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Redox heterogeneities in a subducting slab: example from the Monviso meta-ophiolite (Western Alps, Italy)

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Highlights

- Heterogeneous oxygen fugacity recorded in serpentinites of the Monviso meta-ophiolite
- Subducting slab redox gradient set up during serpentinite dehydration at eclogite facies P-T conditions
- Carbonaceous matter precipitation enhanced by carbonate reduction in the slab

Abstract

Variations of redox conditions (i.e., oxygen fugacity, fO_2) accompanying slab dehydration in subduction zones are subject to ongoing controversies, especially since the interplay between redox sensitive elements during prograde metamorphism remains complex and, likely, variable at the slab scale. Here we investigate fO_2 variations during serpentinite dehydration and their feedback on the stability of sulfur and carbon compounds by studying the eclogitic Monviso meta-ophiolite (Western Alps, Italy). Despite a complex metamorphic history, the Monviso massif has preserved a complete section of oceanic lithosphere, from seafloor metasediments, meta-ophicarbonates and metabasites to deep-seated metagabbros and metaserpentinites. By bringing new estimates in the northern massif, we show that these lithologies have recorded a homogeneous pressure and temperature (P-T) climax, at 520-570°C and 2.6-2.7 GPa, on the whole meta-ophiolite. Despite this homogeneous P-T record, serpentinite forming minerals imply strong variations in fO_2 according to their position in the slab, from high fO_2 conditions (\sim FMQ +2) in the deep-seated lithologies made of heazlewoodite-magnetite-olivine assemblages to low fO_2 (\sim FMQ -4) in the paleoseafloor lithologies made of pentlandite-awaruite-olivine. This redox gradient is opposed to what is expected at mid-ocean ridges and is

29 therefore likely set up during serpentinite dehydration. Such variations of fO_2 conditions also
30 influenced carbon distribution and redox state within the lithosphere. In particular, reducing
31 conditions associated with brucite breakdown in paleoseafloor serpentinites promote the formation
32 of disordered carbonaceous matter over inorganic carbonates. Newly-formed disordered
33 carbonaceous matter could subsequently be recycled in the deep mantle, with the potential to play a
34 major role on the deep carbon cycle.

35 1. Introduction

36 Fluid/rock interactions between the slab and the mantle wedge are central in understanding
37 geochemical cycles in subduction zones. These are particularly sensitive to redox processes and oxygen
38 fugacity (fO_2) that govern both element speciation in fluids and mineral equilibria at high pressure and
39 high temperature (HP-HT). Strong redox gradients are observed in HP-HT slab relicts in mountain
40 ranges (meta-ophiolites) and in active or orogenic mantle wedge areas (e.g., Tumiati & Malaspina,
41 2019). Although the latter were clearly shaped during subduction by slab-derived fluid percolation,
42 ongoing controversies concern the origin of redox variations in meta-ophiolites and whether or not
43 these are inherited from an abyssal stage (e.g., Bretscher et al., 2018; Vieira Duarte et al., 2021) or
44 settled during prograde metamorphism (Debret et al., 2015; Padrón-Navarta et al., 2021).

45 Serpentinites have the potential to record redox evolution within the subduction system. These rocks
46 are observed in both slab and mantle wedge relicts, and have preserved a high level of redox
47 heterogeneities (i.e., strong variations in fO_2), with samples equilibrated between -4 to +3 relative to
48 Fayalite-Magnetite-Quartz buffer (FMQ; Debret et al., 2015; Debret & Sverjensky, 2017; Evans et al.,
49 2017; Evans & Frost, 2021; Evans & Powell, 2015; Galvez et al., 2013; Piccoli et al., 2019; Vitale
50 Brovarone et al., 2017). For example, the observation of graphite-like horizons at the contact between
51 metaserpentinites and metasedimentary rocks in slab related Alpine meta-ophiolites (Galvez et al.,
52 2013; Vitale Brovarone et al., 2017) suggests that fluid/rock interactions can promote carbonate
53 reduction into methane and/or graphitic material constraining the assemblage observed in

54 metaserpentinites to FMQ -4. At the opposite, highly oxidizing conditions were recorded in chlorite-
55 harzburgites formed during antigorite breakdown in the Cerro del Almirez massif (Spain; Debret et al.,
56 2015). There, the formation of hemo-ilmenite, chlorite, olivine and orthopyroxene could have been
57 equilibrated up to FMQ +3. To complement these observations, thermodynamic and experimental
58 studies have recently investigated fO_2 variations during serpentinite dehydration and highlighted the
59 role of protolith (i.e., abyssal serpentinite) composition and mineralogy influencing metamorphic
60 reactional pathways during subduction (Debret & Sverjensky, 2017; Evans et al., 2017; Evans & Frost,
61 2021; Evans & Powell, 2015; Iacovino et al., 2020; Lazar, 2020; Maurice et al., 2020; Vieira Duarte et
62 al., 2021). However, when extrapolated to subduction systems, these models must be taken with
63 caution as they often compare fO_2 retrieved from bulk compositions and phase assemblages from
64 various geological settings, with sometimes large uncertainties regarding the geodynamical setting
65 (e.g., Cerro del Almirez, Spain).

66 The Western Alps are a relevant natural laboratory to study the oceanic lithosphere cycle in subduction
67 zones. They are among the best subduction archives in the world, with abundant eclogitic meta-
68 ophiolites (500-650°C, 2.0-2.5 GPa) preserving fragments of oceanic mantle peridotites, gabbros,
69 thinned continental margin and pelagic sediments partly within their pre-collisional architecture
70 (Agard, 2021; Bernouilli et al., 2003). Subducted fragments experienced conditions typical of mature
71 subduction worldwide before exhumation and juxtaposition during Alpine orogeny. Here we
72 investigate the redox variations recorded in ultramafic rocks (i.e., not only metaserpentinites but also
73 meta-ophicarbonates and chloriteschists) composing the Monviso meta-ophiolite (Italy). This meta-
74 ophiolite is a well-characterized section of oceanic lithosphere (Angiboust et al., 2012; Balestro et al.,
75 2011, 2013; Locatelli, Federico, et al., 2019; Lombardo et al., 1978) that was subducted to eclogite
76 facies P-T conditions before being exhumed during the Alpine orogeny. Based on thermodynamic
77 models and petrological observations, we show that the meta-ophiolite recorded strong redox
78 heterogeneities at eclogite facies conditions, from basal serpentinites equilibrated at about FMQ +2 as
79 opposed to paleoseafloor serpentinites equilibrated at about FMQ -4. This redox gradient is opposed

80 to what is expected at mid-ocean ridges in modern settings suggesting that it was settled during
81 subduction. Interestingly, reducing conditions associated with paleoseafloor lithologies are likely
82 promoted by carbonate reduction into disordered carbonaceous matter.

83 2. Geological setting

84 The Monviso meta-ophiolite is a mafic/ultramafic unit extending over 30 km along strike at the French–
85 Italian border (Figure 1). It belongs to the Ligure Piemontese domain of the Western Alps, which
86 regroups fragments of the Tethys oceanic lithosphere later subducted with the European continental
87 crust under the Apulian margin, and exhumed during the Alpine orogeny (see review by Agard, 2021).

88 The Monviso meta-ophiolite is separated from the blueschist-facies Queyras Schistes Lustrés Complex
89 to the West and from the eclogite-facies Dora Maira continental unit to the East by two ductile normal
90 faults (Ballèvre et al., 1990; Blake & Jayko, 1990). The first modern geological map of the southern part
91 of the Monviso massif was made by Lombardo et al. (1978) and was completed by Balestro et al. (2013)
92 and Locatelli, Federico, et al. (2019). The northern part of the massif was more recently mapped by
93 Balestro et al. (2011).

94 The Monviso massif is mainly made of calcschists, pillowlavas, metabasalts, metagabbros and
95 metaserpentinites. The original lithostratigraphical subdivision of the Monviso meta-ophiolite was
96 defined in the southern part of the massif by Lombardo et al. (1978). These authors distinguished six
97 N-S striking and W-dipping subunits disrupted by shear zones, namely, from East to West, the Basal
98 Serpentinite Unit, the Lago Superiore Unit, the Viso Mozzo Unit, the Passo Gallarino Unit, the Costa
99 Ticino Unit, and the Vallanta metabasite Unit. This division was supported by P-T estimates on
100 metagabbros, whereby ad hoc thermo-barometers (Ellis & Green, 1979; Pattison & Newton, 1989)
101 showed a heterogeneous metamorphic record along the massif, ranging from $450 \pm 40^\circ\text{C} - 1.2 \pm 0.3$
102 GPa in the Passo Gallarino Unit to $620 \pm 50^\circ\text{C} - > 2.4$ GPa in the Lago Superiore Unit (Blake et al., 1995;
103 Schwartz et al., 2001). However, this model was revised by Angiboust et al. (2012) who tested potential
104 heterogeneities within and between the various subunits using thermodynamic models applied to

105 metagabbros and Raman Spectroscopy of Carbonaceous Material (RSCM) thermometry in
106 metasedimentary rocks. These new P-T estimates rather suggest the existence of two main coherent
107 tectonometamorphic subunits extending over 20 km long, namely the Upper and Lower Tectonic Units
108 (also named Monviso and Lago superior Units in Angiboust et al., 2012; Figure 1). Each
109 tectonometamorphic subunits has recorded a difference in temperature of about 70°C, with the Upper
110 Tectonic Units being equilibrated at 480°C-2.2 GPa and the Lower Tectonic Units recording a
111 metamorphic climax at 550°C-2.6 GPa. They were then juxtaposed at epidote–blueschist facies during
112 Alpine orogeny and are now separated by an Alpine-related West-dipping shear zone, namely the
113 Upper Shear Zone (USZ) (Figure 1a; Angiboust et al., 2012). More recently, Balestro et al. (2018) and
114 Festa et al. (2015) proposed that the Lower Tectonic Unit could have been derived from an oceanic
115 core complex, with some major shear zones resulting from the reactivation of pre-Alpine structures
116 (e.g., oceanic detachment fault, ODF). These structures were evidenced in the northern part of the
117 massif where the contact between metasedimentary rocks and (ultra)mafic units has been interpreted
118 as a paleo-ODF (Figure 1a-c) separating seafloor (ophicarbonates, basalts and sedimentary rocks) and
119 deep-seated (serpentinites and gabbros) oceanic lithologies. In the southern part of the Lower Tectonic
120 Unit, metasedimentary units are quasi-absent and the continuation of these paleoseafloor structures
121 remains unclear (Figure 1a). Indeed, these were intensively reworked and overprinted by Alpine-
122 related shear zones, namely the Intermediate and Lower Shear Zones (ISZ and LSZ, respectively; Figure
123 1d-e; Angiboust et al., 2012, 2014). It is interesting to note that, despite numerous studies focusing on
124 the Monviso meta-ophiolite over the last 30 years, the lack of systematic P-T estimates on the northern
125 part of the massif does not allow a truthful comparison of the metamorphic record from North to
126 South in the massif.

127 3. Field occurrence of the studied samples

128 Our study aims at comparing the metamorphic and redox record of ultramafic rocks
129 (metaserpentinites, meta-ophicarbonates, chloriteschists) along the Monviso Lower Tectonic Unit. The

130 studied rocks were sampled along four cross sections (Figure 1b-e), namely from North to South, Colle
131 del Baracun, Colle Armoine, Lago Superiore/Lago Fiorenza and Rifugio Quintino Sella cross sections. In
132 addition, few metasedimentary rocks were sampled at the contact with ultramafic rocks for RSCM
133 thermometry purpose.

134 3.1 Northern massif sampling

135 Both Colle del Baracun and Colle Armoine cross sections are characterized by a high amount of
136 metasedimentary rocks stratigraphically sitting on metaserpentinites (thereafter referred to as
137 paleoseafloor serpentinites, Figure 1b-c). The Colle del Baracun cross section represents an overturned
138 fold, with the core of the fold consisting of paleoseafloor lithologies including metasedimentary rocks
139 and few metabasalts overlying metaserpentinites (Figure 1b). Toward to the East, the limbs of the fold
140 are composed of a ~ 300 m thick metaserpentinite layer made of foliated serpentinites embedding
141 metagabbroic pods of several metres in length. This deep-seated sequence is referred to as a basal
142 serpentinite layer, outcropping from North to South (Lombardo et al., 1978) and stratigraphically
143 sitting below the paleoseafloor lithologies. The Colle Armoine cross section is characterized by a
144 recumbent geometry with the core of the synformal anticlines consisting of metaserpentinites, and
145 the limbs of metasedimentary rocks (Figure 1c). To the East, these paleoseafloor lithologies are
146 separated from basal serpentinites by the LSZ.

147 Paleoseafloor lithologies were sampled at the Colle del Baracun and the Colle Armoine sensus stricto
148 (Figure 1a). In these areas, the contacts between metasedimentary rocks and metaserpentinites are
149 marked by intensively sheared metasomatic chloriteschist layers of several metres in length. The
150 chloriteschists are highly foliated and can display diopside and/or tremolite layers of several
151 centimetres thickness, associated with numerous magnetite crystals of millimetre size (Figure 2a).
152 Massive centimetric to metric blocks of lawsonite-rich eclogites and meta-ophimagnesites (Figure 2b)
153 are embedded within chloriteschist foliation in both localities. Below the metasomatic shear zone, the
154 paleoseafloor serpentinites can be associated with a pervasive network of brown veins mainly made
155 of olivine, sometimes associated with centimetric titanoclinohumite crystals (Figure 2c).

156 Basal serpentinites were collected nearby the Rifugio Barbara Lowrie and toward to the North nearby
157 Villanova village (Figure 1a-b). At Rifugio Barbara Lowrie, metaserpentinites were sampled along a cliff
158 made of an alternance of metric to centimetric brown olivine-rich and dark blue serpentine-rich layers
159 (Figure 2d). The brown layers form a dense anastomosed network of veins that cross-cut the dark-blue
160 host serpentinite. Meta-rodingite dykes are also observed along the cliff. They display a black chlorite
161 wall of about 10 cm in width, mainly made of chlorite, diopside, magnetite and andradite in contact
162 with the host serpentinites. The Villanova metaserpentinites are intensively sheared and finely
163 recrystallized. The rock foliation is materialised by small brown planes of several millimetre in width
164 with sigmoidal shapes mainly made of olivine. The rock foliation can embed decimetre to metre sized
165 boudins of massive serpentinite with a pale green colour.

