



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

ARCHIVIO ISTITUZIONALE
DELLA RICERCA

Alma Mater Studiorum Università di Bologna Archivio istituzionale della ricerca

In situ Sr isotope analysis of mantle carbonates: Constraints on the evolution and sources of metasomatic carbon-bearing fluids in a paleo-collisional setting

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

In situ Sr isotope analysis of mantle carbonates: Constraints on the evolution and sources of metasomatic carbon-bearing fluids in a paleo-collisional setting / Consuma G.; Braga R.; Giovanardi T.; Bersani D.; Konzett J.; Lugli F.; Mazzucchelli M.; Tropper P.. - In: LITHOS. - ISSN 0024-4937. - ELETTRONICO. - 354-355:(2020), pp. 105334.1-105334.15. [10.1016/j.lithos.2019.105334]

Availability:

This version is available at: <https://hdl.handle.net/11585/765813> since: 2020-07-13

Published:

DOI: <http://doi.org/10.1016/j.lithos.2019.105334>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

This is the final peer-reviewed accepted manuscript of:

Giulia Consuma, Roberto Braga, Tommaso Giovanardi, Danilo Bersani, Jürgen Konzett, Federico Lugli, Maurizio Mazzucchelli, Peter Tropper (2020). In situ Sr isotope analysis of mantle carbonates: Constraints on the evolution and sources of metasomatic carbon-bearing fluids in a paleo-collisional setting, Lithos, 354–355

The final published version is available online at
<https://dx.doi.org/10.1016/j.lithos.2019.105334>

Rights / License:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

***In situ* Sr isotope analysis of mantle carbonates: constraints on the evolution and sources of metasomatic carbon-bearing fluids in a paleo-collisional setting**

Giulia Consuma^a, Roberto Braga^{a,*}, Tommaso Giovanardi^b, Danilo Bersani^c, Jürgen Konzett^d, Federico Lugli^c, Maurizio Mazzucchelli^b, Peter Tropper^d

^a Department of Biological, Geological and Environmental Sciences, University of Bologna, Piazza di Porta San Donato 1, 40126 Bologna, Italy

^b Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Via Campi 103, 41125 Modena, Italy

^c Department of Mathematical, Physical and Computer Sciences, University of Parma, Parco Area delle Scienze 7/A, 43124, Parma, Italy

^d Institute of Mineralogy and Petrology, University of Innsbruck, Innrain52, 6020 Innsbruck, Austria

^e Department of Cultural Heritage, University of Bologna, Via degli Ariani 1, 48100 Ravenna, Italy

*Corresponding author: r.braga@unibo.it (Roberto Braga)

ABSTRACT

1 Carbonate-bearing wedge peridotites attest the mobilization of carbon (C) by slab fluids/melts
2 circulating in a subduction setting. In general, COH fluids are thought to derive from the
3 dehydration/partial melting of the crustal portions of slabs, especially during the exhumation of
4 crust-mantle mélanges along continental subduction channels. In this study we combined textural
5 observations with *in-situ* Sr isotope analyses of mantle carbonates occurring in different
6 microstructural sites to test whether the fluids responsible for the carbonation of a mantle wedge
7 derived from the subducted continental crust or not. We focus on the Ulten Zone peridotites
8 (Eastern Italian Alps) associated with high-grade felsic rocks, where carbonates occur mainly as
9 dolomite and minor magnesite and calcite. Analyses by a laser ablation system coupled to a
10 Neptune MC-ICP-MS on peridotites representing different episodes of a complex metasomatic
11 history, indicate that Sr isotopic variations can be linked to the different microstructural positions of
12 carbonates. The C-metasomatism of UZ peridotites can be outlined in two stages. The first stage is
13 the *HP*-carbonation at peak (eclogite-facies) conditions, with formation of interstitial matrix
14 dolomite in textural equilibrium with hornblende to pargasite amphibole and Cl-apatite. This

15 dolomite exhibits relatively unradiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ present day values of 0.70487 ± 0.00010 ,
16 requiring different sources with respect to the associated migmatites and the overhanging mantle
17 wedge. Carbonation continued during exhumation, with local injection of C-rich fluids forming
18 dolomite veins in association with tremolite and chlorite. The dolomite vein shows a wide range of
19 $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7036-0.7083), reflecting both the primary composition of carbonates and the consequent
20 interaction with crustal fluids as expected in a crust-mantle mélange. The second stage is C-
21 remobilization during the final exhumation by dolomite dissolution and precipitation of brucite
22 intergrowths with calcite, that exhibits a quite similar Sr composition of the precursor dolomite.
23 The mantle wedge is therefore capable to store carbonates representing a complex metasomatic
24 evolution from eclogite-facies conditions to very shallow structural levels. Fluids released from
25 subducting slabs of continental lithosphere might be responsible for the crystallization, in the
26 overlying ultramafic rocks, of metasomatic minerals such as amphibole, phlogopite and zircon, but
27 their role on the carbonation of mantle wedge is most likely overestimated. The combination of
28 geochemical, isotopic and textural evidence suggests the contribution of a distinct source of C-
29 bearing fluids for included and interstitial dolomite, which could be related to depleted mantle
30 wedge sources and/or trondhjemitic igneous activity. Differently, residual COH-fluids released by
31 the associated stromatic gneisses and orthogneisses acted during the end of exhumation, providing
32 the highest Sr isotope values for the dolomite veins.

33 **Keywords:** Carbon Cycle; peridotite; mantle-wedge; In situ Sr isotope; metasomatism; Ulten Zone

34 **1 Introduction**

35 At convergent plate boundaries, the interface between subducting slab and overhanging mantle
36 wedge represents a complex region, where a mix of slab- and wedge-derived lithologies plays a key
37 role in the surface-to-mantle volatiles budget on Earth (Bebout and Penniston-Dorland, 2016). In
38 this tectonic setting, the subduction of carbon (C) stored in organic matter and carbonate minerals is

39 partly returned to the surface by slab fluids (Manning, 2014). The occurrence of hydrous and
40 carbonated phases, and the enrichment in incompatible elements of the lithospheric mantle wedge
41 above a subducting slab, testify the fluid-mediated large-scale cycling of elements. The C transfer
42 among different reservoirs is usually related to fluids or melts expelled from the crustal portion of
43 the subducted oceanic lithosphere (carbonated serpentinite, altered crust and sediments). However,
44 many of the studied mantle wedge peridotites are now exposed within variable migmatized felsic
45 gneisses, as a result of continental collision (Brueckner and Medaris, 2000; Zheng, 2012 and
46 references therein). Accordingly, several studies highlight the importance of subducted continental
47 crust as source of metasomatic C-bearing fluids/hydrous melts reacting and enriching the
48 overhanging mantle wedge (Zanetti et al., 1999; Zheng, 2009; Hermann et al., 2013). An
49 appropriate identification of the C sources during interactions between mantle wedge and subducted
50 continental lithosphere is therefore essential in order to develop a quantitative understanding of the
51 global C flux.

52 In this study we take advantage of the wealth of data already available on the multiple metasomatic
53 history of the Ulten Zone (UZ) peridotite (northern Italy) to illustrate the formation and the
54 dissolution-precipitation of carbonates at relatively shallow ($P < 3$ GPa) and cold ($T < 850^{\circ}\text{C}$)
55 conditions. The UZ peridotites record the transition from mantle wedge, coarse-grained, spinel-
56 peridotite to high-pressure, fine-grained, garnet-bearing amphibole-peridotite and, finally to low- P ,
57 low- T serpentinitized peridotites (Förster et al., 2017; Ionov et al., 2017; Gudelius et al., 2018).
58 Therefore, these rocks offer the opportunity to investigate fluid-driven carbonation at different P - T
59 conditions, along the complex metasomatic evolution of a paleo-mantle wedge involved in
60 continental collision. We combined microstructural observations, major elements compositions,
61 micro-Raman analyses of carbonates and associated minerals, with in situ $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic
62 composition of carbonates as a tracer for investigating the potential sources of C-bearing fluids. The
63 choice of using elemental Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to shed more light on C-metasomatism is based on

64 the fact that: (i) it is relatively abundant in the carbonates structure due to its easy substitution with
65 Ca^{2+} ; (ii) the partition of Rb into the carbonate crystal structure is hampered because of its large
66 ionic size, and we therefore assume that carbonates may inherit the Sr isotopic composition of C-
67 bearing fluids at the time of their formation and their release from the sources (Dickin, 2018 and
68 references therein); (iii) its concentration and isotopic composition may provide information about
69 fluid sources, elements partitioning, isotopic mixing behavior and extent of fluid-rock interaction
70 (Banner, 1995). *In situ* approaches applied to carbonates can therefore provide the spatial resolution
71 to better constrain the carbon-volatile-element mobilization in a crust-mantle interface and the
72 element exchange at grain-scale.

