ridge, and intruded by lower Eocene dolerite sills of EMORB  
115 affinity (Cluzel et al. 2018).

116 The serpentinization processes of the Peridotite Nappe have never been studied in-depth, while  
117 peridotites are highly serpentinized. Orloff (1968) highlighted, for the first time, the decreasing  
118 degree of serpentinization from bottom to the top of the ophiolite. More recently, Frost et al. (2013)  
119 identified three generations of serpentine veins in a dunite sample: two-first generations of lizardite  
120 and the last one of chrysotile. The transformation of lizardite to chrysotile would have been  
121 accompanied by the release of Fe and the subsequent formation of magnetite. Mothersole et al. (2017)  
122 used NC serpentinites as proxies of mantle wedge serpentinites and compared them with those from  
123 the 15°20'N fracture zone in the Mid-Atlantic Ridge to evaluate the effect of hydrothermal alteration  
124 on a budget of major and minor elements in the two different geodynamic settings (Mothersole et al.  
125 2017). They concluded that serpentinization was nearly identical in the two environments, except  
126 more oxidized Fe as well as enrichments in Cl, S, and C in abyssal serpentinites compared to the  
127 forearc serpentinites. Serpentine-bearing faults were extensively studied i) to characterize their  
128 kinematics and the mechanisms of NC ophiolite emplacement on the continental basement (Gautier  
129 et al. 2016; Quesnel et al. 2016b), and ii) to constrain the carbonation and silicification of the  
130 serpentinite sole in relation to meteoric fluid percolation (Quesnel et al. 2016a; 2013; Ulrich et al.  
131 2014) and iii) to understand the formation of secondary Ni-rich phyllosilicates, mostly talc-like  
132 phases, in serpentine-filled fractures at the top of the ophiolite (Cathelineau et al. 2016; 2015; Fritsch  
133 et al. 2016; Muñoz et al. 2019). High temperature, slab-derived fluids are proposed for the origin of  
134 syntectonic tremolite-antigorite veins, which are widespread in the Peridotite Nappe (Cluzel et al.

135 2019). But the source and nature of fluids in equilibrium with the main serpentinization episode that  
136 affected the whole ophiolite remains, however, unconstrained.

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## 138 **MATERIALS AND METHODS**

### 139 *Sampling and analytical strategies*

140 A collection of 30 samples, collected from five different massifs (the Massif du Sud, Kopeto,  
141 Koniambo, Tiébaghi and Poum), includes serpentinized harzburgites, lherzolites and dunites referred  
142 to as "upper serpentine" hereafter, as well as serpentinites from the sole of the Peridotite Nappe. They  
143 represent most rock types and serpentine occurrences of the NC ophiolite. The serpentinites were  
144 characterized by: 1) Raman spectroscopy, to identify serpentine species, 2) major and trace element  
145 chemistry of primary minerals and serpentines crystals, to evaluate the chemical mobility during  
146 fluid-rock interactions, 3) oxygen and hydrogen isotope geochemistry of each serpentine variety to  
147 discuss the source of fluids involved in the serpentinization processes.

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### 149 *Raman Spectroscopy*

150 Raman spectra were acquired at ENS Lyon (France) using a Horiba Jobin-Yvon LabRam  
151 HR800 spectrometer and a visible ionized argon laser source with a wavelength of 514 nm. Output  
152 laser power was 100 mW, and measurements were performed using an Olympus lens of 100x to focus  
153 the laser beam onto an area that was 1  $\mu\text{m}$  in diameter. Analyses were carried out on 30  $\mu\text{m}$  polished  
154 thin sections. Spectra result from the average of 5 acquisitions of 10-20 s for each point measured to  
155 optimize the signal/noise ratio. Raman spectra were recorded in two spectral intervals: 200-1250  $\text{cm}^{-1}$   
156 for structural bonding characterization and 3550-3800  $\text{cm}^{-1}$  for the characterization of hydroxyl  
157 groups. Serpentine species were mainly identified by comparing spectra with those already published  
158 (Auzende et al. 2004; Lemaire 2000), focusing on the OH stretching range.

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### 160 *Mineral Chemistry*

161 Electron microprobe analyses of minerals were carried out with a Cameca SX 100 at Service  
162 Commun de Microscopie Électronique et de Microanalyses (SCMEM, Nancy, France). All analyses  
163 of major elements, Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, were made against natural and synthetic  
164 mineral standard: albite (Si, Na), corundum (Al), andradite (Ca), olivine (Mg), hematite (Fe), MnTiO<sub>3</sub>  
165 (Mn, Ti), NiO (Ni), orthoclase (K), with the exception for serpentine measurements for which Mg  
166 was calibrated using natural clinocllore. Acceleration voltage and beam current were 15 kV and 12  
167 nA, respectively, the counting time was 10 s, and standard correction procedures were applied. The  
168 beam diameter was focused to 1  $\mu\text{m}$ . Total Fe content is calculated on a divalent basis, as FeO.  
169 Structural formulae were calculated based on of the following number of oxygens: olivine, 4;

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170 pyroxene, 6; lizardite, chrysotile and polygonal serpentine, 7. Antigorite has a general formulae  $Mg_{3m-}$   
171  $3Si_{2m}O_{5m}(O.H.)_{4m-6}$  that differs from the idealized serpentine formula  $Mg_3SiO_5(OH)_4$  by a minor  
172  $Mg(OH)_2$  depletion,  $m$  being the number of tetrahedra along an entire wavelength. Structural formulae  
173 for antigorite were calculated based on  $m=17$ .

174  $Fe^{2+}$  and  $Fe^{3+}$  contents in serpentine were calculated using the approach described by Beard and  
175 Frost (2017). Thus, in the  $(Mg+Fe_T)$  pfu vs.  $(Si+Al)$  pfu space, the microprobe analyses of serpentine  
176 lie along a linear trend that extends from pure Mg serpentine (lizardite/chrysotile or antigorite) to  
177 brucite ( $Mg(OH)_2$ ). The trend towards brucite is a consequence of extremely fine-grained serpentine-  
178 brucite intergrowths. According to Beard and Frost (2017), the deviation of a serpentine analysis from  
179 the brucite trend reflects the stoichiometric effects of ferric iron substitutions in the crystal chemistry  
180 of serpentine. Here, a full dioctahedral substitution is assumed, meaning that ferric iron is  
181 accommodated in the serpentine structure by substitution for divalent cation plus the addition of a  
182 vacancy in the octahedral sheet. In this case, a serpentine that integrates a significant amount of ferric  
183 iron would deviate from the brucite trend, showing lower  $(Mg+Fe_T)$  pfu at a given  $(Si+Al)$  pfu.  
184 Considering that this deviation is only caused by ferric iron substitution, the following equation  
185 provides  $Fe^{3+}$  pfu:

$$Fe^{3+} = -x \times (Si + Al) + 7 - (Mg + Fe_T) \quad (1)$$

188 where  $x$  is the ideal number of Si cations when the serpentine formula is calculated for seven oxygens  
189 (i.e., 2 in lizardite/chrysotile and 2.05 in antigorite).

190 A High-Resolution Laser Ablation Inductively Coupled-Plasma Mass Spectrometer (HR-LA-  
191 ICP-MS) at the Geosciences Ocean laboratory (Brest, France) composed of a 193 nm MicroLas  
192 CopexPro Coherent coupled with an Element II ICP-MS has been used for trace element analyzes.  
193 Laser ablations were performed with a constant 5 Hz pulse rate, with an ablation crater of 90 to 120  
194  $\mu m$  in diameter. The number of pulses was 200, which is sufficient to form a long and stable signal  
195 for integration. The ablated material is transported using a constant He flow and mixed with Ar in a  
196 cyclone coaxial mixer before entering the ICP torch and being ionized. The ions are then sampled,  
197 accelerated and focused before being separated and analyzed in the mass spectrometer.  $^{29}Si$  content  
198 — known from prior electron microprobe analyses — was used as internal standard and  
199 concentrations were calibrated against the NIST 612 rhyolitic glass using reference values from  
200 Pearce et al. (1997). Data reduction was carried out by using SILLIS software, following the standard  
201 methods of Longerich et al. (1996). Detection limits were between <1 and 60 ppb for most trace  
202 elements, <0.5 ppm for B, Li, Mn, Co, Ni, As and between 1 and 50 ppm for Mg, Ca, Ti considering  
203 a spot size of 120  $\mu m$ .

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### *Stable isotope measurements*

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Stable oxygen and hydrogen isotope compositions were measured from separated serpentine fragments at the Stable Isotope Laboratory at the University of Lausanne. Separated powders were obtained by micro-drilling using a drill of 500  $\mu\text{m}$  of diameter for the largest veins of antigorite and chrysotile. A smaller drill of 100  $\mu\text{m}$  of diameter was used to sample the mesh core of lizardite. Serpentine samples were then purified from magnetite grains by using a hand-held magnet and potential denser primary minerals were separated by settling in water. Oxygen isotopes were measured according to a method adapted after Sharp (1992). Between 1 and 2 mg of powder are loaded in a Pt sample holder and heated with a  $\text{CO}_2$ -laser under a F atmosphere and a pressure of 50 mbar. The liberated oxygen is analyzed as O on a Finnigan MAT 253 mass spectrometer. Hydrogen isotope were measured by applying the method of Sharp et al. (2001). Between 0.5 and 1 mg of sample powder is loaded in a tin capsule and reduced by reaction with glassy carbon at 1450°C in a helium carrier gas-producing H and CO. Produced gases are separated in a gas chromatograph and analyzed in a Finnigan MAT Delta Plus XL mass spectrometer configured to make hydrogen isotope analyses in continuous flow mode. Results are given in the standard  $\delta$ -notation, expressed relative to  $V_{\text{SMOW}}$  in permil (‰). Replicate oxygen isotope analyses of the standards (UWG-2 garnet) yielded an average precision of  $\pm 0.25\%$  for  $\delta^{18}\text{O}$  values. The precision of the G1 biotite in-house standards for hydrogen isotope analyses was  $\pm 2\%$ .

## RESULTS

### *Serpentine petrography*

In agreement with the work of Orloff (1968), whereas the degree of serpentinization is moderate to high throughout the ophiolite (>50%, "facies normal", **Figure 2a, b**), it is close to 100% near the base, giving to the rock a typical dark color ("facies de base"; **Figure 2c**). Locally, near the top of the massifs, the degree of serpentinization is less than 10% ("facies superieur"). There, serpentine occurs along fracture walls and also forms mm-thick black veins pervasively surrounding preserved grains of olivine and pyroxene.

The base of the ophiolite consists of a schistose and intensely brecciated serpentinite sole of 20 m to 300 m thick. Breccias are composed by mm to dm-scale blocks (phacoids) of totally serpentinized peridotite embedded in a matrix of sheared serpentinite. Several generations of serpentine can be identified even at naked eye: massive serpentinite is crosscut by mm to cm-thick, yellow to light-green serpentine veins (**Figure 2d**). These veins are systematically surrounded by dark seams of magnetite and the overall is frequently crosscut by mm-thick fibrous veins, the latter being occasionally replaced by veins of greenish to white serpentine (**Figure 2e, f**). This greenish to



240 white serpentine may also compose large amounts of the breccia matrix. In thin section, the latest  
241 generations of serpentine occur almost exclusively as limited domains or veins formed after  
242 microfracture infilling (**Figure 3b, c, d**). Larger domains of replacement can be found, but they  
243 usually correspond to the strongly deformed area where secondary serpentine composes the breccia  
244 matrix.

245 In the less serpentinized samples, serpentinization starts at the boundaries of olivine grains and  
246 along micro-fractures (**Figure 3**). It progressively extends from the rim to the core of the grains as  
247 the serpentinization degree increases, giving the rock a typical mesh texture (see S1 in **Figure 3a**). In  
248 general, olivine is strongly affected by serpentinization, while orthopyroxene remains relatively  
249 preserved or develop bastite rims around fresh cores. Iron released during serpentinization  
250 crystallized as magnetite rimming olivine grains and along mm-scale fractures, forming dark seams  
251 (**Figure 3a**).

252 Six generations of serpentine have been identified in the sole (S1-S6 in **Figure 3**). The first  
253 generation of serpentine after the primary mesh texture (S1) forms homogeneous domains that display  
254 the same grey color as the mesh texture under cross-polarized light (S2, **Figure 3b, d**). Black veins  
255 of magnetite identical to those observed in the mesh texture are present in S2, and extend parallel to  
256 the S2 borders. The limits of the S2 domain are diffuse, suggesting progressive replacements of the  
257 mesh texture S1. Both serpentine generations are closely associated with  $\mu\text{m}$  to mm-thick veins of  
258 serpentine of a characteristic bluish-grey color under cross-polarized light (S3, **Figure 3b, c, d**). S3  
259 veins are made of decussate blades of tens of micrometers in size, giving these veins a typical  
260 interlocking texture. The borders of S3 veins are marked by the accumulation of magnetite grains,  
261 both inside and outside the veins. S4 veins occasionally crystallize in tension gashes, similarly to S5  
262 veins and exhibit transitional texture between the decussate blades of S3 and the fibrous habitus that  
263 characterizes S5. Fibers can reach  $\sim 200 \mu\text{m}$  in size and have a grey to yellow birefringence under  
264 cross-polarized light (**Figure 3b, c**). They are commonly oriented perpendicularly to the vein edges.  
265 The latest serpentine generation (S6) occurs as replacement of previous serpentine generations,  
266 forming veins (**Figure 3c**) or covering large domains that form the matrix of breccias as shown by  
267 Ulrich et al. (2014) and Quesnel et al. (2016b).

### 268 269 *Nature of serpentine polymorphs*

270 The typical Raman spectra for the different generations of serpentine (i.e., from S1 to S6, as  
271 previously described) are displayed in Figure 4. Their specific spectral signatures allow identifying  
272 serpentine species (Figure 4; Auzende et al. 2004; Lemaire 2000). Except for minor changes in the  
273 low wavenumber region, the discrimination and identification of serpentine minerals are mainly based  
274 on the OH stretching bands located in the range  $3600\text{-}3750 \text{ cm}^{-1}$ . Lizardite characterized by peaks at

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275 3685 and 3706  $\text{cm}^{-1}$ , is the most abundant variety, forming the S1 and S2 generations. In contrast, the  
276 typical Raman spectrum obtained for S3 veins corresponds to antigorite, with characteristic peaks at  
277 3670 and 3699  $\text{cm}^{-1}$ . S5 perfectly matches with the spectral signature of chrysotile, and S4  
278 corresponds to a mixture of antigorite (S3) and chrysotile (S5). Finally, the serpentine S6 is identified  
279 as polygonal serpentine, characterized by a weak band at 3648  $\text{cm}^{-1}$  and a doublet at 3690 and  
280 3697  $\text{cm}^{-1}$  (Cathelineau et al. 2016).

### 281 282 *Chemistry of primary minerals*

283 The representative compositions in major and trace elements of primary minerals and each  
284 serpentine variety identified are presented in Tables 1 and 2. The supplementary table S1 provides all  
285 the data. Standard deviations are  $2\sigma$ . Analyses of the primary minerals are consistent with those  
286 previously published for the NC peridotites (Frost et al. 2013; Mothersole et al. 2017; Pirard et al.  
287 2013). Olivine is  $\text{Fo}_{91}$  (**Figure 5**) and has a NiO content of  $\sim 0.4$  wt.% (Ni=0.1 pfu) and MnO content  
288 of  $\sim 0.16$  wt.%. Olivine is also characterized by an extreme depletion in trace elements so that they  
289 are usually close, or below, the detection limit. High-field strength elements (HFSE) have Primitive  
290 Mantle (PM)-normalized concentrations varying between  $10^{-3}$  and  $10^{-1}$  (**Figure 6**). Orthopyroxene is  
291 mainly enstatite and has a constant Mg# similar to olivine (0.91). CaO content ranges between 0.42  
292 and 2.79 wt. % with an average value of 1.06 wt. % (Ca=0.04 pfu).  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  have  
293 concentrations ranging between 2.27 and 4.51 wt. % and 0.56 and 0.88 wt. %, respectively, and a  
294 corresponding Cr# of  $\sim 0.12$  and down to 0.09, reflecting a high degree of depletion of the peridotite.  
295 PM-normalized trace element patterns show that orthopyroxene is strongly depleted in light rare-earth  
296 elements (LREE), with  $\text{Ce}_N/\text{Yb}_N < 0.05$ . Clinopyroxene is diopside and is mainly present in spinel and  
297 plagioclase lherzolite, although some occurrences may be observed in harzburgite, mostly from  
298 exsolution in orthopyroxene. Clinopyroxene is characterized by slightly higher Mg# ( $\sim 0.93$ ) and  
299  $\text{Al}_2\text{O}_3$  of  $\sim 4.16$  wt. % (Al=0.2 pfu) and  $\text{Cr}_2\text{O}_3$  of 0.94 wt.% (Cr#  $\sim 0.13$ ). PM-normalized trace  
300 element patterns show a strong fractionation of LREE relative to heavy (H)REE ( $\text{Ce}_N/\text{Yb}_N < 0.01$ )  
301 and a nearly flat HREE pattern ( $\text{Dy}_N/\text{Yb}_N \sim 0.8$ ). Slight Sr and Eu anomalies are observed and reflect  
302 equilibrium with plagioclase.

### 303 304 *Chemistry of serpentine*

305 Lizardite replacing primary minerals in the upper parts of the massif (upper serpentines) has  
306 been divided in four types: lizardite after olivine (i.e. in the mesh core), lizardite in the mesh rim,  
307 lizardite after orthopyroxene and lizardite after clinopyroxene. All have  $\text{H}_2\text{O}$  content of  $\sim 13$  wt. %,   
308 which is consistent with the hydroxyl stoichiometry of lizardite. Lizardite after olivine shows rather  
309 homogeneous compositions with  $\sim 41$  wt. %  $\text{SiO}_2$  and MgO (Si=2.0 pfu, Mg=2.9 pfu) and  $\sim 4$  wt. %

310 FeO ( $\text{Fe}^{2+}=0.2$  pfu). Compared to olivine, mesh cores have higher  $\text{Al}_2\text{O}_3$  content ( $\sim 0.3$  wt. %) and  
311 lower NiO content ( $\sim 0.2$  wt. %). Mesh rims are characterized by lower  $\text{SiO}_2$  and MgO contents (38  
312 wt. % and 37 wt. %, respectively). FeO content is higher ( $>10$  wt. %,  $\text{Fe}^{2+}=0.5$  pfu) and may reflect  
313 the presence of minute grains of magnetite in the mesh rims. Bastite contains 38 to 42 wt. %  $\text{SiO}_2$ ,  
314 and is usually characterized by lower Si at a given  $\text{Mg}+\text{Fe}_T$  compared to lizardite after olivine, and  
315 displays higher Cr and Al contents. Mg# varies between 0.91 and 0.97, with an average of 0.92  
316 (**Figure 5**). Bastites formed either after orthopyroxene or clinopyroxene do not show any difference  
317 in the major element concentrations. Regarding the Fe oxidation state in upper serpentines, our  
318 estimates show that Fe is mostly divalent ( $\text{Fe}^{3+}/\text{Fe}_T < 0.1$ , **Figure 5d**), consistently with previous  
319 estimates made by Beard and Frost (2017).

320 Primitive Mantle normalized trace element patterns of upper serpentines are presented in  
321 **Figure 6**. Despite some slight differences (particularly some enrichments in large ion lithophile  
322 elements, LILE), PM-normalized trace element patterns of serpentines match well those of primary  
323 minerals. Minor and trace elements in lizardite after olivine is highly depleted (Ti: 10.0-85.8 ppm;  
324 Mn: 125-1059 ppm; Co: 18.7-81.1 ppm; Y: 0.060-0.375 ppm), with a strong fractionation between  
325 LREE and HREE ( $0.008 < (\text{Ce}/\text{Yb})_N < 0.132$ ). Lizardite after orthopyroxene is slightly less depleted in  
326 minor and trace elements (Ti: 158-174 ppm; Mn: 568-635 ppm; Co: 26.8 ppm; Y: 0.907-0.994 ppm)  
327 but still shows LREE depleted patterns and strong LREE/HREE fractionation  
328 ( $0.02 < (\text{Ce}/\text{Yb})_N < 0.162$ ) similar to lizardite after olivine. LREE are depleted in serpentine after  
329 clinopyroxene. Elements such as Y (7.81 ppm), Ti (2163 ppm), Mn (1460 ppm) and Co (67.4 ppm)  
330 are enriched compared to lizardite after olivine and orthopyroxene. Only one occurrence of lizardite  
331 after clinopyroxene was found, confirming that the clinopyroxene is more frequently transformed into  
332 amphibole (tremolite) than serpentine during the hydration processes. Regarding fluid-mobile  
333 elements (FME), upper serpentines are enriched in B (4.71-24.3 ppm), Sb (0.007-0.016 ppm) and U  
334 (0.854-2.74 ppm) and depleted in Li and Sr with respect to Depleted Mantle (DM) values (Figure 7).  
335 More specifically, Pb and Sr concentrations are similar to those previously published for NC  
336 serpentinized peridotites (Secchiari et al. 2016; 2019; Ulrich et al. 2010), and overlap the fields of  
337 abyssal serpentinites and subducted serpentinites with some sedimentary contributions. Upper  
338 serpentinites display B, Li and Sb concentrations lower than those of other serpentinites worldwide  
339 (Figure 7). Arsenic is always below the detection limits.