166 3.2 Southern massif sampling

167 The Lago Superiore/Lago Fiorenza and Rifugio Quintino Sella cross sections display similar
168 lithostratigraphic structures. They consist, from West to East, of metabasalts structurally overlying a
169 thick sequence of metagabbros and metaserpentinites (Figure 1d-e). Relative to those of the northern
170 part of the massif, these cross sections are characterized by scarce metasedimentary rocks and a large
171 amount of metabasites. To the East, the cross sections are cut by the LSZ that separates metabasites
172 from basal serpentinites (Angiboust et al., 2012; Locatelli, Verlaquet, et al., 2019). The LSZ includes
173 highly deformed meta-ophidolomites within a serpentinite matrix (thereafter named LSZ-
174 serpentinites). The LSZ-serpentinites are highly foliated and can embed massive serpentinite blocks of
175 several metres in width. They are composed of an alternance of antigorite-rich and olivine-rich layers
176 with sigmoidal shapes that contribute to a S-C fabric (Figure 2e – see also Schwartz et al., 2013). To the
177 West, the USZ (Figure 1a) also includes large block of meta-ophidolomites of metric size.
178 Metasedimentary rocks, meta-ophidolomites and LSZ-serpentinites were sampled at the Lago
179 Superiore/Lago Fiorenza and nearby the Rifugio Quintino Sella. Beyond the LSZ to the East, the basal
180 serpentinites are variably foliated with a West-dipping foliation and includes metre sized eclogitic

181 lenses. This unit was not resampled as sufficient data are already provided in the literature for this
182 specific area (Gilio et al., 2020; Schwartz et al., 2013).

183 4. Methods

184 4.1 Bulk rock analyses

185 Bulk rock major and volatile (carbon and sulfur) elements were analysed at the SARM (Service
186 d'Analyses des Roches et des Minéraux, Nancy, France) by Inductively Coupled Plasma Optical Emission
187 Spectrometry (Thermo Scientific iCAP 6500) and HORIBA EMIA-320V2 Carbon/Sulfur Analyser,
188 respectively. Sample digestions for major elements (SiO_2 , Al_2O_3 , Fe_2O_3 , MnO, MgO, CaO, Na_2O , K_2O ,
189 TiO_2) were performed using LiBO_2 flux fusion process following the procedure described by Carignan
190 et al. (2001). The analyses were accurate within 1–5% for SiO_2 , Al_2O_3 , Fe_2O_3 , MnO, MgO, CaO, Na_2O ,
191 K_2O and within 1–10% for TiO_2 based on repeated analyses of U.S. Geological Survey and CRPG
192 standards (Carignan et al., 2001).

193 4.2 Silicate and sulfide in situ analyses

194 In situ major element concentrations of the rock forming minerals were obtained in punctual mode on
195 C-coated petrographic thin sections using a CAMECA SXFive electron microprobe at the CAMPARIS
196 platform, Sorbonne Université (Paris, France; accelerating voltage 15 kV, beam current 10 nA). For
197 representative analyses of major mineral phases, the reader is referred to Supplementary Table S1.
198 Scanning Electron Microscope (SEM) observations were performed at the platform PARI of the Institut
199 de physique du globe de Paris of Université Paris Cité (IPGP-UPC, France) using a Zeiss EVO MA-10 and
200 a Zeiss Auriga FEG-FIB on Au-coated petrographic thin sections. Images were collected using a
201 backscattered electron (BSE) detector (NTS BSD) at 15 kV accelerating voltage and high current. Energy
202 dispersive X-ray spectrometry (EDS) measurements were performed using a Bruker Quantax 200
203 detector (125 eV resolution).

204 4.3 Carbonaceous compound characterization

205 Sample preparation for in situ carbon compound characterization was performed at IPGP-UP. Rock
206 samples were sawed with a cleaned Cu-core diamond blade and sterile ultrapure water to extract the

207 inner core, free of possible post-sampling organic contamination. The inner core was then manipulated
208 using clean pliers, thinned and polished on both faces (down to a thickness of tens of micrometres)
209 with pure ethanol using alumina polishing disks without any use of resin or glue.

210 SEM observations were performed on Au-coated samples at the platform PARI of the IPGP-UP using a
211 Zeiss Auriga 40 field emission scanning electron microscope. Backscattered electron images were
212 collected at high current with accelerating voltage ranging from 10 kV to 15 kV, at respectively low and
213 high currents (from 10 pA to 1 nA), using a NTS BSD detector. EDS maps were collected at 15 kV
214 accelerating voltage using a Bruker Quantax 200 detector. Elemental distributions were processed
215 using the ImageJ software (Schneider et al., 2012). False colour images were obtained using PhotoFiltre
216 7 software.

217 Raman spectroscopy was performed on resin-free samples at the platform PARI of the IPGP-UP with a
218 Renishaw InVia spectrometer using the 514nm wavelength of a 20 mW argon laser focused through
219 an Olympus BX61 microscope with a x50 objective (numerical aperture: 0.75). This configuration yields
220 a planar resolution close to 1 μm . The laser power delivered at the sample surface was 0.5 mW with
221 integration times of 150 s, well below the critical dose of radiation that can damage carbonaceous
222 matter (Beysac et al., 2003). Light was dispersed by a holographic grating with 1800 grooves mm^{-1}
223 and the signal analysed with a RENCAM charge-coupled device detector. Acquisition times were set at
224 $5 \times 30\text{s}$. Raman was used to identify and characterize both silicates (e.g., serpentine minerals) and
225 carbonaceous matter and for RSCM thermometry. As the chemical and structural evolution of
226 carbonaceous matter after a temperature increase is irreversible, RSCM thermometry is a convenient
227 tool to estimate maximum temperature experienced by sedimentary organic matter in the range of
228 330-640 (± 50) $^{\circ}\text{C}$. For each metasediment sample, 10 spectra were averaged to smooth out the within-
229 sample structural heterogeneity. Spectra were then fitted using PeakFit software (Systat Software,
230 Inc.), based on the method of Beysac et al. (2002).

4.4 Thermodynamic models

231 We use a Gibbs free energy minimization strategy (Connolly, 2005, 2009) to compute, using Perplex
232 software, phase equilibria in metaserpentinites during subduction. Pseudosections were calculated for
233 four representative samples of paleoseafloor (VIS18-5A1 and VIS18-7 samples), LSZ- (VIS18-3 sample)
234 and basal (VIS20-1 sample) serpentinites (Table 1 and Supplementary Table S2). These samples were
235 selected as they host contrasted HP parageneses, made of antigorite-olivine (VIS18-3, VIS18-5A1 and
236 VIS20-1 samples) or antigorite-chlorite-diopside/tremolite (VIS18-7 sample), and redox-sensitive
237 accessory phases, made of awaruite-pentlandite (VIS18-3 and VIS18-5A1 sample) or heazlewoodite-
238 magnetite (VIS20-1 sample). This sample set is considered as representative of the mineralogical
239 variations observed in the metaserpentinites constituting the Monviso meta-ophiolite.

241 Phase diagrams in $\text{SiO}_2\text{-FeO-MgO-CaO-H}_2\text{O} [\text{CO}_2\text{-NiO-S}_2\text{-O}_2]$ systems were calculated using the Holland
242 & Powell 1998 (revised in Holland & Powell, 2003) thermodynamic database. Al_2O_3 was not considered
243 as the main Al-bearing phase would be chlorite, stable in all the studied rocks, whatever the considered
244 P-T conditions. Although Al_2O_3 contents can enlarge the stability field of antigorite to higher
245 temperatures (Padrón-Navarta et al., 2013), these effects were considered negligible at the
246 investigated temperatures, i.e., below temperatures of antigorite breakdown (620°C). This therefore
247 does not affect the phase relationships, neither the dehydration reactions at the considered
248 conditions. In calculations with Ni-S bearing species, awaruite, heazlewoodite, vaesite, millerite,
249 pentlandite, pyrite and pyrrhotite have been implemented in the database (Supplementary Table S3).
250 The thermodynamic data of these pure species have been compiled from Evans et al. (2017), Holland
251 & Powell (1998) and Klein & Bach (2009) and were previously benchmarked by Evans et al. (2017). A-
252 X relationships are from Holland & Powell (2003) for olivine (with the addition of a Ni-olivine species
253 “fran”), clinopyroxene, orthopyroxene, and amphibole (tremolite and Fe-tremolite); from Padrón-
254 Navarta et al. (2013) for antigorite; from Sack & Ghiorso (1991) for magnetite-magnesioferrite; from
255 Franzolin et al. (2011) for carbonates, with an enthalpy of formation of $-5.74 \text{ kJ mol}^{-1}$ for ordered
256 dolomite (Navrotsky & Capobianco, 1987), which is considered to be in good accordance with natural

257 examples (e.g., Scambelluri et al., 2016, Debret et al. 2018). The fluid considered (COH-fluid, see
258 perplex.ethz.ch) uses a hybrid equation of state derived from Connolly & Cesare (1993) and includes
259 H₂S and SO₂ species. Carbon-bearing species were not considered in the thermodynamic modelling as
260 current thermodynamic knowledge of organic compounds at HP-HT is limited to methane (CH₄) and
261 acetate (CH₃COO⁻) in fluids (Sverjensky et al., 2014), while several recent natural or experimental
262 studies have highlighted that the later these simple organic species are likely to decompose to solid
263 carbonaceous compounds, for which no thermodynamic database is available (e.g., Szlachta et al.,
264 2022).

265 Few adjustments of serpentinite bulk rock composition were performed depending on the considered
266 solution models. Pseudosections were calculated considering FeO, therefore excluding Fe₂O₃ linked to
267 magnetite according to Kempf et al. (2020), and CaO bounded to silicates (Supplementary Table S2).
268 The amount of FeO was calculated considering a constant Fe³⁺/Fe_{total} ratio of 0.4, coherent with
269 previous estimates in the eclogitic Alpine meta-ophiolites (Debret et al., 2014), and a ratio of 0.66 for
270 magnetite. This was with the exception of pseudosections calculated in SiO₂-FeO-MgO-CaO-H₂O-NiO-
271 S₂-O₂ system that attempt to model Fe-bearing accessory phases (i.e., magnetite, sulfides) during
272 thermodynamic calculations. The amount of CaO was calculated removing CaO bounds to carbonate,
273 based on CO₂ concentrations measured in bulk rock. This was with the exception of pseudosections in
274 SiO₂-FeO-MgO-CaO-H₂O-CO₂ in which carbonates were implemented during thermodynamic
275 calculations – assuming that all carbon contained in the samples is inorganic.

276 5. Thin section observations and in situ analyses

277 The studied cross sections show from East to West a succession of deep-seated oceanic lithologies
278 (basal serpentinites and metagabbros) to paleoseafloor lithologies (including calcschists, metabasalts,
279 meta-ophicarbonates and paleoseafloor serpentinites; Figure 1). Here we describe the thin section
280 petrography of metasedimentary and ultramafic rocks composing the massif from top to bottom: (i)
281 metasedimentary rocks, (ii) the metasomatic contacts made of chloriteschists embedding blocks of

282 meta-ophimagnesites, (iii) paleoseafloor serpentinites, (iv) LSZ-serpentinites and associated meta-
283 ophidolomites related to shear zones in the southern part of the massif and (v) basal serpentinites.

284 5.1 Metasedimentary rocks

285 Metasedimentary rocks were sampled all along the massif, at the contact with ultramafic rocks in the
286 northern massif and within the USZ and LSZ in the southern massif (Table 1). These rocks are mainly
287 made of calcite, quartz, white micas and graphite. Metasedimentary rocks from the northern massif
288 were selected to perform RSCM thermometry (Beyssac et al., 2002). Few variations in Raman spectra
289 are observed passing from one sample to another (Figure 3). The obtained spectra are characterized
290 by a broad disordered band (D) of low intensity at 1355 cm^{-1} and a sharp and more intense graphite
291 band (G) at 1578 cm^{-1} . Temperatures obtained through the deconvolution of the D and G bands are
292 shown in Figure 1a. Considering the errors of 50°C associated with these estimates (Beyssac et al.,
293 2002), these temperatures overlap, ranging from 519°C at the Colle del Baracun to 558°C at the Colle
294 Armoine.

295 5.2 Metasomatic contacts

296 Metasomatic contacts made of chloriteschists embedding meta-ophimagnesites (Figure 2a-b) were
297 sampled at the interface between metasedimentary and ultramafic units in the northern part of the
298 massif. The chloriteschists present an alternance of diopside (Di2)-rich and chlorite-rich folded layers
299 (Figure 2a). Diopside layers are widely associated with large crystals of tremolite, interstitial talc and
300 sulfides of more than $50\text{ }\mu\text{m}$ in width and can contain rare calcite relicts in their centre (Figure 4a-b).
301 Both diopside and chlorite crystals are orientated along rock foliation and are associated with
302 abundant magnetite. Di2 grains of about $100\text{ }\mu\text{m}$ in width with a XMg value ($=\text{Mg}/(\text{Mg} + \text{Fe})$) ranging
303 from 0.89 to 0.96 have low Al_2O_3 and Cr_2O_3 ($<0.2\text{ weight\%, wt\%}$) contents relative to mantle
304 clinopyroxene (Supplementary Table S1), supporting a metamorphic origin (Nozaka, 2010). Chlorite
305 crystallized as orientated lamellae of $200\text{ }\mu\text{m}$ in length. They have Al_2O_3 contents of 13.0-14.6 wt% and
306 XMg values of 0.90-0.92. Raman and SEM analyses highlight the presence of carbonaceous matter in
307 both diopside- and chlorite-rich layers (Figure 4c). Carbonaceous matter consists of dense aggregates

308 of about 10 μm in width with a gel-like texture and enclosed within diopside or chlorite crystals (Figure
309 4c). Associated Raman spectra are characterized by a broad and relatively intense D band at 1369 cm^{-1}
310 ¹ and a relatively sharper G band at 1591 cm^{-1} (Figure 3). Based on these spectra, these are named
311 disordered carbonaceous matter (DCM) hereafter.

312 Meta-ophimagnesites are made of large magnesite crystals of up to 10 cm in width surrounded by
313 white metamorphic coronas (Figure 2b). The latter includes large magnetite crystals, up to 1 cm in
314 width, associated with finely recrystallized assemblages made of antigorite-chlorite and dolomite-
315 tremolite/diopside \pm chlorite \pm talc (Figure 4d). Antigorites are systematically associated with chlorite
316 in their centre. Antigorites are characterized by variable Al_2O_3 contents ranging from 0.1 to 2.3 wt%
317 and XMg values ranging from 0.90 to 0.93 (Supplementary Table S1). Chlorites have higher Al_2O_3
318 contents of 12.0 to 15.1 wt% and XMg values ranging from 0.88 to 0.92. DCM was also observed in the
319 recrystallized assemblages, as embedded in chlorite. The associated Raman spectra are similar to those
320 observed in chloriteschists and are marked by two broad D and G bands at 1369 cm^{-1} and 1591 cm^{-1} ,
321 respectively (Figure 3).