73 **2.Geology and petrology of the Ulten Zone**

74 In the Ulten Valley and Non Valley (Trentino-Alto Adige, Italy), the Ulten Zone is a tectono-
75 metamorphic complex belonging to the Tonale Nappe, Upper Austroalpine domain of the Eastern
76 Alps (Fig.1). The Tonale Nappe forms a SW-NE oriented narrow belt of Variscan metamorphic
77 rocks, bounded by Alpine faults such as the Tonale and Giudicarie lines to the South and the Peio
78 Line to the North (Müller et al., 2001). The UZ consists of strongly foliated garnet-kyanite gneisses
79 and migmatites enclosing lenses of peridotites and pyroxenites (Obata and Morten, 1987). The main
80 metamorphic overprint is Variscan in age whereas the evidences of a weak Eo-Alpine overprint
81 mostly occur along the main tectonic lines (Godard et al., 1996).

82 Considering the different grain size and metamorphic assemblage, Obata and Morten (1987)
83 classified the UZ peridotites as ranging from less deformed coarse-grained spinel peridotites to
84 foliated fine-grained garnet-amphibole/chlorite-amphibole peridotites: the latter are interpreted as
85 deformed and recrystallized derivatives of the former.

86 The UZ petrology and metasomatic evolution is the subject of several studies well summarized in
87 Scambelluri et al. (2010) and the sketch of Figure 2 contains the main features of an otherwise

88 complex sequence of events. In stage 1 (Fig. 2), coarse-grained peridotites made of olivine +
89 enstatite + diopside + Cr-Al spinel with protogranular texture (Obata and Morten, 1987) were
90 percolated by hydrous basic melts from deeper lithospheric mantle before the Variscan orogeny,
91 leading to LREE and LILE enrichment at spinel facies conditions (1200°C and 1.3-1.6 GPa; Nimis
92 and Morten, 2000).

93 During stage 2, related to the Variscan subduction, corner flow dragged the coarse-peridotites close
94 to the slab-wedge interface and caused the transition to porphyroclastic to fine-grained equigranular
95 peridotites. The porphyroclastic type shows garnet corona around spinel and the occurrence of pale
96 green amphibole in the peridotite matrix (Obata and Morten, 1987). However, well preserved
97 spinel-facies coarse-peridotites are fairly rare in the field and the transitional evolution of the
98 different lithotypes is still somewhat enigmatic.

99 Fine-grained peridotites show different mineral assemblages, mainly distinguished by the
100 presence/absence of garnet and clinopyroxene, ranging from olivine + orthopyroxene +
101 clinopyroxene + garnet + Ca-amphibole \pm spinel to olivine + orthopyroxene + Ca-amphibole +
102 chlorite (Obata and Morten, 1987). Phlogopite, apatite, dolomite and rare dissakisite-(La) are
103 accessories (Tumiati et al., 2007). Fine-grained peridotites resulted from mylonitization and
104 hydration of the coarse-peridotites that interacted with slab-derived fluids during the Variscan
105 continental collision. The metamorphic peak was estimated around 850°C and 2.0-2.5 GPa in
106 eclogite-facies conditions (Nimis and Morten, 2000; Braga and Sapienza, 2007), concomitant to a
107 widespread crystallization of LILE- and LREE-rich amphibole, in textural equilibrium with garnet
108 (Scambelluri et al., 2006). The timing of tectonic emplacement into the crust is still uncertain:
109 garnet-whole rock and garnet-clinopyroxene isochrones Sm-Nd ages of Tumiati et al. (2003)
110 suggest that garnet-facies equilibration and metasomatism in peridotite, and country rocks
111 migmatization occurred at the same time, about 340-330 Ma. This argument supported the notion
112 that the tectonic insertion of peridotite into the subducted continental crust occurred at peak

113 conditions (Tumiati et al., 2003). Conversely, Scambelluri et al. (2006) stressed that the
114 incorporation of mantle wedge peridotites into the crustal slab to form a crust-mantle mélange
115 likely occurred shortly after the metamorphic peak.

116 Stage 3 (Fig. 2) represents the retrograde evolution of the crust-mantle association, recorded by (i)
117 kelyphitic coronas around garnet in fine-grained garnet-amphibole peridotites (Godard and Martin,
118 2000) and (ii) the occurrence of fine-grained spinel/chlorite-amphibole peridotite, interpreted as
119 retrograde derivatives from garnet-peridotites (Obata and Morten, 1987; Braga and Sapienza 2007;
120 Marocchi et al., 2007). All the UZ lithotypes experienced a post-Variscan exhumation and were
121 subjected to variable degrees of serpentinization that in some instances erased the previous texture
122 of peridotites.

123 The petrographic evidence of amphibole and minor dolomite requires carbon bearing hydrous
124 metasomatic agents. The origin of the hydrous metasomatic fluids with a CO₂ component were at
125 first interpreted by Rampone and Morten (2001) as residual fluids left after the crystallization of
126 leucosomes of the host migmatite during the Variscan subduction. On the other hand, Scambelluri
127 et al. (2006) emphasized that fluids interacted with the peridotites while the latter still resided in the
128 mantle wedge (i.e. not within a crust-mantle mélange); moreover, the origin of metasomatic fluids
129 were related to the reaction of hydrous anatectic melts with wedge peridotite at the slab-wedge
130 boundary. This reaction produced an orthopyroxene-rich layer and LILE-rich residual fluids
131 forming the garnet + amphibole peridotites. Later studies (Marocchi et al., 2007; Ionov et al., 2017)
132 suggested that the migmatization of the host gneisses plausibly acted only during late stages of
133 metasomatism, while the main metasomatic episodes were governed by slab-derived crustal fluids
134 equilibrating with the lithospheric mantle prior to the Variscan subduction.

135 Dolomite, previously found in all UZ textural types, is the main C-repository (Sapienza et al., 2009;
136 Förster et al., 2017; Gudelius et al., 2018). Trace elements analyses of dolomite from stage 2 and
137 stage 3 peridotites indicate that dolomite represents the major repository also for Sr, Ba, Pb and

138 subordinately LREE (Sapienza et al., 2009). Smaller amounts of magnesite are reported by
139 Malaspina and Tumiati (2012) in a fine-grained porphyroclastic garnet peridotite and by Förster et
140 al. (2017) in a coarse-grained protogranular peridotite. Only recently, evidences for carbonate
141 dissolution-precipitation processes in these peridotites have been reported (Förster et al., 2017).

142 **3. Analytical methods**

143 **Scanning electron microscopy (SEM), Electron probe microanalysis (EPMA)**

144 Silicates, carbonates, oxides and sulfides were investigated with SEM and EPMA. Petrographic
145 thick sections (ca. 100 μm of thickness) and peridotite chips with 5 mm of thickness were gold
146 coated for SEM analyses. BSE images were acquired at the Dipartimento di Scienze Biologiche
147 Geologiche e Ambientali, Università di Bologna, using a Scanning Electron Microscope (SEM)
148 Philips 515B fitted with an EDAX DX4 microanalytical device. The operating conditions were:
149 accelerating voltage of 15kV, beam current of 2nA and a spot size $\sim 1\mu\text{m}$. Major element
150 compositions were determined with the JEOL 8100 SUPERPROBE electron microprobe at the
151 Institute of Mineralogy and Petrography, University of Innsbruck, with the analytical conditions: 15
152 kV accelerating voltage, 10 nA beam current, using wavelength-dispersive spectroscopy (WDS). F-
153 topaz (F), jadeite (Na_2O), orthoclase (K_2O), rutile (TiO_2), rhodonite (MnO), MgO, diopside (CaO),
154 chromite (Cr_2O_3), almandine (FeO), corundum (Al_2O_3), atacamite (Cl), baryte (BaO), Ni-olivine
155 (NiO), and quartz (SiO_2) were used as standards for silicates and oxides analyses, while calcite
156 (CaO), diopside (MgO), strontianite (SrO), rhodonite (MnO) and almandine (FeO) standards were
157 used for carbonates analyses. To avoid carbonate devolatilization during EPMA, the electron beam
158 was defocused to an approximate size of 10x10 microns.

