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► To cite this version:

Antoine Boutier, Alberto Vitale Brovarone, Isabelle Martinez, Olivier Sissmann, Sara Mana. High-pressure serpentization and abiotic methane formation in metaperidotite from the Appalachian subduction, northern Vermont. *Lithos*, 2021, 396-397, pp.106190. 10.1016/j.lithos.2021.106190 . hal-03388726

HAL Id: hal-03388726

<https://ifp.hal.science/hal-03388726v1>

Submitted on 9 May 2023

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1 **High-pressure serpentinization and abiotic methane formation in metaperidotite from the**
2 **Appalachian subduction, northern Vermont**

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1 Introduction

2 Alteration of ultramafic rocks by aqueous fluids, or serpentinization, produces serpentine-
3 rich rocks and may be accompanied by redox reactions leading to the formation of H₂ and
4 abiotic light hydrocarbons (Mével, 2003; Moody, 1976; Seyfried et al., 2007). Oxidation of
5 Fe²⁺ in mantle minerals and formation of Fe³⁺ minerals such as magnetite produces H₂,
6 which may then promote the conversions of dissolved carbon-bearing species into abiotic
7 CH₄ (Andréani et al., 2013; Berndt et al., 1996). Serpentinization is well documented at mid-
8 ocean ridges and on land (Andréani et al., 2007; Cannat et al., 2010; Etiope et al., 2011; Klein
9 et al., 2014; Schrenk et al., 2013), where H₂ and CH₄ produced through serpentinization can
10 support biological communities and could be linked to the emergence of early life on Earth
11 (Kelley et al., 2005; Ménez et al., 2018; Sleep and Bird, 2007). Serpentinization processes
12 may also happen at much greater depths and affect subducted mantle sections and the
13 overlying mantle wedge at convergent margins (Guillot et al., 2015, 2000; Vitale Brovarone
14 et al., 2017; Wada et al., 2008), owing to the availability of aqueous fluids (Bebout and
15 Penniston-Dorland, 2016; Deschamps et al., 2013). However, the patterns of
16 serpentinization reactions at high-temperature (HT) and high-pressure (HP) conditions, here
17 defined with respect to the serpentine stability field, and the associated fluid-rock redox
18 budgets are still largely unconstrained. The possibility that HT-HP serpentinization may not
19 involve Fe oxidation and genesis of H₂ at 400-600°C has been proposed (Evans, 2010).
20 However, natural case studies of slab and mantle wedge-derived serpentinized peridotites
21 suggest that magnetite, H₂ and abiotic CH₄ can be produced at these conditions (Vitale
22 Brovarone et al., 2020). Ultramafic bodies in metamorphic belts can provide insights on the
23 mechanisms of HP-HT serpentinization and the resulting fluids (Evans et al., 2017), and

24 therefore make good case studies for the investigation of the mechanisms of
25 serpentinization in subduction zones.

26 The Belvidere ultramafic complex, Vermont, USA, is a fragment of the former Iapetus ocean
27 that was involved in the Taconic orogeny and recorded subduction-related HP
28 metamorphism during Cambrian-Ordovician (Chew and van Staal, 2014; Gale, 1980;
29 Honsberger et al., 2017). This complex includes variably serpentinized peridotites containing
30 antigorite, the HT serpentine minerals stable at subduction zone HP conditions (e.g., Evans,
31 2004; Schwartz et al., 2013), therefore making a potential example of HT-HP
32 serpentinization. In this work, we integrate field, microstructural, thermodynamic, and fluid
33 inclusions data to investigate the patterns and timing of serpentinization of the Belvidere
34 ultramafic complex, with particular focus on the HP fluid-rock interactions recorded by
35 these rocks.

36 **1. Geologic setting**

37 The Belvidere Mountain complex (BMC) area is part of a North-South trending belt of
38 mafic/ultramafic rocks belonging to the Appalachian Mountain system and extending from
39 Newfoundland to Georgia (Gale, 2007; Hibbard et al., 2006)(Fig. 1). These ultramafic bodies
40 mainly consist of variably serpentinized peridotites, and associated metabasic and
41 metafelsic rocks tectonically embedded within Cambrian-Ordovician metasedimentary and
42 metavolcanic formations (Chidester et al., 1978; Gale, 1986, 1980; Laird et al., 1984; Van
43 Baalen et al., 2009). The BMC, as well as other mafic/ultramafic complexes such as the
44 Tillotson Peak and the Pennington complexes, may represent remnants of an ocean-
45 continent transition zone associated with the extension of the Laurentian margin (Chew and

46 van Staal, 2014). These terranes were successively involved in the closure of the Iapetus
47 Ocean during the Ordovician Taconic orogeny (Doolan et al., 1982; Honsberger et al., 2017;
48 Karabinos et al., 1998; Laird et al., 1984; Stanley et al., 1984). The BMC forms a 6.5 km long
49 body that structurally overlies the metasedimentary Ottawaquechee and Stowe Formations
50 to the East and is overlain by the Hazen Notch formation to the West. The Stowe Formation
51 is late Cambrian, composed of gray-green quartz-chlorite-sericite +/- magnetite schists. The
52 Ottawaquechee Formation consists of middle Cambrian carbonaceous pyritiferous phyllites.
53 The Neoproterozoic to Cambrian Hazen Notch Formation includes graphitic and non-
54 graphitic quartz-albite-sclerite-chlorite schist, along with medium-grained, massive, quartz-
55 albite-muscovite gneiss. The internal architecture of the BMC comprises, from top to
56 bottom, variably serpentinized dunite and harzburgite, coarse-grained and fine-grained
57 amphibolite, greenstone, muscovite schist, and albite gneiss (Gale, 1986, 1980; Van Baalen
58 et al., 2009). Lenticular bodies composed of talc-carbonate rocks and steatite, often
59 including cores of relatively un-serpentinized peridotite, are observed within the BMC, and
60 range in size from a few meters to several tens of meters (Chidester et al., 1978). The BMC
61 rocks underwent Taconic blueschist-facies peak metamorphic conditions constrained at 0.9-
62 1.3 GPa and 510-520 °C in metabasic rocks (Honsberger, 2015; Laird et al., 1993). Higher P
63 metamorphic conditions, up to coesite ultra high-pressure (UHP) conditions, are recorded
64 by the Tillotson Peak mafic rocks located just north of the BMC (Gonzalez et al., 2020; Laird
65 et al., 1993, 1984). In the BMC, the HP tectonometamorphic event has been dated at 505-
66 473 Ma by $^{40/39}\text{Ar}$ amphibole and mica geochronology (Castonguay et al., 2012; Laird et al.,
67 1993).

68 **2. Methods**

69 Quantitative energy-dispersive X-ray spectroscopy (EDS) analyses and backscattered
70 electron (BSE) imaging were carried out using the JSM-IT300LV Scanning Electron
71 Microscope Oxford Inca Energy Dispersive Spectrometer at the Department of Earth
72 Sciences of Turin University. Data were processed with the INCA software from Oxford
73 Instruments. Quantitative analysis employed 15kV accelerating voltage and a beam current
74 of 50 nA and 20 s to 40 s counting total time. Natural and synthetic mineral and oxide
75 standards were employed. EDS calibration was made using Cobalt standard.

76 Quantitative wavelength-dispersive spectrometer (WDS) analyses were carried out using a
77 JEOL 8200 Super Probe at the Department of Earth Sciences "Ardito Desio" of Milan
78 University. The microprobe was using a 15kV accelerating voltage under 5 nA, with 30s
79 counting time under maximum emission peak. Sixteen oxide composition were measured,
80 using synthetic and natural standards: grossular (Si, Al and Ca), omphacite (Na), K-feldspar
81 (K), fayalite (Fe), forsterite (Mg), rhodonites (Mn), niccolite (Ni), ilmenite (Ti), galena (Pb and
82 S), pure Cr, pure Zn and pure Cu.

83 MicroRaman spectroscopy of minerals and fluid inclusions was done at the Department of
84 Earth Sciences, University of Turin, with a LabRAM HR (VIS) (HORIBA Jobin Yvon) equipped
85 with a 532.11 nm, solid-state Nd laser, a Super Notch Plus filter with spectral resolution of 1
86 cm^{-1} , and a grating of 600 grooves/mm. The laser of emission power was set at 80 mW and
87 focused to 5 μm with a 100x objective with a laser power on the sample < 5 mW. Calibration
88 was performed using the 520.6 cm^{-1} band of a silicon standard for the 100-2000 cm^{-1} range,
89 and the 2331 cm^{-1} band of atmospheric N_2 for the 2000-4000 cm^{-1} range. Four
90 accumulations of 30–60 s were collected for each spectrum. Raman spectra of fluid
91 inclusions were performed on double-polished thick sections unless otherwise specified.

92 Isotopic composition measurements of methane were performed on a MAT 253 (Thermo
93 Fisher) mass spectrometer, coupled with gas chromatography (GCC-IRMS) device as CO₂
94 gas, at a specific retention time, on masses 44 (for $\delta^{12}\text{C}$), 45 (for $\delta^{13}\text{C}$) and 46 (for $\delta^{18}\text{O}$),
95 after the methane is completely oxidized into CO₂ through combustion at 1000°C. This is
96 because it is not possible to directly measure methane isotopologues ($^{12}\text{CH}_4$, $^{13}\text{CH}_4$, $^{12}\text{CH}_3\text{D}$)
97 on a “classical” magnetic sector IRMS, due to interferences on masses 16, 17 and 18 in the
98 source (such as CH₅⁺, H₂O ...). The value of the CO₂ internal reference gas was determined
99 using multiple IAEA carbonate standards (IAEA-603, 610, 611, 612) on an EA-IRMS device.
100 On the GCC-IRMS, the efficiency of CH₄ oxidation into CO₂ is checked before each analytical
101 session by injecting, as a sample, two different commercial external methane isotopic
102 standard (such as Air Liquide Thermo 1.2 and Air Liquide Bio 1.0 gases). If the analytical
103 value of the commercial standards is within 0.1‰ of their independently determined value,
104 then the combustion process is deemed valid and without fractionation. The samples
105 collected from fluid inclusions can then be analyzed. The gas phase was extracted and
106 measured after crushing 20 to 30 gr of rock sample under vacuum.

107 Thermodynamic modelling was performed using the Deep Earth Water (DEW) Model
108 (Huang et al., 2019; Sverjensky et al., 2014) and the EQ3/EQ6 software (Wolery and Jarek,
109 2003) with a modified Berman database (Berman, 1988). The speciation-solubility code EQ3
110 was used to calculate the composition of a fluid in equilibrium with a given mineral
111 assemblage at fixed $f\text{O}_2$, P and T, and in the K-Na-Ca-Mg-Fe-Al-Si-O-H-C-N-S-Cl system. The
112 reaction path modeling code EQ6 was used to model the irreversible reaction between 1kg
113 of fluid as derived from EQ3 (see section 3.5 for details on different buffering assemblages),
114 and a given number of moles of minerals constituting a rock reservoir and determining an

115 initial fluid/rock (F/R) ratio for each calculation. The chosen EQ6 mineral assemblage
116 corresponds to a dunite with mineral modal proportions comparable with the most
117 preserved study samples and consisting of 92% olivine (forsterite 90%, fayalite 10%), 5.4%
118 orthopyroxene (enstatite 90%, ferrosilite 10%), 2.5% clinopyroxene (diopside 90%,
119 hedenbergite 10%) and 0.1% spinel. Additional details regarding the modeling strategy are
120 presented in Section 3.5.

121 **3. Sample description and mineral chemistry**

122 In this section, we present the petrography, microstructures and mineral chemistry of
123 samples collected in the BMC (Fig. 2). The selected samples range from weakly
124 serpentinized dunite (V18-2a and V18-2b) to partially serpentinized dunite including layers
125 of boudinaged meta-pyroxenite (V18-3a and V18-3b), to fully serpentinized peridotite (V18-
126 B3). One sample of rodingites consisting of carbonates, garnet, epidote and chlorite is also
127 presented.

128 ***Microstructural characterization***

129 Sample V18-2a (least serpentinized dunite) consists of olivine (~80 vol.%), antigorite (~10
130 vol.%), Cr-spinel (>5 vol.%), magnetite (<5 vol.%), chlorite (<1 vol.%), sulphides (<1 vol.%),
131 and alloys (<1 vol.%) determined from visual estimate in thin section. Primary olivine forms
132 crystals ranging in size from 0.25 to 1 mm (Fig. 3A) partially replaced by antigorite, as
133 identified by MicroRaman spectroscopy (Fig. 4), along fractures (Fig. 3A-C). Antigorite is
134 present as elongated crystals, up to 200 μm in length, which statically overgrew the olivine
135 (Fig. 3C). Magnetite is present in three microstructural domains: as large, millimeter scale

136 crystals rimming chromite relicts, as grains of $\sim 50 \mu\text{m}$, and as millimeter scale crystals in
137 antigorite veins. Chlorite is found, together with magnetite, around Cr-spinel relicts (Fig. 3B).