322 5.3 Paleoseafloor serpentinites

323 Paleoseafloor serpentinites are observed directly below the metasomatic contacts separating
324 metasedimentary and ultramafic units. These rocks present highly variable amount of olivine or
325 diopside either at sample or thin section scales (Figures 2c and 5). Diopside-rich layers are made of
326 antigorite, two generations of diopside (Di1 and Di2), magnetite, chlorite, calcite and pentlandite \pm
327 ilmenite, hydroandradite, tremolite and talc. It must be noted that olivine is usually absent in diopside-
328 rich layers (Figure 5a). The antigorites crystallized as lamellae of 50 to 200 μm in length oriented along
329 rock foliation. They have Al_2O_3 contents ranging from 0.05 to 3.80 wt% and XMg values of 0.94-0.96
330 (Supplementary Table S1). Chlorite flakes can be observed in the centre of antigorite lamellae,
331 sometimes completely replacing the latter (Figure 5c-d). These chlorite cores display Al_2O_3 contents
332 ranging from 12.1 to 14.6 wt% and XMg values of 0.95, similar to those of antigorite. Rare and large
333 diopside crystals (Di1) of up to 1 mm in length, often presenting kink band structures, are disseminated

334 within the antigorite matrix. They display mantle clinopyroxene like composition (e.g., Nozaka, 2010),
335 with Al₂O₃ contents of 1.7-6.7 wt%, Cr₂O₃ contents of 0.3-1.4 wt% and XMg values of 0.90-0.95. A
336 second generation of diopside (Di2) is either present as layers of about 300 µm in width orientated
337 along rock foliation (Figure 5a) or as small interstitial needles of 10-100 µm in length disseminated
338 within the antigorite matrix and orientated along rock foliation (Figure 5e-f). Di2 have lower Al₂O₃ (<
339 0.7 wt%) and Cr₂O₃ (<0.2 wt%) contents and higher XMg values (> 0.95) than those of Di1
340 (Supplementary Table S1). Di2 can be intimately associated with carbonates, most of the time calcite
341 but dolomite was also analysed in one sample (Figure 5b-d and Table 1). Carbonates is observed as
342 small indented veins crenulated along rock foliation (Figure 5b) and as porphyroclasts of hundreds of
343 micrometres (Figure 5d) to millimetre size (Figure 5c) embedded within rock foliation. The carbonates
344 are always overgrown by antigorite lamellae (Figure 5b, d). The calcite veins are associated with thin
345 coronas made of pentlandite, hydro-andradite, ilmenite and magnetite. The sheared tails of the
346 porphyroclasts are made of diopside (Di2), tremolite and talc (Figure 5c). At the contact with
347 porphyroclasts tails, the antigorite is partly to fully replaced by chlorite (Figure 5c-d). It is interesting
348 to note that both carbonate veins and porphyroclast rims are associated with DCM. The associated
349 Raman spectrum is marked by two broad D and G bands at 1369 cm⁻¹ and 1591 cm⁻¹, respectively,
350 identical to that observed in chloriteschists and meta-ophimagnesites (Figure 3).

351 Olivine-rich layers are made of granoblastic olivine (Ol2), magnetite, titanochondrodite (TiChn),
352 titanoclinohumite (TiCl), brucite, pentlandite and awaruite (Figure 5e-g). Granoblastic olivines
353 crystallized as grains of variable width ranging from 10 to 400 µm. They display low NiO content (below
354 detection limit up to 0.28 wt%) and XMg values (0.77 to 0.87, on average 0.82 in 15 analyses) relative
355 to mantle olivine (e.g., Nozaka, 2010). Brucite aggregates of up to 500 µm in width are observed within
356 olivine-rich layers in few samples (Table 1). Brucites have XMg values ranging from 0.92 to 0.94.
357 Olivines can be associated with large humite crystals of 300 µm in length (Figures 2c and 5e-f). Electron
358 microprobe analyses show that these crystals are highly heterogeneous, having compositions
359 spreading between titanochondrodite and titanoclinohumite endmembers. This agrees with previous

360 studies that have shown that both humite varieties can be associated at micrometric scales in HP-
361 serpentinites (e.g., López Sánchez-Vizcaíno et al., 2005). Titanochondrodites have TiO₂ contents
362 ranging from 6.18 to 7.80 wt% and X_{Mg}^{TiChn} values from 0.85 to 0.86
363 ($X_{Mg}^{TiChn/TiCl} = Mg / (Mg + Fe + Mn + Ni)$). Titanoclinohumites have TiO₂ contents ranging from 4.32 to 7.01
364 wt% and X_{Mg}^{TiCl} values from 0.85 to 0.90. Titanochondrodites and titanoclinohumites are chlorine and
365 fluorine-free (Supplementary Table S1). Olivines are also intimately associated with small interstitial
366 magnetite crystals and large automorphic pentlandite (about 50 μm in width) and/or awaruite (50-100
367 μm in width; Figure 5g).

368 5.4 Lower Shear Zone serpentinites

369 LSZ-serpentinites were sampled in the southern part of the Monviso massif in the Lower Shear Zone
370 separating metabasites and basal serpentinites. These rocks are composed of an alternance of
371 antigorite-rich and olivine-rich layers (Figure 6a) forming sigmoidal plans, contributing to a S-C fabric
372 at the sample and thin section scales (Figure 2e, see Schwartz et al., 2013 for more details). The
373 antigorite-rich layers are made of orientated antigorite lamellae of 100 μm in length with Al₂O₃
374 contents ranging from 1.5 to 1.9 wt% and X_{Mg} values of 0.96 (Supplementary Table S1). The olivine-
375 rich layers are made of olivine (Ol2), magnetite, brucite, titanoclinohumite, pentlandite and awaruite.
376 Olivines crystallized as grains of variable width, from 20 μm to 400 μm. They have similar X_{Mg} values
377 of 0.84 – 0.88 and low NiO contents (<0.12 wt%) (Figure 6a). Brucite is observed as patches composed
378 of lamellae of about 200 μm in length and surrounded by small grains of Ol2 of about 20 μm in width.
379 Brucites have high X_{Mg} values ranging from 0.94 to 0.97. They are closely associated with magnetite
380 grains of about 400 μm in width. Titanoclinohumite crystallized as small grains of about 50 μm
381 disseminated within olivine-rich layers. They have TiO₂ contents of ~6.2 wt%, X_{Mg}^{TiCl} values of ~0.90,
382 and are fluorine and chlorine-free (Supplementary Table S1). Awaruite crystals of 50 μm in width and
383 pentlandite grains of 100 μm are observed surrounding magnetite (Figure 6b). Some massive
384 serpentinite blocks have preserved early oceanic-like textures such as mesh and bastite textures
385 replacing mantle olivine and pyroxenes, respectively (Supplementary Figure S1). These textures are

386 crosscut by chrysotile veins. Mantle olivines in LSZ-serpentinites have higher NiO contents compared
387 to Ol₂, ranging from 0.31 to 0.46 wt%. They have a XMg value of 0.89.

388 Meta-ophidolomites were sampled in both the USZ and the LSZ, near the Rifugio Quintino Sella. They
389 consist of an alternance of dolomite-rich and diopside-rich layers interbedded by antigorite. Antigorite
390 lamellae of about 100 µm in length display Al₂O₃ contents ranging from 1.4 to 2.2 wt% and XMg values
391 of 0.94 (Supplementary Table S1). The dolomite-rich layers are made of dolomite crystals of up to 1
392 cm in width surrounded by metamorphic coronas made of diopside (Di₂) or calcite and magnetite. It
393 must be noted that Gilio et al. (2020) also reported the existence of meta-ophimagnesites within the
394 LSZ; those were not studied here.

395 5.5 Basal serpentinites

396 Basal serpentinites were sampled in the northern part of the Monviso massif near Villanova and the
397 Rifugio Barbara Lowrie. These rocks are made of an alternance of antigorite- and olivine-rich layers
398 (Figure 2d). They are composed of antigorite, metamorphic olivines, magnetite, brucite, chlorite,
399 heazlewoodite and rare diopside (Di₁ and Di₂) (Figure 7). In antigorite-rich layers, antigorites crystallize
400 as lamellae of 100 µm in length orientated along rock foliation. Their Al₂O₃ contents range from 1.2 to
401 2.1 wt% and their XMg values from 0.96 to 0.98 (Supplementary Table S1). Antigorites are intimately
402 associated with thinly crystallized (<10 µm width) olivine and micrometric grains of magnetite (Figure
403 7a-b), giving a dusty aspect in thin sections (Figure 7a). Dusty olivines display NiO contents ranging
404 from 0.03 to 0.22 wt% and XMg values ranging from 0.90 to 0.94. Chlorites, which have XMg values of
405 0.95, crystallized as orientated lamellae of 200 µm in length displaying a strong zoning, with a brown
406 core and a dark blue rim. Brown chlorites are also observed in the centre of antigorite lamellae (Figure
407 7b). Rare brucites crystallize as small flakes of 100 µm in length aggregated within patches (Figure 7b).
408 They display XMg values of about 0.97. The contact between brucites and antigorites is always
409 underlined by dusty olivine/magnetite assemblages (Figure 7b). Rare diopsides are also observed
410 either as (i) isolated crystals of about 400 µm in width (Di₁), deformed along the foliation and
411 sometimes presenting kink band structures or (ii) large crystals of 200 µm in width with a brown colour

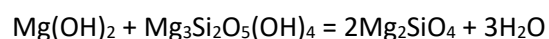
412 and numerous inclusions of magnetite (Di2). Di2 are Al_2O_3 and Cr_2O_3 free (< 0.1 wt%) and have XMg
413 values of about 0.97-0.98. Olivine-rich layers are mainly made of euhedral olivine crystals (Ol2) of
414 about hundreds of micrometres in width containing numerous fluid, andradite and antigorite
415 inclusions (Figures 7c). Euhedral olivines display low NiO contents (0.02-0.14 wt%) and high XMg values
416 (0.96-0.97) compared to dusty olivines (Figure 7a). Large magnetite and heazlewoodite crystals of 50
417 μm in width are also observed associated with euhedral olivines (Figure 7d).

418 6. Temperature and redox record along the massif

419 6.1 Homogeneous temperature record

420 The Monviso meta-ophiolite has long been considered as a fossilized serpentinite subduction channel,
421 resulting in the formation of tectonic melanges (Blake et al., 1995; Guillot et al., 2004; Schwartz et al.,
422 2001). However, more recent studies have revised this model suggesting that it consists of two main
423 coherent tectonometamorphic subunits, namely the Upper and Lower Tectonic Units (Figure 1),
424 detached at different depths during subduction and later juxtaposed during exhumation along the
425 subduction interface (Angiboust et al., 2012). The existence of two coherent tectonic subunits is
426 notably supported by a good homogeneity of metamorphic peak temperatures recorded within each
427 subunit (Angiboust et al., 2012; Gilio et al., 2020; Locatelli, Federico, et al., 2019; Locatelli, Verlaquet,
428 et al., 2019). However, up to now, most of the metamorphic studies on the Monviso meta-ophiolite
429 have investigated the southern part of the massif (e.g., Angiboust et al., 2012, 2014; Blake et al., 1995;
430 Gilio et al., 2020; Groppo & Castelli, 2010; Guillot et al., 2004; Locatelli et al., 2018; Locatelli, Verlaquet,
431 et al., 2019; Schwartz et al., 2001), while the northern part is the subject of only a few ones (Balestro
432 et al., 2015, 2018). Although the continuation of tectonic structures from North to South remains
433 unclear (Figure 1a), the temperatures obtained here on sedimentary organic matter by RSCM
434 thermometry suggest a homogeneous temperature record for the metasedimentary rocks all along
435 the massif with temperature estimates overlapping within an interval of 50°C (i.e., within the
436 associated errors; Beyssac et al., 2002) from North to South (Figure 1).

437 The ultramafic rocks of the Lower Tectonic Unit are characterized by the occurrence of an antigorite-
438 olivine ± brucite paragenesis from North to South (Figures 2, 5, 6 and 7). The granoblastic textures
439 (Figures 6a, 7a-b), the presence of mineral inclusions, such as antigorite within olivine (Figure 7c), and
440 the highly variable NiO contents and XMg values (Figure 8a) of olivines are coherent with a
441 metamorphic origin, as already proposed by several studies on the southern part of the Monviso meta-
442 ophiolite (Gilio et al., 2020; Schwartz et al., 2013). The preferential crystallization of olivine at the
443 contact between brucite and antigorite (Figures 6a and 7b), as well as the rare occurrences of brucite
444 in the studied samples (Table 1), suggest that metamorphic olivines formed after antigorite and brucite
445 according to the following reaction in MgO-SiO₂-H₂O systems (Evans, 2004; Schwartz et al., 2013):



448 In a system containing aluminium, brucite breakdown is also expected to stabilize chlorite, as
449 supported by the observation of this mineral with antigorite and/or olivine in the studied samples (e.g.,
450 Figures 7b). Brucite breakdown was previously inferred to occur nearby 400°C at 2.0-2.5 GPa in MgO-
451 SiO₂-H₂O systems (Evans, 2004). However, new estimates in the FeO-Al₂O₃-MgO-SiO₂-H₂O system
452 extends the stability field of brucite up to 550°C (Kempf et al., 2020). In agreement with these previous
453 studies, our P-T pseudosection calculations in the CaO-FeO-MgO-SiO₂-H₂O system show that Eq. (1)
454 can occur over a large range of temperatures in the Monviso meta-ophiolite, from 400 to 550°C at 2.3-
455 2.7 GPa (Figure 9a and Supplementary Figure S2). These temperatures estimates are poorly sensitive
456 to pressure and overlap with the metamorphic conditions recorded by carbonaceous matter in
457 metasedimentary rocks (516-565°C; this study and Angiboust et al., 2012; Figure 1a) and calculated by
458 thermodynamic modelling in metabasites (~550°C, 2.6–2.7 GPa; Angiboust et al., 2012). It must
459 however be noted that olivine amounts are highly variable at either the sample (e.g., Figure 5), outcrop
460 (Figure 2) or massif scale (Table 1), olivine being notably absent in diopside/tremolite-rich layers
461 forming paleoseafloor serpentinites. Using thermodynamic calculations in the CaO-FeO-MgO-SiO₂-H₂O
462 system and compositional variations in bulk rock metaserpentinites, we identified two metamorphic

463 sequences during subduction. These are characterized by a climax paragenesis (520-570°C and 2.6-2.7
464 GPa) at either Olivine-Brucite-Antigorite (Figure 9a) or Diopside-Talc-Antigorite (Figure 9b). These
465 different metamorphic pathways can be attributed to variable amounts of brucite in metaserpentinites
466 during prograde metamorphism (Figure 9c). Brucite abundance in serpentinites is highly sensitive to
467 silica activity (Frost & Beard, 2007) and is therefore sensitive to SiO₂ abundance relative to MgO in bulk
468 rock and/or to the circulation of SiO₂-rich fluids in shear bands at HP. In agreement with previous
469 observations, Figure 9c shows that olivine appearance can be pushed up to 600-650°C (i.e., antigorite
470 breakdown) in SiO₂-rich systems, while it decreases to 480-490°C in MgO-rich systems. However, in
471 these models, the diopside modal amount is controlled by CaO concentrations in metaserpentinites,
472 which are poorly variable in mantle peridotite (0-4 wt%; (Bodinier & Godard, 2013). Hence, such
473 models cannot account for large variations of diopside modal amount and CaO variations (from 0.1 to
474 9 wt%) observed in bulk rock (Supplementary Table S2) at the massif scale, calling for other sources of
475 CaO and reactional pathways. In fact, a variation of carbon dioxide activity (a_{CO_2}) also favours the
476 formation of diopside and talc at the expense of carbonates and antigorite in ultramafic systems
477 (Figure 9d). It is therefore plausible that the high amount of metamorphic diopside (Di2) found in
478 metaserpentinites reflects carbonated paleo-horizons (i.e., meta-ophicalcites) in the massif
479 subsequently devolatilize during subduction (see section 6.3 for more details about carbonate role
480 during brucite breakdown). Such an observation is coherent with Balestro et al. (2018) that argued for
481 the preservation of ODF paleo-structures in the northern part of the massif.