159 **Micro-Raman spectroscopy**

160 Micro-Raman spectroscopy was performed for the identification of the serpentine phases and
161 calcite + brucite intergrowths at the Department of Mathematical, Physical and Computer Sciences,
162 University of Parma. Polished thick sections and rock chips were investigated with a Horiba Jobin-
163 Yvon LabRam apparatus, equipped with an Olympus microscope with 10x, 100x and ultra long
164 working distance (ULWD) 50x objectives and motorized x-y stage. The 473.1 nm line of a doubled
165 Nd:YAG diode pumped laser was used as excitation source with a spectral resolution of about 2 cm⁻¹.
166 The 473.1 nm source was selected to work in the spectra range with the maximum sensitivity of
167 the detector to enhance the OH stretching signal of the water molecules in the high wavenumber
168 range (3000-4000 cm⁻¹). The spectra were collected using the ULWD 50X objective with repeated
169 acquisition. The background subtraction of each spectrum was performed with the LabSpec[®]
170 software.

171

172 *In situ* Laser Ablation MC-ICP-MS analyses

173 In situ Sr isotopes of carbonates occurring in three thick sections and four rock chips of 5 mm
174 thickness, representing both fine- and coarse- grained peridotites, were measured at the Centro
175 Interdipartimentale Grandi Strumenti (CIGS) of the University of Modena and Reggio Emilia
176 (Italy) using a double focusing MC-ICP-MS with a forward Nier-Johnson geometry (Thermo
177 Fisher Scientific, NeptuneTM), coupled to a 213 nm Nd:YAG laser ablation system (New Wave
178 ResearchTM). The analytical procedure is the same as of Giovanardi et al. (2018).

179 Laser ablation parameters consisted of a laser spot ranging from 55 μm to 100 μm (see Table 4), a
180 fluence of ~10 J/cm², a laser frequency of ~10 Hz and a He flux of ~0.5 L/min. Signals were
181 acquired in static mode with a block of 250 cycles (including laser warm-up, ~50–80 cycles of
182 analysis and washout) and an integration time of 0.5 s. Collected *m/z* were 82Kr, 83Kr, 84Sr, 85Rb,
183 85.5, 86Sr, 86.5, 87Sr and 88Sr. Masses 85.5 and 86.5 were measured to check doubly charged Yb
184 interferences. Kr was corrected measuring 60 s of gas blank with the laser off. After background

185 subtraction, the remaining signal on mass 82 was used to check the formation of Ca dimers and
186 argides; while mass 83 to check the presence of Er^{2+} . Rb was corrected by calculating the ^{87}Rb
187 contribution to mass 87 by measuring the interference-free ^{85}Rb signal, correcting for instrumental
188 mass fractionation, and using the natural $^{87}\text{Rb}/^{85}\text{Rb}$ ratio. Mass bias normalization was performed
189 through exponential law and a $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of 8.375209. The accuracy of the analyses was
190 checked using an in-house reference material (modern marine shell) (see Table X in Supplementary
191 Material), which yielded a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.709174 ± 0.000064 (2σ ; $n = 19$), in agreement with
192 modern seawater (0.70917). Three analyses of a second in-house carbonate reference material
193 yielded a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.707562 ± 0.000018 (2σ), equal to the solution reference value (0.70756
194 ± 0.00003 ; 2σ) (Weber et al., 2019). Data reduction was performed using a customized excel
195 spreadsheet.

196

197 **4 Results**

198 **4.1 Sample description and petrography**

199 Peridotite samples were collected from the Northeastern part of the UZ (Figs 1 and 3), from
200 outcrops or boulders very close to the outcrops (Table 1 for sample description, location) (Fig.3).
201 Each sample underwent weak up to very strong serpentinization that in some instances overprinted
202 the previous textures. All the samples investigated contain carbonates such as dolomite and, locally,
203 magnesite and calcite (see Table 1). From now on, the numbers 1 and 2 refer to first and second
204 generation respectively of olivine, orthopyroxene, clinopyroxene and spinel.
205 Samples 18LP1 and MOL1-C are coarse-type spinel peridotites consisting mainly of large (1-4 mm)
206 olivine₁, orthopyroxene₁ and spinel₁. Sample 18LP1 shows orthopyroxene₁ with undulose
207 extinction and kink bands and they are usually surrounded by a chlorite rim with a diameter of
208 about 150 μm . Clinopyroxene₁, exhibiting amphibole and spinel exsolutions, is associated with
209 nearly-dark vermicular spinels₁. The studied chip rock contains a 300 μm wide veinlet crosscutting

210 the matrix and filled with dolomite associated with colorless amphibole and chlorite; here, dolomite
211 occurs as lobate-shaped grains (Fig. 5a). This veinlet is perpendicularly crosscut in several places
212 by thin (ca. 50 μm wide) serpentine veins that locally contain dolomite streaks (ca. 25 μm wide)
213 (Fig. 5b). Sample MOL1-C does not contain clinopyroxene₁ and mainly consists of strongly
214 fractured olivines₁ and orthopyroxenes₁ showing kink bands. Vermicular dark spinel is often
215 included in coarse green amphiboles. The sample shows a ca. 300 μm wide veinlet consisting of
216 magnesite, serpentine, colorless amphibole and opaque minerals (Fig. 5c) cuts by a dolomite vein
217 (ca. 200 μm long) (Fig. 5d). When the magnesite + serpentine + colorless amphibole vein
218 encounters coarse crystals of orthopyroxene₁, serpentine minerals grow along orthopyroxene₁
219 cleavages promoting a black-colored needle-like serpentine microstructure (Fig.s 4a and 5c). Both
220 coarse peridotites probably escaped full mineralogical equilibration under eclogite-facies
221 conditions, as indicated by the absence of garnet.

222 Fine-grained peridotites are the most common textural rock type in the UZ. They show grain sizes
223 smaller than 0.7 mm and exhibit porphyroblastic to equigranular textures. Sample VM10A is a fine-
224 grained mylonitic garnet-amphibole-peridotite with a main foliation defined by the preferred
225 orientation of matrix minerals. The main mineralogical association consists of fine-grained olivine₂,
226 orthopyroxene₂, green amphibole, spinel₂ with accessory matrix dolomite (ca. 60 μm) (Fig. 5e)
227 associated with apatite and green amphibole. Allanite locally occurs in the matrix. A porphyroclast
228 (ca. 1cm) of highly fractured reddish zircon occurs in this rock; it contains a mm-sized dolomite
229 inclusion associated with apatite. Rare small-sized pinkish-garnets occur.

230 Samples KL2.4-2b and KL2.4-3 are fine-grained garnet-amphibole peridotites and contain
231 porphyroblasts of coarse pink garnet (ca. 1cm of size) surrounded by a kelyphitic corona made of
232 orthopyroxene + amphibole + clinopyroxene \pm spinel (Fig. 4b). These garnets are highly fractured
233 and contain mm-sized spinel₁ inclusions. This spinel₁ locally hosts polycrystalline aggregates

234 consisting of (i) apatite, ilmenite, pentlandite, calcite-brucite intergrowths and phlogopite; (ii)
235 ilmenite, chlorite, apatite, pentlandite. The KL2.4-2b sample description is reported in detail by
236 Förster et al. (2017), who also documented the occurrence of a dolomite inclusion (ca. 70 μm) in a
237 primary spinel included in coarse-grained garnet. Matrix dolomite (ca. 40 μm) occurs commonly in
238 association with green amphibole and apatite. In both samples, calcite occurs as thin veins in the
239 matrix (Fig. 5g), included in chlorite and, in some instances, forming intergrowths with brucite.
240 Two generations of serpentine minerals occur, with the first one represented by mesh structure in
241 olivine₂ and bastite in orthopyroxene₂ and the second one forming thin veins crosscutting the matrix
242 with the porphyroblastic garnet and kelyphitic corona.

243 Sample KL1-A is a fine-grained garnet-amphibole peridotite with the same mineralogy of the
244 previous samples but equigranular texture (ca. 300 μm) (Fig. 4c). Here, intergrowths of calcite +
245 brucite associated with relict dolomite occur in the matrix (Fig. 5f). Widespread small-sized
246 pinkish-garnets (200-300 μm) occur interstitially in the matrix, always exhibiting a kelyphitic
247 corona of orthopyroxene + amphibole + clinopyroxene \pm spinel. This peridotite sample shows
248 mesh and bastite replacement textures of olivine and pyroxene respectively. This sample is also
249 pervaded by thin veins of serpentine and chlorite crosscutting the matrix (Fig. 4c).

250 Sample MM1 is a fine-grained amphibole-chlorite peridotite. This sample comes from a well-
251 studied outcrop which provided sample 300B studied by Morten and Obata (1990), Scambelluri et
252 al. (2006) and Braga and Sapienza (2007). Particularity of the sample is the presence of a ca. 1 cm
253 wide serpentine vein showing concentric zonation with a core filled by magnetite and pentlandite
254 and minor dolomite and calcite, and a border zone including matrix minerals consisting of olivine₂,
255 orthopyroxene₂, green amphibole and spinel₂ (see Figs. 5a-b-c-d and S1a-b-c-d in Supplementary
256 Material). Matrix dolomite is estimated to occur with an abundance of 2%, with a grain-size range
257 of about 50-100 μm and commonly associated with apatite (Figs. 5h and S1b in Supplementary
258 Material).