340 In the serpentinite sole, all serpentine species display homogeneous major and trace element  
341 compositions. They contain  $\sim 44$  wt.%  $\text{SiO}_2$  ( $\text{Si} = 2.0$  pfu),  $\sim 40$  wt.% MgO ( $\text{Mg} = 2.8$  pfu),  $\sim 13$  wt.%  
342  $\text{H}_2\text{O}$  and they are characterized by very low FeO ( $\sim 2$  wt.%,  $\text{Fe} \leq 0.1$  pfu) and  $\text{Al}_2\text{O}_3$  ( $< 0.1$  wt.%,  $\text{Al}$   
343  $< 0.005$  pfu; **Figure 5**) and very high Mg# ( $\sim 0.98$ ) compared to upper serpentines. Calculated  
344  $\text{Fe}^{3+}/\text{Fe}_T$  ratio shows that serpentines from the sole integrate significant amounts of ferric iron: On

345 average, lizardite and chrysotile have  $Fe^{3+}/Fe_T$  ratio of ~0.2, antigorite, 0.35, and polygonal  
346 serpentine, 0.7 (up to 1). They also show HFSE depletion similar to that described in upper  
347 serpentines. However, they are slightly more depleted in HREE and significantly more enriched in  
348 LREE, except Ce which has a similar concentration to that of moderately serpentinized NC  
349 peridotites. Serpentines from the sole display a strong Ce negative anomaly ( $Ce/Ce^*=0.009-0.739$ ,  
350 **Figure 7**). They also display enriched concentrations in FME relative to upper serpentines (B: 2.13-  
351 8.52 ppm; Sb: 0.005-0.057 ppm; Li: 0.054-0.543; Cs: 0.004-0.022; Rb: 0.014-0.275 ppm; Ba: 0.066-  
352 0.952 ppm; Pb: 0.002-0.133; Sr: 0.202-4.05 ppm) with a pronounced U positive anomaly (U: 0.001-  
353 0.043 ppm; **Figure 6**). Similarly to upper serpentines, As concentrations in the serpentinite sole were  
354 too low to be determined (**Table 2**).

### 356 *O and H stable isotope composition*

357 The  $\delta^{18}O$  and  $\delta D$  values of fresh peridotites are 5.5‰ and -70‰ respectively, which are  
358 consistent with mantle rock compositions (Deloule et al. 1991; Eiler 2001). Serpentines display a  
359 wide range of  $\delta^{18}O$  values from 1.7‰ to 13.9‰. In contrast,  $\delta D$  values are quite homogeneous (-107  
360 to -88‰). No systematic difference can be observed between serpentine species.

361 The upper serpentines (i.e., lizardite) display a narrow range of isotopic compositions:  
362  $5.4‰ < \delta^{18}O < 6.9‰$  and  $-103‰ < \delta D < -97‰$ . In the serpentinite sole, the  $\delta^{18}O$  and  $\delta D$  values of  
363 lizardite are somewhat broader:  $\delta^{18}O_{liz} = 2.2$  to  $5.7‰$  and  $\delta D_{liz} = -107$  to  $-97‰$ . The whole range of  
364 values including other serpentine species from the sole is 1.7 to 12.2‰ for oxygen, -107 to -88‰ for  
365 hydrogen. Two samples (Ti 51a-1, -2, Poum 4-6, -2, -3) have traces of amorphous silica, and also the  
366 highest  $\delta^{18}O$  values. Such high values are likely due to amorphous silica, which has high  $\delta^{18}O$  values  
367 around 30‰ (Quesnel et al. 2016a). For this reason, these data will not be considered further in the  
368 following discussion. The isotopic compositions of serpentines are thus assumed to range between  
369 1.7 to 7.9‰ for  $\delta^{18}O$ , and from -107 to -88‰ for  $\delta D$ .

## 471 **DISCUSSION**

### 472 *Deciphering the source of serpentinization fluids and conditions of serpentinization from the* 473 *serpentine chemistry: a new modeling approach*

474 The New Caledonia serpentines plot away from the field of oceanic serpentines defined in the  
475 literature (Sakai et al. 1990; Wenner and Taylor 1973), therefore excluding the involvement of  
476 seawater in the serpentinization process (**Figure 8a**). Some trace element concentrations also confirm  
477 this inference (**Figure 7**), since abyssal serpentines are usually characterized by a high U/Th ratio,  
478 attributed to seawater interaction with peridotite (Deschamps 2010; Frisby et al. 2016). U and Th are  
479

380 highly depleted in the mantle (e.g., Salters et al. 2002), but U is enriched in seawater relative to Th  
381 (Chen et al. 1986), leading to a significant fractionation between these elements when seawater is  
382 involved in serpentinization process. The Ce negative anomaly ( $Ce/Ce^* < 1$ , with  $Ce/Ce^*$  equals to  
383  $Ce_N / [(La_N * Pr_N)^{1/2}]$ ) is typical of the seawater where  $Ce^{3+}$  is oxidized into the less soluble  $Ce^{4+}$   
384 (Elderfield and Greaves 1982). Low  $Ce/Ce^*$  is also a common feature in abyssal serpentines  
385 (Delacour et al. 2008; Frisby et al. 2016; Rouméjon et al. 2015). Frisby et al. (2016) have recently  
386 shown that seawater influences the LREE budget of serpentine through the addition of La and Pr, and  
387 that  $Ce/Ce^*$  decreases in abyssal serpentines with increasing U/Th. NC serpentines, more specifically  
388 those from the serpentinite sole, are characterized by high U/Th and low  $Ce/Ce^*$  ratios compared to  
389 moderately serpentinized NC peridotites (**Figure 7**). However, U/Th ratio never exceeds 10 in our  
390 samples whereas it is  $\gg 10$  in abyssal serpentines (up to 10,000). Also, most of our samples display  
391 much larger Ce negative anomalies than that of abyssal serpentines, thus providing additional  
392 evidence that seawater was unlikely involved in the formation of NC serpentines.

393 Serpentine with  $\delta D$  values as low as -100‰ have been identified in other places worldwide,  
394 forming the "Ophiolite serpentines" field defined by Wenner and Taylor (1973) where NC serpentines  
395 plot (**Figure 8a**). These Ophiolite serpentines are commonly assumed to result from the interaction  
396 of peridotite with meteoric or metamorphic fluids either during obduction or during exhumation and  
397 retrograde re-equilibration of the peridotites (Früh-Green et al. 1996; 2001; Kyser et al. 1999;  
398 O'Hanley 1996). Typically, very low  $\delta D$  values for serpentine minerals ( $< -100$ ‰) are attributed to  
399 late serpentinization events due to the circulation of meteoric waters under subsurface conditions. On  
400 the other hand,  $\delta D$  values in the range of -100 to -70‰ are better explained by the presence of  
401 composite fluids (Burkhard and O'Neil 1988; Früh-Green et al. 2001).

402 The O and H isotope compositions of a given serpentine depend on three main parameters: 1)  
403 the isotopic composition of the serpentinizing fluid ( $\delta^{18}O_{fluid}$  and  $\delta D_{fluid}$ ), 2) the serpentinization  
404 temperature (T), and 3) the water-rock ratio (W/R) during the reaction. The complex relationships  
405 between these three parameters on the one hand, and the isotopic fractionation factors on the other  
406 hand, have been characterized experimentally and from the study of natural samples (e.g. Saccocia et  
407 al. 2009; Sakai and Tsutsumi 1978; Savin and Lee 1988; Wenner and Taylor 1973; Zheng 1993). The  
408 isotopic compositions of serpentinizing fluids may be calculated using calibrated serpentine-water  
409 isotopic fractionation factors, and assuming W/R values and temperature (e.g., Alt et al. 2012; Alt  
410 and Shanks Iii 2006; Früh-Green et al. 2001; Kyser et al. 1999; Rouméjon et al. 2015; Sakai et al.  
411 1990; Thakurta et al. 2009). Alternatively, W/R can be determined if the composition of the  
412 serpentinizing fluid is known (Agrinier and Cannat 1997; Alt et al. 2007; Burkhard and O'Neil 1988;  
413 Magaritz and Taylor 1974; Rouméjon et al. 2015; Wenner and Taylor 1973). Conversely, the  
414 approximative temperature of serpentinization can be estimated by using the serpentine-magnetite

415 geothermometer, based on the oxygen isotope fractionation between these two co-genetic minerals  
 416 (Wenner and Taylor 1971). Actually, this approach is somewhat unsatisfactory because it requires  
 417 knowing or arbitrarily setting at least one of the parameters listed above. For example, in the oceanic  
 418 context, serpentine fluids are relatively well constrained because they are either seawater or seawater  
 419 modified by hydrothermal fluids (Agrinier and Cannat 1997). But for fluids derived from ancient  
 420 lithospheric remnants,  $\delta^{18}\text{O}_{\text{fluid}}$  and  $\delta\text{D}_{\text{fluid}}$  are generally unknown and need to be assumed or  
 421 calculated. It follows that the serpentine-magnetite geothermometer can hardly be used in the case of  
 422 multiple serpentinization events since the related generations of magnetite are challenging to identify  
 423 and separate.

424 In this study we developed a new approach based on Monte Carlo simulations to constrain the  
 425 source of fluids in equilibrium with NC serpentines based on their oxygen and hydrogen isotope  
 426 compositions. Figure 8 (b to d) shows the result of one million Monte Carlo simulations using the  
 427 isotopic fractionation factors of Wenner and Taylor (1973) (as modified by O'Hanley 1996) for  
 428 oxygen isotopes:

$$1000\ln\alpha_{\text{serpentine-water}}^{18\text{O}-16\text{O}} = 1.69 \times 10^6/T^2 - 4.23 \quad (2)$$

429 and of Saccocia et al. (2009) for hydrogen isotopes:

$$1000\ln\alpha_{\text{serpentine-water}}^{D-H} = 3.436 \times 10^6/T^2 - 34.736 \times 10^3/T + 21.67 \quad (2)$$

432 where T is the temperature in Kelvin. It should be noticed that the use of oxygen isotope fractionation  
 433 factors from Saccocia et al. (2009) provides quite similar results to those of Wenner and Taylor (1971)  
 434 in the temperature range of 250-450°C. However the serpentine-water  $^{18}\text{O}-^{16}\text{O}$  fractionation factor  
 435 of Wenner and Taylor (1971) is applicable for a wide range of temperature, contrarily to the  
 436 experimental approach of Saccocia et al. (2009) whose fractionation factor was calibrated for  
 437 temperatures >250°C. As a consequence, the use of the Wenner and Taylor fractionation factor was  
 438 found more consistent with calculating the  $\delta^{18}\text{O}$  composition of serpentinizing fluids when no other  
 439 constraint on serpentinization temperature is available.

440 The O and H isotope compositions of a serpentine can be calculated by applying Sheppard et  
 441 al. (1969) mass-balance equation:

$$\delta_{\text{serpentine}} = \frac{\delta_{\text{mantle}} + W/R \times (\delta_{\text{fluid}} + 1000\ln\alpha_{\text{serpentine-water}})}{1 + W/R} \quad (4)$$

449 with  $\delta_{serpentine}$ ,  $\delta_{mantle}$  and  $\delta_{fluid}$  are the O and H isotope compositions of the serpentine, the mantle and  
450 the serpentinizing fluid, respectively, W/R is the fluid-rock ratio and  $1000\ln\alpha$  is the fractionation  
451 factor calculated with equations (2) and (3). Mantle values of  $\delta^{18}\text{O} = +5.5\text{‰}$  and  $\delta\text{D} = -80\text{‰}$  have  
452 been chosen for the composition of the starting material (Deloule et al. 1991; Eiler 2001). Other  
453 parameters are defined randomly for each simulation in the following ranges:  $50 < T^{\circ}\text{C} < 450$ ,  
454  $0.13 < \text{WR} < 1000$ ,  $-40 < \delta^{18}\text{O}_{\text{fluid}} (\text{‰}) < 40$  and  $-200 < \delta\text{D}_{\text{fluid}} (\text{‰}) < 20$  (see **Figure 8**). Although  
455 serpentine can be stable at temperature up to  $\sim 700^{\circ}\text{C}$ , the temperature of serpentinization rarely  
456 exceeds  $350^{\circ}\text{C}$  at spreading centers and  $400\text{-}500^{\circ}\text{C}$  in subduction zones (e.g., Evans 2004; Klein et  
457 al. 2013; Ulmer and Trommsdorff 1995). Low-temperature serpentinization remains poorly  
458 documented, even though some authors argued for serpentinization might occur at temperature lower  
459 than  $80^{\circ}\text{C}$  (e.g., Agrinier et al. 1995; Bonatti et al. 1984). Thus, a low-temperature threshold of  $50^{\circ}\text{C}$   
460 was chosen arbitrarily. The range of fluid-rock ratios was chosen considering that 0.13 is the  
461 minimum ratio required to convert an olivine into a serpentine stoichiometrically, and  $\delta_{serpentine}^{WR=1000} \approx$   
462  $\delta_{serpentine}^{WR=\infty} \cdot \delta_{\text{fluid}}$  thresholds were chosen so that almost all compositions of terrestrial fluids were  
463 covered (Hoefs 2009). In our modeling approach, a simulation is considered to be valid when the  
464 modeled serpentine displays  $\delta^{18}\text{O}$  and  $\delta\text{D}$  compositions that are in the range of NC serpentinites  
465 ( $1.7\text{‰} < \delta^{18}\text{O} < 7.9\text{‰}$ ;  $-107\text{‰} < \delta\text{D} < -88\text{‰}$ ). Results are provided in supplementary materials and  
466 are presented in **Figure 8**: **Figure 8b** reports the calculated  $\delta^{18}\text{O}$  and  $\delta\text{D}$  compositions of fluids that  
467 are able to reproduce a serpentine that matches the O and H compositions of NC serpentines. Among  
468 1 million random simulations,  $\sim 6500$  were consistent with the O and H signatures of NC serpentines.  
469 **Figure 8c** and **Figure 8d** show, respectively, the calculated  $\delta^{18}\text{O}_{\text{fluid}}$  and  $\delta\text{D}_{\text{fluid}}$  as a function of the  
470 correspondent temperatures of serpentinization. Results of Monte-Carlo simulations show that fluids  
471 in equilibrium with NC serpentines extend between the meteoric water line and an area defined  
472 between  $3\text{‰}$  and  $8\text{‰}$  in  $\delta^{18}\text{O}$  and  $-80\text{‰}$  and  $-60\text{‰}$  in  $\delta\text{D}$  in which most of the results plot ( $\sim 40\%$  of  
473 6500 simulations, see the red, white cross-hatched area in Figure 8b). Fluids that fall into this area  
474 have interacted with the mantle at temperatures between  $\sim 250^{\circ}$  and  $430^{\circ}\text{C}$  (the white cross-hatched  
475 areas in Figure 8c,d), while interactions with fluids showing negative  $\delta^{18}\text{O}$  and higher  $\delta\text{D}$  signatures  
476 ( $> -60\text{‰}$ ) occurred at lower temperatures ( $100\text{-}200^{\circ}\text{C}$ ; **Figure 8c, d**). With a few exceptions, our  
477 calculations show that NC serpentines were formed at relatively high W/R ( $>1$ ) (see Figure S1 in  
478 supplementary materials).

### ***Origin of NC serpentinites***

#### ***From deep serpentinization...***

482 Based on the new petrological, mineralogical, geochemical and modeling data presented here,  
483 the chronology of serpentinization of NC peridotites would be as follows. First, the decreasing

484 serpentinization degree from bottom to the top of the Peridotite nappe is good evidence for a fluid  
485 circulation mainly located at the base of the ophiolite. Since the NC ophiolite was in the forearc  
486 position for ~20 Ma before its obduction on the Norfolk Ridge, the most likely source of the fluids  
487 forming pervasive lizardite S1 would come from dehydration of the subducting slab. As our results  
488 fall into the Alpine Ophiolite-type field of Wenner and Taylor (1973), they are consistent with this  
489 assumption. Consequently, three potential sources of fluids present in the recycled oceanic  
490 lithosphere can contribute to hydrating the mantle wedge: the altered oceanic crust (AOC), the  
491 subducted sediments and the subducted abyssal serpentinites. The fluids in equilibrium with all of  
492 these components have distinct signatures in trace elements and stable isotopes that also sharply differ  
493 from the composition of the mantle wedge (Eiler et al. 1998; Kodolanyi et al. 2012; Peters et al.  
494 2017). One of the best examples documented worldwide is provided by the formation of serpentine  
495 mud volcanoes along the Marianna Trench (Fryer 1992). The geodynamics in this region  
496 approximates the one assumed for the South Loyalty Basin at the subduction time, and the occurrence  
497 of serpentinite seamounts provide a unique window for studying fluid circulations into the forearc  
498 mantle. Alt and Shanks III (2006) used typical  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for the AOC, oceanic sediments,  
499 and abyssal serpentinites to predict the isotopic compositions of fluids in equilibrium with each  
500 subducted component, and determine the source of serpentinizing fluids in the Marianna forearc  
501 mantle. In their modeling, they assumed that the metasomatized basaltic basement has  $\delta^{18}\text{O} = +8$  to  
502  $+11\text{‰}$  and  $\delta\text{D} = -90$  to  $-120\text{‰}$  (Alt 2003), and used a simplified AOC mineralogy with 49% albite,  
503 49% chlorite and 2% calcite. The dehydration of metabasalts having these isotopic compositions and  
504 mineralogy would produce, therefore, fluids with  $\delta^{18}\text{O}$  values of  $+2$  to  $+8\text{‰}$  (up to  $+10\text{‰}$  at  $400^\circ\text{C}$ )  
505 and  $\delta\text{D}$  values of  $-50\text{‰}$  to  $-90\text{‰}$ . Similarly, the authors calculated higher  $\delta^{18}\text{O}$  ( $+12$  to  $+16\text{‰}$ ) and  
506  $\delta\text{D}$  ( $-20$  to  $-40\text{‰}$ ) values for sediment-derived fluids and  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in the range of  $+5$  to  $+9\text{‰}$  and  
507  $-5$  to  $-30\text{‰}$  respectively for serpentine-derived fluids at  $\sim 200\text{-}350^\circ\text{C}$  (**Figure 8b**). By comparison,  
508 the main O and H isotope values calculated for fluids in equilibrium with NC serpentinites (the red,  
509 white cross-hatched area in Figure 8b) are consistent with fluids coming from the dehydration of an  
510 AOC. On the contrary, neither sediment-derived fluids nor serpentine-derived fluids fit our modeled  
511 serpentinizing fluids. Our simulations also predict that AOC-derived fluids interacted with the forearc  
512 peridotites at temperatures of  $250\text{-}430^\circ\text{C}$  (**Figure 8c, d**). These temperatures are close to those of  
513 AOC dehydration usually proposed in forearc settings ( $200\text{-}450^\circ\text{C}$ ; Alt and Shanks Iii 2006; Rüpke  
514 et al. 2004). Additionally, the maximum temperature of  $430^\circ\text{C}$  estimated by our simulations may be  
515 lowered to  $\sim 350^\circ\text{C}$  based on field observations: lizardite is commonly replaced by antigorite at  
516 temperature  $>350^\circ\text{C}$  in (supra)-subduction environments (Evans et al. 1976; Evans 2004; Ulmer and  
517 Trommsdorff 1995; 1999). This replacement has never been observed in the NC ophiolite, where



518 lizardite is the dominant serpentine variety, while antigorite is mainly restricted to synkinematic crack  
519 seals (Cluzel et al. 2019; Quesnel et al. 2016b).