482 Few robust thermodynamic constrains on pressure exist within ultramafic rocks. However, the
483 observation of both titanoclinohumite and titanochondrodite (this study, e.g., Figures 2c and 5e-f, as
484 well as Gilio et al., 2020) is coherent with a HP equilibration above 2 GPa (Shen et al., 2014). For Gilio
485 et al. (2020), the absence of titanoclinohumite in LSZ-serpentinites suggests that these rocks
486 equilibrated below Eq. (1) curve ($T < 500^\circ\text{C}$; Figure 9c) during the Monviso retrograde path. However,
487 the stability of titanoclinohumite phases are also controlled by TiO₂ concentrations in the protolith,
488 TiO₂ mobility in fluids, carbonate activity and F concentrations (Evans & Trommsdorff, 1983; Savko &

489 Skryabin, 1999). All of these parameters being unknown and likely variable at the massif scale, the
490 variable occurrence of humite phases is more likely to reflect chemical heterogeneities than a
491 variability of pressure recorded in the metaserpentinites.

492 Overall, from North to South, temperature estimates based either on metasedimentary rocks,
493 metabasites and metaserpentinites overlap within a range of 50°C suggesting that the different
494 lithologies composing the Lower Tectonic Unit recorded homogeneous P-T conditions, with a
495 metamorphic climax nearby 520-570°C and 2.6-2.7 GPa. Our observations further support previous
496 studies (Angiboust et al., 2012, 2014; Gilio et al., 2020; Locatelli et al., 2018; Locatelli, Verlaguet, et al.,
497 2019) showing that the Monviso constitutes a large oceanic lithosphere section eclogitized during
498 subduction and partly dismembered during Alpine orogeny. The Monviso lithostratigraphic sequence
499 includes, from East to West, a succession of deep-seated lithologies, including gabbroic intrusions into
500 an extended section of serpentinized lithospheric mantle (i.e., basal serpentinites), to paleoseafloor
501 lithologies, including metasediments sitting on serpentinites in the North or metabasalts sitting on
502 metagabbros in the South. This sequence is coherent with the preservation of a heterogeneous crustal
503 section such as the ones observed at slow-spreading ridges (Cannat, 1995) or in other Western Alps
504 (meta-)ophiolites (Lagabrielle & Cannat, 1990).

505 6.2 A contrasted redox record in metaserpentinites

506 Although they result from the same metamorphic reaction (Eq. 1), metamorphic olivines display highly
507 variable NiO contents (below detection limit up to 0.28) and XMg values (0.77-0.97) along the massif
508 (Figure 8a and Supplementary Table S1). The low NiO contents in Monviso olivines relative to mantle
509 olivine are typical of metamorphic processes (Nozaka, 2010). Also relative to mantle olivines, olivines
510 from basal serpentinites have higher XMg values, up to 0.97, while olivines from paleoseafloor and
511 LSZ-serpentinites have lower and extremely variable XMg values, down to 0.77. Kempf et al. (2020)
512 ascribe XMg value variations in metamorphic olivine to variable temperatures of crystallization during
513 brucite breakdown, where Fe-rich olivine becomes progressively more Mg-rich with increasing
514 temperature. These authors report XMg value variations between 0.93 and 0.97 in the Zermatt-Saas

515 eclogitic meta-ophiolite (Swiss Alps). The highest XMg values (nearby 0.97) are ascribed to
516 metamorphic vein crystallization equilibrated with metamorphic fluids, while XMg value variations in
517 host rock olivines (in the range 0.93 to 0.96) are ascribed to a narrow temperature range, between 10
518 to 20°C. Similar XMg value variations between metamorphic veins and host rock olivines are observed
519 in the Monviso basal serpentinites (Figure 7a). However, according to Kempf et al. (2020)
520 thermometer, a jump in temperature of about 75°C and up to 150°C is required to account for XMg
521 value variations from 0.77 to 0.94 at 2.6 GPa in the whole massif (Figure 9a). This is not consistent with
522 the apparent homogeneous P-T recorded by associated metasedimentary rocks and metabasites
523 (Figure 1). Similarly, such XMg dependency on temperature suggests that only the first stages of brucite
524 breakdown may produce XMg values lower than 0.85 (Kempf et al., 2020), while in the Monviso meta-
525 ophiolite, olivine with low XMg values were analysed in several samples presenting high modal amount
526 of metamorphic olivines (Figure 8a-b), calling for other processes. Interestingly, the accessory phases
527 associated with metamorphic olivines composing paleoseafloor and LSZ- serpentinites are made of
528 pentlandite and awaruite (Figures 5g and 6b), while heazlewoodite and magnetite are present in basal
529 serpentinites (Figure 7d). Pentlandite, awaruite, heazlewoodite and magnetite appearance are
530 primarily controlled by fO_2 and/or fS_2 variations and Fe partitioning between metamorphic phases
531 rather than variations in P or T (Evans et al., 2017). In order to better characterized Fe exchanges
532 between silicates, Fe-oxides, Ni/Fe-alloys and sulfides, we attempted to model brucite breakdown in
533 the S-NiO-CaO-FeO-MgO-SiO₂-H₂O system (Figure 10). In these models, pentlandite and awaruite can
534 only be equilibrated at low oxygen fugacity ($<-27 \log(fO_2)$; \sim FMQ -4; Figure 10), which agrees with
535 previous thermodynamic studies (Evans et al., 2017). At such conditions, the presence of awaruite and
536 pentlandite during brucite breakdown leads to low-Ni olivine, as shown by NiO content in olivine
537 isopleths (Figure 10) and in accordance with the low NiO contents of metamorphic olivines composing
538 the paleoseafloor and LSZ- serpentinites, overall suggesting that these phases crystallized at
539 equilibrium. In contrast, basal serpentinites forming olivines display relatively high NiO contents and
540 are associated with magnetite and heazlewoodite. These rocks are also characterized by the absence

541 of awaruite, which, according to thermodynamic calculations, requires lower fO_2 conditions, i.e.,
542 $\log(fO_2)$ around -24 (\sim FMQ; Figure 10). Pseudosections show that the disappearance of awaruite leads
543 to an increase of NiO contents in olivines, explaining the high NiO concentrations in olivine formed in
544 basal serpentinites relative to paleoseafloor and LSZ- serpentinites (Figure 8a). This therefore suggests
545 that paleoseafloor, LSZ- and basal serpentinites have recorded a strong redox gradient, varying from
546 around -27 to -22 $\log(fO_2)$. These redox variations also influence the fate of magnetite during brucite
547 breakdown and therefore the XMg value variations of metamorphic olivines (XMg values isopleths in
548 Figure 10). Paleoseafloor and LSZ- serpentinites preserved interstitial magnetite and automorphic
549 awaruite and pentlandite (e.g., Figure 5g). This textural relationship suggests that olivine, awaruite and
550 pentlandite are concomitantly formed during brucite breakdown, while the interstitial magnetite could
551 represent the last steps of brucite breakdown, associated with a decrease of rock porosity and the
552 precipitation of the less fluid mobile elements such as Fe. Similarly, the observation of both awaruite
553 and pentlandite surrounding large magnetite crystals (Figure 6b) also suggests that magnetite is poorly
554 stable during brucite breakdown in these lithologies and at low fO_2 conditions, as predicted by
555 thermodynamic calculations (Figure 10). At the opposite, in basal serpentinites, magnetite is abundant
556 (Figure 7) and olivine displays relatively high XMg values and NiO contents (Figure 8a-b) coherent with
557 high fO_2 conditions (Figure 10). Hence, as shown by thermodynamic models, XMg isopleths are
558 controlled by fO_2 conditions, with Olivine-Antigorite-Heazlewoodite-Magnetite assemblages being
559 equilibrated with XMg values of 0.89-0.93, while Olivine-Antigorite-Pentlandite-Awaruite assemblages
560 are equilibrated over a large range of lower XMg values, from 0.77 to 0.85 (Figures 10).

561 6.3 Role of carbon during redox variations accompanying serpentinite 562 dehydration at high pressure

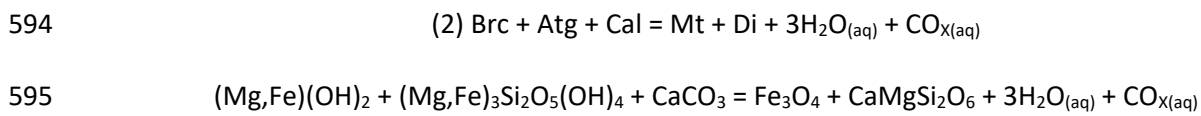
563 The Monviso ultramafic rocks are associated with different types of carbonates, namely calcite,
564 magnesite and dolomite (e.g., Figure 2b, 4b, d, 5b, c and Table 1), reflecting different stages of carbon
565 mobilisation along the massif history (e.g., Gilio et al., 2020). Here we discuss carbonate origin and
566 metamorphic reactions leading to carbonate destabilization during either subduction- (prograde)

567 and/or exhumation- (retrograde) related metamorphism. We also link the different stages of
568 carbonate devolatilization to the precipitation of DCM during the evolution in pressure and
569 temperature of the massif.

570 6.3.1 Abyssal calcite destabilization during prograde metamorphism

571 As shown by thermodynamic modelling (Figure 9d), the presence of carbonate in paleoseafloor
572 serpentinites is likely to influence the metamorphic reaction pathways during subduction. In the
573 Monviso meta-ophiolite, rare calcite relicts are observed as crenulated veins (Figure 5a-b),
574 porphyroclasts embedded in rock foliation (Figure 5c-d) or in the centre of diopside-rich layers (Figure
575 4b) in both paleoseafloor serpentinites and chloriteschists. These textural relationships show that the
576 formation of calcite occurred prior to Alpine-related deformation and metamorphism. Indeed, calcites
577 are commonly observed close to the seafloor in abyssal settings and are interpreted as paleoseafloor
578 related in ophiolites (Lafay et al., 2017) when they are associated with sediments and serpentinites
579 (referred as the “Steinman trinity” in Alpine meta-ophiolites, see Bernoulli et al., 2003 for a review).
580 During subduction, calcite is unlikely to form in ultramafic systems as the precipitation of metamorphic
581 Ca-bearing silicates (e.g., diopside or tremolite) controls the chemical potential of Ca. This reduces the
582 concentration of Ca in metamorphic fluids and therefore the stability and the formation of HP-related
583 meta-ophicalcites (Menzel et al., 2020). In agreement with thermodynamic modelling (Figure 9d),
584 calcite porphyroclasts are surrounded by complex reaction rims made of diopside (and/or tremolite),
585 talc, magnetite and chlorite (Figures 4b, 5c-d). The diopside (Di2) observed either in paleoseafloor
586 serpentinites or chloriteschists display low Al_2O_3 and Cr_2O_3 contents and high XMg values relative to
587 large kink band diopside crystals (Di1; Figure 8b), coherent with a metamorphic origin. The formation
588 of chloriteschists and diopside-rich layers in paleoseafloor serpentinites can therefore be explained by
589 a progressive decrease in a_{CO_2} favouring the formation of diopside-magnetite-chlorite at the expense
590 of carbonate and antigorite (Debret et al., 2018). Indeed, the large amount of fluids released during
591 brucite breakdown at HP can induce such a decrease in a_{CO_2} in fluids and therefore enhance calcite

592 dissolution (Kelemen & Manning, 2015). This can be expressed in the Monviso meta-ophiolite
593 according to the simplified reaction:



596 Additional Al_2O_3 component that can be present in antigorite will allow chlorite formation as shown
597 by the occurrence of flakes made of chlorite at the contact of diopside-rich layers (Figures 4a-b and
598 5ad). Brucite breakdown in carbonate-rich lithologies is therefore expected to stabilize a chlorite-
599 diopside/tremolite-magnetite paragenesis at HP.

600 Considering the reasoning above, the chloriteschists made of an alternance of diopside- and chlorite-
601 rich layers preserving level of calcite in their centre (Figure 4a-b) can be interpreted as former seafloor-
602 related ophicarbonates horizons formed at the contact between metasedimentary rocks and
603 serpentinites (Figure 1) and partly to fully devolatilized at HP during brucite breakdown. This is in good
604 agreement with recent observations in the Queyras meta-ophiolites where diopside-rich serpentinites
605 are also interpreted as meta-ophicarbonates (Debret et al., 2018). In Eq. (2), the exact form of carbon
606 in fluids is highly speculative as this is intimately related to $f\text{O}_2$ conditions at HP, with reduced
607 conditions possibly favouring the abiotic formation of organic compounds (e.g., hydrocarbons
608 including methane or organic acids such as formate, HCOO^-) at the expense of carbonates (Sverjensky
609 et al., 2014; Vitale Brovarone et al., 2017).