259 4.2 Major element compositions and micro-Raman spectroscopy

260 Representative major element compositions of silicate minerals and apatites are listed in **Table 2**
261 (for all the EPM analyses see Supplementary Material ST-I and ST-IX) while all the carbonates
262 major element compositions are listed in **Table 3**. The major element compositions commonly do
263 not exhibit variations between coarse-grained and fine-grained rocks and minerals of different
264 generations. *Olivine* is unzoned with $\text{Fo}_{88-90}\text{Teph}_{0-2}$. *Orthopyroxene* is commonly $\text{En}_{90-92}\text{Fs}_{8-10}\text{Wo}_{0-1}$
265 with Al_2O_3 reaching values up to 2.80 wt.%. Two textural-types of *spinel* are recognized: a first
266 generation of coarse spinel_1 included in porphyroblastic garnets exhibits $\text{Cr}\# \sim 0.43$, where $\text{Cr}\#$ is
267 $\text{Cr}/(\text{Cr}+\text{Al})$, while the second generation of matrix smaller spinel_2 has $\text{Cr}\#$ of about 0.35.
268 *Clinopyroxene* is always diopside ($\text{En}_{46-49}\text{Fs}_{2-3}\text{Wo}_{47-50}$). Green *amphibole* in the matrix is commonly
269 Mg-hornblende and minor pargasite (in samples KL2.4-2b and KL2.4-3). Pargasite is often rimmed
270 by colorless *tremolitic amphibole* ($\text{Al}_2\text{O}_3 \sim 0.25$ wt.%). Considering the three amphibole-types,
271 Na_2O and Al_2O_3 contents range from 0.1 to 1.6 wt.% and from 0.25 to 16.6 wt.%, respectively.
272 When amphibole occurs in veinlets, its composition is always tremolitic (i.e. magnesite vein with
273 tremolite and serpentine). Unzoned *garnet* is pyrope-rich ($\text{Py}_{51-70}\text{Alm}_{17-30}\text{Sps}_{1-4}\text{Grs}_{11-15}$) showing
274 little to no compositional variations between porphyroclasts and small-sized garnets. *Apatite*,
275 always in association with dolomite, exhibits a high Cl content of about 5 wt.%. Serpentine
276 (*lizardite*) replacing olivine and pyroxenes exhibits a Fe content ranging from 1.53 to 9.02 wt.%
277 FeO. In the fine-grained amphibole-chlorite peridotite sample MM1, a composite serpentine vein
278 was characterized by micro-Raman spectroscopy showing lizardite and mixed lizardite/chrysotile
279 compositions (Fig. S1 in Supplementary Material). Sheet silicates, represented by chlorite and
280 phlogopite, show Fe contents of 2.22-2.55 and 3.45-5.03 wt.% FeO respectively. The Na_2O content
281 of phlogopite reaches values of 0.13 wt.%.

282 Carbonate compositions are given in the $\text{MgCO}_3\text{-CaCO}_3\text{-FeCO}_3$ ternary diagram (Fig. 6). Unzoned
283 *dolomite* does not exhibit any compositional variations between the different peridotites and
284 microstructural domains. It can be classified as ferroan-dolomite, with X_{FeCO_3} of about 0.02 in all
285 the samples. Similarly, magnesite veinlet shows high Fe content, with X_{FeCO_3} of about 0.05. *Calcite*
286 (together with brucite) was identified using micro-Raman spectroscopy (see Fig S2 in
287 Supplementary Material for the Raman spectrum), and it also occurs as thin veins cutting the matrix
288 or as intergrowths with brucite in association with dolomite (Fig. 7). Calcite composition is close to
289 the Ca-carbonate endmember (Fig. 6).

290 **4.3 Sr isotope composition of Ulten Zone carbonates**

291 *In situ* $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio analyses are listed in **Table 4**. Carbonates were previously chosen and
292 detected considering the grain size, the Sr concentration and the microstructural domain. Dolomite
293 is the main C-repository, showing a grain size of mostly 30-70 μm . Calcite veins are too narrow (ca.
294 20-30 μm wide) to be measured by LA-MC-ICP-MS, while magnesite does not contain Sr (see
295 Table IX in Supplementary Material). For this study we performed thirty-nine *in situ* analyses. Spot
296 size analyses ranges between 55 and 100 μm , in relation to the carbonate size (see Table 4). The
297 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios obtained for all the dolomites are reported in Figure 8 and range between
298 0.70360 ± 0.00007 and 0.71184 ± 0.00026 (n=36). The distribution of Sr isotopic compositions of
299 all carbonates analyzed is shown in Figure 8.

300 In the coarse-type spinel peridotite *18LPI*, the dolomite vein associated with tremolite and chlorite
301 exhibits highly variable Sr isotopic values ranging from 0.70360 ± 0.00007 to 0.70830 ± 0.00015
302 (n=12) (Figs. 8 and 9). Two lobate-shaped dolomite grains (spots 5, 8) shown in Figure 9 exhibit
303 the lowest values of all UZ carbonates analyzed. In *MOLI-C* late vein dolomite cutting a magnesite
304 vein (Fig. 5d) gives an average value of 0.71184 ± 0.00026 (n=2), representing the highest
305 radiogenic ratio obtained by the *in-situ* Sr measurements of all Ulten carbonates-bearing peridotites
306 of this study.

307 In three fine-grained peridotites, both dolomite and (when possible) calcite were analyzed. In Figure
308 8 it can be observed that the Sr isotopic ratio of matrix dolomite is nearly-homogeneous within the
309 same sample and, conversely, different values were obtained from the different fine-type
310 peridotites. In the mylonitic garnet-amphibole peridotite *VM10A*, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of matrix
311 dolomite is 0.70529 ± 0.00011 (n=4). In the same sample, a large dolomite inclusion (ca. 7 mm
312 long) occurring in a zircon porphyroclast exhibits a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70597 ± 0.00007 , obtained
313 by analyzing a line scan along the carbonate grain. In the fine-grained garnet-amphibole peridotite
314 *KLI-A*, the dolomite $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.70671 ± 0.00021 whereas calcite (associated to brucite)
315 gives slightly higher radiogenic values of about 0.70719 ± 0.00018 (n=3). It is worth noting that,
316 given the small size of calcite and brucite and their textural interconnection, both of them were
317 included in the spots analyses. However, brucite is not supposed to incorporate Sr^{2+} and we
318 therefore consider our data as exclusive for calcite. Average value of matrix dolomite in fine-
319 grained amphibole-chlorite peridotite *MMI* is 0.70487 ± 0.00010 (n=16).

320 **5. Discussion**

321 Petrographic data indicate that the UZ peridotites, during their complex metasomatic history,
322 underwent carbonation and, locally, dolomite dissolution and calcite reprecipitation. To date, the
323 crustal portion of the subducted continental slab has been considered as the source of the several
324 metasomatic fluids that interacted with the UZ peridotites (Rampone and Morten, 2001;
325 Scambelluri et al., 2006; Sapienza et al., 2009). The presence of hydrous phases (dissakisite-Ce,
326 amphibole and minor phlogopite) enriched in LILE, Th, U, and LREE compared to other
327 incompatible trace elements, as well as the occurrence of large zircon grains (Forster et al., 2017;
328 this study), strongly support this interpretation. On the basis of textures, bulk rock and mineral
329 major and trace element compositions, Ionov et al. (2017) suggested that most of the “crustal”
330 overprint of the UZ occurred into the mantle wedge well below the crust (ca. 850°C at 60-90 km

331 depths), in a supra-subduction setting similar to the mantle wedge sampled by harzburgite xenoliths
332 from the western Pacific. Given the uncertainty of ‘crustal’ vs ‘mantle’ origin of metasomatizing
333 fluids, the Sr concentration and isotopic signature of carbonates of the UZ peridotites may help to
334 shed light on these contrasting views.

335 We will focus on C-related processes by simply dividing the metasomatic evolution into two main
336 stages: (1) the *HP* carbonation of mantle wedge peridotites at peak (eclogite-facies) conditions and
337 during their early exhumation up to mid-crust depth and (2) the carbon re-mobilization via fluid-
338 rock interaction during the final exhumation of the crust-mantle mélange, which formed after the
339 incorporation of mantle slivers into the subducted continental crust. The tectonic insertion of the
340 peridotites into the host gneiss is believed to have occurred after peak pressure conditions
341 (Scambelluri et al. 2006). We discuss these two processes separately, referring to them as Stage 1
342 and Stage 2.