520 Regarding trace elements, the evolution of the mantle wedge composition interacting with slab-  
521 derived fluids is evaluated by proposing a single-step process where the fluids that migrate from the  
522 descending slab are mixed with the overlying forearc mantle. Trace element concentrations of a slab-  
523 derived fluid  $C_f$  can be estimated by applying the following equation:

$$524 \quad C_f = \frac{C_0 \times M}{F} \quad (5)$$

525 where  $C_0$  is the concentration of an element in the subducted component (i.e., the AOC, the sediments  
526 or the serpentinites),  $M$  is the mobility (in percent) of an element during the dehydration of a  
527 subducted component, and  $F$  is the weight fraction of fluid extracted from the subducted component  
528 (Sano et al. 2001). All parameters used for the modeling of trace elements, references and results of  
529 calculations are summarized in **Table 4**. The weight fraction of fluids released from the AOC and  
530 sediments is assumed to be 1.5 and 3 wt.% respectively, in agreement with estimates previously  
531 published (Peacock 1990; Rüpke et al. 2004). The lizardite-antigorite transition in the subducting slab  
532 could have released fluids at temperatures below 350°C in the forearc subducted slab. Thus, pure Mg-  
533 lizardite contains 13 wt.% H<sub>2</sub>O, while pure Mg-antigorite (m=17) only contains 12.3 wt.% H<sub>2</sub>O.  
534 Consequently, the weight fraction of serpentine-derived fluids was set to ~0.7 wt.%. Data of element  
535 mobility during dehydration processes are taken from experimental studies on natural pelite for  
536 sediments (Aizawa et al. 1999), natural amphibolite for AOC (Kogiso et al. 1997; Sano et al. 2001)  
537 and natural antigorite for serpentinite (Tenthorey and Hermann 2004). U, Th, B and Zr are used  
538 because of their behavior during dehydration and their respective concentrations in the slab  
539 components: Th and Zr mobilities are rather low in hydrous fluids, while B is highly mobile. U  
540 mobility depends on its oxidation state: it is immobile in its reduced form U<sup>4+</sup> while it is mobile in its  
541 oxidized form U<sup>6+</sup> (Brenan et al. 1995). Actually, the high solubility of uranium in subduction zone  
542 fluids has been reported by several studies (e.g., Bailey and Ragnarsdottir 1994; Bali et al. 2010). All  
543 of these elements are enriched in sediments (Plank 2014) and depleted in the mantle (Salters and  
544 Stracke 2004; Secchiari et al. 2019). The U/Th ratio is low in sediments, but is roughly similar in  
545 AOC and abyssal serpentinites (**Table 4**). However, the U/Th ratio is more fractionated during  
546 serpentine dehydration than during AOC dehydration (Kogiso et al. 1997; Tenthorey and Hermann  
547 2004). As a consequence, the U/Th ratio is higher in serpentine-derived fluids than in AOC fluids,  
548 and is the lowest in sediment-derived fluids (**Figure 9**). Subducted serpentinites have a high B/Zr  
549 ratio (>20), contrarily to subducted sediments and AOC, which are characterized by low (<1) to very  
550 low (<0.1) B/Zr ratios, respectively. Considering these ratios and the high mobility of B in fluids  
551

553 compared to Zr, the addition of subduction zone fluids in the mantle wedge leads to an increase of  
554 B/Zr ratio towards ~50 for AOC-derived fluids, ~370 for sediment-derived fluids and up to ~8,200  
555 for serpentine-derived fluids. Consistently with the conclusions drawn from the stable isotope study,  
556 the trace element modeling suggests that NC upper serpentines were likely formed by the interaction  
557 with AOC-derived fluids, with nevertheless some addition of sediment-derived fluids (<30%, **Figure**  
558 **9**). This result is consistent with the highly radiogenic strontium isotope compositions of some NC  
559 serpentines from which a metasedimentary contribution was inferred (Cluzel et al. 2019). The  
560 modeling also indicates that the amount of slab-derived fluids that interacted with NC peridotites in  
561 the forearc was low, in the range of <0.1-3 wt.% (**Figure 9**). The amount of sediment-derived fluids  
562 in the mantle wedge was consequently in the order of 0.9 wt.% or less. Such a low amount of  
563 sediment-derived fluids is unresolvable by our modeling approach based on stable isotopes (**Figure**  
564 **8**). On the contrary, the Sr budget of sediments is high compared to the mantle so that a minute amount  
565 of sediments can buffer the Sr isotope system. These results together with the very low concentrations  
566 of As and Sb, which are proxies of the sedimentary contribution in serpentine chemistry (Deschamps  
567 et al. 2013; Deschamps et al. 2011; Hattori and Guillot 2007), imply that the amount of subducted  
568 sediments was low at the time of forearc peridotite hydration. The limited influence of sediment-  
569 derived fluids in the serpentine signature is also inferred by the lack of sedimentary prism, the latter  
570 being replaced by slices of basaltic rocks (i.e., the future Poya Terrane) scrapped off the down going  
571 plate during the Eocene NE-dipping subduction of the SLB (Cluzel et al. 2001; 2012b). In Figure 9,  
572 the domain of the serpentinite sole is more widespread than that of upper serpentines, with some  
573 samples plotting away from the modeling trends. This could reflect the effects of a later episode of  
574 fluids circulation (see the next section below) rather than those of slab-derived fluids contribution.

575 The subduction inception occurring at (or near to) the ridge axis in the SLB led to the  
576 development of a forearc magmatic activity from 55 to 47 Ma (Cluzel et al. 2006; 2016). During this  
577 period, thermal conditions in the forearc were high, causing the melting of the mantle wedge rather  
578 than its hydration. The continuous influx of fluids released from the dehydration of the oceanic crust  
579 of the subducting slab progressively cooled the forearc mantle, leading to the cessation of the forearc  
580 magmatism about 10 Ma after subduction inception (Cluzel et al. 2012a; Cluzel et al. 2016; Ulrich et  
581 al. 2010; Whattam et al. 2008). This period was long enough to alter significantly the oceanic crust  
582 exposed at the seafloor (Staudigel et al. 1981) Then, the AOC entering the subduction zone releases  
583 fluids in the overlying mantle wedge. Such fluids finally cause the massive serpentinization of the  
584 future NC ophiolite (**Figure 10a**). It is worth noting that based on these results, no trace of oceanic  
585 serpentinization related to the opening of the SLB was identified so far. It is possible however that  
586 the serpentinized upper part of the upper plate (the Loyalty Basin) was removed early (i.e., soon after  
587 subduction inception) when the hot and buoyant lower plate had to force its way beneath the future

588 Loyalty fore-arc. Such a feature could account for the absence of MORB-type basaltic crust on top  
589 of the peridotites in the Massif du Sud and the occurrence of fore-arc cumulates directly overlying  
590 highly depleted harzburgites and dunites.

591  
592 *... to (sub-) surface serpentinization.*

593 The development of multiple serpentine generations in the tectonic sole likely reflects changes  
594 in crystallization conditions, including the fluid composition and the formation events, both being  
595 connected with the tectonic history of the Peridotite Nappe. Consistently, the significant differences  
596 in the chemical compositions from S1 to S2 serpentines (e.g., increasing Mg#, different trace element  
597 patterns) may reveal a change in the elemental budget of serpentinizing fluids. On the other hand, the  
598 transition from the lizardite-antigorite assemblage (S2-S3/S4) to chrysotile-polygonal serpentine (S5-  
599 S6) without significant changes in the serpentine chemistry is in favour of a sole development under  
600 cooling temperatures. Our modeling approach of stable isotopes suggests that AOC-derived fluids  
601 alone cannot explain the formation of the serpentinite sole. Low temperature fluids (~100-250°C) of  
602 a meteoric origin can be considered (**Figure 8b**). The involvement of meteoric fluids is also suggested  
603 by major and trace element compositions of sole serpentines. The high  $\text{Fe}^{3+}/\text{Fe}_T$  ratio in serpentines  
604 from the sole (**Figure 5**) indicates a formation under more oxidizing conditions than in the upper  
605 system, which may be interpreted in term of formation depth.

606 Interestingly, Muñoz et al. (2019) showed that secondary serpentines, which are formed close  
607 to the surface by the circulation of meteoric fluids during the early stages of laterization display an  
608 increasing amount of ferric iron from lizardite ( $\text{Fe}^{3+}/\text{Fe}_T = 0.4$ ) to polygonal serpentine  
609 ( $\text{Fe}^{3+}/\text{Fe}_T = 0.95$ ).  $\text{Fe}^{3+}/\text{Fe}_T$  ratios in serpentines from the sole are very comparable to those measured  
610 in the regolith. Polygonal serpentine was also the latest serpentine variety to form and it has the  
611 highest  $\text{Fe}^{3+}/\text{Fe}_T$ . We thus interpret the increase of ferric iron in serpentines from the sole as evidence  
612 of their formation under near-surface conditions (i.e., low temperature, high  $f\text{O}_2$ ). The behavior of  
613 LREE provides additional proof of meteoric fluid involvement in the formation of the serpentinite  
614 sole. Serpentines from the serpentinite sole are LREE-enriched, except Ce. The exact opposite, i.e.,  
615 LREE depletion and strong Ce positive anomaly (**Figure 7**), is observed in laterites on top of the NC  
616 regolith and is explained by the very low mobility of  $\text{Ce}^{4+}$  relative to all other REE (Ulrich et al.  
617 2019). Also, the downslope migration of elements from the regolith can explain the high U/Th ratio  
618 in serpentines from the sole. Indeed, U is mobile under oxidizing surface conditions, while Th is  
619 insoluble (e.g., Dequincey et al. 2002). As a consequence, U/Th ratio is lower in laterites than in the  
620 initial peridotite (**Figure 7**). Meteoric fluids may thus transport LREE, and potentially other FME,  
621 released during weathering. A high U/Th ratio and a low Ce/Ce\* ratio in serpentine is therefore not  
622 necessarily a marker for the influence of seawater solely.

623 Lateritization has been considered as rather early and was active during or slightly after the  
624 ophiolite emplacement by Quesnel et al. (2013), based on a coupled isotopic and structural analysis  
625 of magnesite veins. Following our Monte-Carlo simulations, the O and H isotope signatures of the  
626 meteoric fluids involved during serpentinization ( $\delta^{18}\text{O} = -6 \pm 2\text{‰}$ ,  $\delta\text{D} = -40 \pm 10\text{‰}$ ; **Figure 8b**) are  
627 comparable with present-day rainwater (Nicolini et al. 2016). The current discharge of  $\text{H}_2$ ,  $\text{CH}_4$ , and  
628  $\text{N}_2$ -enriched hyperalkaline spring waters reveals active and low-temperature serpentinization at the  
629 base of the NC ophiolite (Deville and Prinzhofer 2016; Monnin et al. 2014). Thus, the serpentinization  
630 of the serpentinite sole was partly formed in response to the circulation of meteoric fluids during the  
631 late stages of its emplacement (**Figure 10b**). After the crystallization of lizardite 2 in microfracture  
632 networks, antigorite veins may have crystallized under moderate temperatures ( $<250^\circ\text{C}$ ), and high  
633 deformation conditions, such as documented by Ribeiro Da Costa et al. (2008). Finally, as the  
634 obduction proceeded, the progressive cooling temperatures may have led to the replacement of  
635 antigorite into lower temperature species, such as chrysotile and polygonal serpentine, as shown by  
636 Quesnel et al. (2016b).

## 637 638 **CONCLUSIONS**

639 The new mineralogical and geochemical data presented here, on the serpentinites from the  
640 peridotite nappe and the sole of NC ophiolite, provide evidence for a polyphasic history of fluid-rock  
641 interactions. By using trace element concentrations and a new modeling approach based on Monte  
642 Carlo simulations applied on oxygen and hydrogen isotope compositions, we propose that the main  
643 serpentinization event (lizardite formation) mostly occurred during the NE-dipping subduction in the  
644 SLB due to slab dehydration and subsequent hydration of forearc mantle wedge (i.e., the future  
645 Peridotite Nappe). Also, our simulations shift serpentinization temperatures in the fore-arc mantle in  
646 the range of  $250\text{--}450^\circ\text{C}$ , with an upper threshold that may be lowered to  $\sim 350^\circ\text{C}$ , as inferred by the  
647 lack of antigorite.

648 Other serpentine species present in the serpentinite sole recorded retrogression during fore-arc  
649 cooling and obduction. These serpentinization events occurred under high strain conditions and at  
650 lower temperature, from  $\sim 250^\circ\text{C}$  to  $< 100^\circ\text{C}$ . From the oxygen and hydrogen isotope composition of  
651 these serpentines, we suggest a meteoric contribution for the late stage serpentinizing fluids. Thus,  
652 this study demonstrates that serpentine in ophiolite may record a long history of fluid-rock  
653 interactions, from early fluid circulations deep into the forearc mantle to late meteoric fluid  
654 percolation at shallow depth during obduction

## 655 656 **Acknowledgements**

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657 We thank Claire Bassoulet for her help during LA-ICP-MS measurements at Géosciences  
658 Ocean laboratory (Brest, France). We also thank Olivier Rouer (SCMEM, Nancy, France) for his help  
659 during electron microprobe analyses. Marie-Camille Caumon (Géoresources, Nancy, France), and  
660 Gilles Montagnac (Laboratoire de Géologie, ENS Lyon, France) are thanked for their contributions  
661 during Raman spectroscopy analyses. Benita Putlitz and Thorsten Wennemann (ISTE, University of  
662 Lausanne, Switzerland) are acknowledged for their help during the measurement of O and H isotopes.

663 Sampling in New Caledonia was partly funded by the National Centre for Technological  
664 Research CNRT “Nickel et son environnement” based in Nouméa, New Caledonia (Project grant:  
665 8PS2013-CNRT.CNRS/SCANDIUM) and Labex Ressources21 (supported by the French National  
666 Research Agency through the National Program Investissements d’Avenir, reference ANR-10-  
667 LABX-21–LABEXRESSOURCES 21). The fieldwork benefited from the help of Koniambo S.A..

668 Juan Carlos de Obeson, an anonymous reviewer and the editor Othmar Müntener are warmly  
669 acknowledged for their detailed and constructive suggestions that helped to improve the manuscript.

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## Figure Captions

**Figure 1:** Simplified geological map of New Caledonia, showing the exposures of Paleocene-Eocene terranes, (adapted from Maurizot and Vende-Leclerc, 2009). Pre-obduction situation is modified from Cluzel et al. (2012).

**Figure 2: a, b.** Slightly (<20%) to moderately (~50%) serpentinized peridotite, respectively corresponding to the "facies supérieur" (b) and "facies intermediaire" (a) described in Orloff (1968). **c.** Serpentinite from the base of the ophiolite nappe, just above the serpentinite sole. **d, e, f.** Serpentinite from the serpentinite sole showing multiple generations of serpentine in the form of veins and fracture infilling. These serpentines include centimeter-scale greenish veins (d) that are crosscut by millimeter-scale veins filled by fibrous serpentine and/or light green to white-colored massive serpentine (e, f).

**Figure 3: a.** Microphotography (cross-polarized) of the typical mesh texture (S1) observed in serpentinized peridotite and serpentinites from the upper parts of the Peridotite Nappe. Black veins correspond to magnetite (sample MS60). **b.** Microphotography (cross-polarized) of the serpentinite sole showing the primary mesh texture (S1) crosscut by 4 successive generations of serpentine veins (S2 to S5; sample xx3786). **c.** Microphotography (cross-polarized) of the serpentinite sole showing the primary mesh texture (S1) crosscut by S3 veins, itself crosscut by fiber-habitus S5 veins and the close association between S5 and S6 serpentines (sample xx3758). **d.** Schematic representation of (b). mgt: magnetite; chr: chromite.

**Figure 4:** Raman spectra of the main serpentine species identified in this study.

**Figure 5:** Plots of **a.** Si+Al cations vs. Mg+Fe<sub>T</sub> cations; **b.** Mg cations vs. Fe<sub>T</sub> cations; **c.** Fe<sub>T</sub> cations vs. Al cations; and **d.** Mg# ( $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ ) vs. Fe<sup>3+</sup>/Fe<sub>T</sub> (lower right), showing that serpentine from the sole integrates less Al and Fe<sub>T</sub> and more oxidized iron than upper serpentines. Compositions of primary minerals are also shown. Ol: olivine; Opx: orthopyroxene; Cpx: clinopyroxene. Atoms per formula units are calculated based on 7 oxygens for serpentine minerals, except for antigorite which is calculated based on 6.823 oxygens. Olivine and pyroxene structural formulas are calculated based on 4 and 6 oxygens, respectively, and then converted to 7 oxygens for comparison with serpentine minerals. Brucite and Fe<sup>3+</sup> dioctahedral substitution trends are from Beard and Frost (2017).

705 **Figure 6:** PM-normalized extended trace element patterns of serpentine minerals. **a.** Lizardite from  
706 upper serpentines compared to their magmatic mineral precursors (olivine, orthopyroxene,  
707 clinopyroxene). The first serpentine generation (lizardite S1) preserves the initial trace element  
708 patterns. **b.** Trace element patterns of lizardite from the serpentinite sole (S2) compared to lizardite  
709 S1. **c.** Trace element patterns of antigorite (S3) from the serpentinite sole compared to lizardite S2.  
710 **d.** Trace element patterns of chrysotile (S5) and polygonal serpentine (S6) from the serpentinite sole  
711 compared to lizardite S2. S1 to S2 transition is marked by an enrichment in fluid-mobile elements (in  
712 blue), especially with a pronounced U positive anomaly and an enrichment in LREE except for Ce.  
713 S2 to S6 transitions occurred isochemically. Primitive-mantle values are from McDonough and Sun  
714 (1995).

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716 **Figure 7:** Plots of concentrations of selected fluid-mobile elements (B, Li, Sb, Pb, and Sr), U/Th and  
717 Ce/Ce\* ratios in serpentines from Upper serpentinites and from the serpentinite sole. Primitive and  
718 depleted mantle values are from McDonough and Sun (1995) and from Workman and Hart (2005),  
719 respectively, except for B, Li and Sb concentrations in the depleted mantle which are from Salters  
720 and Stracke (2004). Global subducted sediments (GLOSS II) concentrations are from Plank (2014).  
721 Other concentration ranges are from Frisby et al. (2016) and Peters et al. (2017) for abyssal  
722 serpentinites; Lafay et al. (2013) and Peters et al. (2017) for serpentines with sedimentary imprints;  
723 Ulrich et al. (2010) and Secchiari et al. (2016; 2019) for NC serpentinitized peridotites; Ulrich et al.  
724 (2019) for laterites.  $Ce/Ce^* = C_{eN} / [(La_N * Pr_N)^{1/2}]$ .

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726 **Figure 8: a.**  $\delta D$  vs.  $\delta^{18}O$  of NC serpentines. Blue and green fields represent the isotopic compositions  
727 of oceanic serpentinites and ophiolite serpentinites, respectively (Wenner and Taylor, 1973; Früh-  
728 Green et al., 2001). The black arrow shows the trend formed by samples contaminated by supergene  
729 silica ( $\delta^{18}O > 29\%$ ; Quesnel et al., 2016). Grey areas indicate the range of mantle compositions in  
730  $\delta^{18}O$  and  $\delta D$ , with average values of 5.5‰ and -80‰ respectively (Deloule et al., 1991; Eiler et al.,  
731 2001). **b.** Calculated  $\delta D$  vs.  $\delta^{18}O$  compositions of serpentinizing fluids (represented as a density field)  
732 in equilibrium with NC serpentines (~6500 positive results, i.e., consistent with the isotopic  
733 compositions of NC serpentines, over 1 000 000 Monte-Carlo simulations, see the main text for more  
734 details about the modeling). The O and H compositions of fluids in equilibrium with the altered  
735 oceanic crust at 200-400°C, with subducted sediments (sed. fluids) and with subducted serpentinites  
736 (serp. fluids) at 200-350°C are calculated according to the modeling approach of Alt and Shanks III  
737 (2006). NC meteoric rainwater compositions are from Nicolini et al. (2016). **c. and d.** Calculated  
738  $\delta^{18}O_{fluid}$  and  $\delta D_{fluid}$  vs. temperature of serpentinization. The white cross-hatched area indicates  
739 simulations that fall into the red area in (b) (~40% of >6500 simulations). Colorbar values correspond

740 to the number of pixels in one grid cell of a size of 1‰ ( $\delta^{18}\text{O}$ ) by 10‰ ( $\delta\text{D}$ ) in (b), 50°C (T) by 1‰  
741 ( $\delta^{18}\text{O}$ ) in (c) and 50°C (T) by 10‰ ( $\delta\text{D}$ ) in (d).

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743 **Figure 9:** Plots of **a.** U/Th vs. U and **b.** B/Zr vs. B of NC serpentines. Thick solid lines represent the  
5 bulk mixing between the NC mantle wedge and sediment-derived fluids (in orange), with AOC-  
744 derived fluids (in blue) and with serpentine-derived fluids (in green). Thin dotted lines represent the  
745 bulk mixing between the NC mantle wedge and AOC-derived fluids mixed with various amounts of  
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10 sediment-derived fluids (in orange) and serpentine-derived fluids (in green). Grey dotted lines  
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12 correspond to the percentage additions of slab-derived fluids to the mantle wedge. Compositions of  
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14 the NC mantle wedge and AOC, sediment and serpentine-derived fluids and respective sources are  
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16 listed in Table 4.  
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21 **Figure 10: a.** A simple model for the serpentinization of the New Caledonia ophiolite. **a.** Massive  
22 hydration of the forearc mantle related to the dehydration of the altered oceanic basement of the  
23 subducted plate, leading to the formation of fully serpentinized peridotites (including pyroxenes) at  
24 the slab interface, where fluid flows are the most intense, and partially serpentinized peridotites at  
25 shallower depths where fluid flows are less expressed. **b.** Conceptual model of the serpentinite sole  
26 formation in response to the percolation of meteoric fluids at the base of the NC ophiolite during its  
27 emplacement on the Norfolk continental basement. Note that these meteoric fluids previously  
28 interacted with peridotite the top of the ophiolite, forming a thick regolith since the ophiolite emersion  
29 at 34 Ma. (modified after Lagabrielle et al., 2013). The legend is the same as in Figure 1.  
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## Table Captions

**Table 1:** Representative major element concentrations of primary minerals (olivine, orthopyroxene and clinopyroxene) and serpentines from NC peridotites.