138 Sample V18-2b (serpentinized dunite) consists of antigorite ($\sim 40 \text{ vol.}\%$), olivine ($\sim 40 \text{ vol.}\%$,
139 including primary and metamorphic olivine), magnetite ($>5 \text{ vol.}\%$), chlorite ($>5 \text{ vol.}\%$),
140 brucite ($<5 \text{ vol.}\%$), and alloys ($<1 \text{ vol.}\%$). The structure is similar to V18-2a, but in this case
141 the extent of serpentinization is higher. SEM backscattered-electron imaging reveals the
142 presence of a second generation of olivine, hereafter metamorphic olivine (see Section 4.2
143 for discussion) growing in two different sites: epitaxially on the primary olivine and replacing
144 former orthopyroxene (Fig. 5A-B). Striped zoning is observed in primary olivine (Fig. 5A), as
145 described in Plümper et al., 2012a, alternating thin forsterite-richer and forsterite-poorer
146 olivine composition. The initial presence of orthopyroxene in the rock is inferred based on
147 the presence of clinopyroxene exsolutions preserved in metamorphic olivine-rich
148 pseudomorphs (Fig. 3D and 5B). Antigorite is present as elongated (0.5 mm in length)
149 crystals and as fine-grained aggregates in the matrix. The elongated antigorite crystals are
150 chemically zoned, with bright core and dark rim in backscattered electron imaging (Fig. 5A).
151 Raman spectra of both generations exhibit the characteristic 1043 cm^{-1} band of antigorite,
152 whereas the main OH stretching is at 3664 cm^{-1} in the bright core and at 3673 cm^{-1} in the
153 dark rim (Fig. 4C), both consistent with antigorite Raman features. The higher Raman shift of
154 the dark rim may be linked to variation of pressure condition (Auzende et al., 2004). The
155 dark antigorite generation appears the same forming the fine-grained aggregates. Only the
156 dark generation was observed in contact with primary and metamorphic olivine (Fig. 5A).
157 Magnetite is more abundant relative to sample V18-2a. Brucite was identified by SEM
158 EPMA, and Raman (Fig. 4B) in veins, sometimes associated to metamorphic olivine (Fig. 5C).

159 Alloys and sulphides are present in association with antigorite and are locally associated to
160 magnetite (Fig. 5D).

161 Samples V18-3a and 3b are from a boudinaged layer of clinopyroxenite included in an
162 intensely serpentinized dunite (Fig. 3E-G). The mineral assemblage and microstructures of
163 the serpentinized dunite part of the sample is similar to sample V18-2b, yet more intensely
164 serpentinized. The primary clinopyroxene is fully replaced by diopside aggregates in both
165 the clinopyroxenite layer and the host dunite. The primary clinopyroxene sites in this sample
166 are slightly different from the serpentinized dunite, with less abundant magnetite and
167 characteristic fan-shaped diopside aggregates in the former compared to the latter.
168 Metamorphic olivine is present at the rim of primary clinopyroxene and along its cleavages,
169 together with antigorite (Fig. 5E-F). In the latter case, metamorphic olivine is localized along
170 thin arrays encircled by antigorite (Fig. 5F). Antigorite shows the same chemical zoning as
171 observed in the dunite, with brighter cores and darker rims in backscatter electron imaging
172 (Fig. 5G). Backscattered electron imaging reveals that the dark antigorite shows similar
173 overgrowth microstructural relationships with both primary and metamorphic olivine (Fig.
174 5E). The microstructures reflect either equilibrium between antigorite and the two olivine
175 generations, or overgrowth of both olivine generations by the antigorite. Considering that
176 the amount of primary olivine strongly decreases in favour of antigorite in several samples,
177 which suggests serpentinization of the primary olivine, it is suggested that the dark
178 antigorite generation formed after the growth of metamorphic olivine. It is possible, even
179 though the microstructures could not confirm it, that the first antigorite generation grew
180 prior to or together with the metamorphic olivine. Magnetite is present in four different
181 structural sites: as arrays of $\sim 50 \mu\text{m}$ size crystals scattered in the rock, as trails of $\sim 50 \mu\text{m}$

182 crystals in primary olivine and clinopyroxene pseudomorphoses, as aggregates rimming the
183 primary Cr-spinel, and as millimeter scale aggregates along discordant veins. The Cr-spinel
184 sites are characterized by three different layers: a rather preserved core, a mantle of
185 ferritchromite, and a rim of magnetite (Fig. 5E; see Section 4.2).

186 Sample V18-B3 is a fully serpentinized peridotite. The matrix is composed of a mixture of
187 antigorite and chrysotile (identified by MicroRaman) with magnetite. Brucite is observed
188 replacing pyroxene sites and is associated with magnetite and/or metamorphic olivine (Fig.
189 3H and 5H). Based on the microstructural observations on sample V18-2b, these
190 pseudomorphoses are interpreted as former orthopyroxene crystals replaced by
191 metamorphic olivine and successively hydrated to form serpentine + brucite ± magnetite.

192 **3.1. Mineral chemistry**

193 Primary olivine has Mg# of 0.91-0.92 [$Mg\# = Mg/(Fe+Mg)$], whereas metamorphic olivine is
194 enriched in Mg (Mg# of 0.95) (Table 1, Fig. 6). The Mn# [$Mn\# = Mn/(Mn+Fe+Ni)$] of
195 metamorphic olivine (0.0040 ± 0.0006) is much higher than primary olivine (0.0015 ± 0.0005).
196 Metamorphic olivine analyses in sample V18-B3 show slightly lower Mg# and higher Mn#
197 content relative to metamorphic olivine from other samples. Metamorphic olivine rimming
198 the primary orthopyroxene sites in sample V18-3a has higher CaO content (0.25 wt.%)
199 compared to the metamorphic olivine overgrowing primary olivine in V18-2b (0.02 wt.%).
200 The NiO content of primary olivine (0.38 to 0.49 wt.%) and metamorphic olivine (0.39 to
201 0.46 wt.%) are similar.

202 The incorporation of Mn in olivine appears to be characteristic of metamorphic olivine from
203 several localities worldwide regardless of the olivine formation conditions (dehydration vs.

204 hydration) (Fig. 6) (e.g., Frost and Beard, 2007; Majumdar et al., 2016; Nozaka, 2018, 2003).
205 The Mg# of metamorphic olivine relative to primary olivine may depend upon several
206 parameters such as the stability of different Fe-bearing minerals, the Fe partitioning among
207 them, and P-T and redox conditions. An increase in Mg# (and MnO) in metamorphic olivine
208 relative to primary olivine has been observed in inferred mantle wedge peridotites
209 recording HP serpentinization (Dandar et al., 2019; Guillot et al., 2000). Our data, together
210 with previous work, indicate that iron was not preferentially partitioned into olivine during
211 HT serpentinization (Evans, 2010) but other Fe-bearing minerals, such as serpentine and
212 magnetite, could form. Plümper et al., 2012a report striped Mg# zoning similar to the BMC
213 samples in hydrated supra-subduction mantle rocks as the result of chemical interaction
214 during antigorite serpentinization at high temperature conditions. Metamorphic olivine
215 formed through prograde antigorite + brucite dehydration shows either lower or higher
216 Mg# compared to mantle olivine (Arai et al., 2012; Debret et al., 2013; Iyer et al., 2008;
217 Kempf and Hermann, 2018; Nozaka, 2018; Plümper et al., 2012b; Scambelluri et al., 1995;
218 Shen et al., 2015)(Fig. 6).

219 In samples V18-2b and V18-3a, the core of individual, elongated antigorite crystals exhibits
220 higher FeO (1.6 to 2.6 wt.% [Mg# 0.94-0.96]), Al₂O₃ (1.45-1.77 wt.%) [Mg# =Mg/(Mg+ΣFe)],
221 and Cr₂O₃ (0.25-0.61 wt.%) than the rim (1.2-1.35 wt.% [Mg# 0.97], 0.47-0.52 wt.%, 0.10-
222 0.13 wt.%, respectively)(Table 1). In both samples, unzoned matrix antigorite has a
223 composition equivalent to the rim of the elongated antigorite crystals. The Mn# [Mn# =
224 Mn/(Mn+Fe+Ni)] of antigorite is 0.0006 (±0.0004).

225 The preserved spinel core in sample V18-3a has Cr# [Cr/(Cr+Al)] of 0.79 ±0.001 (Table 2).

226 The mantle overgrowing the primary spinel has a ferritchromite mantle of Cr-magnetite

227 with a Cr# of 0.91 and higher MnO relative to the core. The magnetite rims with no Al₂O₃,
228 but high Cr₂O₃ (1.87 ±1.16 wt.%). The composition of the disseminated and vein magnetite
229 differs from magnetite found in the spinel sites, with very little Cr₂O₃ (Table 2).

230 Diopside in sample V18-3a has a Mg number [Mg# =Mg/(Mg+Fe)] of 0.98. Chlorite in V18-2b
231 and V18-3a has an Mg# [Mg# =Mg/(Mg+ΣFe)] of 0.95, and Cr₂O₃ up to 4.07 wt.% (Table 1).

232 Brucite has up to 3 wt.% FeO (as total Fe), Mg# [Mg# =Mg/(Mg+Fe)] of 0.97 (Table 2). Alloys
233 and sulfides are Ni rich, with various amounts of S, Fe and trace amounts of Pb, Cu, et Co
234 (Table 3). Alloys mainly consist of Cu-bearing FeNi alloy (taenite) (Table 3). Sulphides include
235 Ni, Cu, and Fe sulphides. Only heazlewoodite (NiS) was analysed whereas for other
236 sulphides proper analyses could not be obtain owing to the small grain sizes.

237 **3.2. Fluid inclusion analysis**

238 Primary olivine in all samples is rich in fluid inclusions forming secondary trails (Fig. 7). The
239 fluid inclusion trails are confined within individual crystals and show two alternative
240 structural relationships relative to the antigorite veins, being either cut by them (Fig. 7A) or
241 propagating from them (Fig. 7B-C). These patterns suggest a secondary fluid inclusions
242 entrapment during the antigorite serpentinization event, which appear the dominant
243 hydration event in the rock.

244 Fluid inclusions of 0.5 to 5 µm in size were analyzed and exhibit rounded to elongated
245 shapes (Fig. 7D-E). Optical microscope observations at room conditions suggest that the
246 fluid inclusions are either single-phase and gaseous, or bi-phase with solid and gas.
247 MicroRaman spectra of fluid inclusions are presented in Fig. 8. The spectra show the

248 presence of marked CH₄ bands (2912 cm⁻¹), as well as N₂ (2327 cm⁻¹), NH₃ (3324 cm⁻¹), S-
249 H/H₂S (2575 cm⁻¹). Free H₂O in the fluid inclusions was not detected by MicroRaman.
250 However, the presence of tiny amounts of free H₂O in the fluid inclusions —undetectable by
251 MicroRaman at room conditions— cannot be excluded (Berkesi et al., 2009; Lamadrid et al.,
252 2017).

253 The molar fraction of gas in the gas mixture was estimated using the Raman scattering
254 cross-section and the instrumental efficiency of each species. Using equation presented in
255 Frezzotti *et al.*, 2012, we obtain the following molar proportion: CH₄ = 92±6%, N₂ = 6±5%,
256 H₂S = 1±1% and NH₃ = 1±2% for the mean composition of twenty inclusions in olivine from
257 all samples (supplementary material 1). Composition within the same inclusion trail show
258 molar fractionation variation smaller than 1% but different trail within the same crystal can
259 exhibit up to 10% of molar fraction of CH₄ and could reflect fluid heterogeneity.
260 Alternatively, this effect can be the result of different crystal orientation during data
261 acquisition (Caumon et al., 2019). No clear pattern was observed linked to relationship
262 between inclusion trails and antigorite veinlets.

263 Solid phases were identified in large (2-5 μm) fluid inclusions. MicroRaman analysis revealed
264 the presence of lizardite and brucite but no magnetite was detected. Some inclusions
265 contain graphite as a solid phase in the inclusion in addition (Fig. 7F and Fig. 8B). The only
266 sporadic presence of graphite in the fluid inclusions, and in particular in inclusions resulting
267 from necking processes, suggest that this mineral precipitated as a result of local
268 respeciation of the fluid inclusions, such as post entrapment host-inclusion reaction with the
269 inclusion wall and resulting respeciation of the fluid inclusion composition (Cesare, 1995).
270 This feature is also suggested by the presence of hydrous phases in the inclusions, which

271 indicates interaction of the inclusion fluid with the host olivine. However, the presence of
272 step-daughter minerals in the inclusion is not systematic, suggesting that the initial fluid was
273 already rich in CH₄ (-N₂-NH₃-H₂S) at the time of trapping, and that the reduced fluid species
274 did not form only inside the fluid inclusions.

275 **3.3. Rodingites**

276 Rodingites have been identified inside the BMC and consist of garnet, diopside, epidote,
277 carbonate ± graphite. While not being the focus of this study, the carbonate in the
278 rodingites has abundant fluid inclusions. Fluid inclusions exhibit negative crystal shape and
279 are single-phase gaseous at room conditions. The composition of the carbonate-hosted fluid
280 inclusions, as revealed by Raman spectroscopy, is essentially CH₄ and N₂. The analyses of the
281 collected Raman spectra in carbonates (see section 4.3) yield molar fractions of N₂ = 67±4%,
282 CH₄ = 33±4% on four different inclusions.