343 *5.1 Stage 1: HP carbonation.*

344 *Included and interstitial dolomite*

345 The onset of the metasomatic history of the UZ peridotites started with percolation of melts into the
346 spinel-facies mantle wedge, causing the formation of pyroxenite layers (Nimis and Morten, 2000).
347 At this stage there is no petrographic evidence of carbonation. Conversely, the occurrence of lobate-
348 shaped dolomite inclusion in a porphyroclastic zircon and matrix dolomites in the fine-grained,
349 garnet-bearing peridotites suggests that carbonation occurred when the Ulten peridotites reached
350 peak eclogite-facies conditions (Fig.10). If zircon and dolomite formation are coeval as the
351 petrographic observation suggests, a time constraint for this early episode of carbonation can be
352 provided by the 333 Ma U-Pb age of zircon from metasomatic reaction bands at the Mt. Hochwart
353 gneiss-peridotite contact (Tumiati et al., 2007), the same locality of sample VM10A of this study.

354 Furthermore, in another fine-grained garnet-bearing peridotite we have a unique microstructural
355 evidence of a dolomite inclusion in Cr-spinel, which is included in a porphyroclastic garnet. Major
356 elements composition obtained with EPMA shows that this inclusion has the same composition as
357 the matrix dolomite and dolomite veins. The origin of this inclusion is yet unknown (i.e. mantle
358 provenance or subducted continental crustal derivation), but the occurrence of fractures in the host
359 garnet may suggest that dolomite precipitation could have been induced during C-rich fluids
360 percolation after spinel and garnet crystallization (in contrast to the interpretation of an early melt-
361 related process in the high-*T* spinel stage given by Förster et al., 2017). At peak conditions, fluids
362 prompted the precipitation of interstitial dolomite.

363 During continental collision, the crustal portion of the descending slab consists of the sedimentary
364 cover and its underlying crystalline basement. The subducted lithologies may release fluids into the
365 overhanging mantle wedge and their source can be investigated, at least in part, by considering fluid
366 mobile elements (FME) such as Sr and the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio. Different sources of the
367 metasomatic liquids were considered for the *HP*-dolomite (both included and interstitial), as
368 reported in Figure 11: (i) associated stromatic gneisses and orthogneisses; (ii) Devonian
369 sedimentary cover; (iii) lithospheric mantle; (iv) trondhjemitic dykes and pockets.

370 (i) Based on literature, we expected similar Sr isotopic ratio for the carbonates and the
371 associated crustal rocks. However, the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of stromatic gneisses (i.e.
372 migmatitic paragneisses that suffered 20-30% degree of partial melting according to
373 Braga and Massonne, 2012) and orthogneisses from the subducted crust and now part of
374 the *mélange*, argues against their role as the sources for C-bearing fluids.

375 (ii) It is difficult to assess the role of a sedimentary cover overlying the crystalline basement
376 because of the lack of field evidence of Paleozoic sedimentary successions associated
377 with the UZ crust-peridotite association. Subducted marine carbonates along the oceanic
378 crust subduction prior to the subduction of the continental crust may also play a role in

379 the formation of carbonates in the mantle wedge. However, Sr isotope values reported
380 by van Geldern et al. (2006) for well-preserved Devonian brachiopod shells (Mn < 100
381 ppm; Fe < 400 ppm and Sr > 500 ppm) range from 0.70782 to 0.70804 (during the
382 Emsian-Eifelian boundary and early Famennian respectively), unlikely representing the
383 required sources for the interstitial dolomite in the matrix.

384 (iii) The relatively unradiogenic values of matrix carbonates have Sr isotopic values close to
385 those of the coarse-grained spinel-garnet peridotites of Tumiati et al. (2003), as shown in
386 Fig. 11. Several studies (i.e. Tumiati et al. 2003 and Scambelluri et al. 2006) highlighted
387 that the UZ peridotites were enriched in incompatible elements by reacting with fluids
388 released from a subducting continental lithosphere undergoing partial melting. In
389 particular, the enrichment of the UZ peridotite took place in the mantle wedge above the
390 subduction zone (Scambelluri et al. 2006) by fluids variably equilibrated with mantle
391 rocks (Ionov et al. 2017). In this scenario, the fluids responsible for the formation of
392 matrix dolomite might have variably reacted with a depleted lithospheric mantle and
393 evolved towards slightly lower Sr isotopic compositions before crystallizing matrix
394 dolomite.

395 (iv) The radiogenic Sr signature of few trondhjemitic dykes and pockets described by Del
396 Moro et al. (1999) are close to those reported for the matrix dolomite of the fine-grained
397 mylonitic garnet-amphibole peridotite VM10A from Mt. Hochwart. Based on petrology
398 and whole-rock Sr-Nd isotope geochemistry, Del Moro et al. (1999) interpreted the UZ
399 trondhjemite as melts produced by fluid-assisted anatexis of a metasedimentary lower
400 crust characterized by low Rb/Sr and Sr isotope ratios. Once formed, the trondhjemite
401 melts intruded the UZ migmatitic crust.

402 *Localized carbonation: carbonates veinlets.*

403 The tectonic insertion of mantle material into the crustal portion of the continental slab occurred
404 after the attainment of maximum pressure conditions, i.e. at the beginning of the exhumation
405 (Scambelluri et al., 2006). During this early phase of upwelling of the crust-mantle mélange,
406 dolomite veins associated with tremolite and chlorite and magnesite + lizardite-chrysotile +
407 tremolite vein within the two coarse-type spinel peridotites are indicative that carbonation occurs as
408 local injection of C-rich fluids (Fig. 10) under different retrograde P - T conditions. The mineral
409 assemblage of the dolomite + tremolite + chlorite vein supports the evidence of a retrograde process
410 prior to serpentinization ($650^{\circ}\text{C} \leq T \leq 700^{\circ}\text{C}$ at P of ca. 1 GPa) and, in addition, provides a
411 minimum P - T estimate for the formation of the crust-mantle mélange.

412 The Sr isotopic heterogeneity (0.7035-0.7085; Figs. 8 and 9) measured in different dolomite grains
413 from the dolomite + tremolite + chlorite vein encompasses the $^{87}\text{Sr}/^{86}\text{Sr}$ values measured from
414 matrix and included dolomite. Most of the inter-grain variability can be explained by the interaction
415 of the matrix and the included dolomite, which show low-Sr isotopic values, with progressively
416 more radiogenic fluid, as it would be expected in mantle rocks closely associated with crustal
417 lithologies. Similarly, late-stage carbonate veins in kimberlites from Beinfontein show a large
418 variability of the Sr-isotope composition, reaching values of 0.70957 ± 116 (2σ). These results were
419 interpreted as a consequence of primary carbonates interaction with crustal fluids (Castillo-Oliver et
420 al., 2018), as we speculate for the UZ dolomite veins. It is not easy to explain the occurrence of low
421 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7036-0.7039; Figs. 8 and 9) of two dolomite grains in this vein. As shown in Fig.
422 11, these values approach the MORB signature, thus requiring a distinct metasomatic agent with a
423 Sr signature typical of a mantle reservoir depleted in radiogenic Sr. This metasomatic agent
424 depleted in radiogenic Sr precipitated primary carbonates that did not interact with late-stage
425 metasomatic crustal fluids.

426 The occurrence of a magnesite vein associated with lizardite-chrysotile and tremolite suggests
427 influx of a local carbonaceous fluid at $T < 600^{\circ}\text{C}$ during the retrograde path. This vein is cut by a

428 dolomite vein with the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.7118-0.7119; Figs. 5d and 8), which formed after
429 the previously discussed vein dolomite. The highly radiogenic values of this vein suggest that this
430 episode of injection of C-rich fluids occurred when the orogenic mélange, characterized by mingled
431 crustal and mantle components, was already well developed and that infiltrating C-rich crustal
432 fluids introduced significant amounts of radiogenic Sr (Fig. 11). According to the geodynamic
433 scenario of Ranalli et al. (2005), this mélange was brought to mid-crustal depths between 330 and
434 300 Ma reaching 0.7 GPa at 500°C.

435 *5.2 Stage 2. Carbon re-mobilization via fluid-rock interaction*

436 Following the geodynamic model proposed by Ranalli et al. (2005), after the late Carboniferous fast
437 exhumation, the crust-mantle mélange underwent slow exhumation and cooling during Permian-
438 Triassic times (300-205 Ma). During this slow exhumation, Stage2 carbonation is related to the
439 action of serpentinizing fluids, which in some instances erased the previous mantle texture. Here, C
440 re-mobilization via fluid-rock interaction prevails (blue arrow, Fig. 10) as evidenced by the
441 occurrence of (i) calcite + brucite intergrowths surrounded by serpentine (Figs. 5f and 7) and (ii)
442 thin calcite veins.