**Table 2:** Representative trace element concentrations of primary minerals (olivine, orthopyroxene and clinopyroxene) and serpentines from NC peridotites.

**Table 3:** Oxygen and hydrogen compositions of NC serpentines (US: upper serpentinites; Lhz: lherzolite; Hz: harzburgite; Du: dunite; lz: lizardite; atg: antigorite; ctl: chrysotile; pol: polygonal serpentine; BR: bulk rock).

**Table 4:** Chemical compositions, mobilities and references used for trace element modeling.

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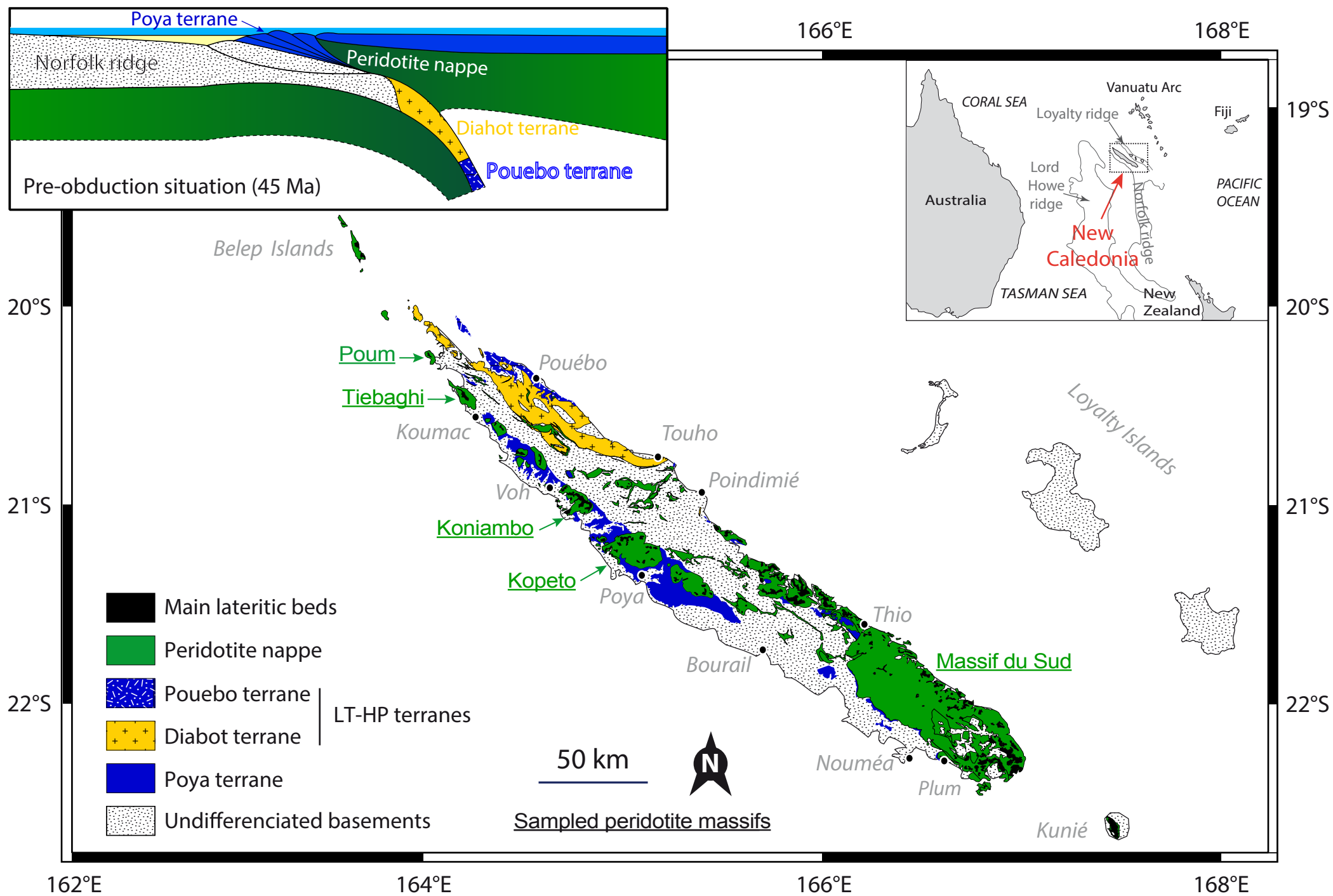
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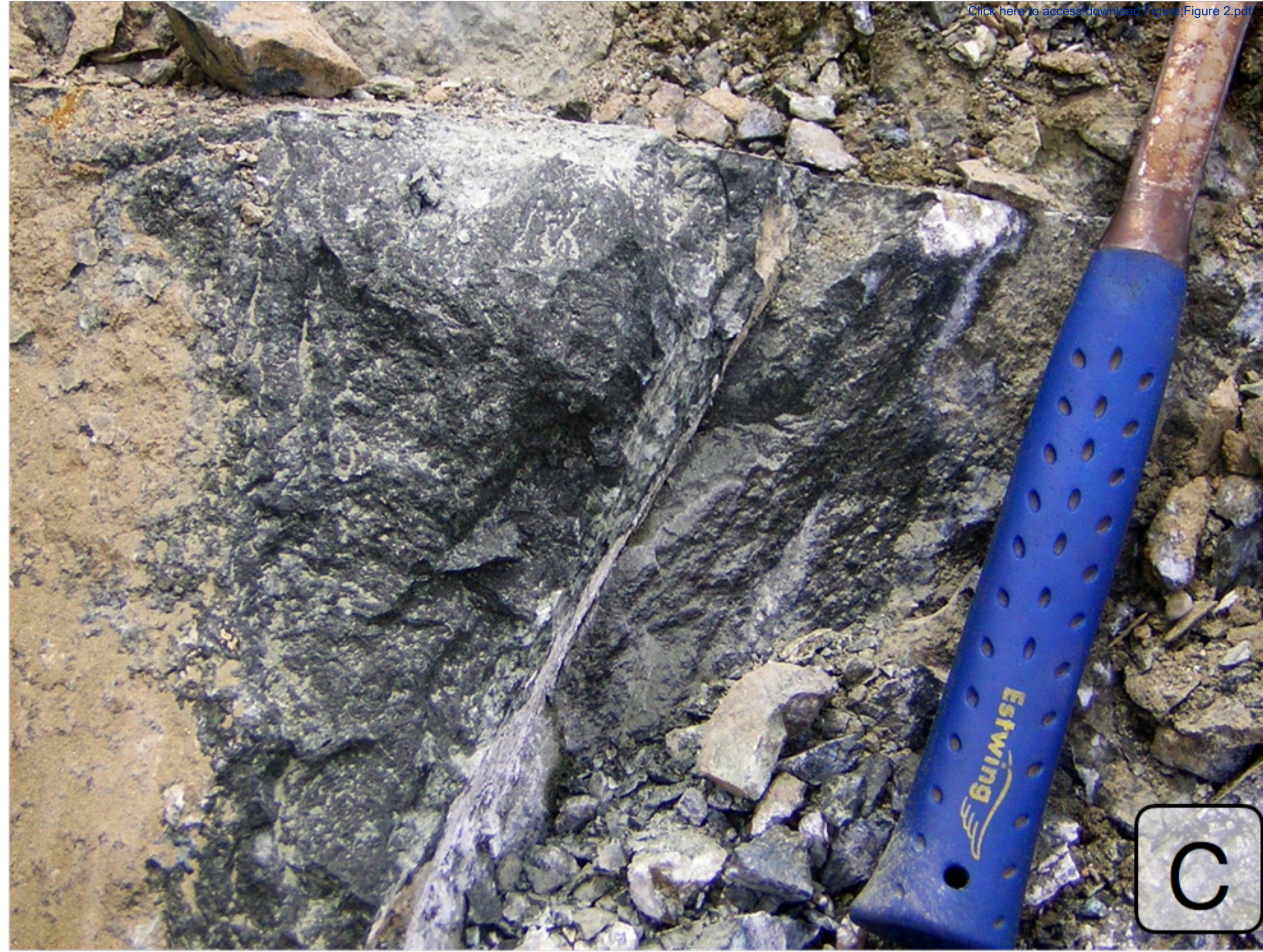
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Figure 1







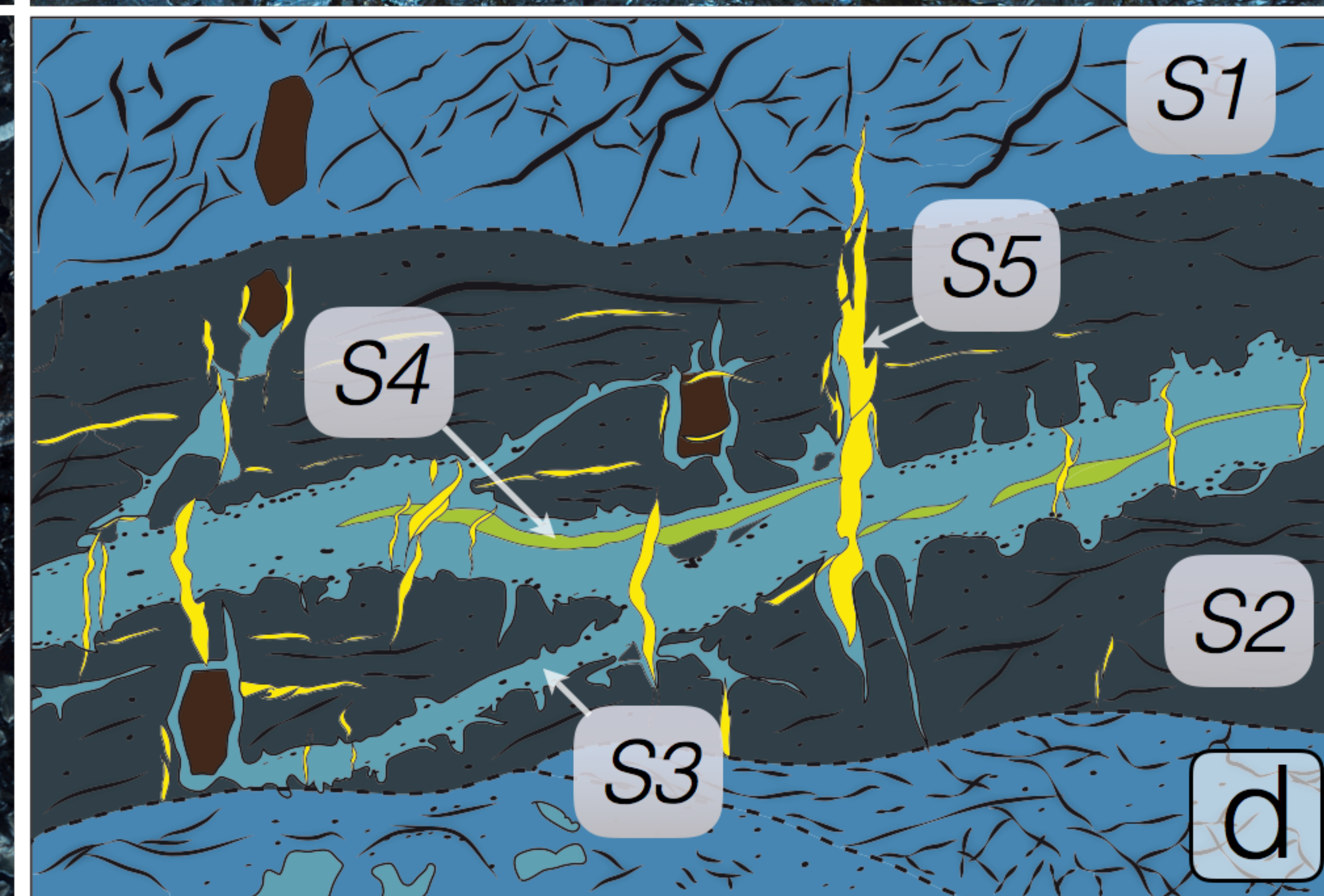
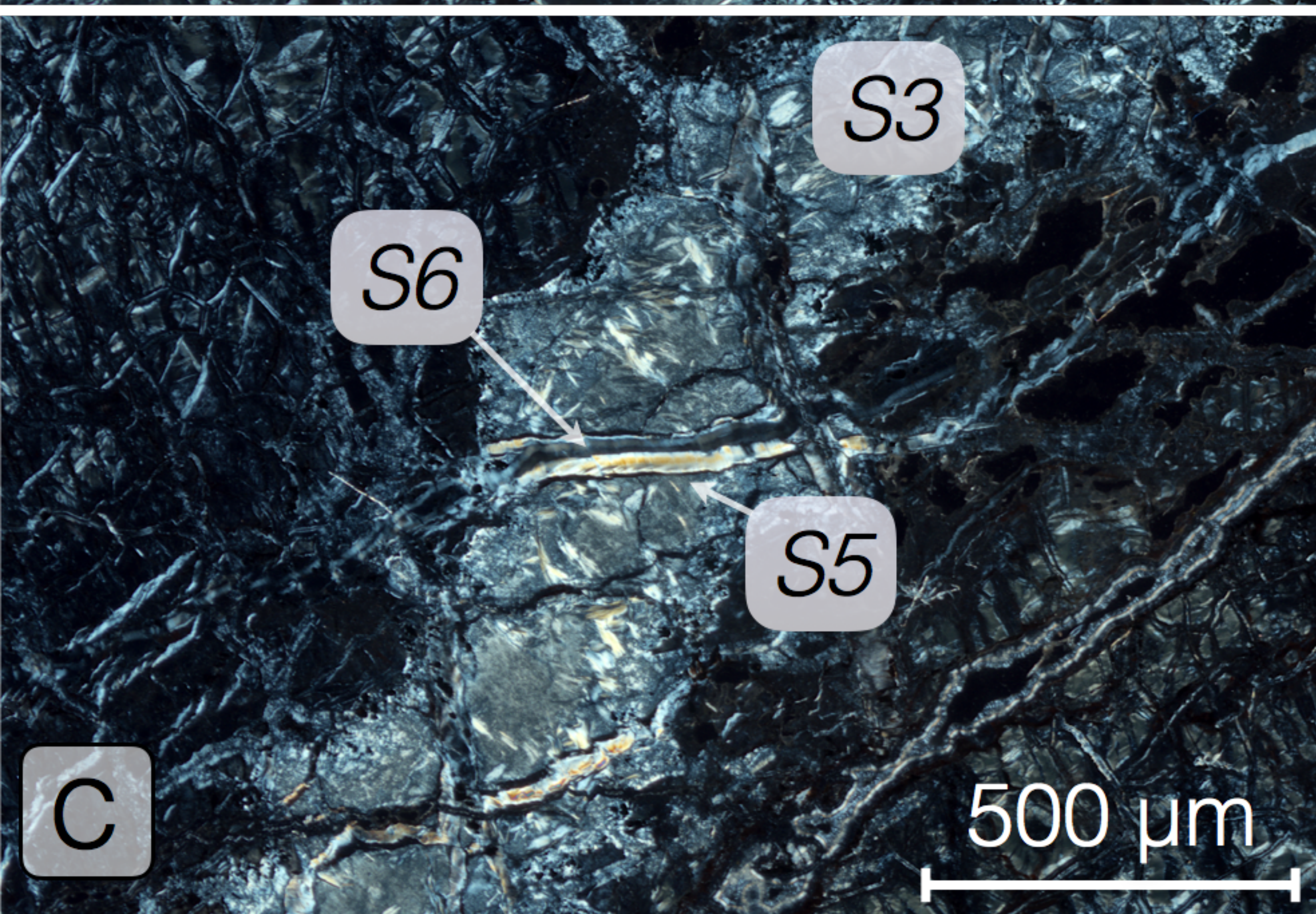
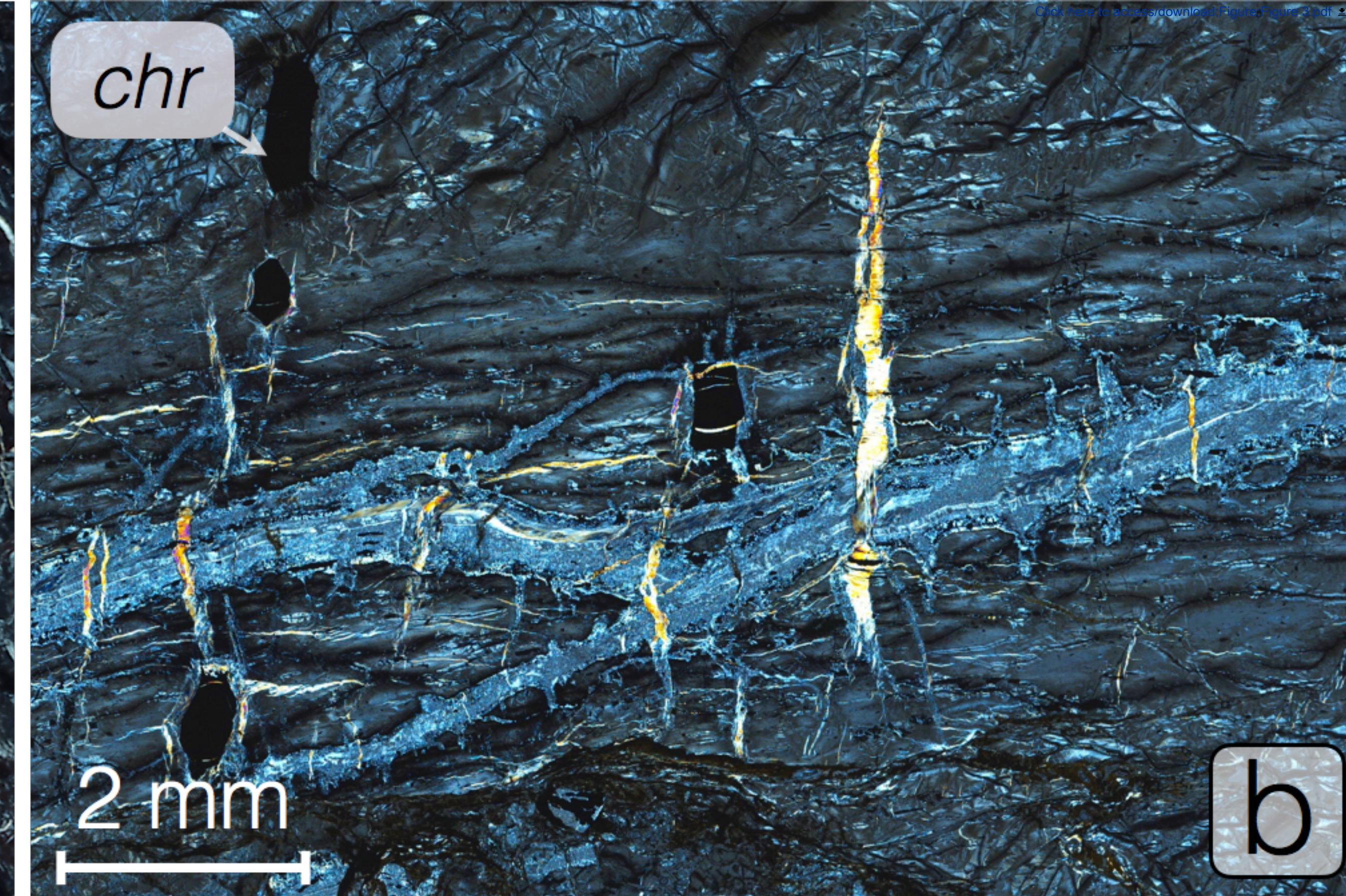
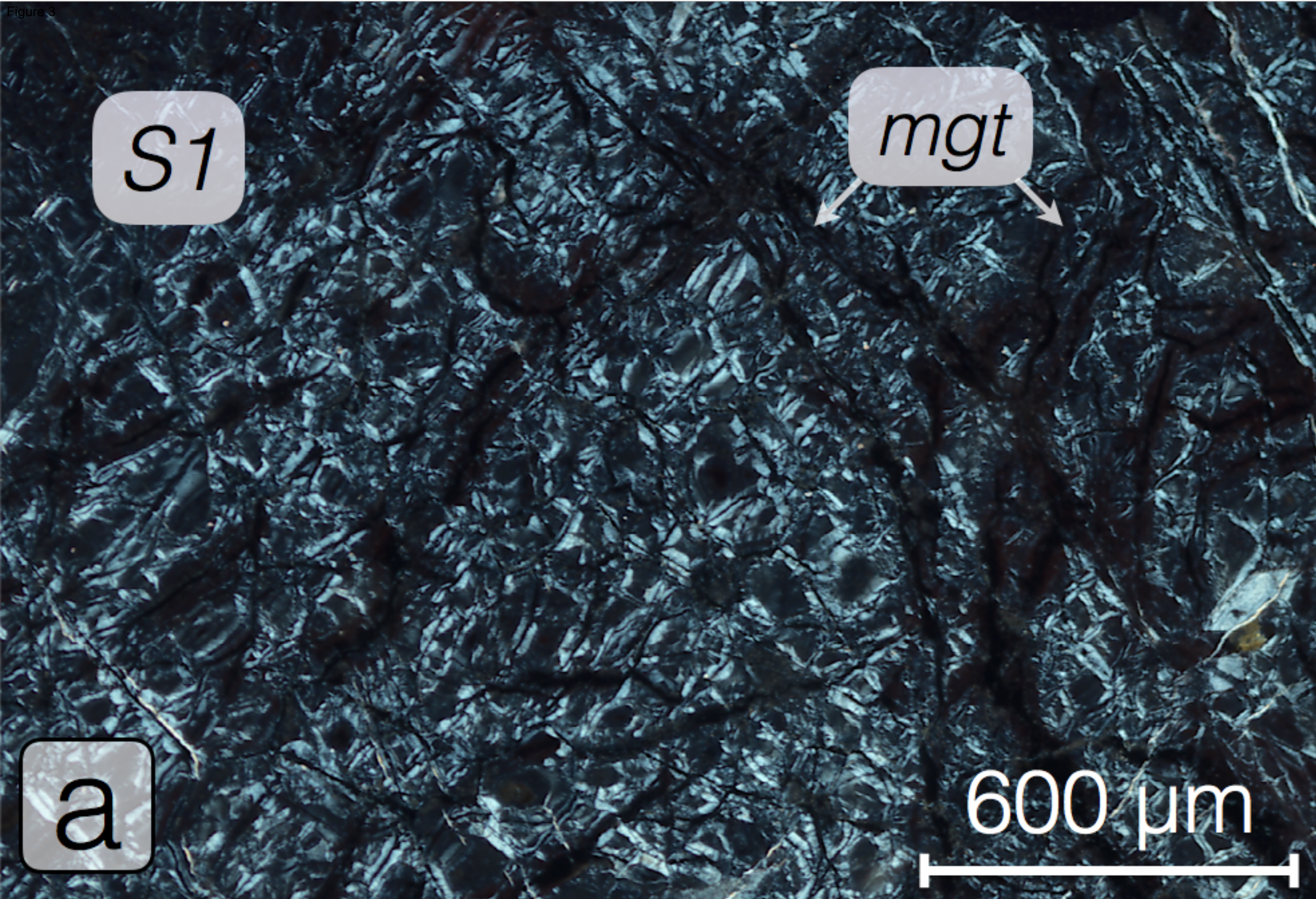