283 **3.4. Thermodynamic modelling**

284 Thermodynamic calculations were performed in order to constrain the mineralogical, fluid
285 and redox evolution of the HP serpentinization. The calculations were done at temperatures
286 consistent with the peak metamorphic conditions estimated for the BMC, i.e., 400 °C to 500
287 °C and 1 GPa (Honsberger, 2015; Laird et al., 1993), and for different F/R ratios (from 0.5 to
288 100). The selected partially serpentinized samples are embedded in strongly serpentinized
289 rocks and, in turn, are included in metasedimentary rocks. For this reason, either ultramafic
290 or metasedimentary were considered to calculate the EQ3 fluid compositions and as
291 possible fluid sources responsible for the metamorphic serpentinization of the BMC rocks.
292 The interaction of EQ3 fluids equilibrated with metasedimentary sources or Si-rich

293 ultramafic sources (e.g. steatite) with the EQ6 dunitic assemblage (cf. Section 2), however,
294 resulted in mineral assemblages inconsistent with the natural samples (Supplementary
295 material 2). For this reason, in the following are presented in detail only the results obtained
296 for EQ3 fluid compositions equilibrated with an ultramafic assemblage consisting of
297 antigorite + magnetite + brucite + chlorite + olivine. The fO_2 of the infiltrating fluid was set
298 at the quartz-fayalite-magnetite (QFM) buffer. Figure 10 shows the mineralogical evolution
299 as a function of reaction progress at 450 °C and 1GPa for a F/R ratio of 1. The model
300 reaction proceeds with progressive transformation of, from the first to the last reacting
301 mineral, mantle spinel, clinopyroxene, orthopyroxene, and olivine. Magnetite starts to form
302 during the early stages of the reaction along with chlorite in response to spinel
303 consumption. Reaction of mantle pyroxenes marks the precipitation of metamorphic
304 clinopyroxene (diopside 93%, hedenbergite 3.35% and clino-enstatite 3.65%), metamorphic
305 olivine, antigorite, and additional magnetite. The late formation of antigorite marks the
306 partial consumption of metamorphic olivine and a decrease in its Mg#, from Mg# 0.90 to
307 Mg# 0.83. These patterns reflect the microstructural features observed in the natural
308 samples. For example, spinel appears intensely replaced by chlorite in rather
309 unserpentinized portions of the rock (Fig. 9A). Similarly, mantle olivine adjacent to fully
310 replaced mantle pyroxenes is commonly little affected by the serpentinization. Both mantle
311 and metamorphic olivine in the natural samples appear texturally replaced by antigorite, as
312 also suggested by the modelling while approaching reaction completion. With the chosen
313 bulk composition and used thermodynamic data set, the formation of antigorite is limited to
314 $T < 470$ °C. The obtained antigorite stability field may be dependent on the absence of iron
315 in the antigorite thermodynamic model considered in the database. The evolution of
316 dissolved elements in the fluid (Fig. 9B) indicates that the total Mg content decreases during

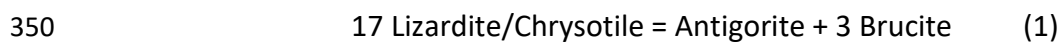
317 the reaction, while Si and Ca increase. The fO_2 decreases progressively during the reaction
318 progress, with a steep decrease during the formation of antigorite down to $\Delta\text{Log QFM} = -1.2$
319 (Fig. 9D). Methane, initially about 1 order of magnitude less concentrated than CO_2 in the
320 reacting fluid, becomes a dominant species at reaction completion (about 1 order of
321 magnitude more concentrated than CO_2). Nevertheless, variations of parameters such as
322 F/R ratio, mineralogy, or temperature, were found to affect the proportion of CH_4 and CO_2 .
323 As an example, increasing the modal proportion of either orthopyroxene or clinopyroxene in
324 the initial rock or decreasing the F/R ratio appears to favor a higher proportion of CH_4 in the
325 fluid in respect to CO_2 . The model predicts high relative concentration of H_2 in the fluids,
326 however H_2 was not detected in natural samples by micro-Raman spectroscopy. This may be
327 due to leakage of H_2 from the inclusions or internal respeciation. Sulphur and nitrogen
328 speciation were also assessed, with HS^- and H_2S and NH_3 being the dominant Sulphur
329 species relative to HSO_4^- and N_2 and NH_4^+ , respectively (Fig. 9C).

330 **4. Discussion**

331 **4.1. Patterns and timing of serpentinization**

332 The timing of serpentinization of slab-derived, exhumed HP serpentinized rocks can span
333 (sub)seafloor or trench conditions prior to subduction, prograde hydration during
334 subduction, or retrograde hydration during exhumation. The BMC complex has been
335 interpreted as a fragment of subducted Iapetus lithosphere, and therefore may have
336 recorded different stages of serpentinization. Although the possibility of at least some
337 (sub)seafloor serpentinization prior to the Taconic subduction cannot be excluded, our data
338 cannot provide any proof of such a pre-subduction event and, instead, suggest a main
339 hydration event at HP-HT conditions in the subduction zone.

340 Besides late chrysotile veinlets, antigorite is the only serpentine mineral identified in the
341 BMC rocks. Although formation of antigorite may occur in a wide range of P-T conditions
342 also as a function of chemical parameters such as the silica activity (Rouméjon et al., 2019),
343 serpentinites dominated by antigorite are generally referred to the HT temperature part of
344 the serpentine stability field, generally above ~300-400 °C (e.g., Evans, 2004; Schwartz et
345 al., 2013). In most subduction zone settings, these conditions also correspond to relatively
346 HP conditions above 1 GPa. However, the presence of antigorite does not necessarily imply
347 the serpentinization event to have happened at HP-HT conditions because it could also have
348 formed as a result of the prograde transformation of lizardite or chrysotile following the
349 reaction:



351 Nevertheless, several lines of evidence indicate that the BMC rocks recorded a stage of HP-
352 HT serpentinization. As a first general consideration, the presence of fresh mantle
353 assemblages throughout the complex (Chidester *et al.*, 1978; this study) represents a
354 suitable condition to promote HP-HT serpentinization in the subduction zone, if aqueous
355 fluids are available. Such a process has already been proposed in other HP ultramafic
356 massifs preserving fresh mantle assemblages (e.g.: Dandar et al., 2019; Früh-Green et al.,
357 2004; Nozaka, 2018; Scambelluri and Tonarini, 2012; Vitale Brovarone et al., 2020, 2017).
358 The BMC rocks provides evidence for such a HP hydration event. Figure 10 summarizes the
359 proposed fluid-rock evolution of the BMC rocks as inferred from the studied samples. The
360 first indication of serpentinization (stage I in Fig. 10) is suggested by the growth of elongated
361 metamorphic olivine on the primary clinopyroxene sites (Fig. 5G), which suggests the former
362 presence of serpentine blades overgrowing the primary clinopyroxene. The selective growth

363 of serpentine at the expense of clinopyroxene rather than primary olivine places this
364 hypothetical event at HT conditions (Klein et al., 2013) and possibly in the antigorite stability
365 field (Fig. 11). Metamorphic olivine is most commonly interpreted to form in response of
366 serpentine dehydration during prograde metamorphism (Plümper et al., 2017; Scambelluri
367 et al., 1991). Figure 11 provides a compilation of generic antigorite dehydration reactions
368 leading to the formation of metamorphic olivine. Although these reactions may be shifted to
369 higher or lower temperatures depending on compositional features (e.g., Padròn-Navarta et
370 al., 2013), the peak metamorphic conditions proposed for the BMC (0.9-1.3 GPa and 520 °C)
371 are consistent with the first olivine-forming reaction involving antigorite + brucite as
372 reactants. Moreover, several studies have shown that olivine can form at T conditions lower
373 than the reactions shown in Figure 11 as a result of local bulk compositional features
374 (Plümper et al., 2017). Alternatively, metamorphic olivine after orthopyroxene may also
375 have formed in response to hydration rather than dehydration reactions, as already
376 proposed for serpentized mantle wedge rocks (Dandar et al., 2019) following the reaction:

377 Orthopyroxene + 0.46 Water + 0.35 Mg²⁺=

378 0.59 M-olivine + 0.06 Antigorite + 0.29 Silica + 0.7 H⁺ (2)

379 The thermodynamic modeling results supports this reaction, as suggested by the decrease
380 of total dissolved Mg and the increase of Si in the fluid during the early growth of
381 metamorphic olivine (Fig. 9A and 10B). In either case (hydration or dehydration), the
382 amount of serpentization predating the formation of metamorphic olivine must have been
383 very low and, if any, related to a HT event.

384 The second, more robustly constrained stage of transformation (stage II in Fig. 10) is
385 characterized by the formation of metamorphic olivine after primary orthopyroxene, and as

386 rim around primary clinopyroxene (now recrystallized into diopside). This reaction was
387 observed in rocks containing rather undisturbed primary olivine, which again point to HT
388 serpentinization conditions (Klein et al., 2013). The partial preservation of clinopyroxene
389 exsolution lamellae inside metamorphic olivine pseudomorphic on orthopyroxene may
390 suggest nearly isovolumetric replacement during this event (Plümper et al., 2012b; Viti et
391 al., 2005). The thermodynamic modeling results suggest that, at 450 °C and 1 GPa, a
392 transient antigorite generation may have formed together with metamorphic olivine early in
393 the fluid-rock interaction, along with spinel breakdown. The Al-Cr-rich antigorite cores
394 (Atg1) observed in the studied samples may testify to this transient antigorite formation.
395 Measured distribution coefficients between antigorite and olivine also suggest different
396 stages of antigorite formation (Supplementary materials 3). The third stage (stage III in Fig.
397 10) is characterized by the growth of a matrix antigorite (Atg2) at the expense of both
398 primary and metamorphic olivine. This event may mark either retrograde hydration along
399 the exhumation path of the BMC, or the progression of the fluid-rock interaction. As
400 indicated by the thermodynamic modeling results, a second antigorite generation is
401 expected to form at 450 °C and 1 GPa after the precipitation of metamorphic olivine (Fig.
402 9A).

403 The fourth stage of serpentinization (IV in Fig. 10) is characterized by the complete
404 serpentinization of primary olivine and partial to full serpentinization of metamorphic
405 olivine. The partial preservation of metamorphic olivine after orthopyroxene in sample free
406 of any primary olivine relict indicates that the largest event of serpentinization of the BMC
407 rocks took place after the formation of metamorphic olivine. The presence of both
408 antigorite and chrysotile + brucite at the expense of metamorphic olivine after

409 orthopyroxene suggests that this event protracted during the cooling of the BMC
410 metamorphic path to temperatures lower than 400 °C (Fig. 11).

411 In summary, based on the collected petrographic and thermodynamic data, the dominant
412 serpentinization event observed in the BMC complex is interpreted to have taken place in
413 the Taconic subduction zone.

414

415 **4.2. Timing of fluid inclusion formation and origin of CH₄**

416 **4.2.1. Timing of fluid inclusion entrapment**

417 Fluid inclusions in the BMC ultramafic and related metasomatic rocks contain reduced fluid
418 species such as CH₄, NH₃, and H₂S. The timing of fluid inclusion formation, as well as the
419 origin of their reduced speciation, is discussed in this section.

420 Reduced fluids have been found to form in ultramafic systems in a wide range of geologic
421 conditions spanning mid-ocean ridges, obducted ophiolitic massifs, orogenic peridotite
422 bodies, in subduction, and in the upper mantle (Andréani et al., 2007; Etiope et al., 2011;
423 Schrenk et al., 2013; Vitale Brovarone et al., 2020). In the BMC rocks, the fluid inclusions
424 may have formed in three different stages of the evolution of the massif and corresponding
425 to three different geodynamic settings: (i) in the mantle prior to the formation of the
426 Iapetus Ocean, (ii) during the (sub)seafloor evolution prior to subduction, and (iii) in the
427 subduction zone.

428 A primary mantle origin can be ruled out because the observed fluid inclusions occur as
429 secondary trails propagating from the antigorite veinlets crossing olivine crystal. A
430 (sub)seafloor origin would match the identification of CH₄-rich fluid inclusions in oceanic
431 peridotite (Cannat et al., 2010; Holm and Charlou, 2001). However, in this case, the fluid

432 inclusions would have been preserved during prograde metamorphism to at least 520 °C
433 and 1 GPa, which is unlikely (Touret, 2001). Moreover, the BMC fluid inclusions are rich in N
434 species (NH₃, N₂), which seems to be an uncommon feature in fluid inclusions from oceanic
435 peridotites (Grozeva et al., 2020; Klein et al., 2019). Instead, N-rich, NH₃-bearing fluid
436 inclusions have been recently documented in CH₄-rich fluid inclusions in HP serpentized
437 peridotites from the Alpine belt and proposed to represent a distinctive feature of
438 subduction zone serpentizing fluids relative to mantle or (sub)seafloor fluids, especially in
439 the presence of metasediment-derived fluids (Vitale Brovarone et al., 2020). Considering the
440 microstructural and petrologic features discussed in Section 5.1, and the abundance of N
441 species, a metamorphic origin in the Taconic subduction is proposed for the studied fluid
442 inclusions.

443 The formation of lizardite and brucite as step-daughter minerals inside the fluid inclusions
444 can be interpreted (1) as a prograde, pre-antigorite inclusion-host interactions, (2) as a
445 retrograde reequilibration of antigorite during cooling of the BMC below ~400 °C with
446 excess brucite (Reaction 1), or (3) as a retrograde host-inclusion interaction below ~400 °C
447 (Fig. 11). Excluding lizardite (meta)stability due to local equilibrium/kinetic features or faster
448 antigorite-lizardite conversion in the inclusions relative to the host rock, we interpret the
449 formation of step-daughter lizardite and brucite as a retrograde host-inclusion interaction.
450 Similar interpretations have been proposed for analogous inclusions from Alpine belt (Vitale
451 Brovarone et al., 2020).

452

453 **4.2.2. Origin of the reducing potential and fluid sources**

454 Another important question is the origin the identified reduced fluids species. In particular,
455 several studies over the last decades have investigated the biotic or abiotic origin of
456 geological CH₄ and associated reduced fluid species (Etiope et al., 2011; Etiope and
457 Sherwood Lollar, 2013; McCollom, 2016; Ménez et al., 2018). Ultramafic systems are
458 generally favorable environments for the genesis of abiotic CH₄ (Section 5.2.1), but other
459 interpretations are also possible.