443 The calcite + brucite intergrowths are the result of dolomite breakdown during interaction with
444 aqueous fluids (Figs. 5f and 7) (Förster et al., 2017) and were found only in highly serpentinized
445 fine-grained garnet-bearing peridotites. Moreover, micro-Raman investigations allowed the
446 identification of lizardite as the serpentine phase surrounding these intergrowths. If serpentinizing
447 fluids were the cause of dolomite dissolution, we therefore argue that the precipitation of calcite +
448 brucite probably occurred at P of about 0.5 GPa and $T < 300^\circ\text{C}$. At this stage the Ulten basement
449 was likely subjected to isostatic adjustment after the conclusion of the Variscan collision (Ranalli et
450 al., 2005).

451 The formation of thin calcite veins occurring in the matrix and in some instances crosscutting
452 spinel, chlorite and phlogopite, was interpreted by Förster et al. (2017) as a consequence of the
453 influx of serpentinizing fluids that triggered dissolution of the former dolomite and crystallization
454 of calcite + brucite intergrowths with concomitant liberation of CO₂, following the reaction
455 $\text{CaMg}(\text{CO}_3)_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{Mg}(\text{OH})_3 + \text{CO}_2$. The release of CO₂ may prompt *in-situ*
456 formation of carbonates (i.e. thin calcite veins) after C saturation was achieved.

457 During fluid-rock interaction, Sr preferentially partitions into the fluid phase (Banner et al., 1995)
458 and the aqueous serpentinizing fluids, characterized by $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7070\text{-}0.7075$, dissolved
459 dolomite that provided the local source of Sr. Eventually, the fluid enriched in C and Sr (from
460 dolomite) precipitated relatively Sr-rich calcite. The higher elemental Sr abundance with respect to
461 dolomite is due to the less incompatible behavior of Sr in calcite (Banner et al., 1995).

462

6. Conclusion and future directions

463 The combination of textural observation of carbonates with *in situ* Sr isotope analyses reveals a
464 more complex metasomatic evolution for the UZ peridotite than previously thought. In particular,
465 two main conclusions can be drawn: (1) at peak (eclogite facies) conditions, there is not a simple
466 carbon transfer between the crustal portion of a subducted continental and the overhanging wedge,
467 but additional C sources have to be considered and (2) at low-pressure conditions, during the final
468 exhumation stages of an already well developed crust-mantle mélange, the main carbonation
469 process implies dolomite breakdown and calcite reprecipitation by H₂O-rich fluids.

470 The relatively unradiogenic Sr isotope ratio recorded by inclusion- and matrix dolomite, with
471 some grains of a dolomite vein, does not support a simple derivation from fluids derived from the
472 migmatite host gneisses (Fig. 11). The first stage of carbonation thus requires *HP* metasomatic
473 fluids (i.e. at ~ 2.5 GPa and 850°C) likely unrelated to the associated crust (stromatic gneisses and
474 orthogneisses), as already recognized by Marocchi et al. (2009; 2007). We suggest that these *HP*

475 fluids may have variably equilibrated with a depleted lithospheric mantle before the crystallization
476 of matrix dolomite. Residual COH fluids originated from the crystallization of trondhjemite liquids
477 intrusion derived from deeper portions of the Ulten crust or fluids released from Paleozoic
478 carbonate succession and involved into the Variscan orogenesis can be considered as alternative
479 sources for the metasomatic agents infiltrating at peak conditions and before the onset of
480 serpentinization.

481 During the first stages of exhumation, C-bearing fluids were channeled into veins, giving rise to the
482 veinlet filled with dolomite associated with tremolite and chlorite, followed at lower *P-T* conditions
483 by the formation of the magnesite + lizardite-crysothile + tremolite veins. The fluids released by the
484 crystallization of leucosomes of the host migmatites, showing variable CO₂/H₂O ratios as inferred
485 by Rampone and Morten (2001), seem to be important metasomatic agents only at the end of the
486 exhumation of the crust-mantle mélange, at temperatures consistent with lizardite stability,
487 providing the highest Sr isotope values for the dolomite veins. The infiltration of serpentinizing
488 fluids represents the last metasomatic episode of peridotites, leading to C-remobilization by
489 dolomite dissolution and calcite precipitation with concomitant liberation of CO₂.

490 Evidences of both HP carbonation and carbonates dissolution-reprecipitation make these rocks an
491 effective carbon locker and a “pit-stop” for C-remobilization through a mantle wedge.
492 Consequently, the results of this study have implications for the global comprehension of the so
493 called “Deep Carbon Cycle”. While in situ Sr isotope data have demonstrated useful to give us
494 additional constrains on an overall complex multiphase metasomatic evolution, their main
495 limitation is the restriction to relatively large grains ($\geq 50\mu\text{m}$) and the less precision compared to
496 dilution techniques. However, our approach ensures the textural control that is mandatory when
497 multiple generations of metasomatic minerals occur in the same sample. The errors obtained for the
498 Ulten carbonates, moreover, are far lower than the variability observed, allowing to clearly

499 distinguish the different isotope patterns. Future higher resolution in-situ C and O isotope analyses
500 of carbonates will allow to better constrain the sources of these C-bearing metasomatizing fluids.

501 **Acknowledgements**

502 G. Gasparotto (University of Bologna), M. Tribus (University of Innsbruck) and Antonio Langone
503 are thanked for assistance during SEM, EPMA and LA-ICP-MS analyses. Constructive reviews by
504 Guillaume Delpech and Andrea Giuliani greatly improved this work. This research was supported
505 by RFO and ALMAIDEA grants (University of Bologna).

506 **References**

- 507 Banner, J.L., 1995. Application of the trace element and isotope geochemistry of strontium to
508 studies of carbonate diagenesis. *Sedimentology* 42, 805–824.
- 509 Bebout, G.E., Penniston-Dorland, S.C., 2016. Fluid and mass transfer at subduction interfaces. The
510 field metamorphic record. *Lithos* 240, 228–258.
- 511 Braga, R., Sapienza, G.T., 2007. The retrograde evolution of a dolomite-bearing hydrous peridotite
512 from the Ulten Zone (Italian Alps). *GeoActa* 6, 37–45.
- 513 Braga, R., Massonne, H.-J., 2012. H₂O content of deep-seated orogenic continental crust: the Ulten
514 Zone, Italian Alps, *International Geology Review* 54, 633–641.
- 515 Brueckner, H.K., Medaris, L.G., 2000. A general model for the intrusion and evolution of
516 ‘mantle’ garnet peridotites in high-pressure and ultra-high-pressure metamorphic terranes.
517 *Journal of Metamorphic Geology* 18, 123–133.
- 518 Castillo-Oliver, M., Giuliani, A., Griffin, W., L., O’Reilly, S., Y., 2018. Characterisation of primary
519 and secondary carbonates in hypabyssal kimberlites: an integrated compositional and Sr-
520 isotopic approach. *Mineralogy and Petrology*, 112, S555–S567.
- 521 Del Moro, A., Martin, S., Prosser, G., 1999. Migmatites of the Ulten Zone (NE Italy), a record of
522 melt transfer in deep crust. *Journal of Petrology* 40, 1803–1826.
- 523 Dickin, A.P., 2018. Radiogenic isotope geology. 3rd edition, Cambridge University Press, 482.
- 524 Evans, B.W., Johannes, W., Oterdoom, H., Trommsdorff, V. 1976. Stability of chrysotile and
525 antigorite in the serpentinite multisystem. *Schweizerische Mineralogische und*
526 *Petrographische Mitteilungen*, 56, 79–93.
- 527 Förster, B., Braga, R., Aulbach, S., Pò, D.L., Bargossi, G.M.G.M., Mair, V., 2017. A petrographic
528 study of carbonate phases in the Ulten Zone ultramafic rocks: insights into carbonation in
529 the mantle wedge and exhumation-related decarbonation. *Ofioliti* 42, 105–127.
- 530 Fumagalli, P., Poli, S., 2005. Experimentally determined phase relations in hydrous peridotites to
531 6.5 GPa and their consequences on the dynamics of subduction zones. *Journal of Petrology*,
532 46, 555–578.
- 533 Gasparrini, M., Bechstädt, T., Boni, M., 2006. Massive hydrothermal dolomites in the southwestern
534 Cantabrian Zone (Spain) and their relation to the Late Variscan evolution. *Marine and*
535 *Petroleum Geology* 23, 543–568.