Figure 4

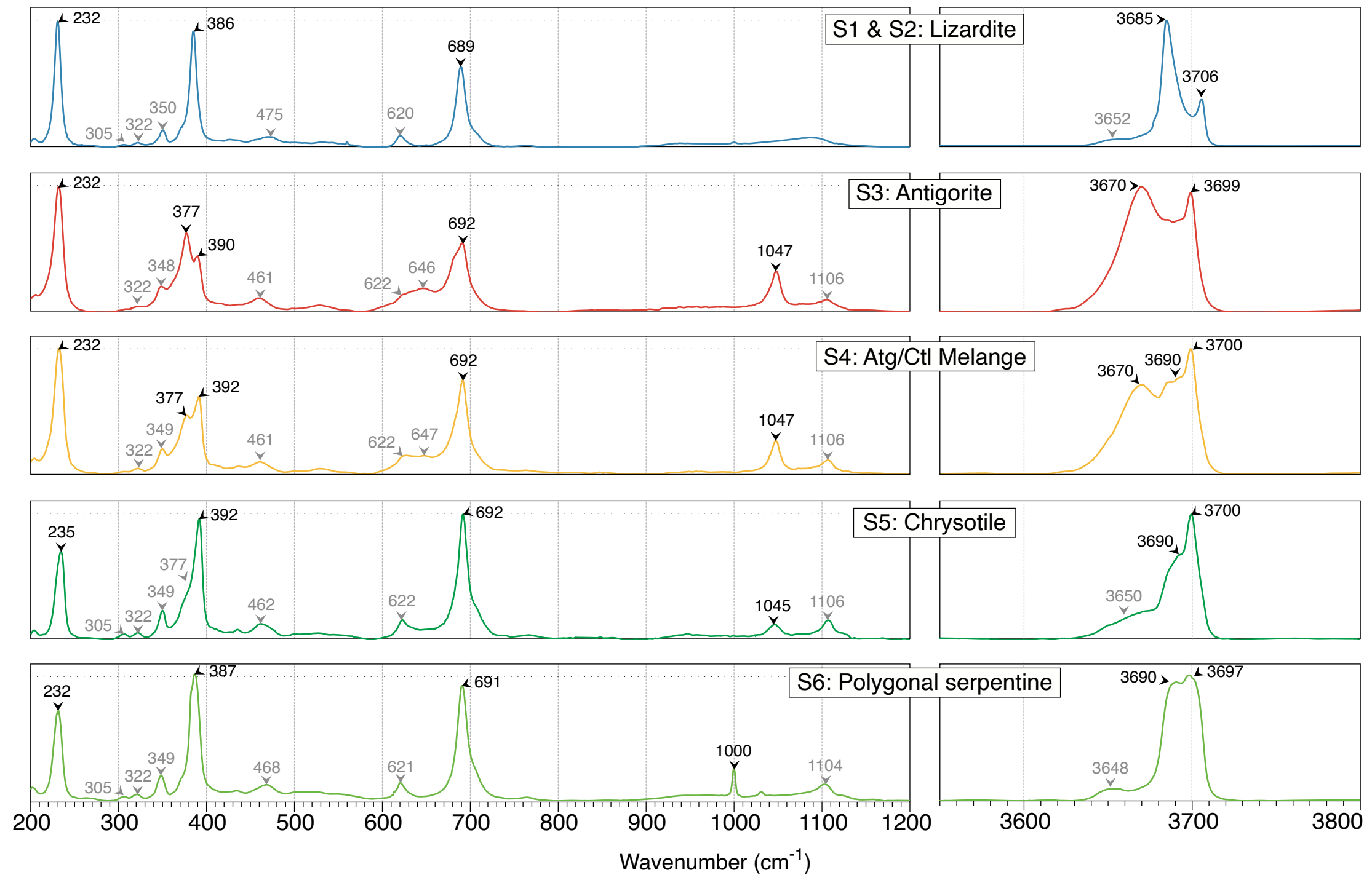
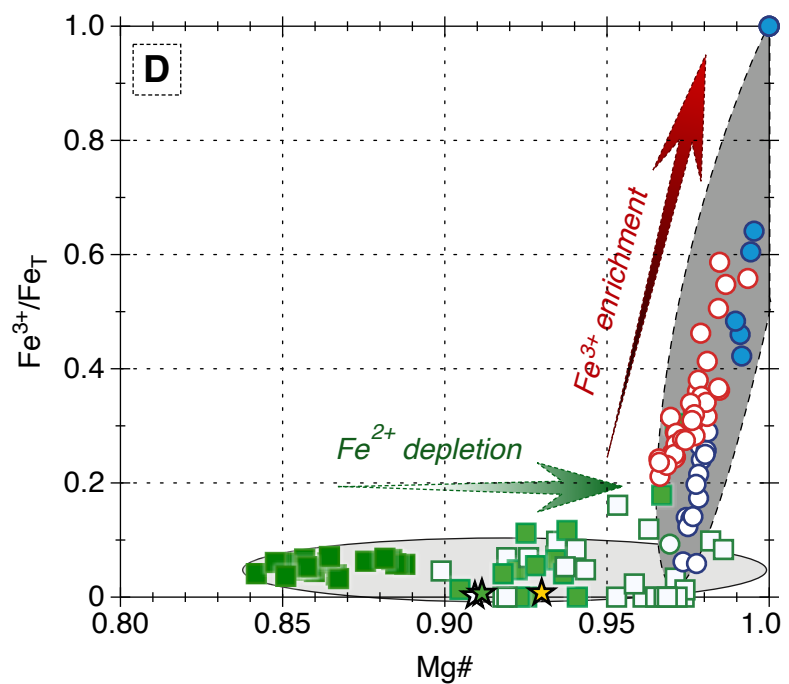
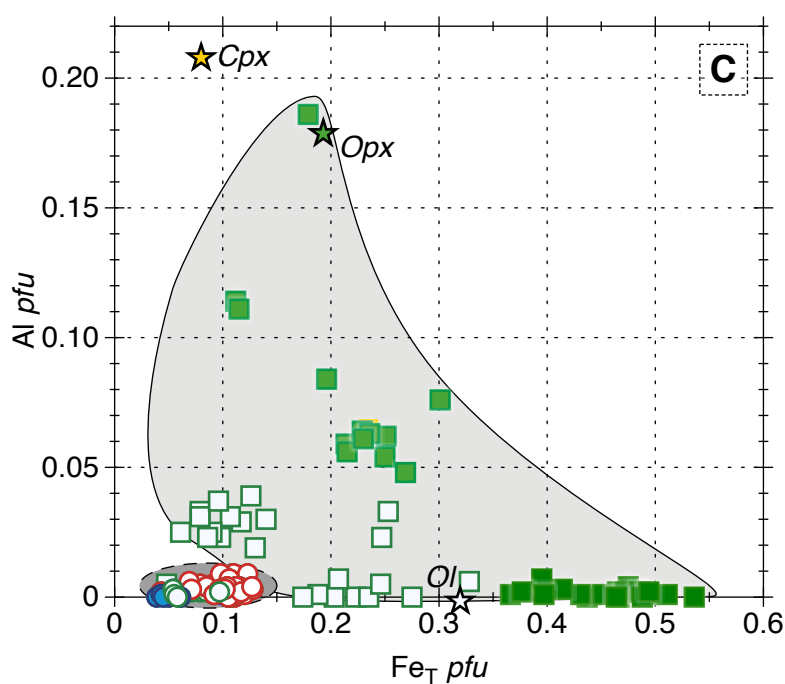
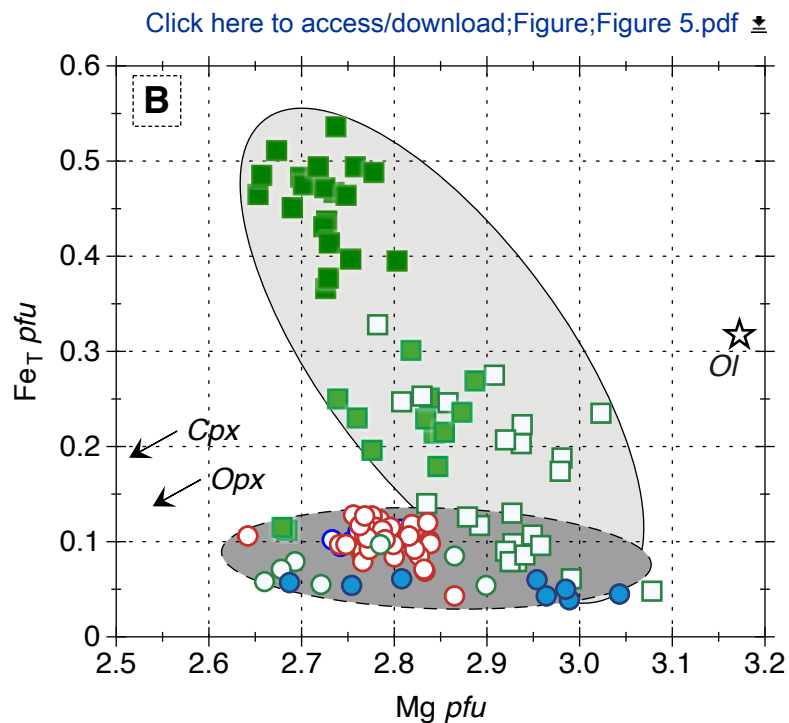
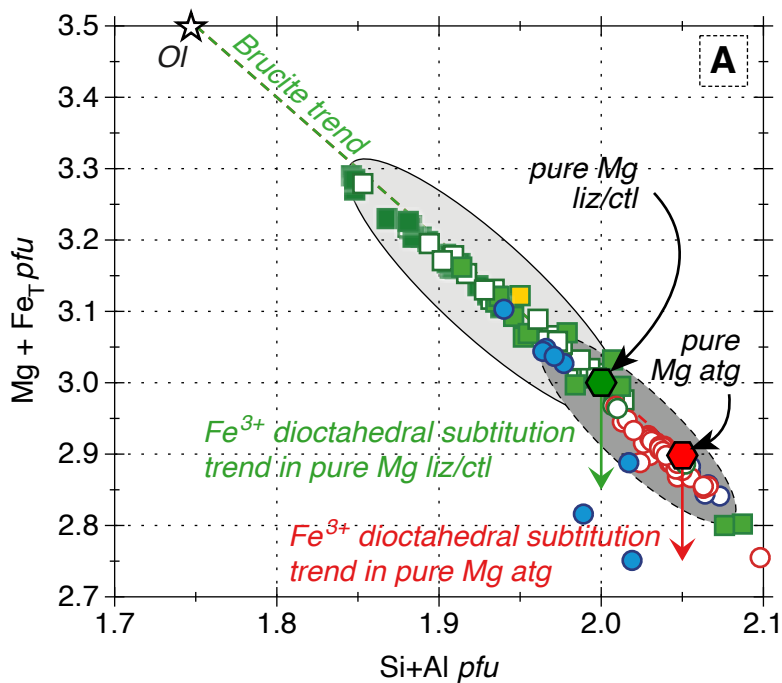


Figure 5

**Upper Serpentines**

- Lizardite (after olivine)
- Lizardite (after orthopyroxene)
- Lizardite (after clinopyroxene)
- Lizardite (mesh)

**Serpentinite sole**

- Lizardite
- Antigorite
- Chrysotile
- Polygonal

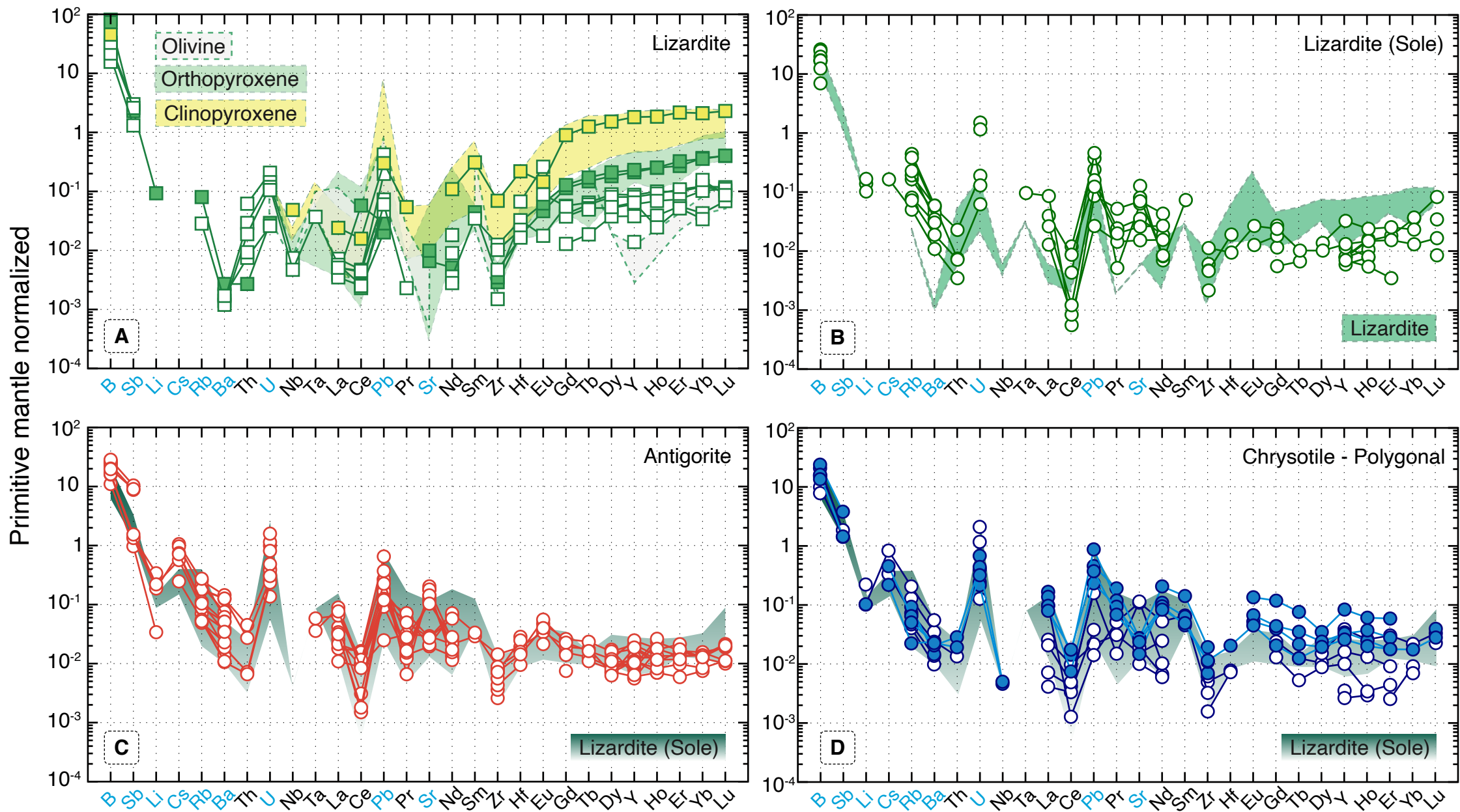
**Primary minerals**

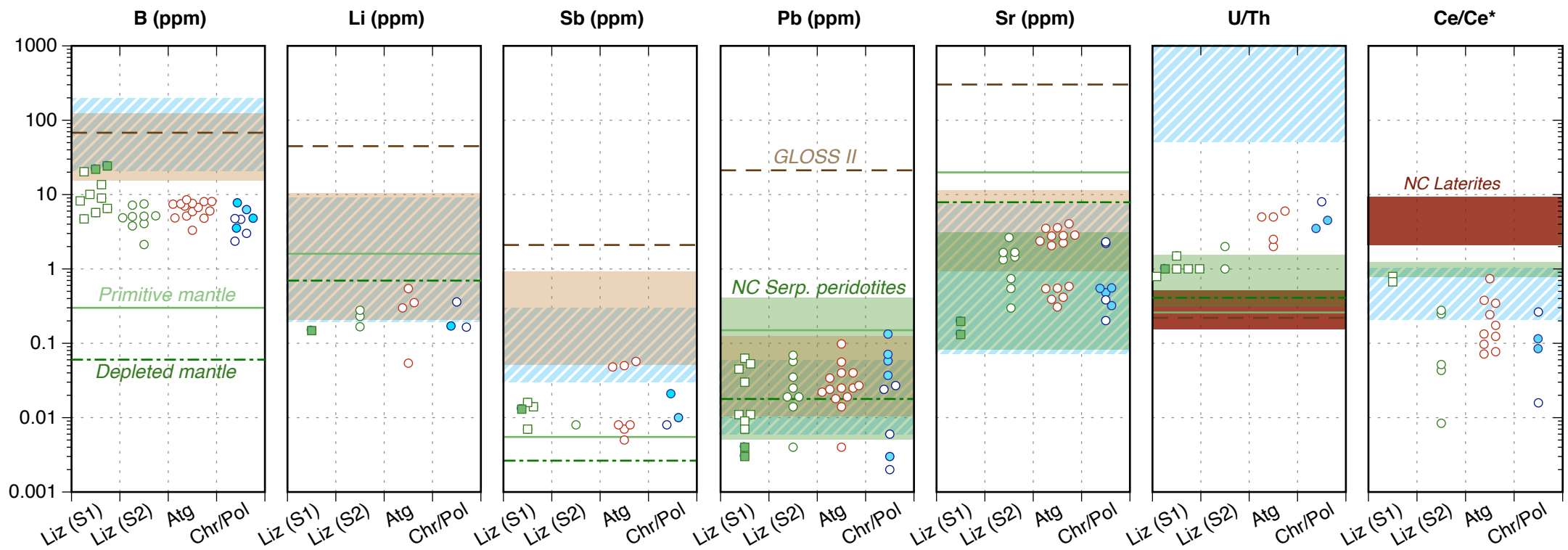
- ☆ Olivine
- ☆ Orthopyroxene
- ☆ Clinopyroxene