460 For example, the abundance of metasedimentary rocks in the study area may have
461 promoted the formation of thermogenic gases during their prograde evolution. This
462 hypothesis would be also consistent with the production of NH₃ through degassing of
463 organic matter in metasedimentary rocks (Bebout and Fogel, 1992; Li et al., 2009). Biotic
464 processes, including thermogenic gas formation, typically show very light $\delta^{13}\text{C}_{\text{CH}_4}$ signatures
465 (Etiope and Sherwood Lollar, 2013), whereas abiotic processes generally result in much
466 heavier $\delta^{13}\text{C}_{\text{CH}_4}$ (~ -50 to 0‰) (Etiope and Sherwood Lollar, 2013). In order to test this
467 hypothesis, we performed reconnaissance $\delta^{13}\text{C}$ analysis of CH₄ in the fluid inclusions
468 (Boutier et al., in preparation). The analyses yielded $\delta^{13}\text{C}$ in the range of -14‰ ($\pm 2\text{‰}$) for
469 inclusions in olivine, and -13‰ ($\pm 1\text{‰}$) for carbonate-hosted methane-rich inclusions from
470 the rodingites. Even though these results must be considered as preliminary test data, they
471 seem to exclude the possibility of a pure thermogenic source.

472 Following the hypothesis of an abiotic origin, two possible mechanisms for the formation of
473 CH₄ can be considered with either external or internal sources, respectively. External
474 sources correspond to the infiltration of CH₄ and other reduced species formed abiotically in
475 other geological reservoirs. A deep mantle origin for the reduced fluids detected in the BMC
476 fluid inclusions appears unlikely if the syn-inclusion, water-rich nature of the serpentinizing

477 fluid is considered. The metasedimentary formations adjacent to the BMC contain
478 carbonate, graphitic carbon, sulphides, and phyllosilicates as potential sources of the C-N-S-
479 H fluid identified in the fluid inclusions. Previous studies along the Appalachian belt have
480 reported evidence of carbon mobilization from these metasedimentary formations or their
481 along-strike equivalents. For example, Zhang *et al.*, 2018 documented metamorphic loss of
482 isotopically light carbon from the Wepawaug schists, Connecticut. The possibility for these
483 carbonate-bearing formations to generate strongly reduced fluids abiotically is not obvious
484 —for reference, water-maximum conditions in graphite-saturated fluids contain roughly
485 equal proportions of CH₄ and CO₂ (Connolly, 1995; Holloway, 1984) —. Nevertheless,
486 evidence for the circulation of CH₄-rich fluids in equivalent formations in East Central
487 Vermont and New Hampshire has been reported (Evans *et al.*, 2002; Rumble III and Hoering,
488 1986). Nevertheless, most petrological studies focusing on New England metasediment-
489 derived fluids point to more oxidized, CO₂-dominated aqueous fluids (Ferry, 2007;
490 Penniston-Dorland and Ferry, 2006). Alternative external sources of reduced fluids would
491 require unidentified processes, including mixing of different carbon reservoirs, or water-
492 rock interactions equivalent to those that took place in the BMC.

493 A reducing potential internal to the BMC, and in particular the hydroxylation of fresh mantle
494 peridotites during the Taconic subduction, appears the most likely interpretation for the
495 genesis of the identified reduced fluid species. The presence of Fe-Ni alloys in the BMC
496 partially serpentinized peridotites indicates that the rock recorded reducing conditions, as
497 already observed in several oceanic and ophiolitic, and some subduction zone serpentinites
498 (Evans *et al.*, 2017; Frost, 1985; Klein and Bach, 2009; Vitale Brovarone *et al.*, 2020).
499 Alternatively, reducing fluids may also be produced by serpentinite dehydration (Evans and
500 Frost, 2021; Piccoli *et al.*, 2019). However, the small amount of metamorphic olivine

501 observed in the BMC rocks seems to contradict this hypothesis. High-pressure syn-
502 serpentization reducing conditions are also suggested by the thermodynamic modelling
503 results presented in this study, which indicates f_{O_2} values as low as $-3.2 \Delta QFM$ at $400^\circ C$
504 and 1 GPa to $-1.2 \Delta QFM$ at $450^\circ C$ and 1 GPa, and the formation of significant amounts of H_2
505 in the fluid (Fig. 9D). The interaction of this H_2 with dissolved carbon, nitrogen, and Sulphur
506 species present in the serpentizing fluid, could have favored the formation of CH_4 , H_2S , and
507 NH_3 from more oxidized species. For NH_3 , the modelling also indicates that this species is
508 already the dominant N species in the infiltrating fluid buffered at QFM. This feature
509 suggests that the N_2 detected in the fluid is most likely formed through post-entrapment
510 respeciation of NH_3 , unless the serpentizing fluid was more oxidized than QFM. The
511 absence of detectable H_2O in the fluid inclusions is interpreted to result from host-inclusion
512 interaction and formation of step-daughter lizardite and brucite, or by the preferential
513 entrapment of immiscible reduced gases relative to aqueous fluids (Huang et al., 2017;
514 Vitale Brovarone et al., 2017). The absence of residual H_2 in the fluid inclusions may be
515 explained by the much faster diffusion H_2 relative to other fluid species through the host
516 olivine, or by selective leakage.

517 The most plausible sources of serpentizing fluid were the metasedimentary formations
518 surrounding the BMC complex. These rock types host substantial amounts of subducted
519 carbon, sulphur, and nitrogen (Bebout and Fogel, 1992; Evans et al., 2014; Kelemen and
520 Manning, 2015; Plank and Manning, 2019). An ultramafic source internal to the BMC would
521 not be consistent with the general retention of N during prograde metamorphism and
522 dehydration of serpentinites (Halama et al., 2014). The hypothesis of a metasediment-
523 derived serpentizing fluid was also suggested by previous oxygen and hydrogen isotopic
524 data on antigorite from the BMC complex (Wenner and Taylor, 1974, 1971). Moreover, the

525 authors proposed antigorite-magnetite equilibration T in the range of 220-460 °C, which is
526 consistent with the prograde P-T of the BMC (Fig. 11). This supports the interpretation of a
527 subduction-related serpentinization related to the infiltration of metasedimentary-derived
528 fluids in a rather dry ultramafic body.

529 **5. Conclusions**

530 Mineralogical, microstructural, and fluid inclusion study of variably serpentinized dunite
531 from the Belvidere Mountain Complex, Appalachian belt, Northern Vermont, provides
532 insight into the process of high-pressure serpentinization in subduction zone and the related
533 fluid-rock redox patterns. Although the BMC underwent a complex tectonic evolution
534 potentially characterized by multiple stages of hydration from the (sub)seafloor to
535 subduction and exhumation, the collected data point to a major event of high-pressure
536 serpentinization that took place in the Appalachian subduction zone. Metamorphic olivine in
537 the BMC serpentinized peridotite is interpreted as the product of rock hydration rather than
538 dehydration, linked to the high-pressure serpentinization event. Our data support the
539 hypothesis that the methane observed in olivine-hosted secondary fluid inclusions is
540 genetically linked to serpentinization in the antigorite stability field consistent with the high-
541 pressure portion of the prograde or retrograde P-T path of the BMC. This favors an abiotic
542 origin for this methane, even though a biotic origin for the C source cannot be excluded. The
543 C- and N-rich composition of fluid inclusions suggests a metasediment-derived origin for the
544 serpentinizing fluid. The high-pressure serpentinization and related abiotic methanogenesis
545 place the Belvidere mountain complex as a suitable proxy for the study of mantle wedge
546 serpentinization. This study confirms the importance of fluid mobility in deep seated

547 ultramafic body in subduction zones for the mobility of C, H, and N, and their implications
548 on large-scale geochemical cycling.

549 **6. Acknowledgments**

550 The authors wish to thank Mark Van Baalen for logistic support and fruitful discussion, and
551 Leslie white for fundamental support during the field work. J.C.M De Hoog is thanked for a
552 very constructive review on an earlier version of this article. AVB acknowledges a MIUR Rita
553 Levi Montalcini grant and a Richard Lounsbery Foundation grant. Simona Ferrando is
554 thanked for her helpful discussions and insights on fluid inclusions. IFP Energies Nouvelles
555 and its helpful personnel is thanked for its help in the acquisition on test isotopic data of
556 methane.

557

558 **Fig. 1:** A: *Simplified geological map of Vermont, modified from Hibbard et al., (2006).* B:
559 *Simplified bedrock geologic map of the Belvidere Mountain Complex and the surrounding*
560 *formations. Modified after Hibbard et al., (2006). Units description from Hibbard et al.,*
561 *(2006) and Gale, (2007).*

562 **Fig. 2:** A-B: *Photographs of the Belvidere serpentized peridotite in outcrop.* C: *Weakly*
563 *serpentized dunite (samples V18-2a and V18-2b).* D: *Serpentized dunite, with boudinaged*
564 *meta-gabbro (samples V18-3a and V18-3b).*

565 **Fig. 3:** A: *Photomicrograph of a partially serpentized dunite.* B: *Partial replacement of*
566 *primary chromian spinel by magnetite and chlorite.* C: *Partial replacement of olivine by*
567 *antigorite.* D: *Inferred primary orthopyroxene being pseudomorphically replaced by*
568 *metamorphic olivine. See also Figure 5B.* E: *Photomicrograph of a pyroxenite layer included*

569 *in the Belvidere peridotite. The photomicrograph shows radial diopside aggregate*
570 *pseudomorphic on primary clinopyroxene. Partially serpentinized olivine is also visible. F:*
571 *Magnetite-rich diopside pseudomorphosis on primary clinopyroxene. Note the growth of*
572 *metamorphic olivine at the rim of the clinopyroxene site. See Figure 5A for SEM-based*
573 *backscattered electron image. G: Metamorphic diopside replacing primary clinopyroxene. In*
574 *this case, note the growth of metamorphic olivine along fractures cutting the*
575 *pseudomorphosis. See Figure 5F for SEM-based backscattered electron image. H: Relict of*
576 *metamorphic olivine pseudomorphic on primary clinopyroxene. The metamorphic olivine is*
577 *then partially replaced by serpentine + brucite + magnetite. A-D: Sample V18-2b, E-G:*
578 *Sample V18-3a; H: sample V18-B3. P-Ol: primary olivine, M-Ol: metamorphic olivine, Atg:*
579 *antigorite, Chl: chlorite, Mgt: magnetite, Di: diopside, Chr: chromite, Br: brucite, Ctl:*
580 *chrysotile.*

581 **Fig. 4:** *Raman spectra of solid phases. A: Antigorite core (Atg1) and rim (Atg2) (see Fig. 5A).*
582 *B: Brucite.*

583 **Fig. 5:** *SEM-BSE images of samples V18-2b, V18-3a and V18-B3. A: Microstructural patterns*
584 *of serpentinization. Two generations of serpentine can be observed based on the BSE*
585 *contrast, a bright core (Atg1) and a dark rim (Atg2). Note also the striped zonation of*
586 *primary olivine and the formation of metamorphic olivine. B: Replacement of an inferred*
587 *primary orthopyroxene crystal by metamorphic olivine. The close-up shows the preservation*
588 *of clinopyroxene relicts interpreted as exsolutions inside the former orthopyroxene. C:*
589 *Formation of brucite at the expense of metamorphic olivine. D: Composite aggregate of Fe-*
590 *Ni and Fe-Cu-Ni alloys and Ni sulphide. E: Growth of metamorphic olivine around a diopside-*
591 *rich primary clinopyroxene pseudomorphosis. A primary chromina spinel partially converted*

592 into magnetite can also be observed. F: Metamorphic diopside replacing primary
593 clinopyroxene. Note the presence of antigorite + metamorphic olivine \pm magnetite along the
594 fractures. In this case, metamorphic olivine occupies the centre of the fractures and is not in
595 contact with diopside, whereas the metamorphic olivine rimming the primary clinopyroxene
596 site is in contact with it. G: Metamorphic olivine growing at the expense of metamorphic
597 diopside (former primary clinopyroxene). The microstructure suggests the former presence of
598 serpentine needles replacing the clinopyroxene and successively replaced by metamorphic
599 olivine. Both Atg1 and Atg2 antigorite generations are present. H: Relict of metamorphic
600 olivine formed at the expense of a primary orthopyroxene site in V18-3b. The metamorphic
601 olivine is partially converted into brucite + serpentine. P-Ol: primary olivine M-Ol:
602 metamorphic olivine Px: pyroxene Di: diopside Mtg: magnetite Chr: chromite Atg: antigorite
603 Br: brucite Ctl: chrysotile NiFeS: nickel and iron sulphite. The presence of antigorite was
604 confirmed by Raman spectroscopy.

605 **Fig. 6:** Mg# versus MnO (wt%) diagram showing the compositional variation of primary and
606 metamorphic olivine. The Mn-richest cluster of metamorphic olivine belongs to sample V18-
607 B3 (fully serpentinized peridotite). Background data from Arai et al., (2012); Dandar et al.,
608 (2019); Debret et al., (2013); Iyer et al., (2008); Nozaka, (2018); Plümper et al., (2012b);
609 Scambelluri et al., (1995); Shen et al., (2015).

610 **Fig. 7:** Photomicrographs of methane-rich fluid inclusion trails in olivine from sample V18-2a.
611 Black arrows indicate fluid inclusion trails. A: Inclusion trail being cut by antigorite veinlets.
612 B: Inclusion trail limited by antigorite veins. C: Secondary trail of fluid inclusions propagating
613 from an antigorite veinlet. D: Photomicrograph showing a fluid-inclusion-rich olivine
614 aggregate. E: Close up of the methane-rich fluid inclusions. F: Close up of a graphite bearing
615 fluid inclusion (red arrow), as confirmed by Raman spectroscopy in (Fig. 8B).

616 **Fig. 8:** Raman spectra of fluid inclusions and step-daughter solid phases. A: Inclusion
617 showing a marked CH₄ band and minor peaks of N₂, NH₃ and S-H bond. Lizardite and brucite
618 O-H bands are also observed. B: Graphite in fluid inclusions (see Fig. 6D). C: Methane-rich
619 fluid inclusion with a close up of O-H bonds of lizardite and brucite.