- 536 Giovanardi, T., Mazzucchelli, M., Lugli, F., Girardi, V.A., Correia, C.T., Tassinari, C.C., Cipriani,
537 A., 2018. Isotopic constraints on contamination processes in the Tonian Goiás Stratiform
538 Complex. *Lithos* 310, 136–152.
- 539 Godard, G., Martin, S., Prosser, G., Kienast, J.R., Morten, L., 1996. Variscan migmatites, eclogites
540 and garnet-peridotites of the Ulten zone, Eastern Austroalpine system. *Tectonophysics* 259,
541 313–341.
- 542 Gudelius, D., Aulbach S., Braga, R., Höfer, H., Woodland, A.B., Gerdes A., 2018. Element transfer
543 and redox conditions in continental subduction zones: new insights from peridotites of the
544 Ulten Zone, North Italy. *Journal of Petrology* 60, 231–268.
- 545 Hermann, J., Zheng, Y.-F., Rubatto, D., 2013. Deep fluids in subducted continental crust. *Elements*
546 9, 281–287.
- 547 Ionov, D.A., Bigot, F., Braga, R., 2017. The Provenance of the Lithospheric Mantle in Continental
548 Collision Zones: Petrology and Geochemistry of Peridotites in the Ulten–Nonsberg Zone
549 (Eastern Alps). *Journal of Petrology* 58, 1451–1472.
- 550 Johannes, W., Puhon, D., 1971. The calcite-aragonite transition, reinvestigated. *Contributions to*
551 *Mineralogy and Petrology* 31, 28–38.
- 552 Malaspina, N., Tumiati, S., 2012. The role of COH and oxygen fugacity in subduction-zone garnet
553 peridotites. *European Journal of Mineralogy* 24, 607–618.
- 554 Manning, C.E., 2014. A piece of the deep carbon puzzle. *Nature Geoscience* 7, 333.
- 555 Marocchi, M., Hermann, J., Morten, L., 2007. Evidence for multi-stage metasomatism of chlorite-
556 amphibole peridotites (Ulten Zone, Italy): constraints from trace element compositions of
557 hydrous phases. *Lithos* 99, 85–104.
- 558 Marocchi, M., Mair, V., Tropper, P., Bargossi, G.M., 2009. Metasomatic reaction bands at the Mt.
559 Hochwart gneiss-peridotite contact (Ulten Zone, Italy): insights into fluid-rock interaction in
560 subduction zones. *Mineralogy and Petrology* 95, 251–272.
- 561 Martin, S., Godard, G., Prosser, G., Schiavo, A., Bernoulli, D., Ranalli, G., 1998. Evolution of the
562 deep crust at the junction Austroalpine/Southalpine: the Tonale Nappe. *Memorie di Scienze*
563 *Geologiche* 50, 3–50.
- 564 Morten, L., Obata, M., 1990. Rare earth abundances in the eastern Alpine peridotites, Nonsberg
565 area, Northern Italy. *European Journal of Mineralogy* 643–654.
- 566 Müller, W., Prosser, G., Mancktelow, N.S., Villa, I.M., Kelley, S.P., Viola, G., Oberli, F., 2001.
567 Geochronological constraints on the evolution of the Periadriatic Fault System (Alps).
568 *International Journal of Earth Sciences* 90, 623–653.
- 569 Nimis, P., Morten, L., 2000. P–T evolution of ‘crustal’ garnet peridotites and included pyroxenites
570 from Nonsberg area (upper Austroalpine), NE Italy: from the wedge to the slab. *Journal of*
571 *Geodynamics* 30, 93–115.
- 572 Obata, M., Morten, L., 1987. Transformation of spinel lherzolite to garnet lherzolite in ultramafic
573 lenses of the Austridic crystalline complex, northern Italy. *Journal of Petrology* 28, 599–
574 623.
- 575 Petrini, R., and Morten, L., 1993. Nd-isotopic evidence of enriched lithospheric domains: an
576 example from the Nonsberg area, Eastern Alps. *Terra Nova* 5, 19–20.
- 577 Rampone, E., Morten, L., 2001. Records of crustal metasomatism in the garnet peridotites of the
578 Ulten Zone (Upper Austroalpine, Eastern Alps). *Journal of Petrology* 42, 207–219.
- 579 Ranalli, G., Martin, S., Mahatsente, R., 2005. Continental subduction and exhumation: an example
580 from the Ulten Unit, Tonale Nappe, Eastern Austroalpine. *Geological Society, London,*
581 *Special Publications* 243, 159–174.
- 582 Salters, V.J.M. and Stracke, A., 2004. Composition on the depleted mantle. *Geochemistry*
583 *Geophysics Geosystems* 5, 1–27.

- 584 Sapienza, G.T., Scambelluri, M., Braga, R., 2009. Dolomite-bearing orogenic garnet peridotites
585 witness fluid-mediated carbon recycling in a mantle wedge (Ulten Zone, Eastern Alps,
586 Italy). *Contributions to Mineralogy and Petrology* 158, 401–420.
- 587 Scambelluri, M., Hermann, J., Morten, L., Rampone, E., 2006. Melt-versus fluid-induced
588 metasomatism in spinel to garnet wedge peridotites (Ulten Zone, Eastern Italian Alps): clues
589 from trace element and Li abundances. *Contributions to Mineralogy and Petrology* 151,
590 372–394.
- 591 Schramke, J.A., Kerrick D.M., Blencoe J.G., 1982. Experimental determination of the brucite =
592 periclase + water equilibrium with a new volumetric technique. *American Mineralogist* 67,
593 269–276.
- 594 Tumiati, S., Thöni, M., Nimis, P., Martin, S., Mair, V., 2003. Mantle–crust interactions during
595 Variscan subduction in the Eastern Alps (Nonsberg–Ulten zone): geochronology and new
596 petrological constraints. *Earth and Planetary Science Letters* 210, 509–526.
- 597 Tumiati, S., Godard, G., Martin, S., Klötzli, U., Monticelli, D., 2007. Fluid-controlled crustal
598 metasomatism within a high-pressure subducted mélange (Mt. Hochwart, Eastern Italian
599 Alps). *Lithos* 94, 148–167.
- 600 Tumiati, S., Fumagalli, P., Tiraboschi, C., Poli, S., 2013. An experimental study on COH-bearing
601 peridotite up to 3.2 GPA and implications for crust-mantle recycling. *Journal of Petrology*
602 54, 453–479.
- 603 Van Achterbergh, E., Ryan, C.G., Jackson, S.E., Griffin, W.L., Sylvester, P., 2001. Laser-
604 Ablation-ICPMS in the Earth Sciences- Principles and Applications. Mineralogical
605 Association of Canada. 239–243.
- 606 van Geldern, R., Joachimski M.M., Day, J., Jansen, U., Alvarez, F., Yolkin E.A., Ma, X.,-P., 2006.
607 Carbon, oxygen and strontium isotope records of Devonian brachiopod shell calcite.
608 *Paleogeography, Palaeoclimatology, Palaeoecology* 240, 47–67.
- 609 Weber, M., Lugli, F., Hattendorf, B., Scholz, D., Mertz-Kraus, R., Guinoiseau, D., Jochum, K.P.
610 (2019) NanoSr-A – new carbonate microanalytical reference material for *In situ* Strontium
611 isotope analysis. *Geostandards and Geoanalytical Research* doi.org/10.1111/ggr.12296.
- 612 Whitney, D.L., Evans, B.W., 2010. Abbreviations for names of rock-forming minerals. *American*
613 *Mineralogist* 95, 185–187.
- 614 Zanetti, A., Mazzucchelli, M., Rivalenti, G., Vannucci, R., 1999. The Finero Phlogopite-Peridotite
615 Massif: An example of subduction-related metasomatism. *Contributions to Mineralogy and*
616 *Petrology* 134, 107–122.
- 617 Zheng, Y.-F., 2012. Metamorphic chemical geodynamics in continental subduction zones.
618 *Chemical Geology* 328, 5–48.
- 619 Zheng, Y.-F., 2009. Fluid regime in continental subduction zones: petrological insights from
620 ultrahigh-pressure metamorphic rocks. *Journal of the Geological Society* 166, 763–782.

621 **Figure captions – Preference color: online only**

622 Fig.1: Geological sketch map of the study area: localization of the Ulten Zone in the Northeastern
623 Alps and simplified geological map of the Ulten Zone from the 1:10.000 sheets Appiano and Rabbi
624 of the Italian Geological Map with samples localization.

625 Fig. 2: *P-T* trajectory of the Ulten Zone peridotites. Infiltration of hot deep melt (red oval) into
626 wedge peridotites in the spinel stage (Stage1); downward flow of wedge peridotites close to the
627 slab-wedge interface due to corner flow (Stage2); exhumation after incorporation of peridotites in a
628 crust-mantle mélange (Stage 3). Redrawn after Nimis and Morten (2000) and Scambelluri et al.
629 (2006).