610 The formation of organic compounds during decarbonation reactions is consistent with the redox
611 record of carbonate free paleoseafloor serpentinites found at the contact with meta-ophicalcites and
612 chloriteschists (Figure 10). It is indeed interesting to note that diopside and chlorite in carbonated
613 paleoseafloor serpentinites and chloriteschists are intimately associated with DCM (Figure 4c),
614 characterized in Raman spectroscopy by a broad D band with relatively high intensity compared to the
615 associated G band (Figure 3). Given the close spatial association of DCM with this paragenesis, it seems
616 reasonable to propose that DCM results from abyssal calcite devolatilization at HP-HT during
617 subduction. The thermal maturation of organic matter during subduction is usually yet misleadingly

618 simplified to kerogen (i.e., insoluble macromolecular organic matter of biological origin dispersed in
619 sedimentary rocks) graphitization upon burial through thermal cracking (allowing C-C bond breaking),
620 as described by Beyssac et al. (2002) for metasedimentary rocks. This is typically associated with the
621 progressive structural evolution of poorly-ordered C-, O-, H-bearing kerogens starting at low
622 temperatures, until the formation of pure C-bearing and well-ordered graphite at 600-700°C
623 (Vandenbroucke & Largeau, 2007). However, the observed DCM preserved here a large amount of
624 structural disorder (Figure 3) which is not compatible with a biological origin and a kerogen like
625 evolution during subduction, therefore calling for new reaction pathways and revisited stability
626 considerations when serpentinite-hosted organic matter is considered. Indeed, recent natural
627 observations have shown that abiotic organic compounds with pure aliphatic structure, i.e., opposed
628 to aromatic graphite-like structure, can be stable and formed at HP-HT in subduction settings (Debret
629 et al., 2022). This suggest that a large diversity of organic compounds of not only biological origin but
630 also formed through HP-HT abiotic processes might exist in subduction zones. However, the
631 mechanisms and diversity of these abiotic solid organic compounds remain at that time poorly
632 investigated. Toffolo et al. (2023) show that the solubility of carbonaceous matter at HP-HT is related
633 to its structure and properties (e.g., oxygen heteroatoms, presence of oxygenated functional groups),
634 with oxidizing conditions and high fluid/rock ratio favouring the dissolution of DCM in fluids. In
635 agreement with this, the experiments of Szlachta et al. (2022) show that acetate, which is
636 thermodynamically predicted at HP-HT under reduced conditions (e.g., Sverjensky et al., 2014), is
637 unlikely to be stable in fluids but rather decomposes to a disordered graphite-like material, with a
638 Raman spectral signature similar to that observed for DCM at the Monviso meta-ophiolite. Similarly,
639 Tao et al. (2018) report the formation of abiotic hydrocarbons and graphite through the reduction of
640 siderite under low fO_2 conditions at 1-6 GPa and 600-1200°C. It is important to note that the graphite-
641 associated Raman spectra reported in Tao et al. (2018) display an important structural disorder which
642 might correspond to DCM or graphitic carbon rather than pure graphite. These results show that solid
643 organic carbon phases could be formed through various processes (i.e., fluid saturation and

644 dissociation of organic compounds or redox processes) along prograde metamorphic pathway in
645 subduction zones. The low fO_2 recorded by paleoseafloor serpentinites and associated chloriteschists
646 could therefore have favoured the preservation and/or the formation of DCM during subduction.

647 6.3.2 Meta-ophimagnesites and meta-ophidolomites

648 Meta-ophimagnesites and meta-ophidolomites form large boudins embedded within the foliation of
649 chloriteschists and LSZ-serpentinites in the northern and southern part of the massif, respectively (e.g.,
650 Figure 2b). Relative to calcite, both magnesites and dolomites are abundant at the massif scale.
651 According to Gilio et al. (2020), the formation of magnesite in the Monviso meta-ophiolite is attributed
652 to subduction-related processes occurring close to metamorphic climax. The same authors report
653 magnesite overprint by dolomite suggesting that dolomite crystallized during massif exhumation. They
654 also report in these rocks the occurrence of minor calcite veins crosscutting rock foliation and attesting
655 for the existence of a second generation of calcite crystallizing during the late stages of massif
656 exhumation.

657 It is interesting to note that magnesite crystals display complex metamorphic rims made of dolomite,
658 magnetite, chlorite, talc, tremolite or diopside (Figure 4d). The stabilization of talc, tremolite or
659 diopside within these metamorphic rims is mainly controlled by aCO_2 rather than P-T conditions (Figure
660 9d), with decreasing aCO_2 leading to the successive formation from talc + carbonate, to tremolite +
661 carbonate, diopside + carbonate until diopside alone (Debret et al., 2018). This suggests successive
662 carbonate leaching and re-precipitation episodes along the massif metamorphic history. These are
663 probably controlled by external fluid circulation along rheological interfaces between different
664 lithologies (e.g., LSZ and/or ODF; Figure 1). Moreover, diopside and chlorite in magnesite metamorphic
665 rims are associated with DCM (Figure 4c) showing that the successive episodes of carbonate leaching,
666 releasing CO_2 in metamorphic fluids, participate to a progressive decrease of both aCO_2 and fO_2 within
667 meta-ophimagnesites, allowing during the last stages (i.e., diopside precipitation) the reduction of
668 carbonate into DCM.

669 6.4 Origin of slab redox gradient

670 Sulfide and Ni-Fe alloys assemblages are key indicators of fO_2 conditions (Evans et al., 2017). In the
671 Monviso serpentinites, they shift from magnetite-pentlandite-awaruite assemblages (indicative of low
672 fO_2) in paleoseafloor lithologies to magnetite-heazlewoodite assemblages (indicative of high fO_2) in
673 the deep-seated lithologies. Both assemblages coexist with metamorphic olivines and are likely
674 equilibrated nearby massif climax at 520-570°C and 2.6-2.7 GPa (Figure 10). This shows the existence
675 of a redox gradient affecting the Monviso oceanic lithosphere at HP-HT during subduction. It has been
676 suggested that pre-subduction composition of serpentinites have major implications on the fO_2
677 evolution during subduction, notably that sulfur- and nickel-bearing phases exercise a major control of
678 fO_2 variations (Debret & Sverjensky, 2017; Evans et al., 2017; Evans & Frost, 2021; Evans & Powell,
679 2015; Iacovino et al., 2020; Lazar, 2020; Maurice et al., 2020; Vieira Duarte et al., 2021). In abyssal
680 settings, deep-seated serpentinites generally display high sulfur and sulfide (mainly as pentlandite,
681 pyrrhotite and pyrite) contents (Alt et al., 2013) due to interactions between
682 metagabbros/serpentinites and fluids. In contrast, serpentinites formed near the seafloor (or nearby
683 ODF) are expected to be equilibrated at higher fO_2 conditions and tend to display low amount of sulfur,
684 mostly in the form of sulfates (Alt et al., 2013; Delacour et al., 2008). Similarly, partially serpentinized
685 peridotites composing the deep part of the oceanic lithosphere are likely to form abundant brucite
686 and serpentine associated with pentlandite, magnetite and awaruite (Schwarzenbach et al., 2016),
687 while both brucite and awaruite disappear near the seafloor under oxidizing conditions associated with
688 the abundant percolation of seawater, which is furthermore undersaturated with respect to brucite
689 (Frost & Beard, 2007; Klein et al., 2020). Overall, this suggests the formation of assemblages
690 equilibrated at relatively low fO_2 at depth and assemblages equilibrated at higher fO_2 toward the
691 seafloor. These observations are opposite to what is observed in the Monviso meta-ophiolite
692 suggesting that the observed redox gradient cannot be inherited from an abyssal stage at mid-ocean
693 ridges and must have been settled during Alpine subduction.

694 The dehydration of serpentinites has the potential to lead to a significant increase of fO_2 conditions up
695 to the total dissolution of sulfides in the presence of metamorphic fluids (e.g., Debret & Sverjensky,
696 2017; Maurice et al., 2020; Evans & Frost, 2021). Although sulfides are still preserved in Monviso
697 metaserpentinites, the co-existence of magnetite and heazlewoodite within basal serpentinite
698 dehydration products agrees with an increase of fO_2 during subduction. Similarly, the presence of
699 heazlewoodite in metamorphic veins also suggests that sulfur is mobilized in fluids equilibrated at high
700 fO_2 during subduction. In contrast, the presence of carbonate in paleoseafloor serpentinites
701 harbouring pentlandite and awaruite tends to buffer the fO_2 at lower level during brucite breakdown.
702 The role of carbonate can be illustrated through the decarbonation reactions Eq. (2) in lithologies
703 composing the metasomatic contact between metaserpentinites and metasedimentary rocks in the
704 Monviso meta-ophiolite. In these carbonated interfaces, the progressive leaching of carbonate in
705 serpentinite derived fluids decreases meta-ophicarbonates redox budget, ultimately leading to a
706 decrease of both aCO_2 and fO_2 nearby seafloor lithologies. It therefore suggests that carbon plays a
707 major role on fO_2 conditions in subducting slab, notably contributing to the emplacement of an inverse
708 redox gradient in the Monviso meta-ophiolite. Interestingly, the observation of solid organic
709 compounds' horizons forming from carbonate under reduced conditions at the contact between
710 serpentinites and metasedimentary rocks (this study and also Galvez et al., 2013; Vitale-Brovarone et
711 al., 2017) shows that these reactions can promote organic carbon formation. These transformations
712 have therefore the potential to affect long term carbon recycling, favouring the transfer of organic
713 carbon to the deep mantle in the form of DCM.

714 Redox variations during serpentinite dehydration were also described in other eclogitic meta-
715 ophiolites, sometimes leading to apparently contrasted conclusions (e.g., Debret & Sverjensky, 2017;
716 Piccoli et al., 2019). As an illustration, in the Lanzo massif (Western Alps), Debret et al. (2016) show
717 that the dehydration of serpentinites can be accompanied by hematite formation suggesting fO_2
718 conditions close to FMQ +3 to +4. In the same meta-ophiolite, Vitale-Brovarone et al. (2017) highlight
719 the formation of graphite and methane rich fluid inclusions in paleoseafloor lithologies (i.e., meta-

720 ophicarbonates), compatible with highly reducing conditions, close to FMQ -4. These apparently
721 contrasted observations can be reconciled by the existence of a redox gradient affecting the
722 lithosphere at HP, such as the one observed here in the Monviso meta-ophiolite. Indeed, the
723 metamorphic olivine of the Lanzo massif also display large XMg variations (from 0.79 to 0.90; Debret
724 et al., 2013; Figure 11), compatible with heterogeneous redox conditions at HP-HT during serpentinite
725 dehydration. It must be noted that such variability in metamorphic olivine composition is not observed
726 for all Alpine meta-ophiolites. For example, metamorphic olivines from Zermatt, Cerro del Almiraz and
727 Erro Tobbio massifs show relatively homogeneous composition (Figure 11). However, large variations
728 of XMg values in metamorphic olivines are observed at the scale of the Alps, passing from one meta-
729 ophiolite setting to another. Given that these massifs have recorded similar temperature conditions
730 (Agard, 2021), such variations might support heterogeneous redox record, therefore calling for further
731 investigations.

732 7. Conclusion

733 We show that the different lithologies (i.e., metasedimentary rocks, metabasites and
734 metaserpentinites) composing the Lower Tectonic Unit of the Monviso meta-ophiolite recorded
735 homogeneous P-T conditions (nearby 520-570°C and 2.6-2.7 GPa) from South to North confirming that
736 the massif constitutes a coherent tectonic unit subducted to eclogite facies P-T conditions during
737 Alpine subduction. Despite a homogeneous P-T record, serpentinites display variable metamorphic
738 assemblages reflecting a redox gradient affecting the massif from East to West. This gradient is
739 probably set up during serpentinite dehydration near metamorphic climax, with basal serpentinites
740 composing the eastern part of the massif recording higher fO_2 conditions relative to paleoseafloor
741 serpentinites associated with meta-ophicarbonates and chloriteschists. This redox gradient is linked to
742 the presence of carbon-bearing phases near the paleoseafloor that buffer down the fO_2 through
743 decarbonation redox reactions, thus confirming that the presence of redox sensitive elements in the
744 initial lithology of the oceanic lithosphere has major implications on the evolution of fO_2 during

745 subduction. A decoupling of carbon behaviour is possible (e.g., Bouilhol et al., 2022), as (i) oxidized
746 carbon-bearing fluids are likely to be leached toward to the mantle wedge after serpentinite
747 dehydration and (ii) the progressive decrease in fO_2 expected through decarbonation redox reactions
748 can potentially form and/or stabilize inherited endogenous carbonaceous compounds atHP and their
749 preferential recycling to the deep mantle.

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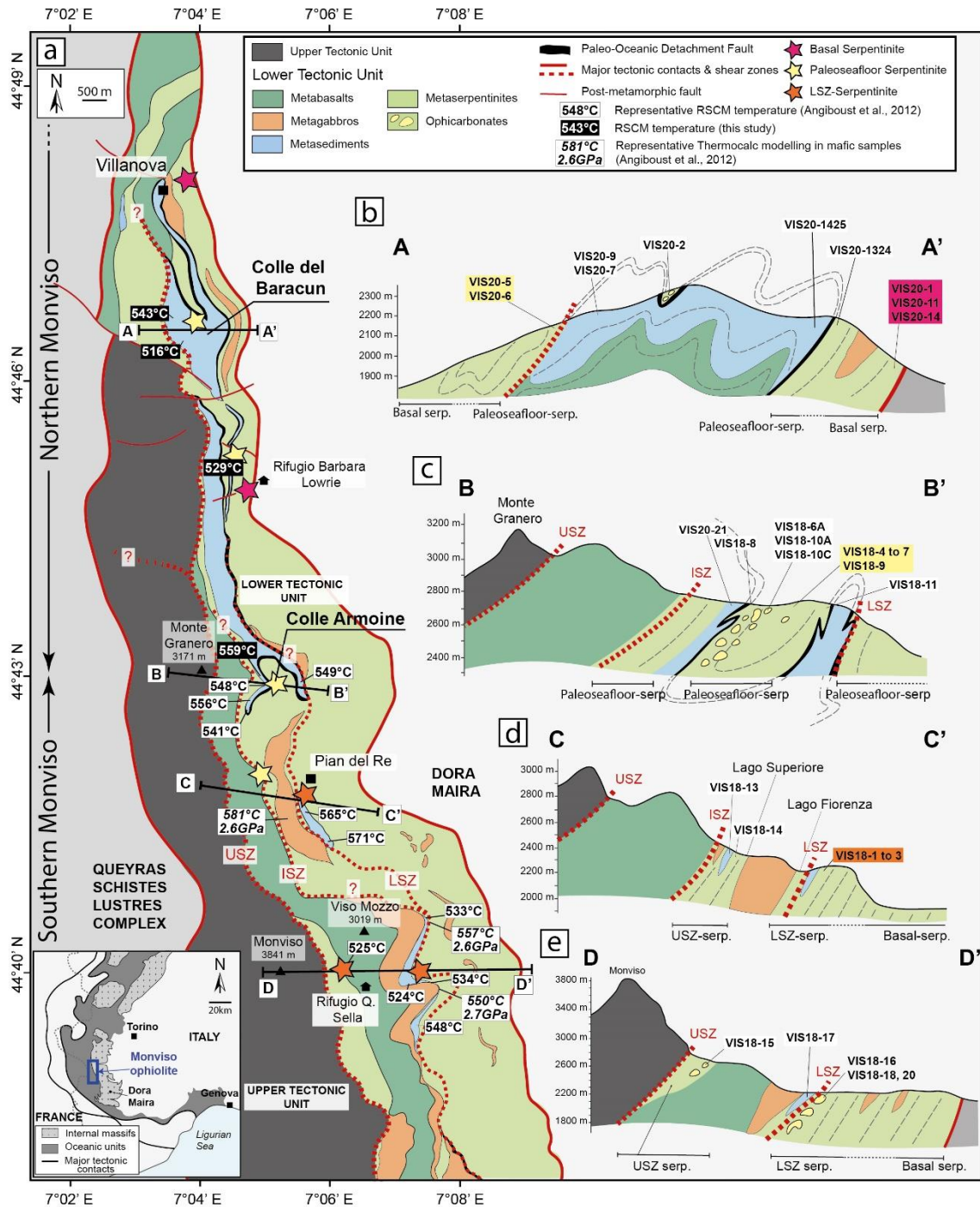
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8. Figures and captions