620 **Fig. 9:** Thermodynamic modelling of HP serpentinization of dunite and related mineralogical
621 and fluid evolution. A: Mineralogical evolution during serpentinization at 450 °C and 1 GPa.
622 B: Evolution of total dissolved elements in the fluid as a function of the reaction progress
623 presented in A. C: Evolution of the nitrogen and sulphur fluid speciation as a function of the
624 reaction progress presented in A. D: Evolution of the fO₂ and H₂, CH₄, and CO₂ concentrations
625 in the fluid as a function of the reaction progress presented in A.

626 **Fig. 10:** Reconstruction of the mineralogical evolution of the BMC partially serpentinized
627 peridotite. An early step of serpentinization is proposed based on the needle-like growth of
628 metamorphic olivine on primary clinopyroxene, suggesting the presence of serpentine prior
629 to the formation of metamorphic olivine. The successive growth of antigorite at the expense
630 of both primary and metamorphic olivine constrains the main serpentinization event to
631 metamorphic conditions. Finally, a late serpentinization event is proposed based on the
632 growth of brucite + antigorite + chrysotile on relict metamorphic. Chr : chromite, P-Ol :
633 primary olivine, M-Ol : metamorphic olivine, Opx : primary orthopyroxene, Cpx : primary
634 clinopyroxene, Chl : chlorite, Mgt : magnetite, Atg : antigorite, Di : diopside, Brc : brucite, Ctl
635 : chrysotile.

636 **Fig. 11:** Simplified stability field of serpentine type minerals and olivine, modified from
637 Guillot et al., (2015) (see references therein for details on the main reactions). The
638 retrograde P-T path of BMC from Honsberger, (2015) is also shown for reference. Atg :

639 *antigorite, Brc : brucite; Ctl : chrysotile; Ilm : ilmenite; Ol : olivine; Tlc : talc; Ticl : titanian*
640 *clinohumite. Diamond graphite transition from Day, (2012).*

641

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1 **Fig. 1:** A: Simplified geological map of Vermont, modified from Hibbard et al., (2006). B:
2 Simplified bedrock geologic map of the Belvidere Mountain Complex and the surrounding
3 formations. Modified after Hibbard et al., (2006). Units description from Hibbard et al., (2006)
4 and Gale, (2007).

5 **Fig. 2:** A-B: Photographs of the Belvidere serpentized peridotite in outcrop. C: Weakly
6 serpentized dunite (samples V18-2a and V18-2b). D: Serpentized dunite, with boudinaged
7 meta-gabbro (samples V18-3a and V18-3b).

8 **Fig. 3:** A: Photomicrograph of a partially serpentized dunite. B: Partial replacement of
9 primary chromian spinel by magnetite and chlorite. C: Partial replacement of olivine by
10 antigorite. D: Inferred primary orthopyroxene being pseudomorphically replaced by
11 metamorphic olivine. See also Figure 5B. E: Photomicrograph of a pyroxenite layer included in
12 the Belvidere peridotite. The photomicrograph shows radial diopside aggregate
13 pseudomorphic on primary clinopyroxene. Partially serpentized olivine is also visible. F:
14 Magnetite-rich diopside pseudomorphosis on primary clinopyroxene. Note the growth of
15 metamorphic olivine at the rim of the clinopyroxene site. See Figure 5A for SEM-based
16 backscattered electron image. G: Metamorphic diopside replacing primary clinopyroxene. In
17 this case, note the growth of metamorphic olivine along fractures cutting the
18 pseudomorphosis. See Figure 5F for SEM-based backscattered electron image. H: Relict of
19 metamorphic olivine pseudomorphic on primary clinopyroxene. The metamorphic olivine is
20 then partially replaced by serpentine + brucite + magnetite. A-D: Sample V18-2b, E-G: Sample
21 V18-3a; H: sample V18-B3. P-Ol: primary olivine, M-Ol: metamorphic olivine, Atg: antigorite,
22 Chl: chlorite, Mgt: magnetite, Di: diopside, Chr: chromite, Br: brucite, Ctl: chrysotile.

23 **Fig. 4:** Raman spectra of solid phases. A: Antigorite core (Atg1) and rim (Atg2) (see Fig. 5A). B:
24 Brucite.

25 **Fig. 5:** SEM-BSE images of samples V18-2b, V18-3a and V18-B3. A: Microstructural patterns of
26 serpentinization. Two generations of serpentine can be observed based on the BSE contrast, a
27 bright core (Atg1) and a dark rim (Atg2). Note also the striped zonation of primary olivine and
28 the formation of metamorphic olivine. B: Replacement of an inferred primary orthopyroxene
29 crystal by metamorphic olivine. The close-up shows the preservation of clinopyroxene relicts
30 interpreted as exsolutions inside the former orthopyroxene. C: Formation of brucite at the
31 expense of metamorphic olivine. D: Composite aggregate of Fe-Ni and Fe-Cu-Ni alloys and Ni
32 sulphide. E: Growth of metamorphic olivine around a diopside-rich primary clinopyroxene
33 pseudomorphosis. A primary chromite spinel partially converted into magnetite can also be
34 observed. F: Metamorphic diopside replacing primary clinopyroxene. Note the presence of
35 antigorite + metamorphic olivine ± magnetite along the fractures. In this case, metamorphic
36 olivine occupies the centre of the fractures and is not in contact with diopside, whereas the
37 metamorphic olivine rimming the primary clinopyroxene site is in contact with it. G:
38 Metamorphic olivine growing at the expense of metamorphic diopside (former primary
39 clinopyroxene). The microstructure suggests the former presence of serpentine needles
40 replacing the clinopyroxene and successively replaced by metamorphic olivine. Both Atg1 and
41 Atg2 antigorite generations are present. H: Relict of metamorphic olivine formed at the
42 expense of a primary orthopyroxene site in V18-3b. The metamorphic olivine is partially
43 converted into brucite + serpentine. P-Ol: primary olivine M-Ol: metamorphic olivine Px:
44 pyroxene Di: diopside Mtg: magnetite Chr: chromite Atg: antigorite Br: brucite Ctl: chrysotile
45 NiFeS: nickel and iron sulphite. The presence of antigorite was confirmed by Raman
46 spectroscopy.

47 **Fig. 6:** Mg# versus MnO (wt%) diagram showing the compositional variation of primary and
48 metamorphic olivine. The Mn-richest cluster of metamorphic olivine belongs to sample V18-
49 B3 (fully serpentinized peridotite). Background data from Arai et al., (2012); Dandar et al.,
50 (2019); Debret et al., (2013); Iyer et al., (2008); Nozaka, (2018); Plümper et al., (2012b);
51 Scambelluri et al., (1995); Shen et al., (2015).

52 **Fig. 7:** Photomicrographs of methane-rich fluid inclusion trails in olivine from sample V18-2a.
53 Black arrows indicate fluid inclusion trails. A: Inclusion trail being cut by antigorite veinlets. B:
54 Inclusion trail limited by antigorite veins. C: Secondary trail of fluid inclusions propagating
55 from an antigorite veinlet. D: Photomicrograph showing a fluid-inclusion-rich olivine
56 aggregate. E: Close up of the methane-rich fluid inclusions. F: Close up of a graphite bearing
57 fluid inclusion (red arrow), as confirmed by Raman spectroscopy in (Fig. 8B).

58 **Fig. 8:** Raman spectra of fluid inclusions and step-daughter solid phases. A: Inclusion showing
59 a marked CH₄ band and minor peaks of N₂ NH₃ and S-H bond. Lizardite and brucite O-H bands
60 are also observed. B: Graphite in fluid inclusions (see Fig. 6D). C: Methane-rich fluid inclusion
61 with a close up of O-H bonds of lizardite and brucite.

62 **Fig. 9:** Thermodynamic modelling of HP serpentinization of dunite and related mineralogical
63 and fluid evolution. A: Mineralogical evolution during serpentinization at 450 °C and 1 GPa. B:
64 Evolution of total dissolved elements in the fluid as a function of the reaction progress
65 presented in A. C: Evolution of the nitrogen and sulphur fluid speciation as a function of the
66 reaction progress presented in A. D: Evolution of the fO₂ and H₂, CH₄, and CO₂ concentrations
67 in the fluid as a function of the reaction progress presented in A.

68 **Fig. 10:** Reconstruction of the mineralogical evolution of the BMC partially serpentinized
69 peridotite. An early step of serpentinization is proposed based on the needle-like growth of

70 metamorphic olivine on primary clinopyroxene, suggesting the presence of serpentine prior to
71 the formation of metamorphic olivine. The successive growth of antigorite at the expense of
72 both primary and metamorphic olivine constrains the main serpentinization event to
73 metamorphic conditions. Finally, a late serpentinization event is proposed based on the
74 growth of brucite + antigorite + chrysotile on relict metamorphic. Chr : chromite, P-Ol : primary
75 olivine, M-Ol : metamorphic olivine, Opx : primary orthopyroxene, Cpx : primary clinopyroxene,
76 Chl : chlorite, Mgt : magnetite, Atg : antigorite, Di : diopside, Brc : brucite, Ctl : chrysotile.