**Fields**

- Upper part of the massifs
- Serpentinite sole

Figure 6



**Upper serpentines**

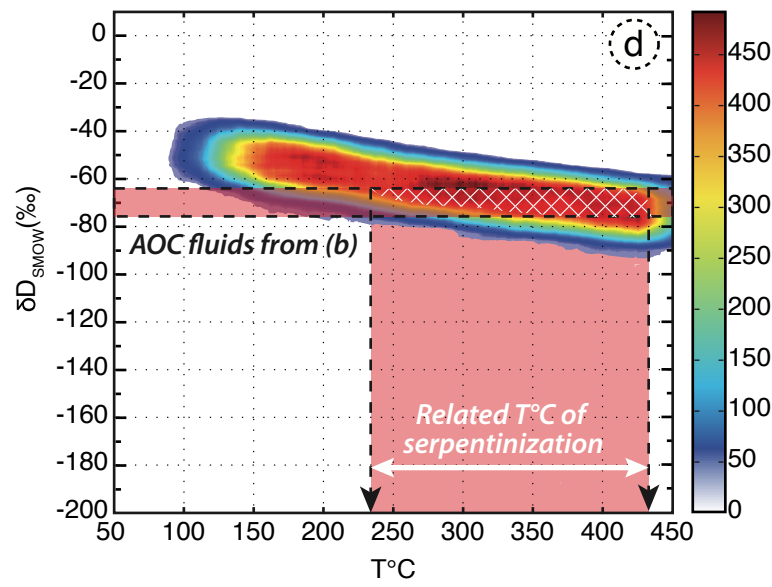
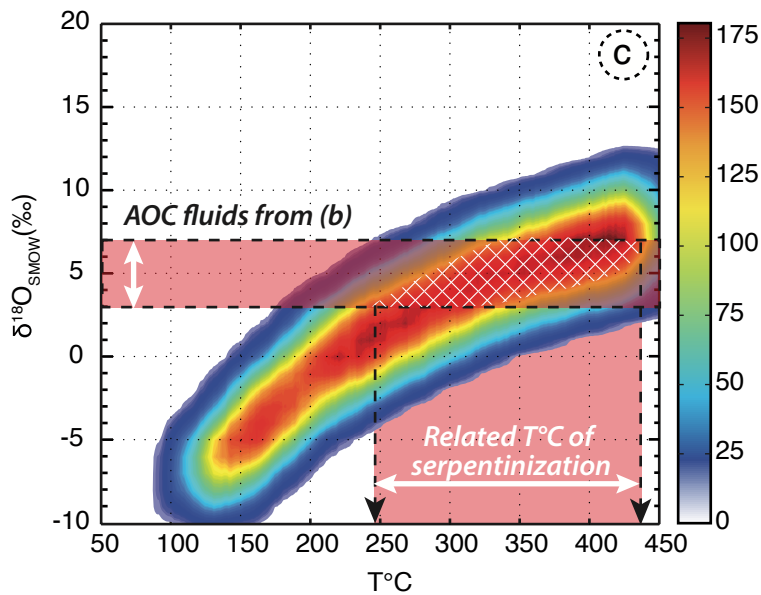
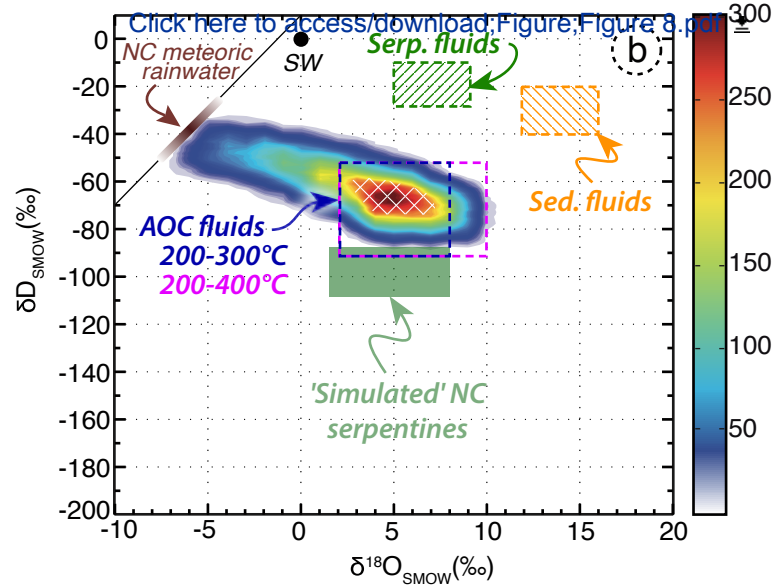
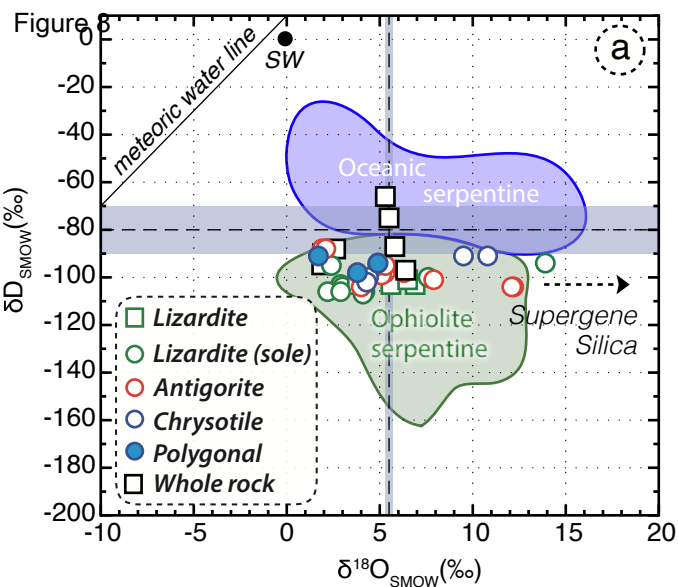
- Lizardite (S1)
- Lizardite (after opx)

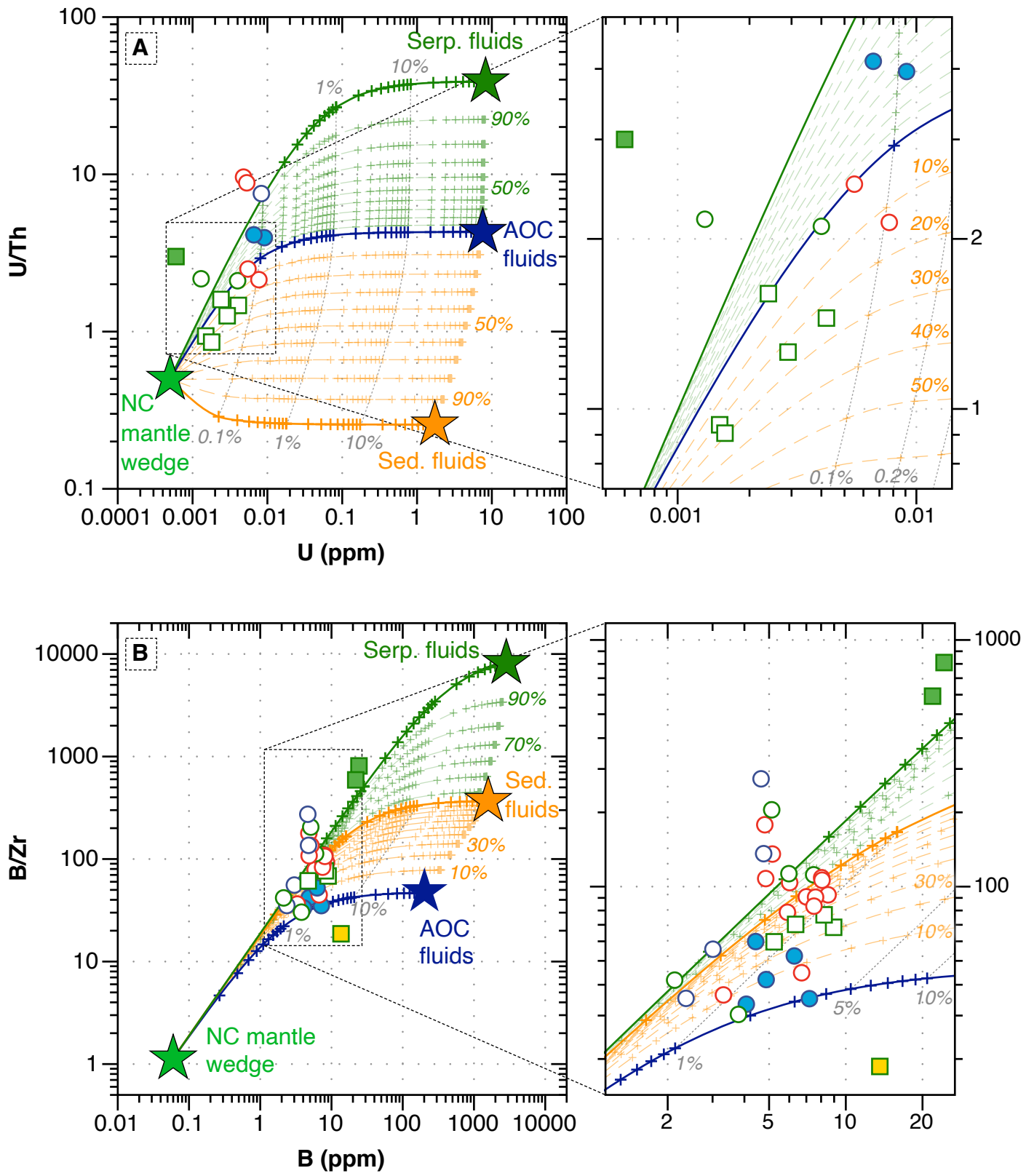
**Serpentinite sole**

- Lizardite (S2)
- Antigorite (S3)
- Chrysotile (S5)
- Polygonal serpentine (S6)

**Literature references**

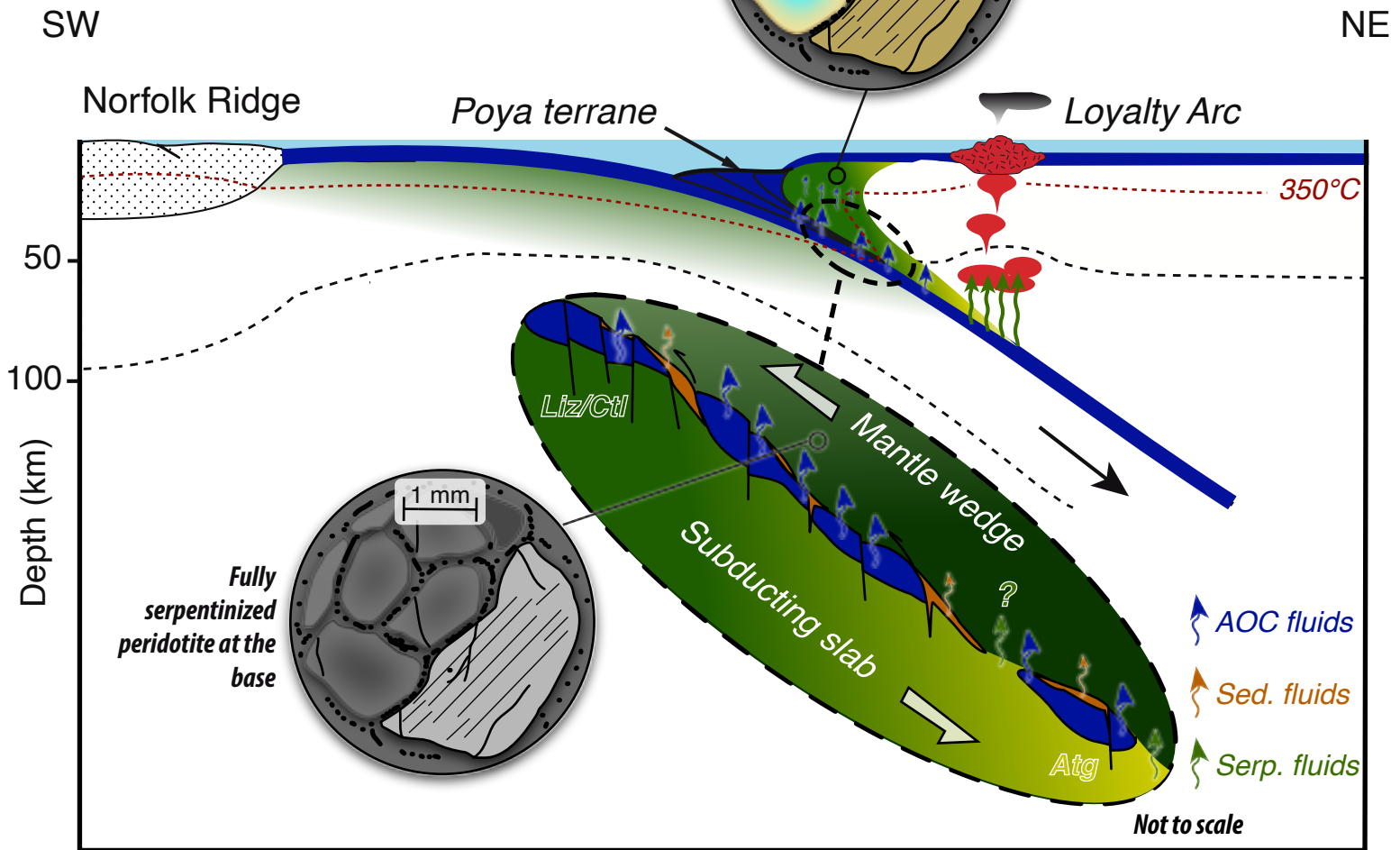
- ▨ Abyssal serpentinites
- ▨ Serpentinized peridotites
- ▨ NC serpenitized peridotites
- ▨ NC laterites



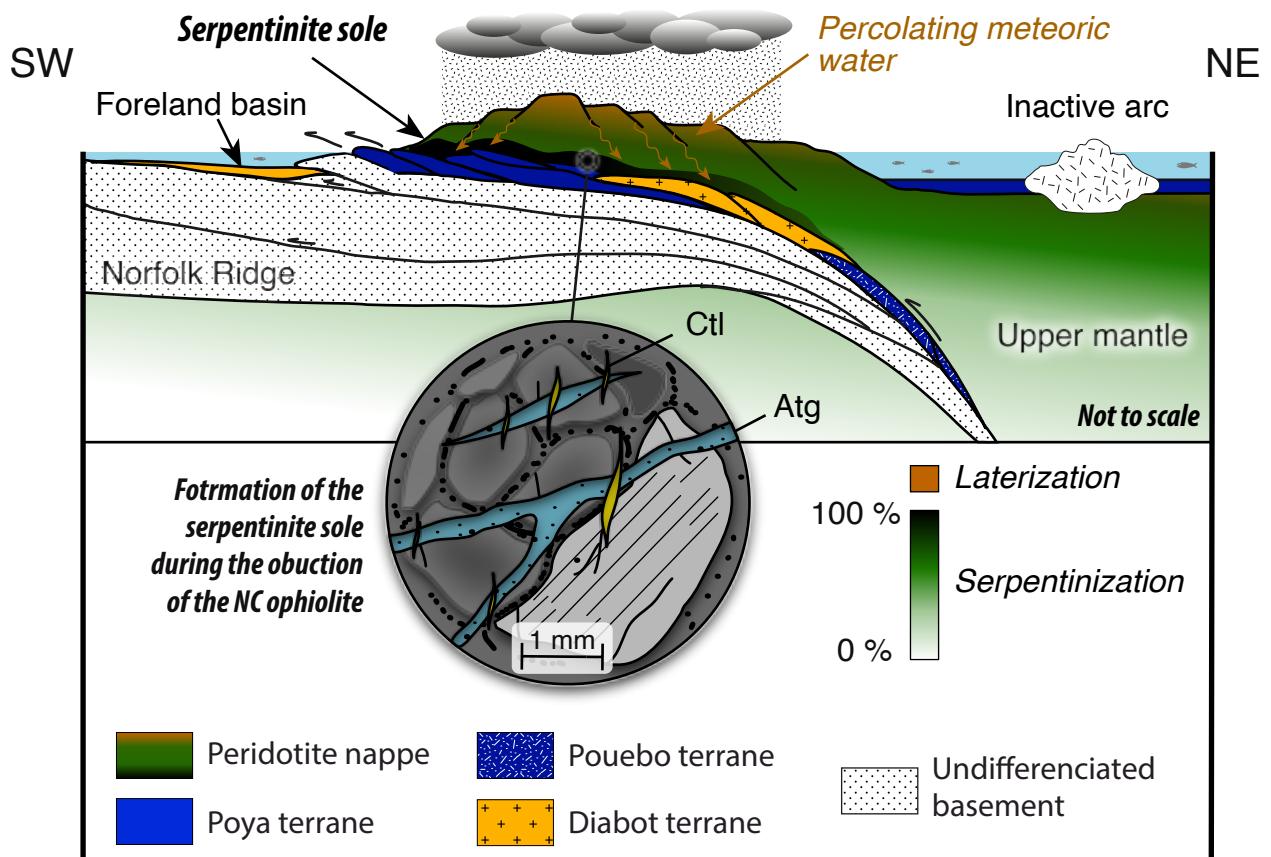




**A : Forearc serpentinitization (45 Ma)**



**B: Serpentinite sole formation (~40 Ma)**



Structural position	Upper part of the ophiolite												
	MS60-1	Ti6-3	Ti50A-07-6	Ti50A-07-9	Ti6-1	Ti50A-07-3	Ti50-2	Ti48	Poum 17	Ti-48	Ti48-06	Poum-13	xx3786A-7
<b>Sample id</b>													
<b>Type</b>	Lizardite		Lizardite		Lizardite	Lizardite	Olivine		Orthopyroxene		Clinopyroxene		Lizarc
<b>Texture</b>	Mesh core		Mesh rim		Bastite	Bastite							Clast and matr
<b>Primary minerals</b>	Olivine		Olivine		Opx	Cpx							
<b>SiO<sub>2</sub></b>	40.0	41.7	38.9	38.5	42.4	39.4	41.0	40.8	55.2	55.1	51.9	51.7	43.2
<b>TiO<sub>2</sub></b>	-	-	-	0.01	0.07	0.04	-	-	0.09	0.11	0.30	0.27	0.04
<b>Al<sub>2</sub>O<sub>3</sub></b>	-	0.57	0.01	-	2.07	1.15	-	-	4.20	3.56	4.77	4.26	0.04
<b>FeO</b>	5.58	2.75	10.97	11.41	2.86	5.88	8.75	8.83	6.01	5.88	2.44	2.07	2.21
<b>MnO</b>	0.02	-	0.19	0.04	0.15	0.18	0.16	0.14	0.16	0.15	0.10	0.12	0.08
<b>MgO</b>	41.3	42.4	36.7	37.5	38.7	40.3	50.0	49.8	33.5	33.1	16.3	16.3	41.4
<b>CaO</b>	-	-	-	-	0.11	-	0.04	0.02	0.47	1.06	23.11	23.01	-
<b>Na<sub>2</sub>O</b>	0.01	0.02	-	-	0.03	-	-	-	0.01	-	0.29	0.38	-
<b>K<sub>2</sub>O</b>	-	-	-	-	0.01	-	-	-	-	-	-	-	0.02
<b>Cr<sub>2</sub>O<sub>3</sub></b>	-	-	-	-	0.95	-	0.01	0.01	0.66	0.88	1.01	1.11	-
<b>NiO</b>	0.38	0.11	0.49	0.47	0.15	0.40	0.41	0.38	0.10	0.10	0.05	0.05	0.48
<b>Total</b>	87.3	87.5	87.3	87.9	87.5	87.3	100.3	99.9	100.4	99.9	100.2	99.3	87.4
<i>Number of oxygen p.f.u.</i>	7		7		7	7	4		6		6		7
<b>Si</b>	1.92	1.95	1.91	1.88	1.97	1.86	1.00	1.00	1.90	1.91	1.88	1.89	2.00
<b>Ti</b>	-	-	-	-	0.002	-	-	-	0.002	0.003	0.008	0.007	0.001
<b>Al</b>	0.018	0.031	0.001	-	0.114	0.064	-	-	0.170	0.146	0.203	0.183	0.002
<b>Fe<sup>3+</sup></b>	-	-	0.027	0.021	0.020	-	-	-	-	-	-	-	0.023
<b>Fe<sup>2+</sup></b>	0.212	0.107	0.424	0.446	0.092	0.313	0.178	0.181	0.173	0.170	0.074	0.063	0.062
<b>Mn</b>	0.002	-	0.008	0.002	0.006	0.007	-	-	0.005	0.005	0.003	0.004	0.003
<b>Mg</b>	2.90	2.95	2.69	2.73	2.68	2.84	1.81	1.81	1.72	1.71	0.88	0.89	2.86
<b>Ca</b>	-	-	-	-	0.006	-	<0.001	<0.001	0.017	0.039	0.897	0.900	-
<b>Na</b>	0.002	0.002	-	-	0.002	-	-	-	<0.001	-	0.020	0.027	-
<b>K</b>	-	-	-	-	0.001	-	-	-	-	-	-	-	0.001
<b>Cr</b>	-	-	-	-	0.035	-	<0.001	<0.001	0.018	0.024	0.029	0.032	-
<b>Ni</b>	0.008	0.004	0.019	0.018	0.006	0.015	0.008	0.007	0.003	0.003	0.001	0.001	0.018
<b>Mg#</b>	0.93	0.96	0.86	0.86	0.97	0.90	0.91	0.91	0.91	0.91	0.92	0.93	0.98
<b>Fe<sup>3+</sup>/(Fe<sup>2+</sup>+Fe<sup>3+</sup>)</b>	-	-	0.06	0.04	0.18	-	-	-	-	-	-	-	0.27