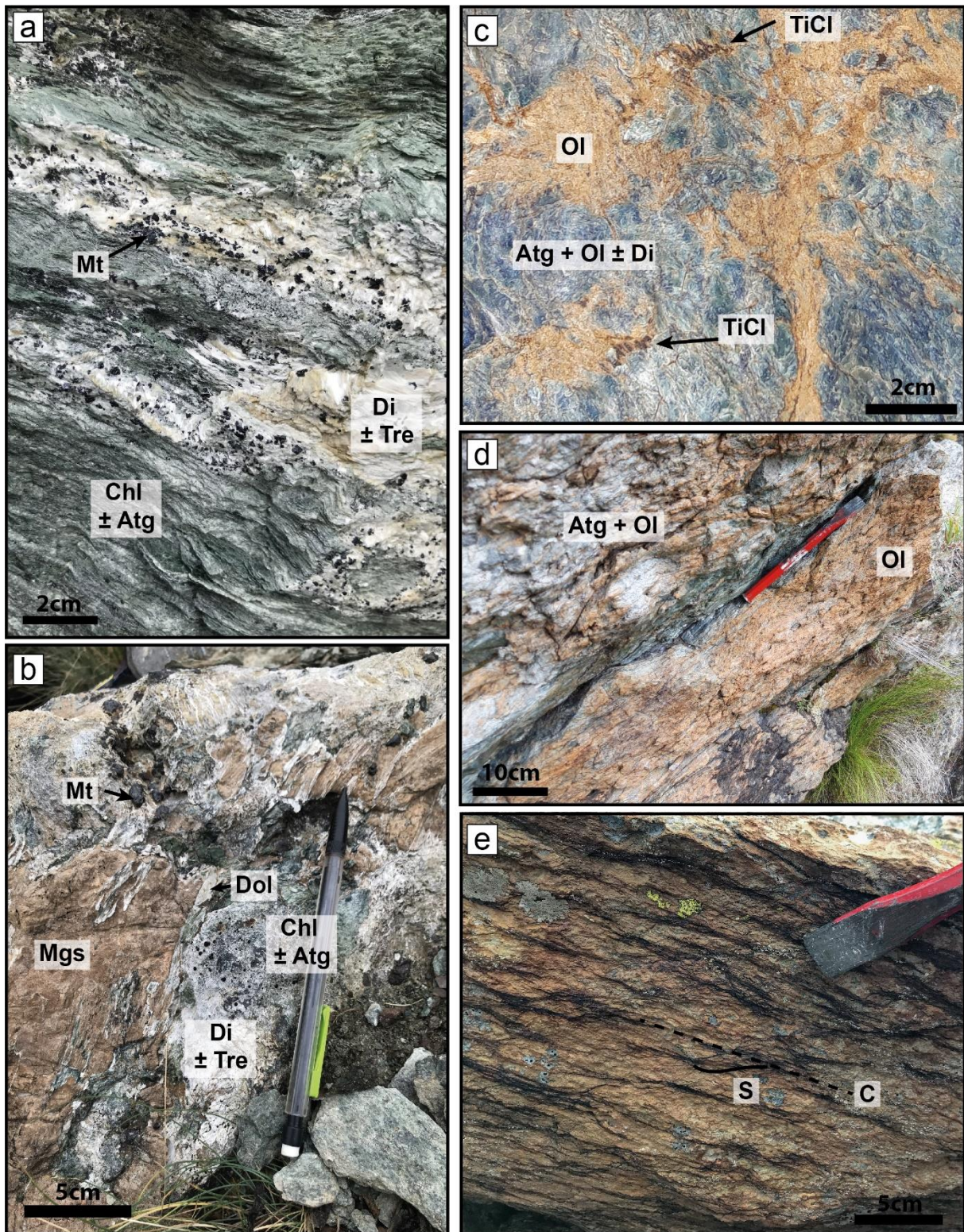


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1014 **Figure 1.** Geological map (a) of the Monviso meta-ophiolite and cross sections of Colle del Baracun (b);
 1015 including a projection of sample locations spanning from Villanova, to the North, to Rifugio Barbara
 1016 Lowrie further South), Colle Armoine (c), Lago Superiore and Lago Fiorenza (d) and Rifugio Quintino
 1017 (Q.) Sella (e) areas (modified after (Angiboust et al., 2012; Balestro et al., 2018; Lombardo et al., 1978;
 1018 Schwartz et al., 2001). The map at the bottom left shows the location of the Monviso meta-ophiolite

1019 in the Western Alps (after Schwartz et al., 2001). (a) The Upper Shear Zone (USZ) (dashed red line
1020 extending from North to South) delimits the main tectonic unit of the Monviso meta-ophiolite, namely
1021 the Upper and Lower Tectonic Units (Angiboust et al., 2012). The solid dark line is interpreted by
1022 Balestro et al. (2015) as a paleo-Oceanic Detachment Fault (ODF) separating crustal and/or
1023 sedimentary lithologies from ultramafic units. Yellow and pink stars correspond to serpentinites
1024 (serp.) sampled near and away the paleo-ODF (LSZ-serpentinites and basal serpentinites, respectively).
1025 Orange stars denote sampling within the USZ, the Lower Shear Zone (LSZ) and the Intermediate Shear
1026 Zone (ISZ). (b-e) Cross sections showing the sample locations along the eclogitic oceanic lithosphere of
1027 the Monviso massif. Sampling for. Representative P-T estimates derived from either RSCM in
1028 metasediments or Thermocalc modelling from Angiboust et al., 2012 and this study are reported in (a)
1029 (white and black boxes, respectively). Additional P-T estimates can be found in Angiboust et al. (2012),
1030 Blake et al. (1995) and Schwartz et al. (2001).

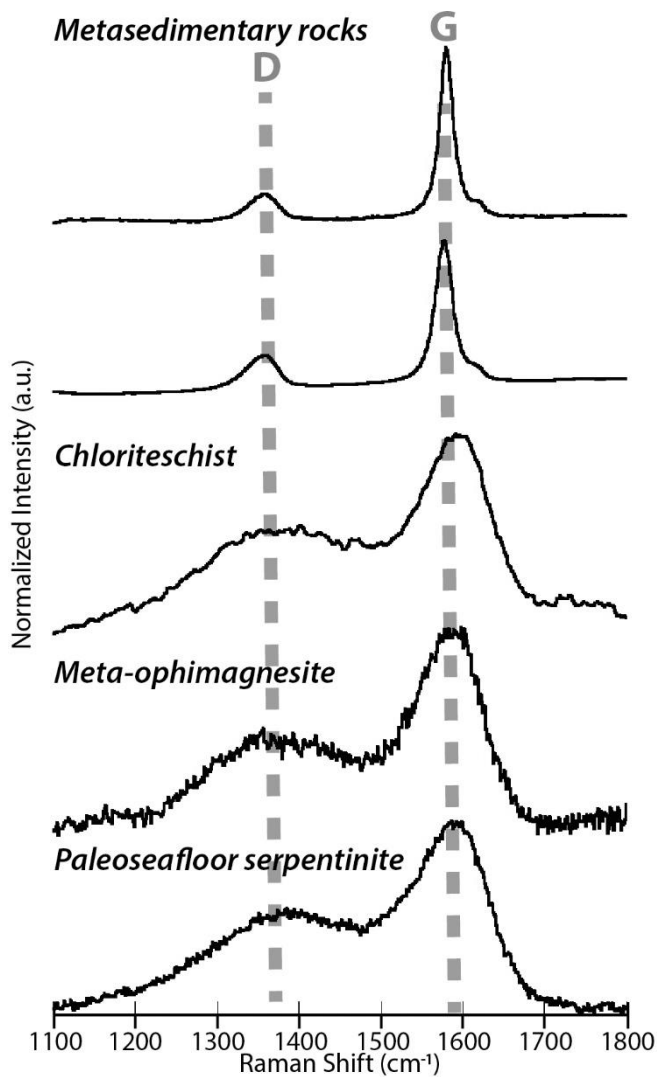
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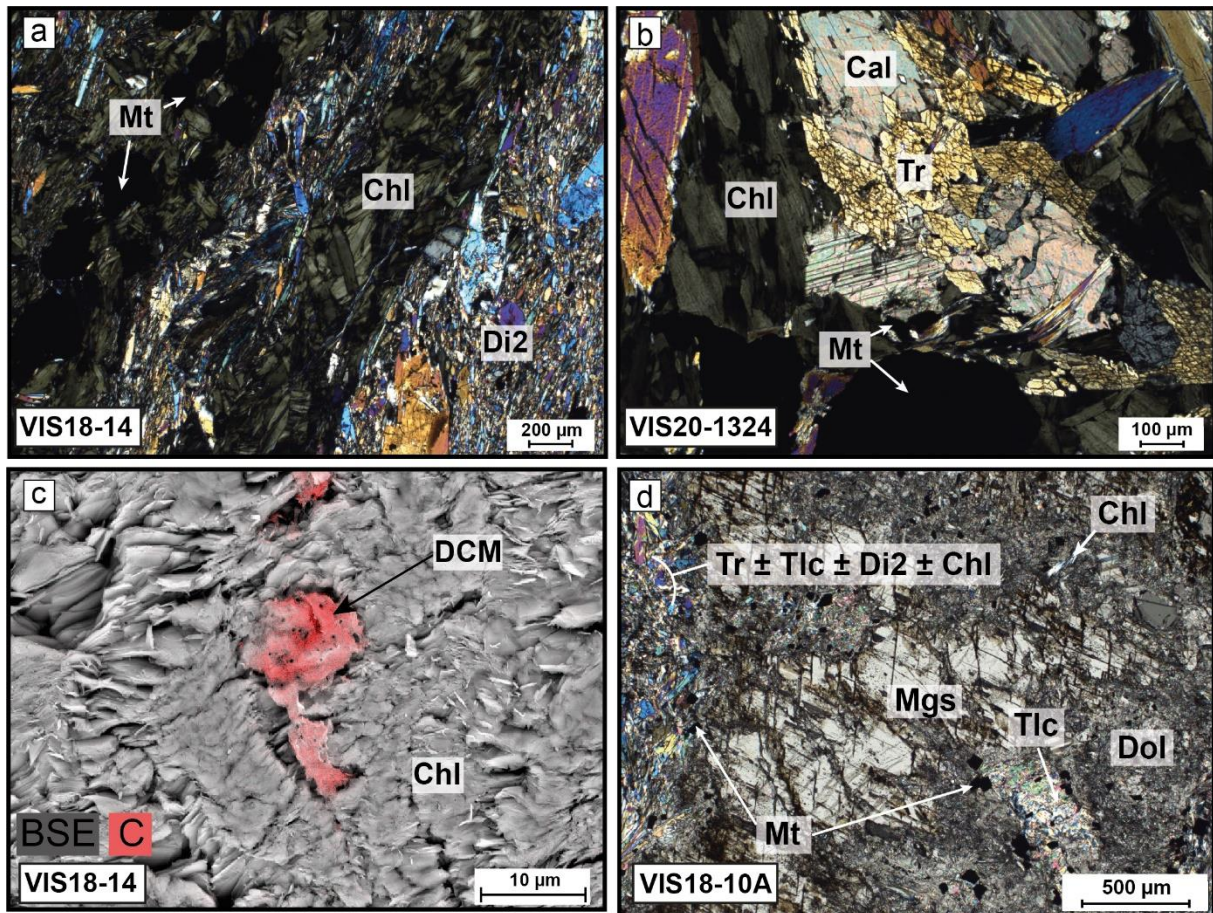
1033 **Figure 2.** Field photographs of ultramafic rocks outcropping in the Monviso meta-ophiolite. (a)
 1034 Chloriteschist made of an alternance of diopside-rich (\pm tremolite) and chlorite-rich (\pm antigorite)
 1035 layers. Note that diopside is associated with abundant magnetite. (b) Meta-ophimagnesite embedded
 1036 within chloriteschist foliation and displaying metamorphic coronas made of dolomite. (c) Olivine-

1037 bearing veins crosscutting paleoseafloor serpentinite. The veins are associated with humite crystals of
1038 centimetre size. (d) Basal serpentinite showing alternance of centimetre to metre sized brown olivine
1039 and serpentinite -rich layers. (e) LSZ-serpentinite where sigmoidal structures, underlined by brown
1040 olivine, contribute to a S-C fabric. See Table 1 caption for mineral abbreviations.



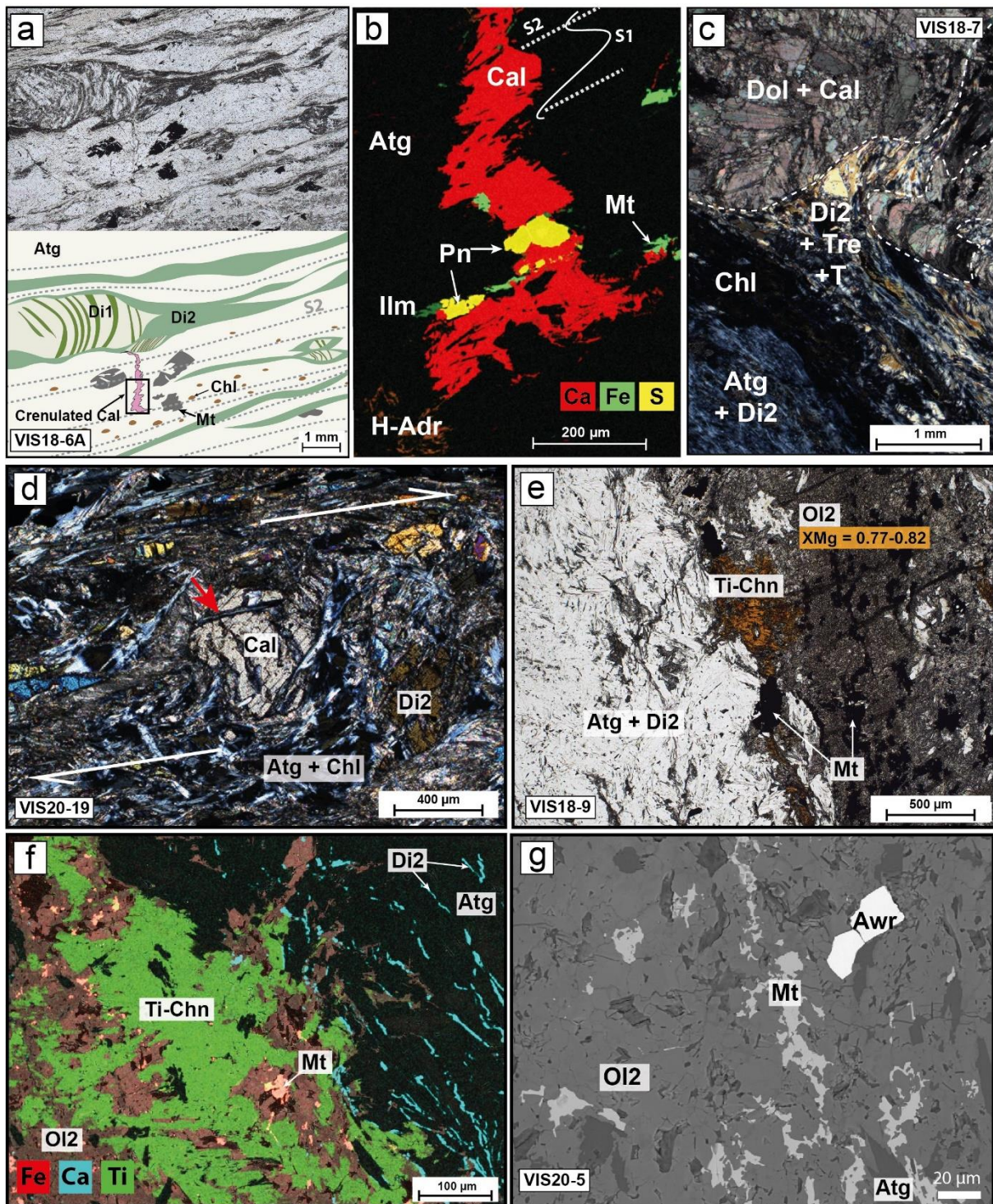
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1042 **Figure 3.** Raman spectra of organic matter composing metasedimentary rocks, chloriteschists, meta-
 1043 ophimagnesites and paleoseafloor serpentinites. Note that the carbonaceous matter in ultramafic
 1044 rocks is characterized by a broad and intense disordered band (D) and a large graphite band (G), while
 1045 that in metasedimentary rocks is characterized by a sharp G band (G) of high intensity compared to
 1046 the associated D band. a.u., arbitrary unit.