77 **Fig. 11:** Simplified stability field of serpentine type minerals and olivine, modified from Guillot
78 et al., (2015) (see references therein for details on the main reactions). The retrograde P-T
79 path of BMC from Honsberger, (2015) is also shown for reference. Atg : antigorite, Brc :
80 brucite; Ctl : chrysotile; Ilm : ilmenite; Ol : olivine; Tlc : talc; Ticl : titanian clinohumite. Diamond
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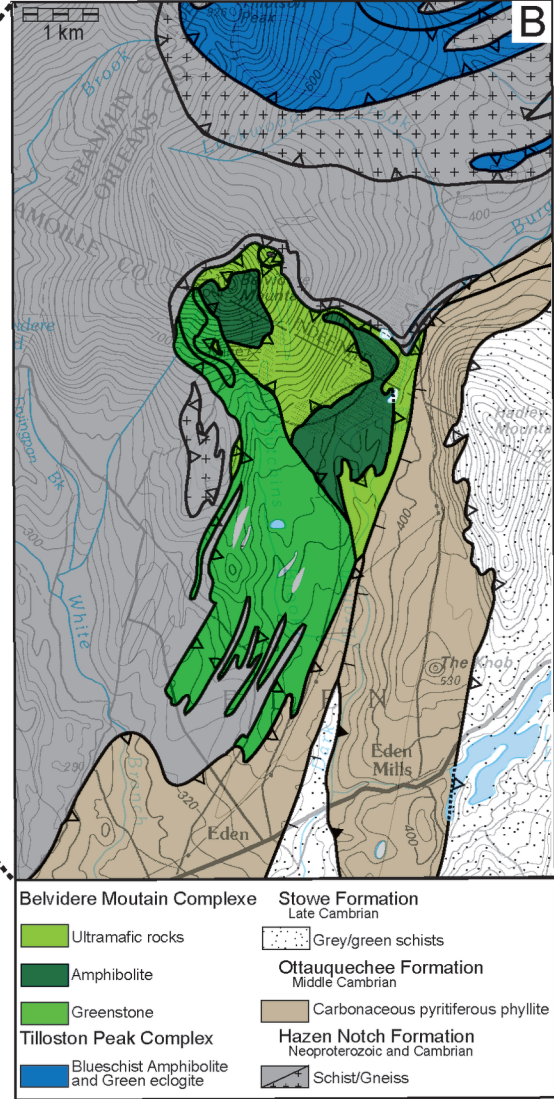
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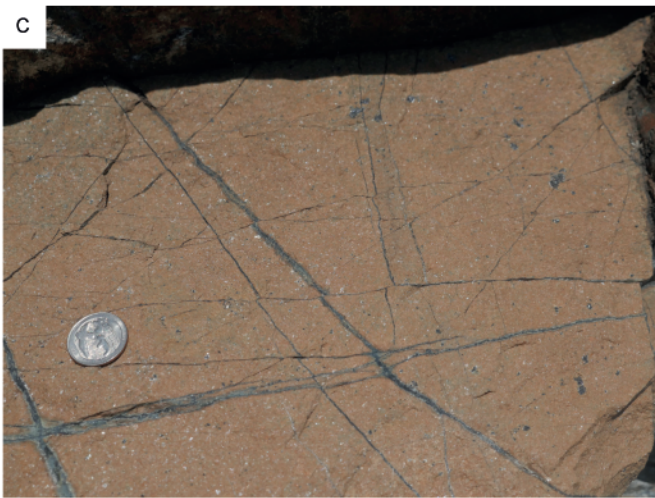
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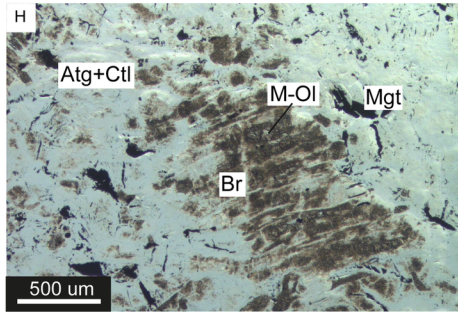
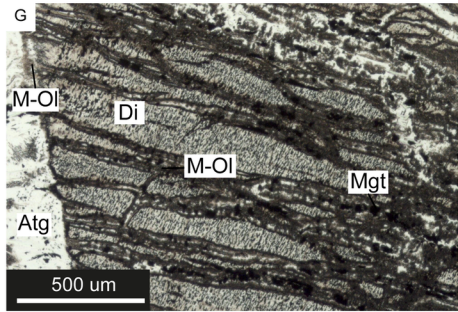
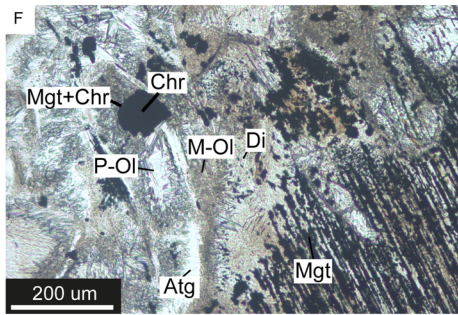
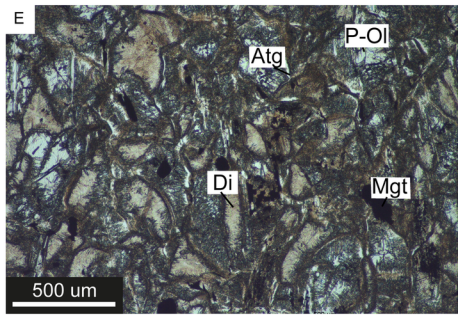
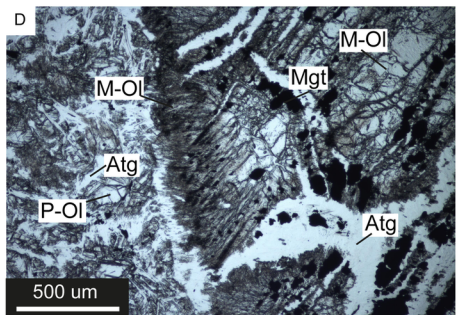
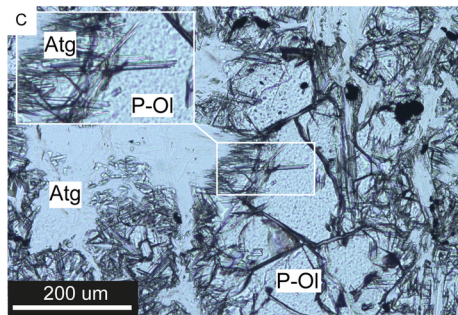
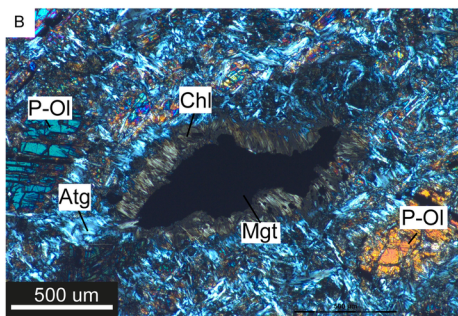
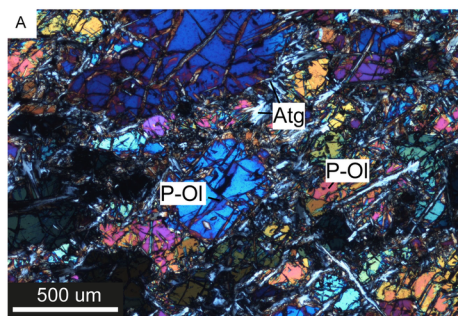
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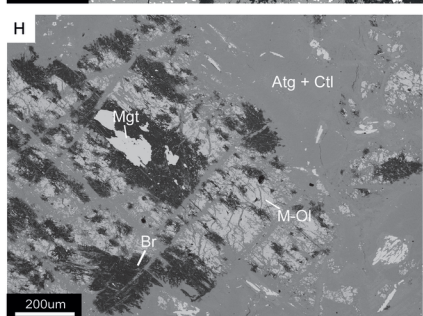
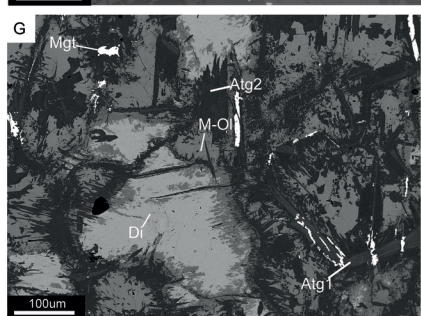
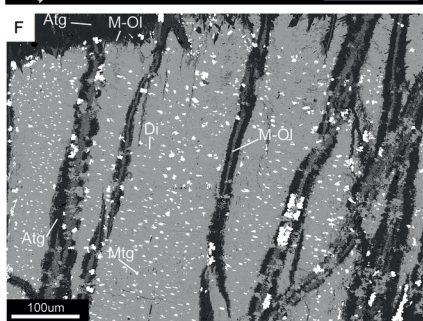
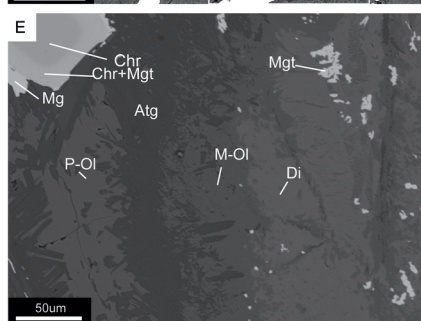
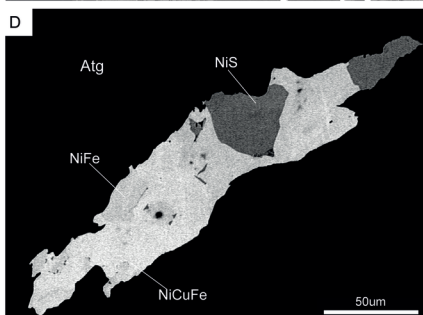
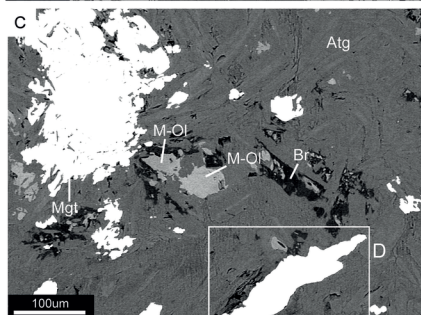
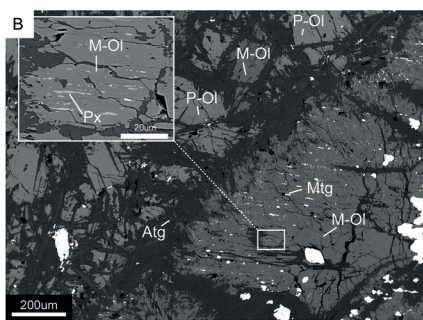
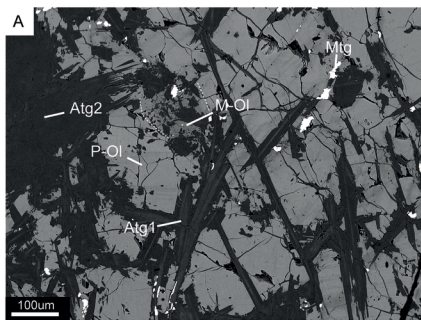
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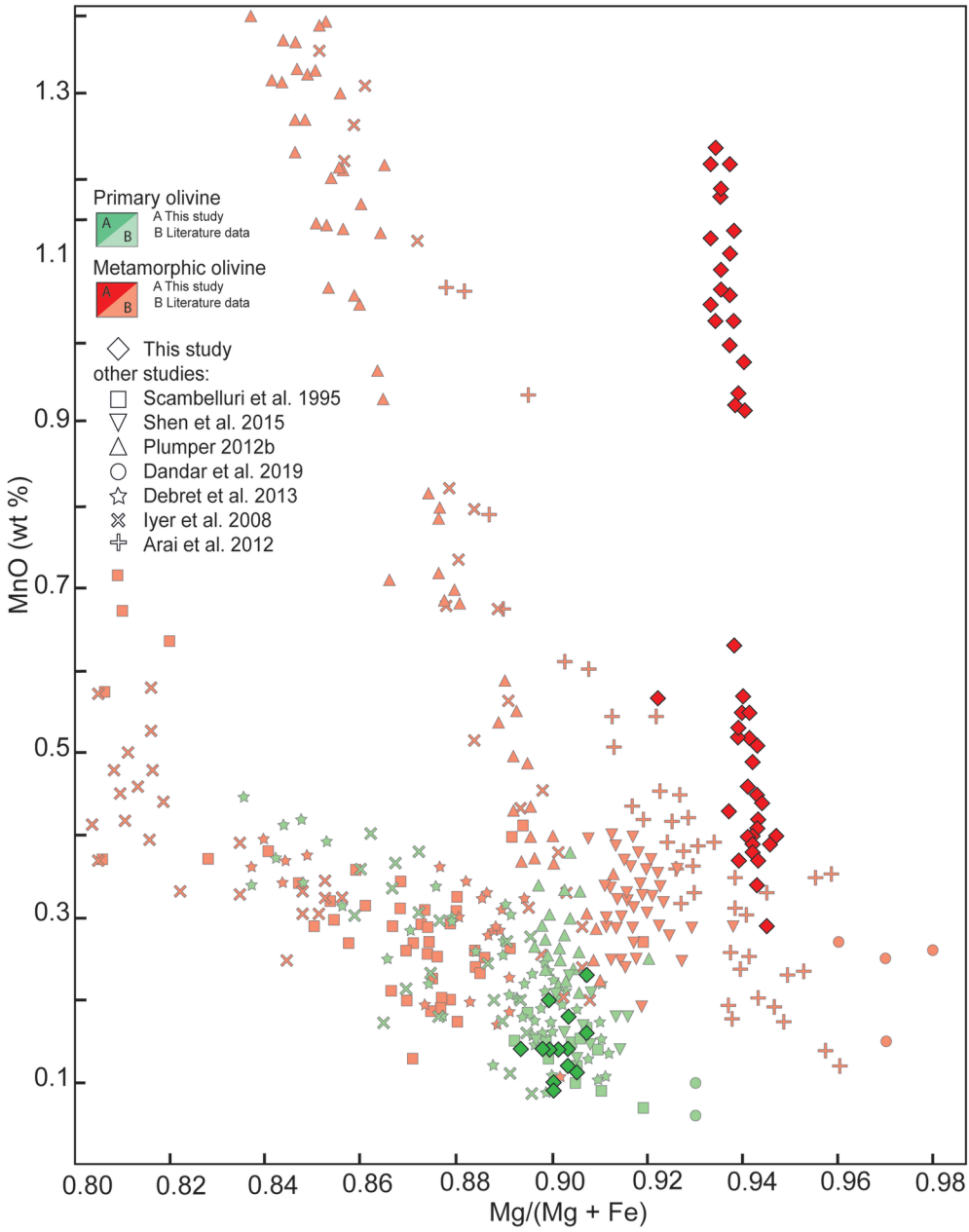
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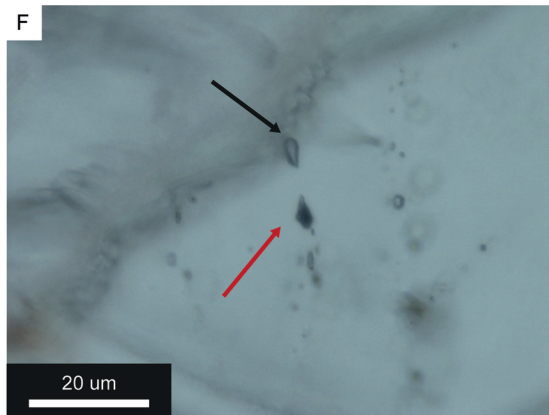
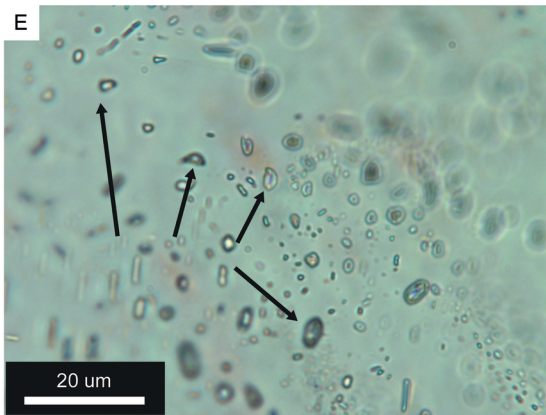
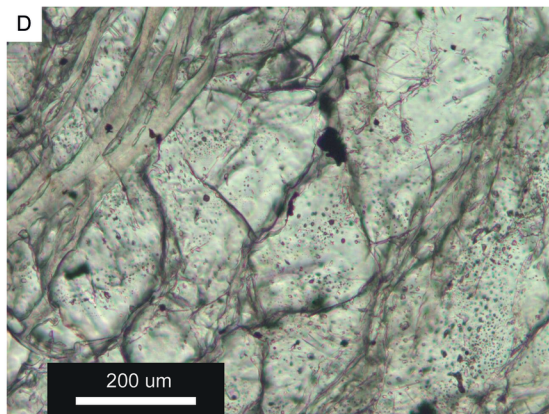
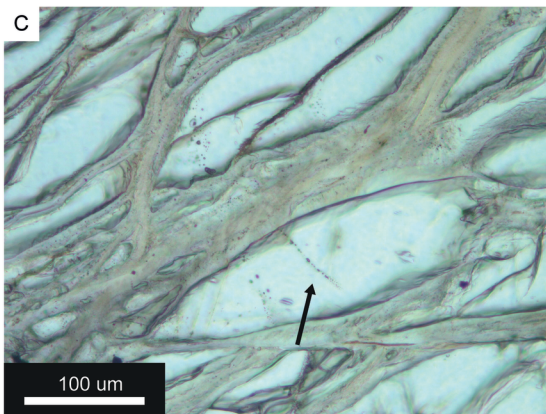
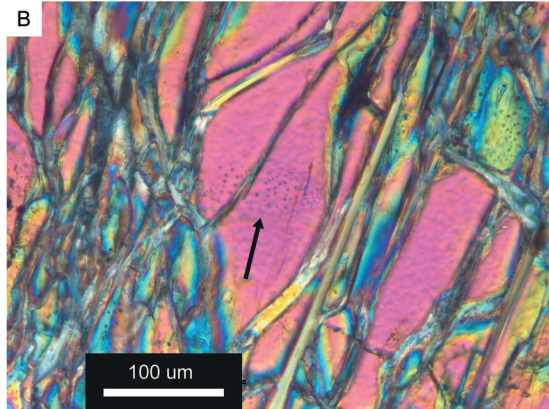
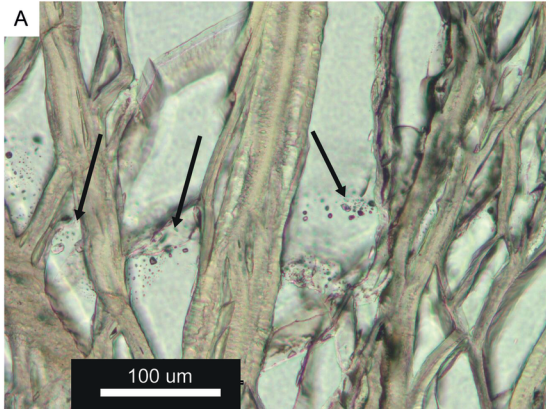