**Serpentinite sole**

KOP-13	xx3786A-13	KOP3-5	xx3758-7	xx3786B-2	KOP3-3	KOP3-4
lite	Antigorite		Chrysotile		Polygonal	
breccia	Vein		Vein		Vein and breccia	
ix					matrix	
44.0	43.5	44.4	44.1	43.5	44.6	45.5
0.01	-	-	0.02	-	-	-
0.05	0.02	0.01	0.06	0.05	0.05	0.01
1.42	2.85	2.42	2.01	2.08	1.46	1.54
0.05	0.01	0.03	0.06	0.02	0.02	-
42.6	39.9	41.4	40.0	40.4	41.5	40.7
0.07	-	0.09	0.11	0.08	0.04	-
0.03	0.06	0.01	0.02	0.05	0.02	0.02
0.01	-	-	0.02	0.01	-	0.02
-	-	0.01	-	0.10	-	0.08
0.29	0.23	0.10	0.05	0.12	0.21	0.21
88.5	86.6	88.4	86.4	86.4	87.9	88.1
	6.823		7		7	
2.01	1.98	1.98	2.06	2.04	1.99	2.02
-	-	-	0.001	-	-	-
0.003	0.001	0.001	0.003	0.003	0.003	0.001
0.017	0.027	0.026	0.011	0.016	0.054	0.057
0.037	0.082	0.065	0.067	0.065	0	0
0.002	0.000	0.001	0.002	0.001	0.001	-
2.90	2.72	2.75	2.78	2.82	2.75	2.69
0.003	-	0.004	0.006	0.004	0.002	-
0.003	0.005	0.001	0.002	0.005	0.002	0.002
0.001	-	-	0.001	0.001	-	0.001
-	-	<0.001	-	0.004	-	0.003
0.011	0.008	0.004	0.002	0.005	0.008	0.007
0.99	0.97	0.98	0.98	0.98	1.00	1.00
0.31	0.25	0.28	0.14	0.20	1.00	1.00

Structural position	Upper serpentinite											
Type	Lizardite		Lizardite	Lizardite	Olivine		Orthopyroxene		Clinopyroxene		Lizardite	
Texture	Mesh core		Bastite	Bastite							Clast and breccia	
Primary minerals	Olivine		Opx	Cpx								
Sample name	Ti-6	Ti 50	Ti-6	Ti-50	TI-50	Poum-13	TI-48	Poum-11	Ti 50	Poum-11	xx-3786a	Ti-47
Li	<0.071	<0.561	<0.088	<0.684	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.088	<0.215
B	5.72	9.89	24.3	13.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.79	5.98
Ti	60.1	60.3	159	2163	14.0	14.0	646	239	1766	542	<1.80	b.d.l.
Mn	166.712	847	635	1460	1057	1004	1090	1096	747	638	80.8	116
Co	31.8628	81.1	27.3	67.4	147	146	63.0	59.0	28.0	24.0	18.2	45.3
Ni	783	4350	576	3068	3127	3179	806	725	415	415	1488	1424
As	<0.156	<2.19	<0.461	<1.85	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.454	<1.23
Rb	<0.010	<0.062	<0.031	<0.113	<0.013	<0.014	<0.017	<0.015	0.054	0.085	0.045	0.120
Sr	<0.032	<0.218	0.131	<0.357	0.02	0.02	1.16	<0.015	0.39	0.92	0.545	1.334
Y	0.260	0.060	0.907	7.809	0.012	0.014	1.72	0.189	8.709	2.053	0.060	0.037
Zr	0.049	<0.084	0.030	0.729	0.025	<0.01	0.022	0.018	0.164	0.137	0.125	0.053
Nb	0.003	<0.021	<0.003	0.032	<0.005	<0.004	0.011	<0.006	0.015	<0.007	<0.002	<0.006
Sn	<0.0512	<0.318	<0.048	<0.526	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.045	<0.212
Sb	0.007	<0.033	<0.008	<0.040	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.009	<0.016
Cs	<0.003	<0.035	<0.008	<0.049	<0.006	<0.009	<0.007	<0.013	<0.006	0.01	<0.008	<0.014
Ba	0.008	<0.044	0.012	<0.039	0.243	<0.018	0.283	0.055	0.864	0.248	0.131	0.406
La	0.004	<0.008	<0.002	0.016	0.006	<0.002	0.133	<0.003	0.041	0.032	0.018	<0.003
Ce	0.004	<0.006	0.004	0.027	0.226	<0.001	0.195	<0.003	0.029	0.038	0.002	0.008
Pr	<0.0007	<0.003	<0.0007	0.014	0.003	<0.002	<0.003	<0.001	0.014	0.01	0.005	0.001
Nd	0.003	0.011	0.006	0.137	<0.017	<0.008	<0.013	<0.013	0.074	0.111	0.035	<0.007
Sm	<0.012	<0.147	<0.014	0.126	<0.008	<0.037	0.015	<0.015	0.152	0.03	<0.017	<0.032
Eu	<0.001	0.040	0.007	0.022	<0.003	<0.003	0.009	0.003	0.105	0.011	0.004	<0.005
Gd	0.005	0.005	0.015	0.124	<0.013	<0.008	0.05	<0.008	0.684	0.116	0.001	<0.005
Tb	0.020	<0.022	0.062	0.488	<0.001	<0.001	0.018	<0.002	0.186	0.026	0.014	<0.012
Dy	0.035	<0.013	0.122	1.028	0.007	<0.005	0.2	0.023	1.307	0.282	0.007	<0.011
Ho	0.010	<0.003	0.037	0.275	<0.003	<0.002	0.053	0.006	0.355	0.075	0.002	0.002
Er	0.032	<0.014	0.118	0.951	<0.008	0.005	0.263	0.039	1.05	0.275	0.007	<0.011
Yb	0.045	0.069	0.162	0.932	<0.027	<0.013	0.453	0.099	1.059	0.388	0.006	<0.015
Lu	0.007	0.006	0.027	0.155	0.002	0.003	0.072	0.017	0.144	0.056	0.001	<0.003
Hf	0.005	0.019	0.005	0.062	<0.006	<0.003	<0.007	<0.003	0.052	0.008	0.003	0.006
Ta	0.001	<0.013	<0.005	<0.019	<0.003	<0.001	<0.001	<0.003	0.003	0.006	<0.003	<0.005
Pb	0.007	0.063	0.003	0.045	0.055	0.028	<0.026	0.039	0.732	0.158	0.019	0.071
Th	0.002	<0.007	<0.001	<0.005	0.006	<0.001	<0.002	<0.001	0.004	0.005	0.001	<0.002
U	0.002	0.002	<0.0004	<0.004	<0.003	0.002	<0.004	<0.001	0.003	0.002	0.001	0.003

**Serpentinite sole**

matrix	Antigorite Vein			Chrysotile Vein		Polygonal Vein and breccia matrix	
	KOP-3	Ti-47	xx-3758	xx-3786a	xx-3758	KOP-3	xx3786a
0.170749	<0.069	<0.209	0.352	<0.048	0.165	<0.173	<0.072
5.12	7.00	8.07	4.85	3.01	4.65	7.20	6.28
2.71	<1.81	12.7	1.95	<1.64	<1.60	<4.56	7.36
84.5	206	289	119	168	158	139	267
7.62289	22.8	85.2	19.9	9.59	14.3	48.1	33.2
905	908	2146	938	471	526	2756	904
<0.259	<0.366	<1.05	<0.209	<0.326	<0.180	<1.20	<0.316
0.051	0.029	0.164	0.053	0.044	0.125	0.057	0.025
1.454	0.416	2.245	2.847	0.384	2.306	0.556	0.308
0.147	0.090	0.028	0.047	0.016	0.044	0.365	0.070
0.025	0.077	0.076	0.045	0.054	0.017	0.205	0.120
<0.002	<0.002	<0.015	<0.001	<0.001	<0.001	<0.009	<0.003
<0.043	<0.070	<0.341	<0.047	<0.051	<0.034	<0.115	<0.037
<0.005	0.048	<0.028	0.008	0.008	<0.005	0.021	0.010
<0.005	<0.005	<0.019	0.012	0.007	0.018	<0.008	<0.007
0.211	0.151	0.405	0.339	0.163	0.370	0.098	0.066
0.058	0.043	<0.008	0.020	0.005	0.014	0.110	0.017
0.001	0.017	<0.010	0.003	0.007	0.008	<0.007	0.017
0.014	0.014	<0.003	0.004	<0.001	0.004	0.049	0.008
0.057	0.082	<0.018	0.021	0.009	0.013	0.262	0.031
<0.008	<0.026	<0.038	<0.012	<0.007	<0.011	0.058	<0.009
0.002	0.007	<0.011	<0.002	<0.002	<0.001	0.021	<0.003
<0.0007	0.002	<0.002	0.001	<0.0008	0.001	0.008	0.001
0.010	0.014	<0.025	<0.005	<0.005	0.007	0.065	0.013
0.010	0.011	0.012	0.005	<0.004	0.006	0.024	0.007
0.004	0.002	<0.002	0.001	<0.0007	0.001	0.009	0.002
0.012	0.006	<0.007	0.004	0.001	0.002	0.026	0.004
0.011	0.006	<0.019	0.004	0.004	<0.008	<0.018	<0.008
<0.001	<0.001	<0.003	0.001	<0.0003	<0.001	<0.005	0.002
<0.004	<0.005	0.007	0.003	0.002	0.002	<0.010	<0.003
0.004	<0.005	<0.010	<0.003	<0.002	<0.003	<0.015	<0.002
0.014	0.025	0.027	0.025	0.027	0.024	0.069	0.003
<0.0003	<0.0008	<0.002	<0.002	0.001	<0.0008	<0.002	<0.0005
0.024	0.010	<0.003	0.016	0.008	0.043	0.014	0.003

Sample	Location	Protolith	Position	Type	$\delta^{18}\text{O}_{\text{SMOW}}$	$\delta\text{D}_{\text{SMOW}}$ (‰)
Por12-1	Massif du sud	Du	US	liz	2.2	-106
Por12-2	Massif du sud	Du	US	liz	4.2	-106
Por12-3	Massif du sud	Du	US	liz	2.9	-106
Por6	Massif du sud	HZ	US	WR	5.3	-66
Por11	Massif du sud	HZ	US	WR	5.5	-75
Por12	Massif du sud	Du	US	WR	2.2	-95
Kop6-1	Kopéto	HZ	Sole	liz	4.1	-107
Kop6-2	Kopéto	HZ	Sole	ant	6.3	-98
Kop6-3	Kopéto	HZ	Sole	ant	3.8	-98
Kop6-4	Kopéto	HZ	Sole	ant	5.3	-98
xx3758	Koniambo	HZ	Sole	ant	4.0	-104
xx3773	Koniambo	HZ	Sole	ant	1.7	-91
xx3778	Koniambo	HZ	Sole	ant	5.1	-
Ko-05-1	Koniambo	HZ	Sole	chrys	4.4	-100
Ko-05-2	Koniambo	HZ	Sole	chrys	4.3	-102
Ti 24-1	Tiébaghi	Lhz	Sole	liz	2.9	-103
Ti 47-2	Tiébaghi	Lhz	Sole	liz	5.7	-97
Ti 48.06-1	Tiébaghi	Lhz	US	liz	5.4	-97
Ti 48.06-2	Tiébaghi	Lhz	US	liz	5.6	-103
Ti 5-1	Tiébaghi	HZ	Sole	liz	2.4	-95
Ti 51c-1	Tiébaghi	Lhz	Sole	liz	3.0	-104
Ti 47-3	Tiébaghi	Lhz	Sole	ant	1.9	-88
Ti 47-3 dup	Tiébaghi	Lhz	Sole	ant	2.1	-88
Ti 52E	Tiébaghi	Lhz	Sole	ant	4.9	-95
Ti 52E dup	Tiébaghi	Lhz	Sole	ant	5.3	-95
Ti 5-3	Tiébaghi	HZ	Sole	chrys	1.7	-
Ti 51a-1	Tiébaghi	Lhz	Sole	chrys	9.5	-91
Ti 51a-2	Tiébaghi	Lhz	Sole	chrys	10.8	-91
Ti 54b	Tiébaghi	Lhz	Sole	chrys	4.9	-94
Ti 51c	Tiébaghi	Lhz	Sole	WR	2.6	-88
Ti 24	Tiébaghi	Lhz	Sole	WR	1.9	-90
Ti 47	Tiébaghi	Lhz	Sole	WR	5.8	-87
Ti 48.06	Tiébaghi	Lhz	US	WR	6.4	-97
Poum 17-1	Poum	Lhz	US	liz	6.8	-103
Poum 17-1 dup	Poum	Lhz	US	liz	6.9	-103
Poum 18-1	Poum	Lhz	US	liz	6.5	-101
Poum 4-5	Poum	HZ	Sole	liz	7.6	-100
Poum 4-6	Poum	HZ	Sole	liz	13.9	-94
Poum 4-1	Poum	HZ	Sole	ant	7.9	-101
Poum 4-2	Poum	HZ	Sole	ant	12.2	-104

Poum 4-3	Poum	Hz	Sole	ant	12.1	-104
UwG-2 gnt (n= 16; valeur theorique: 5.8 ‰)					5.78 ± 0.25	-
G1 Biotite (n=16; valeur théorique: -66 ‰)					-	-67 ± 2

Element	B	Th	U	Zr	U/Th	B/Zr	References
<b>NC mantle wedge</b>	0.06	0.001	0.0005	0.053	0.5	1.13	U, Th, Zr: Secchiari et al. (2016; 2019); B: Salters and Stracke (2004)
<b>AOC</b>	5.2	0.070	0.300	66.5	4.29	0.078	U, Th, Zr: Staudigel et al; (1996); B: Smith et al. (1995)
<b>Mobility (%)</b>	60	37.7	29.1	0.1			Kogiso (1998); Sano et al. (2001)
<b>AOC-derived fluid (F = 1.5%)</b>	208	1.76	5.82	4.43	3.31	46.9	Weight fraction of fluid F: Peacock (1990); Rüpke et al. (2004)
<b>GLOSS II</b>	67.9	8.10	1.73	129	0.214	0.526	Plank (2014)
<b>Mobility (%)</b>	70	2.5	3.0	0.1			Aizawa et al. (1999)
<b>Sed-derived fluid (F = 3%)</b>	1584	6.75	1.73	4.3	0.256	368	Weight fraction of fluid F: Peacock (1990); Rüpke et al. (2004)
<b>Abyssal serpentines</b>	50	0.073	0.569	2.4	7.79	20.8	Peters et al. (2017)
<b>Mobility (%)</b>	39.2	2	10	0.1			Tenthorey and Hermann (2004)
<b>Serp-derived fluid (F = 0.69%)</b>	2841	0.212	8.25	0.348	39.0	8167	Weight fraction of fluid F: Water loss during Lz/Ctl to Atg (2004)



[Click here to view linked References](#)

Marc ULRICH

June, 25 2020

Dear Pr Othmar Müntener,

Please find attached the corrected version of the manuscript written by by myself, Manuel Muñoz, Philippe Boulvais, Michel Cathelineau, Stéphane Guillot and Christian Picard entitled "Serpentinization of New Caledonia peridotites: from depth to (sub-)surface" that we submitted for publication to Contributions to Mineralogy and Petrology.

Following the very helpful comments made by yourself and the two reviewers, we made some substantial changes in the manuscript. They are listed below:

*Dear Marc,*

*I have now received two reviews of your paper. Both reviewers are generally supportive of publication of your paper, but there are numerous issues to be resolved. The recommendation is between moderate to major revisions. I have also read your paper and agree mostly with their evaluations. Both reviewers provided many detailed comments for improving the overall presentation. Please follow their advice. There are, however, several major points that need careful attention. In brief you present a nice dataset, but you have not fully exploited its potential, which is reflected in a relatively general narrative, which lacks rigor of process discussion. This needs improvement along the following lines*

- (i) The paper needs generally a better organisation, more clearly defined research questions, a thorough discussion and then conclusions that take into account this discussion. Looking at the introduction, you invoke large scale processes (non-specific, see problems how you cite below), but in the discussion and conclusions these aspects have not been re-visited. This is too bad, because a reader will not get what are the novel things that one can learn from your study. You need to exploit the data in a more thorough way in order to make your study interesting for the reader.*
- (ii) The introduction on line 78 is poorly formulated, questions about the origin and nature of serpentinizing fluids can mean virtually everything. Please rewrite and be more specific what kind of research question do you want to address with your contribution and then discuss these in terms of the relevant processes. Otherwise a reader will get the impression of a local study. The general relevance of your findings should then be thoroughly discussed.*

[Answer to comments \(i\) and \(ii\): We agree with these comments. The introduction has been rewritten accordingly, and we tried to be more specific on the questions we addressed in this study. The large scale processes we invoked in the introduction are now re-visited in the discussion and the conclusions \(see also our \[detailed answers to reviewers comments below\]\(#\)\).](#)

*(iii) Problems of correctly citing papers, somehow related to point (ii) above. I do not think that listing many many references is necessary. A few key references in the right place are in order. In particular you should cite the original and most important work of Ulmer and Trommsdorff (Science 1995, and Geochemical Society 1999) The works cited on line 70 and 71 refer all to these experimental studies but have not added new insights to this. When you talk about the importance of serpentine then a few papers that address the rheology of serpentine should be incorporated, not only geochemical literature. So focus on a few key references in the right place and do not provide long lists. Be specific when you add citations.*

An effort has been done in correctly citing papers. Original and most important works have been cited (e.g., Ulmer and Trommsdorff papers). A paragraph dealing specifically with the serpentine rheology and its role on rock exhumation has been added to the introduction (lines 79-84).

*(iv) Some of the modelling needs serious rethinking and rewriting as outlined by reviewer #1, and the methods how you have done the calculations needs to be better described and thoroughly discussed*

The modeling has been rewritten and is now described in details (see answer to reviewer #1).

*(v) The discussion of the trace elements and its relationship with the stable isotopes needs to be expanded. As is, this is insufficient. On the one hand you use As, Sb and call these sedimentary traces that are low, but Sr and Sr isotopes are high, derived from sediments. What is the importance of U spikes in panel b,c,d and the Th/U ratio? How important is the high Fe<sup>3+</sup> in sole serpentinites? What is the Ce anomaly telling you? You need to milk these data more thoroughly, and then decide what you can say and what you cannot say. Mobility of incompatible elements depends on many parameters (Eh, pH of fluids) but you associate some anomalies to laterite formation, fair enough. But forming the sole in response to meteoric fluid circulation is not evident and the role of deformation on the trace element composition might be important. Retrogression of antigorite to chrysotile and polygonal serpentine is not isochemical, so what are the changes that you observe?*

A new paragraph dealing with the behavior of trace elements has been added to the discussion, with 2 additional figures (lines 375-392). In addition, we have developed a new modeling that predict the evolution of the mantle wedge budget in trace element during slab dehydration. The results are compared with those of Monte Carlo simulations made on stable isotopes. The origin of U spikes (high U/Th ratios), low Ce/Ce\* (i.e., Ce negative anomaly) and high Fe<sup>3+</sup> in serpentine from the serpentinite sole have been extensively discussed (lines 612-622).

*(vi) The final version needs to be read very carefully by a native English speaker. There are numerous franglisms in the paper, which need to be eliminated.*

Done

*From an editorial point of view, you need to complete the Table in the Electronic Appendix by providing GPS coordinates of all samples. So far I have not found any information where exactly the samples are collected.*

*Tables: It is not appropriate to report values in Tables that are 0.00 or 0.01 with std dev of 0.02. Please replace these by the detection limit of your analysis. (e.g. TiO<sub>2</sub> < 0.01). Relevant digits should be given only, e.g. SiO<sub>2</sub> 41.0 and not 41.04. Bdl in Table 2 should be replaced by the calculated limit of detection (e.g. Li < 0.3 ppm).*

*Figures: please add relevant error bars in the figures. Not on all samples, but representative ones. Figure 5: I do not understand why you plot Fe<sup>3+</sup>/Fetot up to values of 1.1. The range is limited between 0 and 1, the same is true for Mg#, the grey field cannot exceed 1. So the axis should be limited to 1.*

*Figures: In general needs labels for individual panels and these need proper description in the figure caption (see reviewer #2 for improvement). Fig. 8 needs improvement (see reviewer#1)*

All your editorial suggestions have been taken into account and corrected accordingly. In most diagrams, the error bars are not reported because they are smaller than the size of the points.

Note that Contributions to Mineralogy and Petrology has no title numbering and you should consult the webpage for correct formatting of the manuscript, figures, figure captions and tables.