1047

1048 **Figure 4.** Petrological thin section (a,b) and hand-polished section (c,d) images of chloriteschists and
 1049 meta-ophimagnesite from the Lago Superiore (a,c), the Rifugio Barbara Lowrie (b) and the Colle
 1050 Armoine (b) . (a) Photomicrograph in crossed polarized light of a chloriteschist showing an alternance
 1051 of metamorphic diopside (Di2)-rich and chlorite (Chl)-rich layers. Magnetite (Mt) is widely distributed
 1052 in the sample. (b) Photomicrograph in crossed polarized light of a calcite (Cal) relict in chloriteschist.
 1053 Calcite crystals present metamorphic corona made of tremolite and magnetite. (c) Overlay of SEM-BSE
 1054 image and SEM-EDS image showing the distribution of carbon (in red), corresponding to DCM, within
 1055 chlorite. (d) Photomicrograph in crossed polarized light of a meta-ophimagnesite. Magnesite (Mgs)
 1056 metamorphic coronas are made from core to rims of dolomite (Dol), magnetite, talc (Tlc), tremolite
 1057 (Tr), diopside and chlorite assemblages. Few lamellae of antigorite can also be observed within the
 1058 metamorphic rims.

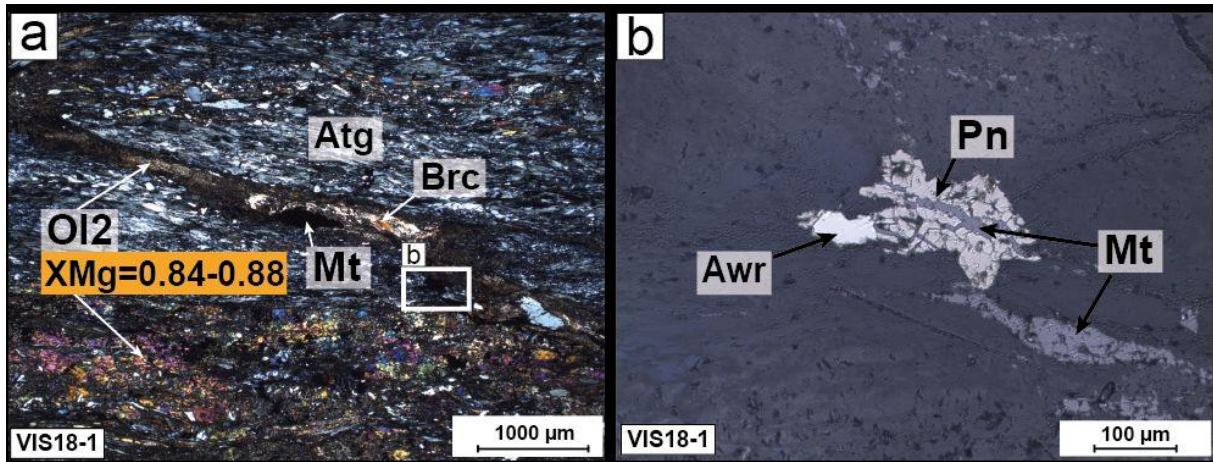


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1060 **Figure 5.** Photomicrographs of thin sections of paleoseafloor serpentinites from the Colle Armoine (a-
 1061 f) and Colle del Baracun (g). (a) Photomicrograph in plane polarized light (top) and associated
 1062 schematic illustration (bottom) of diopside bearing paleoseafloor serpentinites. The box indicates the
 1063 location of the figure 7b. Metamorphic diopside(Di2)-rich layer, orientated along rock foliation (S2),
 1064 embeds first generation of diopside (Di1) associated with antigorite (Atg). Magnetite (Mt) grains

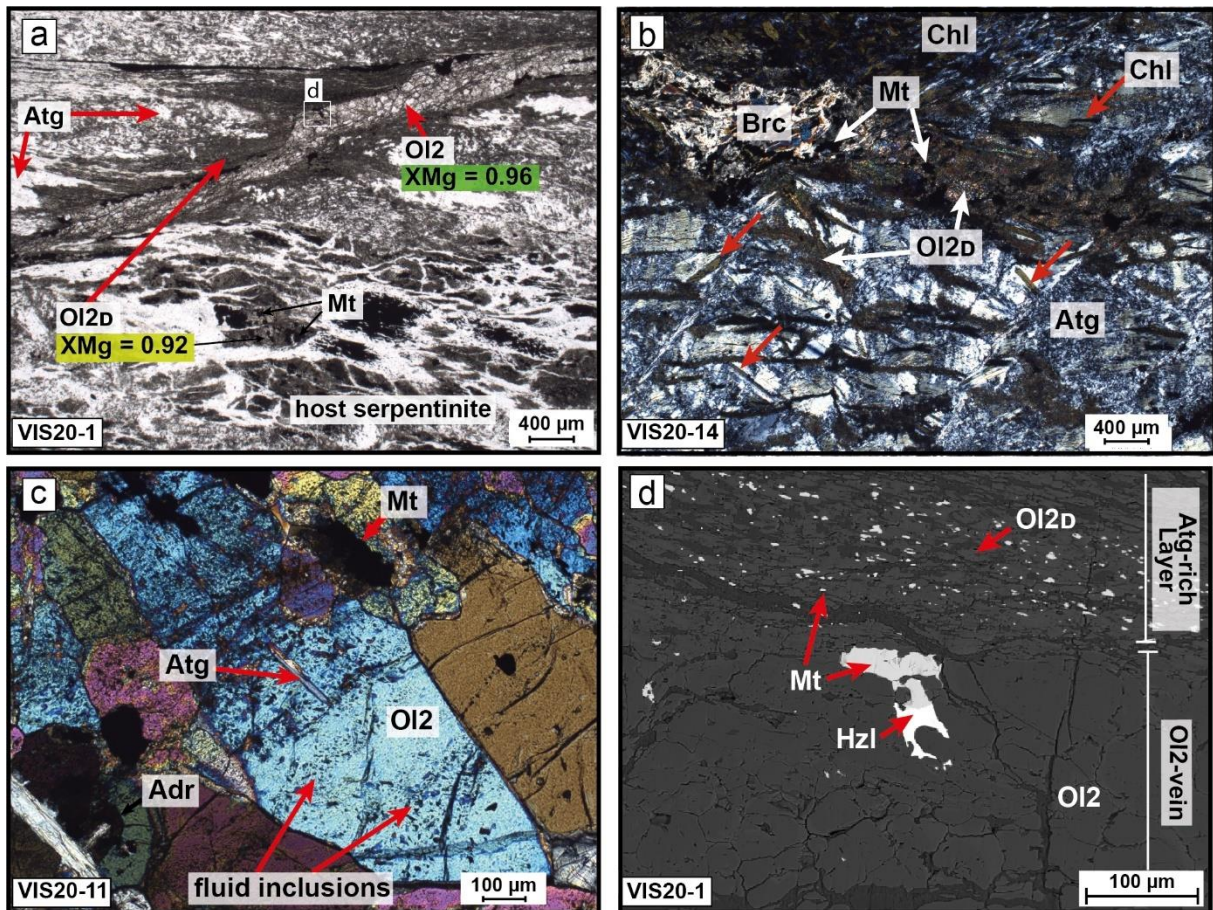
1065 display indented boundaries at the contact with antigorite. Elongated calcite (Cal) crystals of millimetre
1066 size are crenulated by the rock foliation. Chlorites (Chl) flakes can be observed in the centre of
1067 antigorite lamellae. (b) Composite SEM-EDS elemental image (with Ca in red, Fe in green, and S in
1068 yellow) of the elongated calcite shown in (a) and surrounded by a metamorphic rim made of
1069 pentlandite (Pn), hydro-andradite (H-Adr) and ilmenite (Ilm) in contact with antigorite. Calcite veins
1070 are orientated along an early S1 foliation and crenulated along rock S2 foliation. (c) Photomicrograph
1071 in crossed polarized light of a finely recrystallized carbonate porphyroclast made of dolomite (Dol) and
1072 calcite. The tail of the porphyroclast is made of tremolite (Tr), talc (Tlc) and metamorphic diopside. At
1073 the contact with the porphyroclast, the antigorite is fully recrystallized into chlorite. (d)
1074 Photomicrograph in crossed polarized light showing synthetic rotation (depicted by the white arrows)
1075 of a calcite porphyroclast. The metamorphic tail is made of metamorphic diopside, antigorite and
1076 chlorite. Note that calcite is overgrown by antigorite (red arrow). (e) Photomicrograph in plane
1077 polarized light of a partially dehydrated paleoseafloor serpentinite made of an alternance of
1078 metamorphic olivine- and antigorite-rich layers. Antigorite lamellae are associated with finely
1079 disseminated diopside (Di2) needles of 10 to 100 μm in length. Olivines (Ol2), whose XMg values (= $\text{Mg}/(\text{Mg} + \text{Fe})$)
1080 are indicated, are associated with large crystals of titano-chondrodite (TiChn) and
1081 minute grains of magnetite (g). (f) Composite SEM-EDS image showing the distribution of iron (in red),
1082 calcium (in cyan) and titanium (in green) within antigorite- and olivine-rich layers. Antigorite layers are
1083 associated with finely disseminated calcium-rich needles corresponding to diopside (Di2). (g)
1084 Photomicrograph in reflected light of minute and interstitial grains of magnetite disseminated within
1085 olivine-rich layers.

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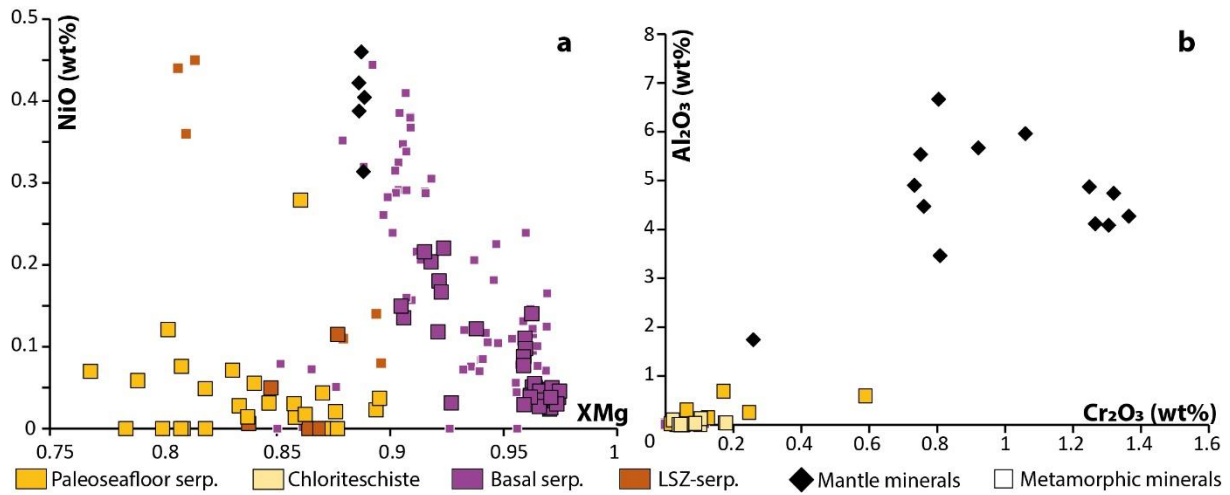
1088 **Figure 6.** Thin section images of a LSZ-serpentinite sampled near the Lago Superiore. (a)
 1089 Photomicrograph in crossed polarized light showing metamorphic olivine, brucite, antigorite and
 1090 magnetite. Olivine-rich layers with associated range of XMg values are located at the contact between
 1091 brucite and antigorite and define S-C structures (Figure 2e). (b) Photomicrograph in reflected light of
 1092 magnetite-pentlandite-awaruite assemblage in olivine-rich layers (location shown in (a)). Note that
 1093 pentlandite and awaruite surround a thin string of magnetite.



1094

1095 **Figure 7.** Thin sections images of basal serpentinites sampled at Villanova (a, d) and Rifugio Barbara
 1096 Lowrie (b, c). (a) Photomicrograph in plane polarized light showing two generations of metamorphic
 1097 olivines (dusty OI2_b and euhedral OI2) and associated XMg values. The first generation is disseminated
 1098 as large aggregates (>500 μm in width) within the host serpentinite. These aggregates are made of
 1099 micrometric olivine grains associated with tiny magnetite (Mt) a few micrometres in width, giving a
 1100 dusty texture in thin sections. The second generation is observed in veins made of euhedral olivines of
 1101 a few hundreds of micrometres in width and that cross-cut the host serpentinite. The mean XMg value
 1102 of the two olivine generations crystalizing in this sample are shown for comparison. (b)
 1103 Photomicrograph in crossed polarized light showing pervasive dusty OI2_b vein network that surrounds
 1104 hundreds of micrometres in width patches made of antigorite (Atg), chlorite (Chl), brucite (Brc) and/or
 1105 magnetite. Flakes of antigorite can include chlorite in their centres (red arrows). (c) Photomicrograph
 1106 in crossed polarized light of a massive OI2-vein. Euhedral olivine crystals contain numerous fluid and
 1107 mineral inclusions. These latter include antigorite, andradite (Adr), magnetite and heazlewoodite (Hzi).