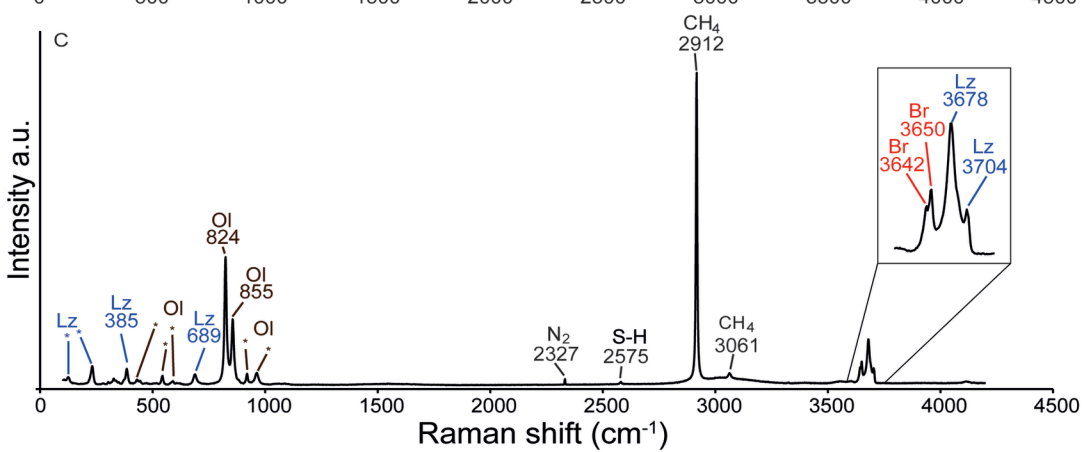
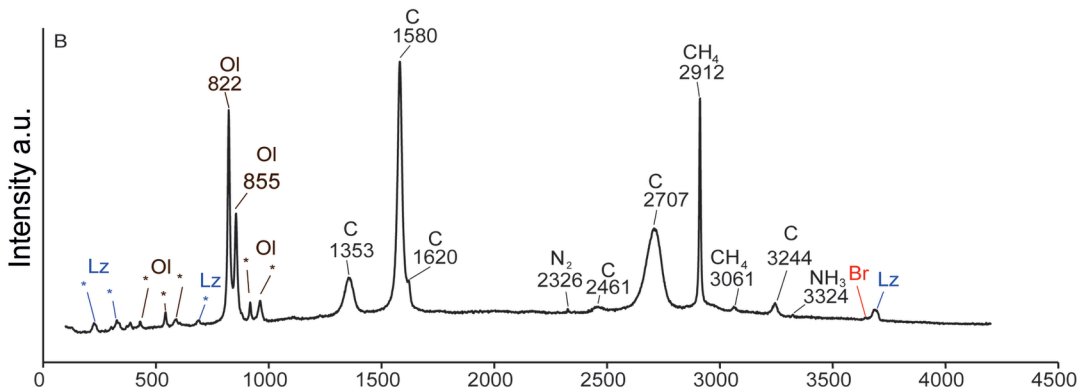
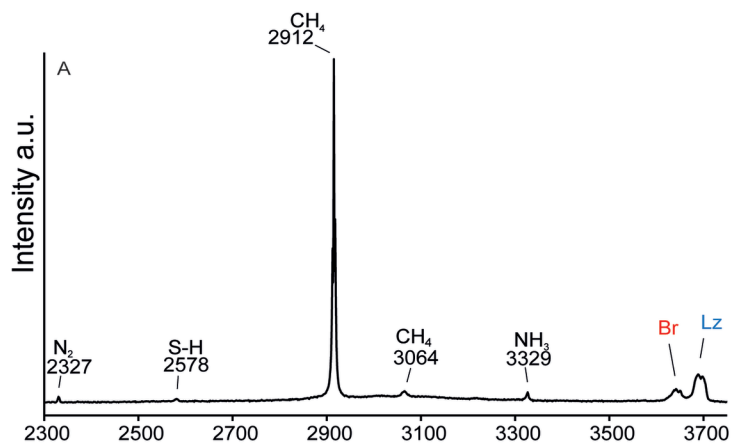


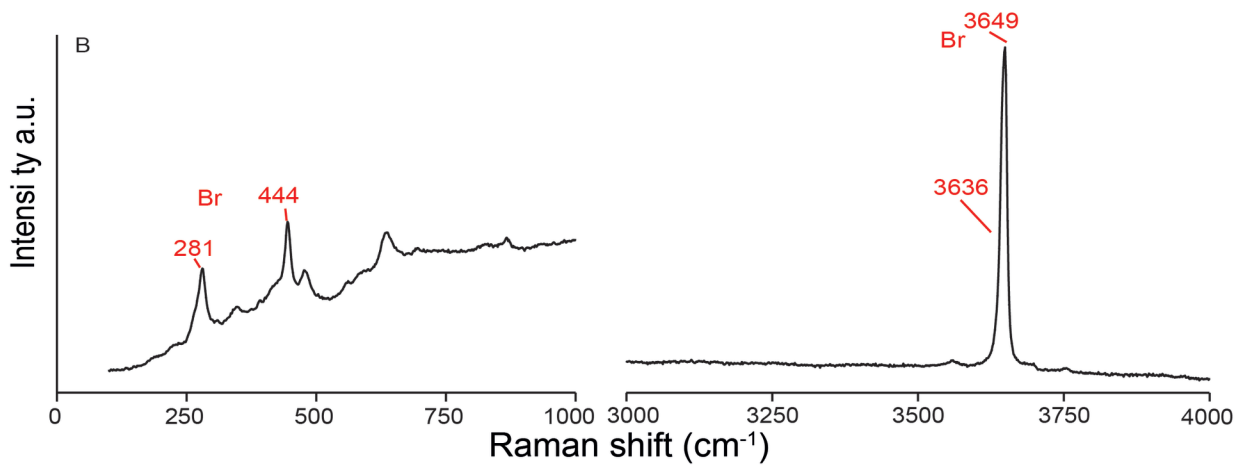
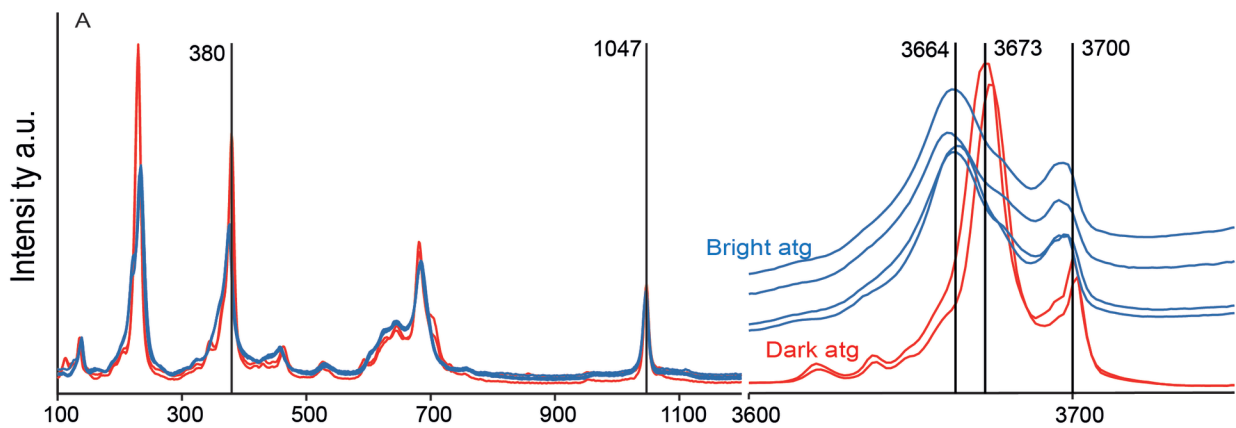


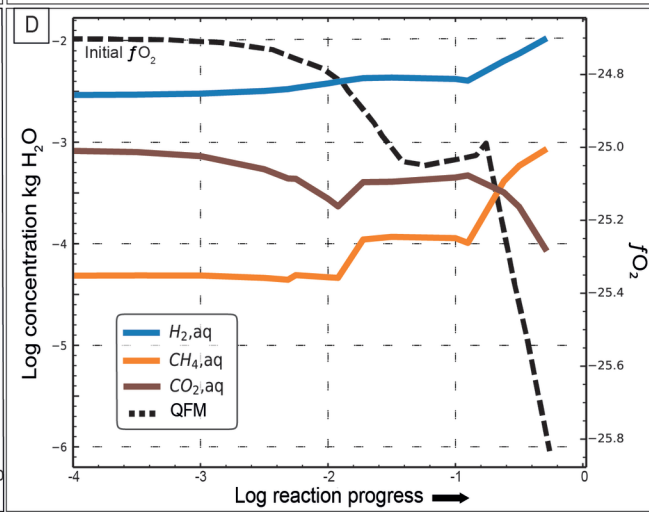
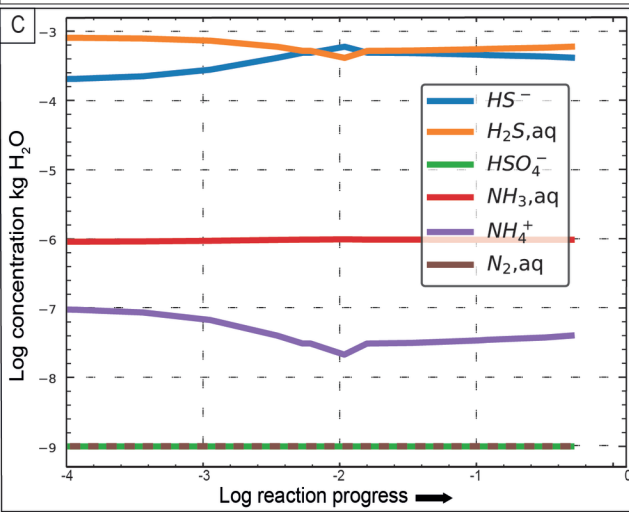
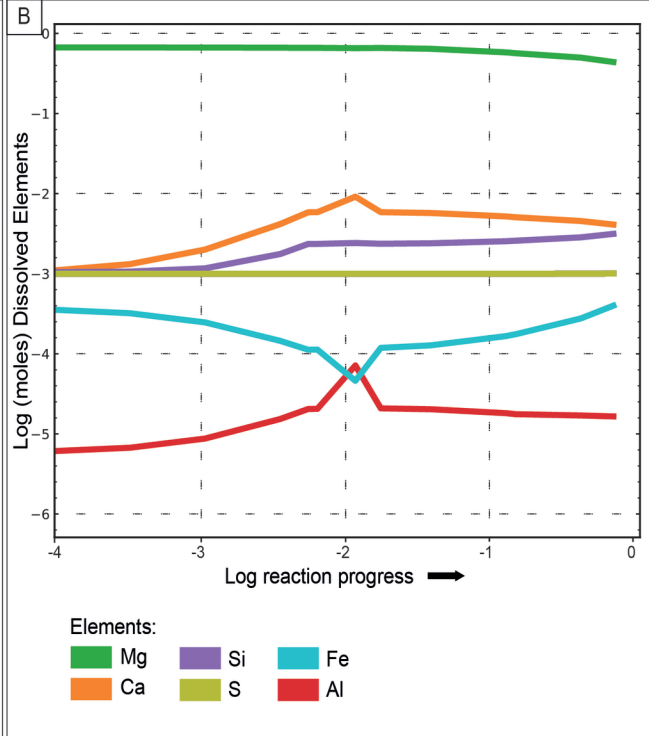
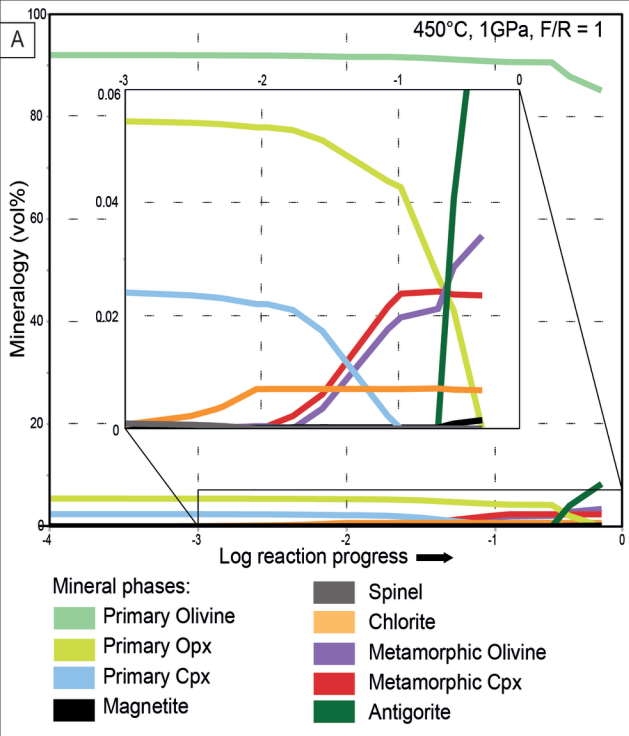