Done

## **Reviewer 1**

*Overall the paper presents interesting work that provides insights into the serpentinization process of the Peridotite Nappe of New Caledonia. The integration of mineralogical, major and trace element geochemistry, and particularly the isotope geochemistry and Monte Carlo and AOC fluid composition modeling is a creative way to develop an interpretation of the serpentinization process. However, there is a general lack of detailed description of the methods and some of the figures need substantial modification to be most effective.*

*Considering these limitations, I cannot recommend publication until after substantial revision and potential re-review.*

### **Major comments:**

*In the introduction, as justification for the work, the significance of the work in general, in regard to understanding plate tectonics and global geochemical cycles is stated. However, these ideas are not revisited in the discussion or conclusions of the manuscript. Thus, the broader significance of what has been learned from this work needs to be developed in more detail.*

We agree with this comment, and the discussion has been revisited accordingly. In particular, we have added a paragraph dealing with and modelling the behavior of some trace elements during the dehydration of subducted slab components and subsequent hydration of the overlying mantle wedge. The behavior of trace elements during late serpentinization events has been discussed more thoroughly, and how serpentines participate to the global geochemical cycles is now better described (e.g., lines 520-574)

*The methods section does not contain enough detailed information. Particularly the methods for the modeling of the  $\delta^{18}O/\delta^D$  are not addressed in the methods section of the paper and are mostly constrained to the caption of Figure 7. This is not adequate and the methods must be much more fully described within the main body text. Similarly, the method for determining  $Fe^{3+}/Fe^T$  is not stated in the method section and needs to be described and/or referenced.*

We do not find appropriate to develop our modeling approach in the Materials and Methods section, particularly because the first paragraph of the Discussion deals with the main limitations of modeling approaches that were previously published in the literature and highlights the benefits of our original approach. However, we agree that the modeling methods have to be better and fully developed, which is now the case in the present version: a new paragraph has been added at the beginning of the Discussion where the modeling approach is fully developed, including the equations used to calculate fractionation factors, the main equation used to calculate the isotopic compositions of serpentine as a function of mantle and fluids compositions, fractionation factors and fluid-rock ratio, and the proper references (lines 424-478).

The method for determining  $Fe^{3+}/Fe^T$  (Beard and Frost, International Geology Reviews, 2016) have been described in details in the Materials and Methods section (lines 174-190).

*Figure 7. Modeling methods should be removed from caption/figure and stated more completely in a dedicated section in the manuscript text. It is not clear enough that there are a couple of different models, that to some degree iterate on one another, involved in determining the temperature of the serpentinizing fluids. There is no justification of using Alt and Shanks 2006 to model the AOC isotopic composition which was then used to narrow the results from the Monte Carlo simulations.*

We agree with this comment and the figure caption has been modified accordingly. In addition, as stated above, the manuscript now includes a section developing the modeling approach. The use of Alt and Shanks III study

(2006) is argued on the basis of the regional geodynamics in the Marianna, which is assumed to be relatively similar to that expected for the South Loyalty Basin at the subduction time. In addition, the Marianna region is the only one so far providing an "access" to fluid circulations in the forearc mantle via the occurrence of serpentinite seamounts. This is now clearly stated in the text (lines 494-519).

*7b – It's not clear if the boundaries of the black box are significant. Please clarify. If they are, please somehow make it easier to interpret the values from the outline of the box.*

*Please list the isotopic values of fluid you are inferring on the plot, as these are the actual results and are difficult to read off of the plot as presented. Remove the AOC crustal mineralogy/composition info from Alt and Shanks, 2006, as this belongs in a better developed methods section in the text vs. only shown on the plot itself.*

The AOC composition and mineralogy has been removed from the figure 7b, and details about the AOC modeling is now given in the text (lines 494-519). Basically, the black box symbolizes the range of O and H isotope compositions of fluids in equilibrium with metabasalts, assuming that the metasomatised basaltic basement has  $\delta^{18}\text{O} = 8\text{-}11\text{‰}$  and  $\delta\text{D} = -90$  to  $-120\text{‰}$  (Alt, Gcubed, 2003), and a simple mineralogy of 48% albite, 48% chlorite and 2% calcite. The dehydration of metabasalts having these isotopic compositions and mineralogy would produce fluids with  $\delta^{18}\text{O}$  values of 2-8‰  $\delta\text{D}$  values of -50‰ to -90‰. Clearly, the boundaries of the black box are dependent of the chosen parameters. However, by keeping the AOC stable isotope composition as defined by Alt (2003), the variation of other parameters (i.e., the mineralogy and the temperature) would lead to increase or reduce the size of the box without significantly moving it. In the modified version of Figure 7, the black box is now in dashed blue lines, and we add a supplementary purple box showing the fluids in equilibrium with the AOC at 200-400°C, which illustrates that increasing the temperature leads to increase the  $\delta^{18}\text{O}$  range up to -10‰ without changing the range of  $\delta\text{D}$ . O and H isotopic compositions of subducted serpentine and sediment-derived fluids as calculated by Alt and Shanks have been also added to the Figure.

The list of isotopic values of fluids inferred on the plot is now provided in a supplementary table. This table also includes T, fluid-rock ratios and isotopic compositions of serpentine for each simulation.

*7c/7d – Please define directly what the cross-hatch pattern indicates. Please directly state why the cross-hatch pattern is constrained to the red area of the density plot of the Monte Carlo simulation results. Please indicate what proportion of total number of simulations is included in that hatched area vs. in the red AOC fluid window.*

The white cross-hatched pattern in Figure 7c/7d corresponds to simulations that plot in the red area in 7b. It represents about 40% of ~6500 random simulations. This is now indicated in the main text and in the figure caption.

*Figure 8 – Either more detailed labelling or indications of process (e.g. labeled arrows) need to be included on the figure itself and/or a more detailed description of the take home message of the figure needs to be included in the caption to make this figure useful. A description of how the rocks and processes from (A) are related to the rocks and processes in (B) would also make this figure more useful.*

The Figure caption has been modified accordingly: It now includes a more detailed description of the take home message.

*The paper needs to be thoroughly reviewed and corrected specifically for English grammar.*

Done

### **Line-by-line comments:**

*Line 32 – 'admitted' is a strange word choice here*

Deleted

*Line 34-35 – ‘their possible association’ what is this referring to? Please state directly.*

Done

*Line 59 – Is ‘mantellic’ actually a word?*

Corrected

*Line 67 – What is ‘huge’ and what are the implications on the geologic system of this water getting into the mantle? It is this that will make the process important.*

The sentence has been modified as follow: "Thus, the uppermost part of the oceanic lithosphere is hydrothermally altered before entering subduction zones. Then, the dehydration of the subducting slab favors the formation of forearc serpentine, which hosts a large amount of water (up to ~13 wt.%). The circulation of such an amount of aqueous fluids may, in turn, transport fluid-mobile elements (FME) deep into the mantle down to ~150 km (Ulmer and Trommsdorff 1995; Wunder et al. 2001). At temperature above ~650°C, serpentine is no longer stable and aqueous fluids are liberated by serpentine breakdown triggered mantle wedge melting that gives rise to arc volcanism (Hattori and Guillot 2003; Iwamori 1998; Reynard 2013; Schmidt and Poli 1998; Ulmer and Trommsdorff 1995; 1999)."

*Line 113-114 – awkwardly worded in English.*

The sentence has been rewritten.

*Line 133 – what exactly does the term “upper serpentine” refer to? The whole package of serpentinitized harz/lherz/dun? Please state this clearly.*

Indeed the term “upper serpentine” refers to the whole package, this is now specified.

Section 3.1

No mention of a method for  $Fe^{3+}/Fe_T$

No mention of the isotope model parameters, etc. in the methods section – they are only briefly touched on in the Discussion section and caption of Figure 7. More development of this is necessary.

The  $Fe^{3+}/Fe_T$  method is now fully developed (lines 174-190)

*Line 232 – Clearly some Fe but how much compared to the Fe content of the primary olivine? E.g. how much Fe is in the serpentine?*

Considering atom per formula unit calculations on the basis of 7 oxygens for both serpentine and olivine in order to compare,  $Fe=0.2$  in average in lizardite vs.  $Fe=0.32$  in average in olivine, which confirms the loss of Fe during serpentinization. This information is available in the supplementary table S1.

*Line 253-255 – awkwardly worded.*

Rephrased

*Line 301-303 –  $Fe_2/Fe_3$  estimated by eprobe analyses. A statement describing this method in more detail and its limitations should be included here or in the methods section. However, it does seem reasonable to use this method if the interpretations are limited and broad as they are in this work.*

Done (see the answer on Major comments above)

*Line 332-334 – serpentines have a wide range of  $\delta^{18}\text{O}$  while  $\delta^{16}\text{O}$  are homogeneous. Why? No systematic difference between serpentine varieties. Why? Upper serpentines (i.e. liz) have a narrow isotope composition while Lizardite in the serpentinite sole have a wider range of isotopic compositions. Why the difference between the two?*

We do not find it appropriate to discuss the reasons why serpentines exhibit chemical heterogeneities in the Results section. The origin of these heterogeneities is widely discussed and addressed in the Discussion section of the manuscript.

*Line 390-392 – The authors state that they do not use the fractionation factors of Saccocia because they are limited to  $T > 250^\circ\text{C}$ . Yet, as stated on lines 403-405, the fluids have been interpreted to have mainly been at 250-430C (which is  $> 250^\circ\text{C}$ )? Additionally, the fractionation factors from all the mentioned sources do converge at  $T$  of  $x$ - $x$ . ask Eric for plot.*

As it is now specified in the manuscript, the use of oxygen isotope fractionation factors from Saccocia et al. (2009) provides quite similar results to that of Wenner and Taylor (1971) in the temperature range of 250-450°C. However the serpentine–water  $^{18}\text{O}$ – $^{16}\text{O}$  fractionation factor of Wenner and Taylor (1971) is applicable at a wide range of temperature, contrarily to the experimental approach of Saccocia et al. (2009) of which fractionation factor was calibrated only for temperatures  $> 250^\circ\text{C}$ . As a consequence, the use of Wenner and Taylor fractionation factor was found more consistent in the aim of calculating the  $\delta^{18}\text{O}$  composition of serpentinizing fluids without any other constraints on serpentinization temperature. Who is Erik?

*Line 404-406 – It isn't at all clear how the Monte Carlo simulations are used to get from the isotope space the values fall into (stated on line 403) to interpreting/knowing that the fluids interacted with the mantle at  $T$  of 250-430C? This isn't clearly described anywhere in the manuscript and must be developed.*

Following the reviewer's recommendations, how the Monte-Carlo simulations have been calculated is now fully developed (see the detailed answer in Major comments and the new section in the manuscript, lines 424-478)

*Line 414-416 – The base is more serpentinized, correct? (At least, it is stated to be such on lines 108-109.) So, this isn't worded correctly because it's saying the serpentinization degree increases from bottom to top thus the bottom is less serpentinized and the top is more serpentinized. If this is not actually the case, there may be some confusion in terminology between the bottom/top of the ophiolite and the sole serpentinites.*

Corrected. Indeed, the serpentinization degree decreases from bottom to top...

*Line 449-452 – If serpentinization of NC occurred prior to entering the subduction zone, is there a signature of this in the isotopes? It was stated earlier that the isotopes fall in the 'ophiolite serpentines' field vs. the oceanic serpentines field which seems to suggest that the processes that occurred in the subduction zone are not represented in the isotopic signature. Please clarify.*

This paragraph has been clarified particularly due to the addition of a new model based on trace elements which confirms the results of the Monte-Carlo simulations, i.e., AOC-derived fluids are mainly responsible to the serpentinization of NC peridotites (see lines 520-574).

*Figure 3. Why mention pyroxene in the caption if not shown in the figure?*

Deleted

3B. Is S1 cut by 3 successive generations of serp veins as stated or by 4 as indicated by the range that is stated (S2 to S5 which would be S2, S3, S4, S5).

S1 is crosscut by 4 serpentine veins, thanks. This is now corrected.

3d. It's not apparent that (d) clarifies anything, the labels on d should be put on b and still be understood.

We do not agree with this comment. We would prefer to leave this figure without any annotations for a better appreciation of the readers.

Figure 5. This caption seems to include less observation/interpretation than captions for other figures and the reader would benefit if it included more observation/interpretation.

Figure 5 caption now includes more details.

Pg. 46 of the compiled pdf doesn't seem to belong in the manuscript.

It belongs to the Table 3 and the trouble is related to the automatic pdf conversion of the manuscript from the journal website.

## **Reviewer 2**

### *General comments*

*This manuscript present details of serpentinization history of the New Caledonia ophiolite using petrological observations and a large geochemical dataset. The manuscript provides details on the formation of serpentinites in the ophiolite identifying multiple generation of serpentinization events based in petrography, geochemistry, stable isotopes and Monte Carlo simulations. They identify an early serpentinization event at high temperatures from AOC fluids during emplacement that is more developed towards the base of the ophiolite with 100% serpentinization and tapers upsection with lower degrees of serpentinization. Further serpentinization involved meteoric fluids result in the formation of chrysotile and polygonal serpentine with geochemical signatures similar to their precursors.*

*The manuscript would be suitable for publication in Contributions of Mineralogy and Petrology after moderate revisions.*

### *Specific comments*

*Comments are arranged by section of the manuscript.*

#### *Geological settings*

*More details on the specific units described in the paper need a little description on this section. Describe the existence of the basal nappe and the upper serpentines. There is no clarity here on the existence of the serpentinite sole and the base of the peridotite nappe and its difference. This applies to Figure 1. If this is classification from the paper it should be more clearly stated in the results or in the discussion.*

Following this comment, the existence of the basal serpentinite sole is clearly indicated in last paragraph of the introduction and the differences between the serpentinite sole and upper serpentines are now widely addressed in the different sections of the manuscript. Unfortunately, at Figure 1 scale, it is not possible to differentiate the serpentinite sole from the serpentinized peridotites in the ophiolitic massifs.

*Line 91 add reference for age of ophiolite. Line 102 Space missing after references*

Done

*Line 106-107 I suggest authors remove asbestos connection. Stating that the serpentinites have not been extensively studied is enough.*

Done

*Lines 106-124 I recommend that this paragraph is reorganized and rewritten to clarify. For readers not familiar with the New Caledonia ophiolite is really difficult to follow. For example in line 114 it is no clear to which group of co-workers is referring and how MAR samples are related to the New Caledonia serpentinites or the important of this combined dataset.*

[This paragraph has been reorganized and rewritten as suggested \(lines 120-127\)](#)

*Materials and methods*

*Line 131 If available it will be good to add sample coordinates either in Table 3 or in a supplementary table. Currently table 3 only list the massif for each sample. Considering that Massif du Sud extends for tens of kilometers having precise locations would be useful.*

[Sample coordinates are now available in supplementary table 1.](#)

*Line 148 Minor suggestion remove thick.*

Done

*Line 148 It is not clear how they make take the average and how it relates to figure 4. Is the average for each point measured, for points in the same vein or each serpentine type?*

[It is for each point measured. This is now specified.](#)

*Line 160 Change french orthose to English orthoclase.*

Done

*Results*

*Line 206-209 This needs some reorganizing. It is confusing as written. If 10% is rare it should be treated as such and state first that moving up section from the base peridotites have moderate to high degrees of serpentinization with some occurrences in the top massifs where it is limited ~10%.*

[The paragraph has been rephrased as suggested \(lines 227-232\).](#)

*Line 210-213 Again this needs some reorganization the paragraph jumps back and forward from the base of the ophiolite and the upper sections making hard to follow. I suggest each unit is described consecutively instead of jumping between them.*

Done



*Line 214-216 This appears out of place. In the previous paragraph you mention the base and then come back to describe it here. Is this a new observation or was it previously describe by others? If the latter is true the difference between the base and the upper sections needs to be incorporated to the Geologic setting.*

We do not fully agree with this comment. The serpentinite sole has never been extensively studied until recently by our group. In addition, this work is the first one identifying several serpentine generations in the serpentinite sole and providing a comprehensive dataset for each generation. Therefore, we would prefer to keep this paragraph at this place.

*Lines 271 Try to be consistent on how numbers in this section are reported. For example, for NiO they report a range and for MnO they report average and confidence interval. This should be consistent across the manuscript. If reporting confidence interval include if it is one or two sigma. This should be done for all sections in the results.*

We agree with this comment. Numbers are now given with a better consistency in all sections in the results.

*Line 275 is there any variation in opx and olivine Mg#? If so add variability. Line 276 Remove ) towards the end of the line.*

There is no variation in opx and olivine Mg# (now specified in the text)

*Line 331 Correct typo on displays*

*Line 332 remove display or show.*

Done

*Line 334 It is not clear when they refer to varieties if it is the same as the generations. If they are the six generations described in the petrography section this needs to be more clearly stated.*

The term varieties has been replaced by species in the manuscript. Species is used to distinguish e.g., lizardite from chrysotile, while generations is used to characterize the chronology of each serpentinization event.

*Line 338 This sentence just repeat what was said in line 333 to 334 and can be removed. Please just confirm which is the correct range for d180 as it differs between the two sentences.*

Not really the same but we agree that it was a bit confusing as it was written. The sentence has been rephrased to be clearer.

*Lines 341-344 How much silica is present in the samples? Is it enough to truly shift the d180 and discard the heavy d180 samples? If silica had d180=30‰ to get to d180=13‰ in the mixture it will require ~30% silica which should be identifiable prior to analysis. In figure 7a they show that all discarded samples except one plot in the ophiolite serpentinite field. This might not affect the results as their Montecarlo simulations have values up to d180=12‰.*

The presence of silica was identified by XRD (not shown in the manuscript) but was not quantified. However, the predicted amount of ~30% you made is consistent with our previous study on the carbonation and silicification processes of the serpentinite sole (Ulrich et al., CTMP, 2014), where we show on the basis of chemical mapping that discrete silicification may easily represent 30% of the rock without significantly modifying its texture. Although it is true that only one of our samples plot off of the ophiolite serpentinite field, these 4 samples are really different from the others in terms of oxygen isotope composition. Thus we find more consistent to discard these samples which likely reflect a later, shallower process than serpentinization.

*Line 343 Global makes this sentence confusing. I recommend it to be removed.*

Done

*Discussion*

*Lines 374-377 talk about of the serpentine-magnetite geothermometer. The next sentence implies multiple approaches for estimating temperature however in this paragraph it only has one (serpentine-magnetite).*

This paragraph has been coupled to the previous one in order to be more clear.

*Line 381 add "fluids derived from....."*

Done

*Line 385-392 This section needs to be rewritten. It is confusing what fractionation factors were used for  $d_{18O}$  and  $dD$ . In line 389 remove "quite". Line 391 it is not clear what authors mean with "is more consistent". If it is a preference based on experimental temperatures it should be said that.*

This section has been deeply rewritten, and we now provide new details on how the Monte-Carlo simulations were calculated.

*Line 392-393 I would add at the beginning of the sentence something like: Neither of this previous work describe.....*

This sentence has been deleted from the manuscript.

*Line 419 Change "et" for "and"*

Done

*Line 438 Change "such materials" for sediments.*

Done

*Line 439 Change "with regards" for "compared"*

Done

*Line 439 Unreadable should be changed to unresolvable*

Done

*Line 473 Missing reference to support idea that sole was formed under more oxidizing conditions. This ties up with the following sentence that attribute high  $Fe^{3+}$  in polygonal serpentine to meteoric fluids and incorporating more than the precursors. This creates a conundrum as in Figure 5 the highest  $Fe^{3+}$  is for antigorite and lizardite that seems to be from S2-S4. This suggest that the late polygonal serpentine has less  $Fe^{3+}$  than the precursor lizardite/antigorite and needs to be clarified.*

We agree with this comment. In the present version of the manuscript,  $Fe^{3+}$  is calculated using an alternative approach (Beard and Frost, 2017) which is clearly more consistent than the approach of Droop (1987) initially used. A direct consequence is that polygonal serpentine has now the highest  $Fe^{3+}$ . The more appropriate

reference that support the idea that sole was formed under oxidizing conditions is already cited (Muñoz et al., JGE, 2019).

*Figures*

*Figure 3 Add sample numbers to panels or caption. For panel C the caption is not clear. When you mean same as B is it the same thin section (insert) or same textures and serpentine generations in different sample?*

The sample numbers have been added to the caption, and the caption for C panel has been corrected.

*Figure 4 I suggest that in the top of the panel is S1 and goes down to S6 instead of the way is presented now.*

Done

*Figure 5 Add letters to panels. It would be good to add some transparency to the symbols. As presented is hard to match description in text with figure. For example line 299 Mg# in bastites range from 88 to 98 is impossible to see in figure.*

Done

*Figure 6 Add letters to panels or caption. Figure 7 Typo in AOC fluids in panels b,c,d*

Done

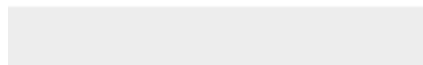
We hope that you will now find this revised manuscript suitable for publication in Contributions to Petrology and Mineralogy. If you have any question, please, let me know at your convenience.

Sincerely yours,

Marc ULRICH



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Supplementary tables.xlsx





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