1108 Secondary fluid inclusions are orientated along plans cross-cutting the olivine crystals. (d) SEM-BSE
1109 image of the contact between a large OI2-vein and the host rock OI1. Note that OI2 are intimately
1110 associated with both magnetite and heazlewoodite.
1111



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1113

Figure 8. Chemical compositions in weight% (wt%) of (a) olivines and (b) diopsides from the Monviso

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metaserpentinites. Data from Schwartz et al. (2013) and Gilio et al. (2020) are shown for comparison

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(small symbols). (a) NiO content vs XMg value in olivines. Olivines of mantle origin have higher NiO

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contents than the ones of metamorphic origin. Paleoseafloor/LSZ- and basal serpentinites have,

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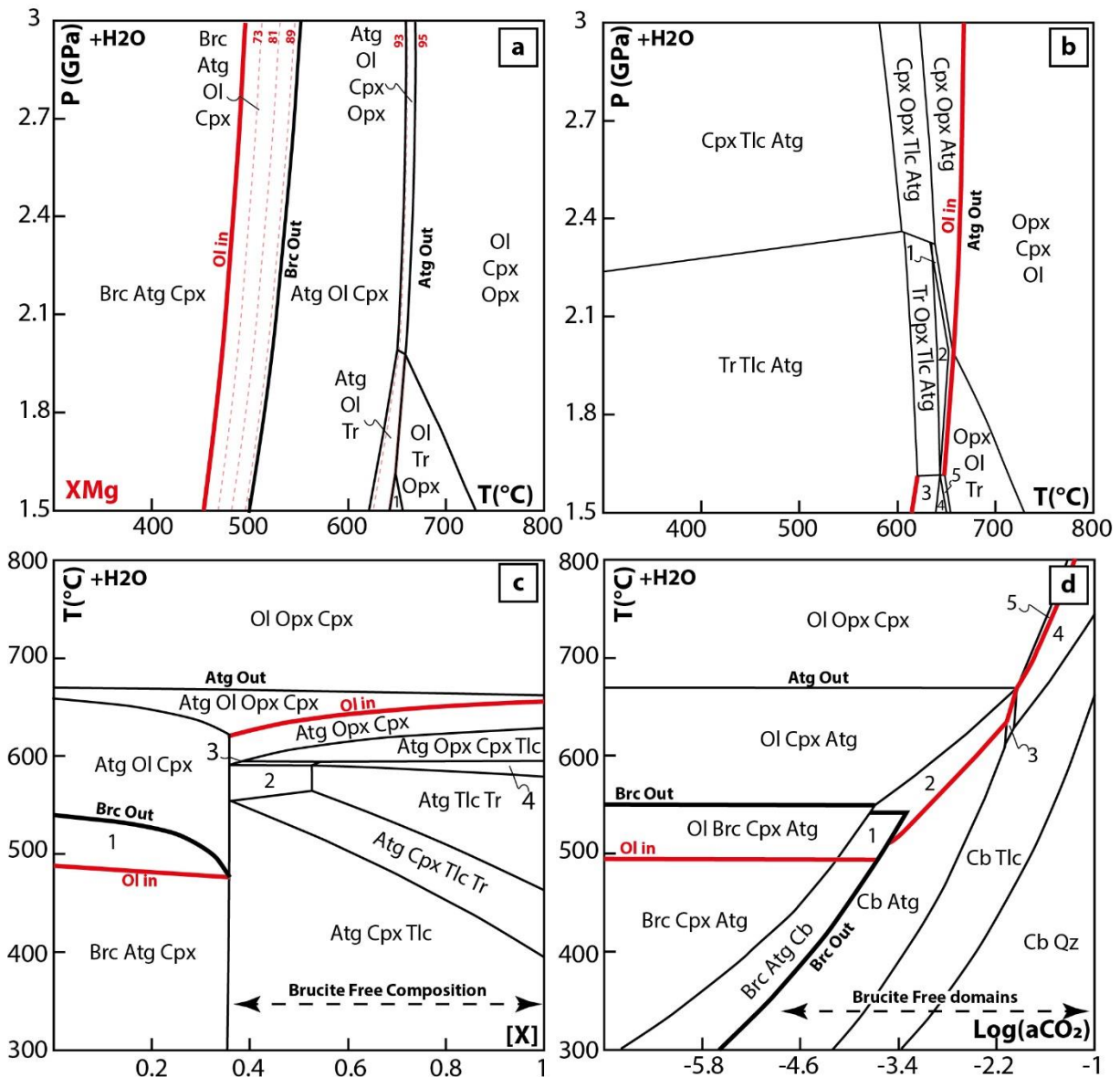
respectively, lower and higher XMg values than the olivines of mantle origin. (b) Al₂O₃ vs Cr₂O₃ in

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diopsides. Metamorphic diopsides (Di2) have lower Al₂O₃ and Cr₂O₃ contents than the primary ones

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(Di1). Uncertainties fall within symbol sizes.



1120

1121 **Figure 9.** Pseudosections based on bulk rock compositions of (a, c, d) olivine-rich (sample VIS18-5A1)

1122 and (b) diopside-rich (sample VIS18-7) paleoseafloor serpentinites. (a-b) P-T pseudosections showing

1123 two metamorphic sequences in paleoseafloor serpentinites influencing the appearance of olivine (Ol

1124 in). (c) T-X pseudosection at 2.5 GPa using MgO variations observed in paleoseafloor serpentinites

1125 (from 36.95 at [X] = 0, to 25.88 wt% at [X] = 1). MgO-rich systems are characterized by a paragenesis

1126 made of Atg-Ol-Cpx at metamorphic climax (520-570°C-2.6-2.7 GPa) while in SiO₂-rich systems, the

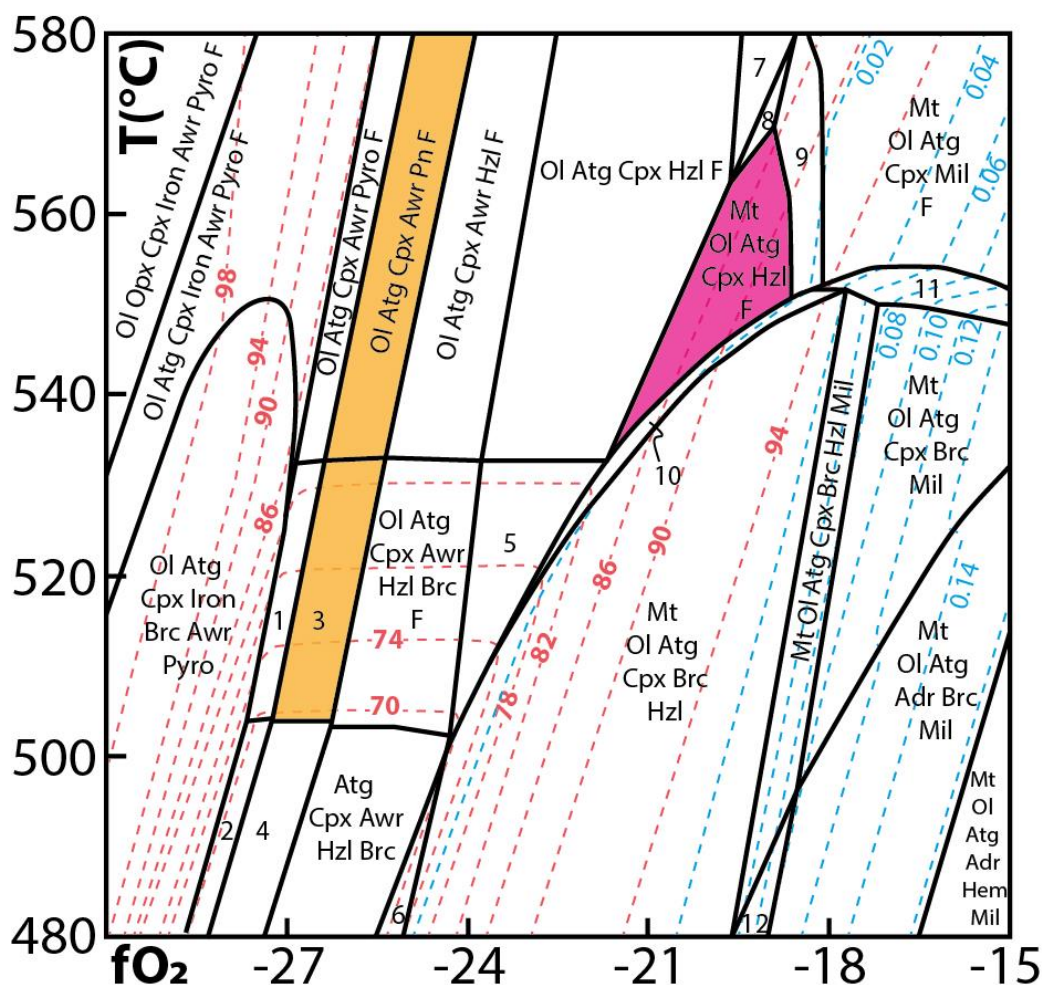
1127 olivine appearance is push back to >620°C. (d) T-Log(aCO₂) pseudosection at 2.5 GPa and a water

1128 activity of 1 in order to report on aCO₂ effects only. The increase of CO₂ activity reduces the divariant

1129 field of brucite, pushing up the appearance of olivine to higher temperatures. Atg, antigorite; Brc,

1130 brucite; Cpx, clinopyroxene; Ol, olivine; Opx, orthopyroxene; Q, quartz; Tlc, talc; Tr, tremolite; Cb
1131 stands for carbonates. (a), 1: Ol-Tlc-Tr; (b), 1: Opx-Cpx-Atg-Tr; 2: Opx-Atg-Tr; 3: Ol- Atg-Tlc-Tr; 4: Ol-Tlc-
1132 Tr; (c), 1: Ol-Brc-Cpx-Atg; 2: Cpx-Atg-Tr; 3: Opx-Tr-Cpx-Atg; 4: Tr-Tlc-Atg-Opx; (d) 1: Ol-Brc-Cb-Atg; 2:
1133 Ol-Cb-Atg; 3: Opx-Cb-Atg; 4: Opx-Cb; 5: Opx-Ol-Cb.

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1136 **Figure 10.** T-Log(f_{O_2}) pseudosection at 2.5 GPa in the S-NiO-CaO-FeO-MgO-SiO₂-H₂O system using
 1137 VIS18-5A1 sample composition. XMg value and NiO content (wt%) isopleths of olivine are in dashed
 1138 red and blue, respectively. Conditions of formation of basal versus ODF-serpentinites (and LSZ-
 1139 serpentinites) are shown in pink and orange, respectively. Atg, antigorite; Adr, andradite; Awr,
 1140 awaruite; Brc, brucite; Chl, chlorite; Cpx, clinopyroxene; Hem, hematite; Hzl, heazlewoodite; Iron,
 1141 native iron; Mil, millerite; Mt, magnetite; Ol, olivine; Opx, orthopyroxene; Pn, pentlandite; Pyro,
 1142 pyrrhotite; suffix F stands for fluids. 1: Ol-Brc-Atg-Cpx-Awr-Pyro-F; 2: Brc-Atg-Cpx-Awr-Pyro; 3: Ol-Brc-
 1143 Atg-Cpx-Awr-Pn-F; 4: Brc-Atg-Cpx-Awr-Pn; 5: Ol-Brc-Atg-Cpx-Hzl-F; 6: Atg-Brc-Ol-Cpx-Mt-Awr-Hzl; 7:
 1144 Atg-Ol-Cpx-Hzl-Pn-F; 8: Atg-Ol-Cpx-Hzl-Pn-Mgt-F; 9: Atg-Ol-Cpx-Hzl-Mil-Mgt-F; 10: Atg-Brc-Ol-Cpx-Brc-
 1145 Mt-Hzl-Mil-F; 11: Ol-Brc-Atg-Cpx-Mt-Mil-F; 12: Ol-Brc-Atg-Mt-Adr-Hzl-Mil.

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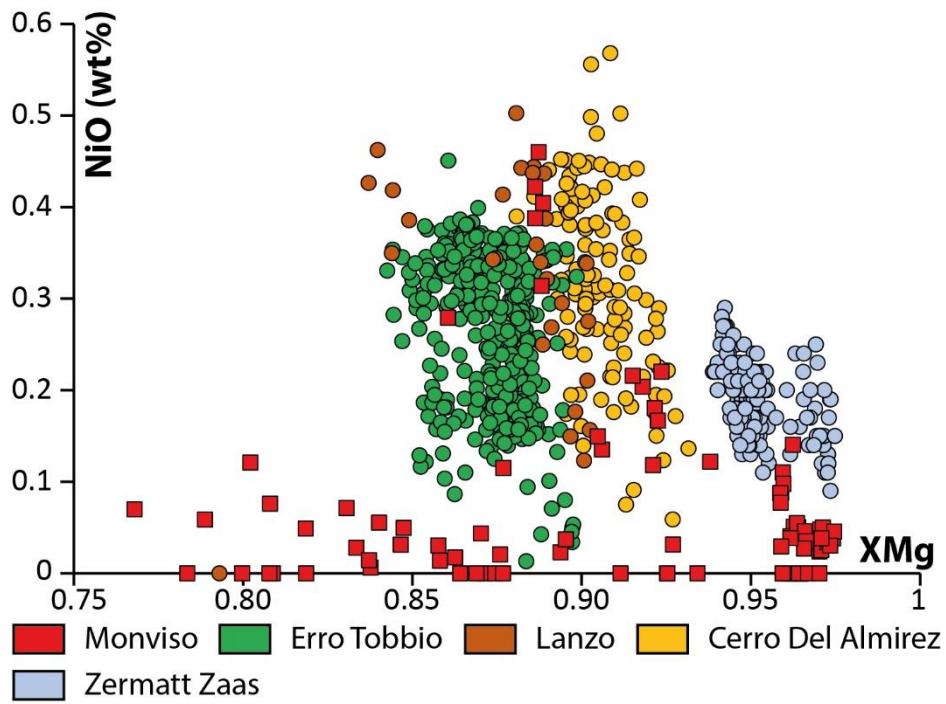


Figure 11: NiO content vs XMg value in metaserpentinite olivines from different alpine eclogitized meta-ophiolite massifs. Data from are from this study and Gilio et al. (2020) for the Monviso, Peters et al. (2020) for Erro Tobbio, Debret et al. (2013) for the Lanzo, Bretscher et al. (2020) for Cerro del Almiraz and Kempf et al. (2020) for Zermatt Zaas.