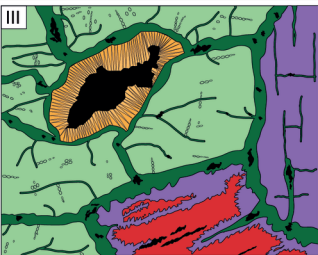
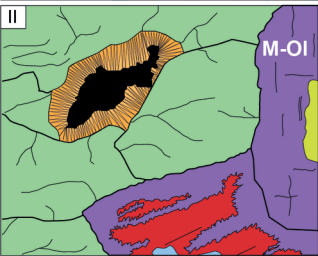
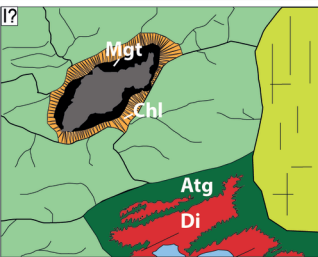
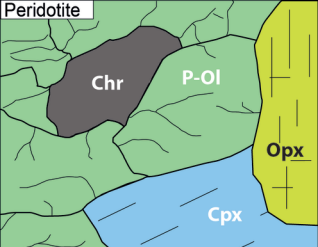






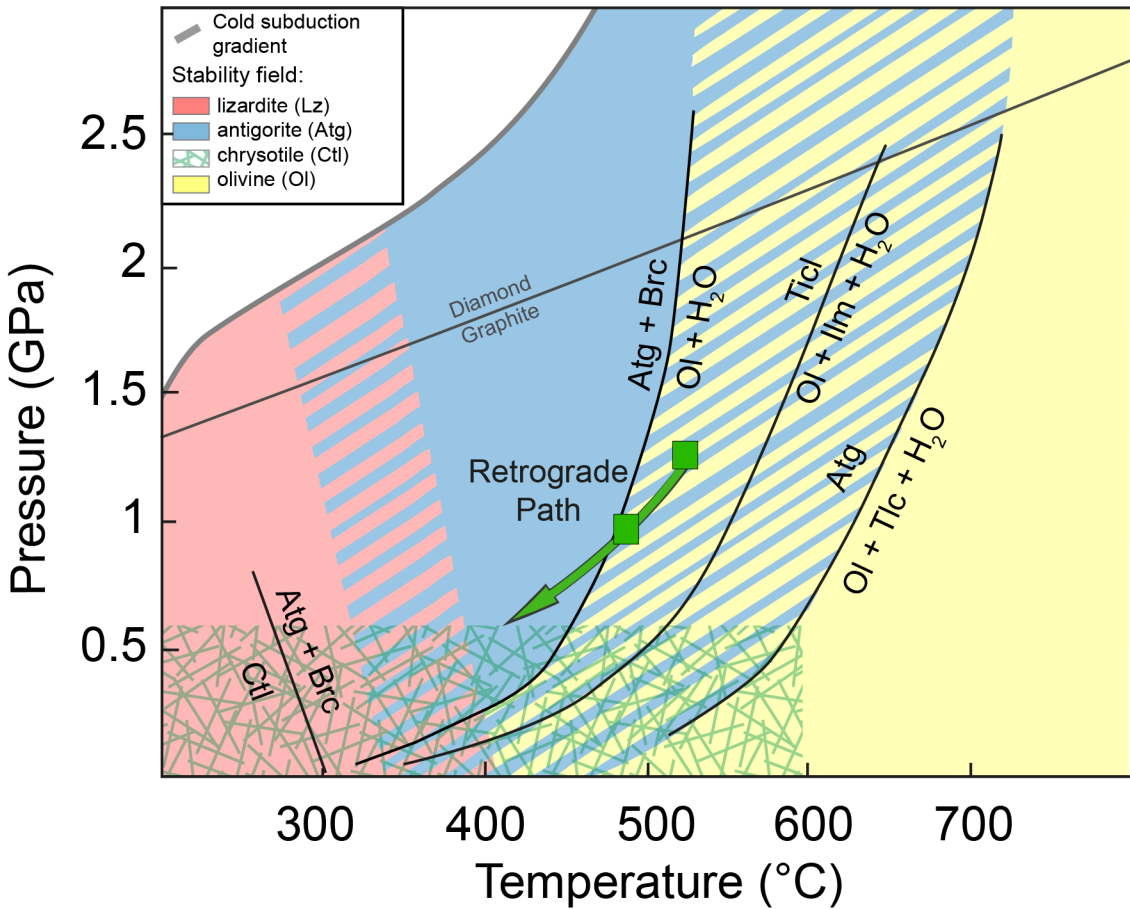


Peridotite



Prograde

Retrograde



1 **Table 1**

MicroProbe analysis. Absence of SD value when n>1 indicates SD<0.01. *EDS analyses normalized at 100.

Minerals	Primary Olivine		Metamorphic Olivine			Pyroxene	Serpentine (Bright core)		Serpentine (Matrix)		Chlorite	
	V18-2b	V18-3a	V18-2b	V18-3a	V18-B3*	V18-3a	V18-2b	V18-3a	V18-2b	V18-3a	V18-2b	V18-3a
Sample (n)	14	11	28	15	25	20	6	2	9	4	11	1
SiO ₂	40.91 (0.25)	40.83 (0.46)	41.31 (0.49)	41.95 (0.63)	42.00 (0.12)	54.96 (0.98)	42.87 (1.21)	43.41 (0.1)	44.15 (0.17)	43.1 (1.35)	32.61 (1.34)	32.03
TiO ₂	0.01 (0.01)	0.02 (0.02)	0.02 (0.01)	0.02 (0.02)		0.03 (0.02)	0.01 (0.01)	0.02 (0.01)	0.02 (0.01)	0 (0)	0.02 (0.02)	0.00
Al ₂ O ₃	0.01 (0.01)	0.01 (0.01)	0.01 (0.02)	0.04 (0.09)		0.15 (0.11)	1.77 (1.22)	1.45 (0.78)	0.52 (0.21)	0.47 (0.26)	14.34 (2.39)	11.78
Cr ₂ O ₃	0.01 (0.02)	0.01 (0.02)	0.06 (0.18)	0.04 (0.03)		0.17 (0.11)	0.61 (0.85)	0.25 (0.19)	0.13 (0.09)	0.1 (0.1)	1.07 (0.56)	4.07
FeO (tot)	8.97 (0.34)	7.93 (0.22)	4.83 (0.30)	5.05 (0.57)	4.71 (0.19)	0.76 (0.16)	2.60 (0.26)	1.58 (0.27)	1.35 (0.22)	1.2 (0.29)	3.31 (0.46)	2.79
MnO	0.15 (0.04)	0.12 (0.06)	0.45 (0.08)	0.37 (0.06)	1.02 (0.18)	0.05 (0.03)	0.04 (0.02)	0.05 (0.05)	0.04 (0.02)	0.02 (0.02)	0.06 (0.10)	0.07
NiO	0.38 (0.03)	0.49 (0.06)	0.43 (0.07)	0.39 (0.06)	0.46 (0.08)	0.03 (0.03)	0.16 (0.02)	0.18 (0.06)	0.15 (0.04)	0.19 (0.02)	0.22 (0.05)	0.24
ZnO	0.04 (0.04)	0.03 (0.04)	0.03 (0.04)	0.03 (0.04)		0.01 (0.02)					0.02 (0.04)	0.00
MgO	50.23 (0.22)	50.91 (0.22)	52.8 (0.64)	51.8 (1.57)	51.80 (0.28)	18.75 (1.15)	37.97 (1.30)	39.81 (0.59)	39.6 (0.77)	40.07 (0.61)	34.34 (1.11)	35.08
CaO	0.02 (0.01)	0.01 (0.02)	0.02 (0.02)	0.25 (0.37)		24.87 (1.43)	0.02 (0.02)	0.05 (0.04)	0.02 (0.02)	0.02 (0.01)	0.02 (0.01)	0.05
Na ₂ O	0.09 (0.22)	0.01 (0.01)	0.02 (0.02)	0.01 (0.01)		0.04 (0.02)					0.02 (0.03)	0.03
K ₂ O	0.01 (0.02)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)		0.01 (0.01)					0.02 (0.02)	0.02
Total,	100.82 (0.36)	100.37 (0.70)	100.06 (1.10)	99.96 (1.63)	100	99.83 (1.12)	86.2 (0.63)	86.93 (0.4)	86.07 (0.82)	85.25 (1.66)	86.14 (0.65)	86.17
Cations												
O*	4.0	4.0	4.0	4.0	4.0	6.0	6.8	6.8	6.8	6.8	28.0	28.0
Si	0.990	0.988	0.991	1.012	1.013	1.989	1.984	2.010	2.044	1.995	6.232	6.165
Ti	0.000	0.000	0.000	0.000		0.001	0.000	0.001	0.001	0.000	0.004	0.000
Al	0.000	0.000	0.000	0.001		0.006	0.091	0.079	0.028	0.026	3.229	2.672
Cr	0.000	0.000	0.001	0.001		0.005	0.026	0.009	0.005	0.004	0.162	0.619
Fe ²⁺ (tot)	0.181	0.161	0.097	0.102	0.095	0.023	0.104	0.061	0.052	0.046	0.529	0.404
Mn	0.003	0.003	0.009	0.008	0.021	0.002	0.001	0.002	0.002	0.001	0.010	0.012
Ni	0.007	0.010	0.008	0.008	0.009	0.001	0.006	0.007	0.006	0.007	0.034	0.037
Zn	0.001	0.001	0.000	0.001		0.000					0.003	0.000
Mg	1.812	1.837	1.891	1.861	1.862	1.012	2.486	2.747	2.733	2.765	9.782	10.063
Ca	0.000	0.000	0.001	0.006		0.964	0.001	0.002	0.001	0.001	0.003	0.011
Na	0.004	0.000	0.001	0.000		0.003					0.007	0.012
K	0.000	0.000	0.000	0.000		0.000					0.005	0.005
Mg#	0.91	0.92	0.95	0.95	0.95	0.98	0.94	0.96	0.97	0.97	0.95	0.96

Mg# = Mg/(Mg+ΣFe)

*As per normalization

3 **Table 2**

MicroProbe analysis. Absence of SD value when n>1 indicates SD<0.01

Minerals	Spinel (nucleus)	Spinel (intermediate)	Magnetite (rim)	Magnetite (mesh and veins)	Brucite	
Sample	V18-3a	V18-3a	V18-3a	V18-3a	V18-2b	
(n)	7	7	7	1	4	10
SiO₂	0.02 (0.02)	0.03 (0.01)	0.06 (0.07)	0.07	0.05 (0.03)	0.78 (2.20)
TiO₂	0.09 (0.02)	0.23 (0.05)	0.03 (0.02)	0.04	0.01 (0.01)	0.01
Al₂O₃	12.63 (0.94)	3.87 (1.34)	0.00	0.03	0.01 (0.01)	0.01 (0.01)
Cr₂O₃	47.51 (0.57)	41.6 (1.29)	1.87 (1.16)	0.01	0.02 (0.02)	0.04 (0.05)
FeO	34.12 (1.1)	48.32 (2.02)	91.45 (0.75)	92.44	92.57 (0.28)	2.91 (0.18)
MnO	0.34 (0.04)	0.95 (0.36)	0.16 (0.03)	0.12	0.19 (0.05)	0.22 (0.04)
NiO	0.09 (0.02)	0.27 (0.05)	1.05 (0.1)	1.11	0.82 (0.09)	0.38 (0.09)
ZnO	0.49 (0.08)	0.3 (0.1)	0.04 (0.06)	0.10	0.04 (0.08)	0.01 (0.02)
MgO	5.99 (0.32)	3.37 (0.22)	0.71 (0.09)	0.62	0.82 (0.19)	75.88 (3.93)
CaO	0.01 (0.01)	0.00	0 (0.01)	0.00	0.00	0.02 (0.03)
Na₂O	0.03 (0.04)	0.02 (0.02)	0.03 (0.03)	0.03	0.02 (0.04)	0.02 (0.02)
K₂O	0.00	0.01 (0.01)	0 (0.01)	0.01	0.00	0.01 (0.01)
Total	101.4 (0.56)	99.03 (0.6)	95.46 (0.5)	94.63	94.56 (0.45)	80.33 (2.70)
Cations						
O*	4.0	4.0	4.0	4.0	4.0	2
Si	0.00	0.00	0.00	0.00	0.00	0.01
Ti	0.00	0.01	0.00	0.00	0.00	0.00
Al	0.49	0.16	0.00	0.00	0.00	0.00
Cr	1.24	1.17	0.06	0.00	0.00	0.00
Fe³	0.26	0.66	1.94	1.99	2.00	0.00
Fe²	0.68	0.78	0.92	0.92	0.92	0.02
Mn	0.01	0.03	0.01	0.00	0.01	0.00
Ni	0.00	0.01	0.03	0.03	0.02	0.00
Zn	0.01	0.01	0.00	0.00	0.00	0.00
Mg	0.29	0.18	0.04	0.03	0.05	0.97
Ca	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00
Cr#	0.79(0.01)	0.92(0.2)	1.00			

4 Cr# = Cr/(Al+Cr)

5 *As per normalization

6 **Table 3**

MicroProbe analysis of alloys

Sample	V18-2b						V18-3a		
	NiFeCu	NiS	NiS	NiS	NiFeCu	NiFeCu	NiS	NiS	NiS
S		24.06	24.25	24.12			24.59	24.52	24.50
Fe	12.21	0.9	0.51	1.35	13.35	20.07	0.84		0.95
Pb				0.13			0.18		
Ni	86.23	72.68	72.71	73.55	86.05	80.03	72.97	72.85	73.30
Cu	1.94				1.75	1.49			
Total:	100.45	97.9	97.59	99.18	101.28	101.71	98.70	97.72	99.04

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