630 Fig.3: The Ulten Zone peridotites in the field. (a) Overview of the geological setting close to Malga
631 Masa Murada with indication of the peridotites outcrop showed in detail in (b); (c)-(d)
632 Serpentinized fine-grained peridotites; (e) Highly altered coarse-grained peridotite with coarse
633 orthopyroxenes.

634 Fig.4: Overview of (a) Coarse-grained spinel peridotite MOL1-C with its characteristic serpentine +
635 magnesite + tremolite vein. See text for detailed description. (b) Fine-grained porphyroblastic-
636 garnet-bearing peridotite KL2.4-3. Pinkish-garnet is surrounded by kelyphytic corona and includes
637 large spinels with polycrystalline aggregates. In this peridotite serpentine is common, in
638 association with magnetite. (c) Fine-grained garnet-bearing peridotite KL1-A. Mineral
639 abbreviations after Whitney and Evans (2010).

640 Fig.5: BSE images of carbonates from the Ulten Zone peridotite. (a) 18LP1. Lobate-shaped
641 dolomite grains constituting a veinlet with tremolite and chlorite; (b) 18LP1. Dolomite streaks into
642 serpentine vein; (c) MOL1-C. Serpentine vein with magnesite and tremolitic amphibole. Infiltration
643 of the vein into orthopyroxene formed spectacular needle-shaped microstructure with opaque
644 minerals; (d) MOL1-C. Dolomite vein cutting the magnesite veinlet; (e) VM10A. Interstitial
645 dolomite with its perfect cleavage; (f) KL1-A. Matrix dolomite associated with apatite. Note the
646 incipient formation of calcite-brucite intergrowths into dolomite; (g) KL2.4-3. Large spinel cut by a

647 thin calcite vein; (h) MM1. Matrix dolomite (with little magnesite inclusions) associated with
648 apatite and serpentine. Mineral abbreviations after Whitney and Evans (2010).

649 Fig.6: Carbonates composition plotted in the $\text{MgCO}_3\text{-CaCO}_3\text{-FeCO}_3$ ternary diagram.

650 Fig.7: BSE image of calcite-brucite intergrowths occurring in fine-grained garnet-amphibole
651 peridotite KL1-A. The stars point out the spots for micro-Raman analyses whose spectra is reported
652 in Fig.9. The yellow arrows indicate the serpentine surrounding calcite-brucite intergrowths.
653 Mineral abbreviations after Whitney and Evans (2010).

654 Fig.8: Sr isotope ratios for dolomites and calcites occurring in different microstructural positions
655 measured by LA-MC-ICP-MS. The error bars represent ± 2 standard errors. Whole rock $^{87}\text{Sr}/^{86}\text{Sr}$
656 for fine-grained garnet-amphibole peridotite A4323 and coarse-grained spinel-garnet peridotite
657 A4454 from the work of Tumiati et al. (2003) are reported for comparison.

658 Fig.9: Partial sketch of a dolomite vein associated with tremolite and chlorite in sample 18LP1 with
659 SEM-BSE images associated. Analyzed spots with Sr isotope ratio are reported.

660 Fig.10: P - T diagram with stages of carbonates formation during the metasomatic evolution of the
661 Ulten peridotites. See text for discussion. Reference curves: Dolomite-in, magnesite-in, dolomite-
662 out, garnet-in curve from Tumiati et al., (2013); tremolite (Tr) + magnesite (Mgs) = enstatite (En) +
663 dolomite (Dol) from Malaspina and Tumiati (2012) for $X_{\text{CO}_2} = 0.5$; brucite (Brc) = periclase (Per) +
664 water (H_2O) from Schramke et al., (1982). Antigorite-out curve and chlorite-out curve from
665 Fumagalli and Poli (2005). Antigorite = chrysotile (Ctl) / Lizardite (Liz) from Evans (1976);
666 aragonite = calcite from Johannes and Puhon (1971). The HP -garnet stage and chlorite-amphibole

667 stage correspond to the thermobarometric data obtained by Nimis and Morten (2000) and Sapienza
668 et al. (2009). Mineral abbreviations after Whitney and Evans (2010).

669 Fig.11: Strontium isotopic compositions of carbonates from the Ulten Zone peridotites in
670 comparison with the potential sources of C-bearing fluids. MORB values taken from Salters and
671 Stracke (2004); the Sr-isotope values of stromatic gneisses and peridotites from Tumiatì et al.
672 (2003) and the stromatic gneisses, orthogneisses and trondhjemitic intrusions from Del Moro et al.
673 (1999) are recalculated for $t=330\text{Ma}$, corresponding to the inferred age of the last isotopic
674 homogenization event. The Sr-isotope values for the brachiopod shell calcites from van Geldern et
675 al. (2006) correspond to Early to Late Devonian (Emsian-Eifelian boundary and early Famennian).

Figure1

Fig.1

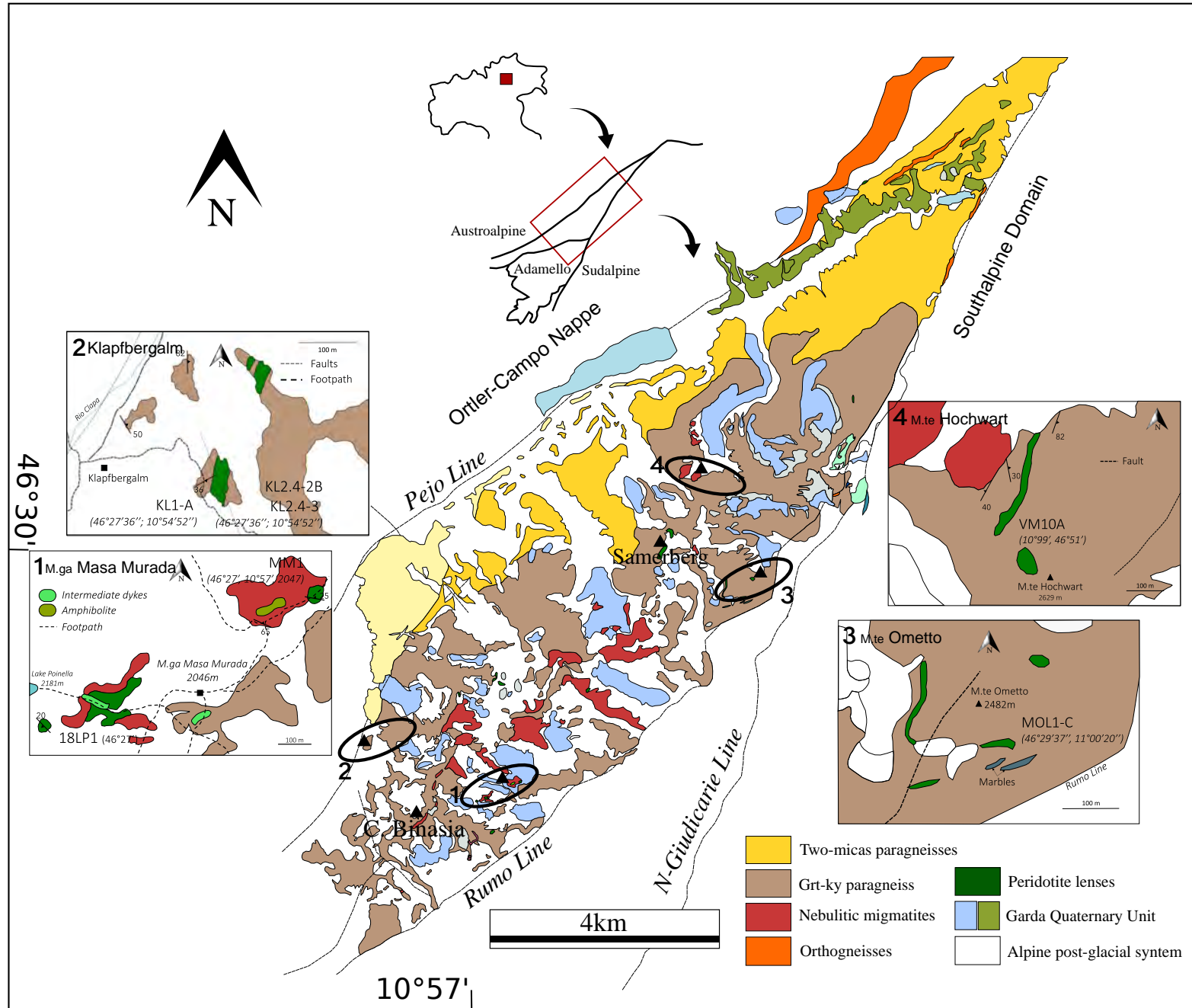


Figure 2

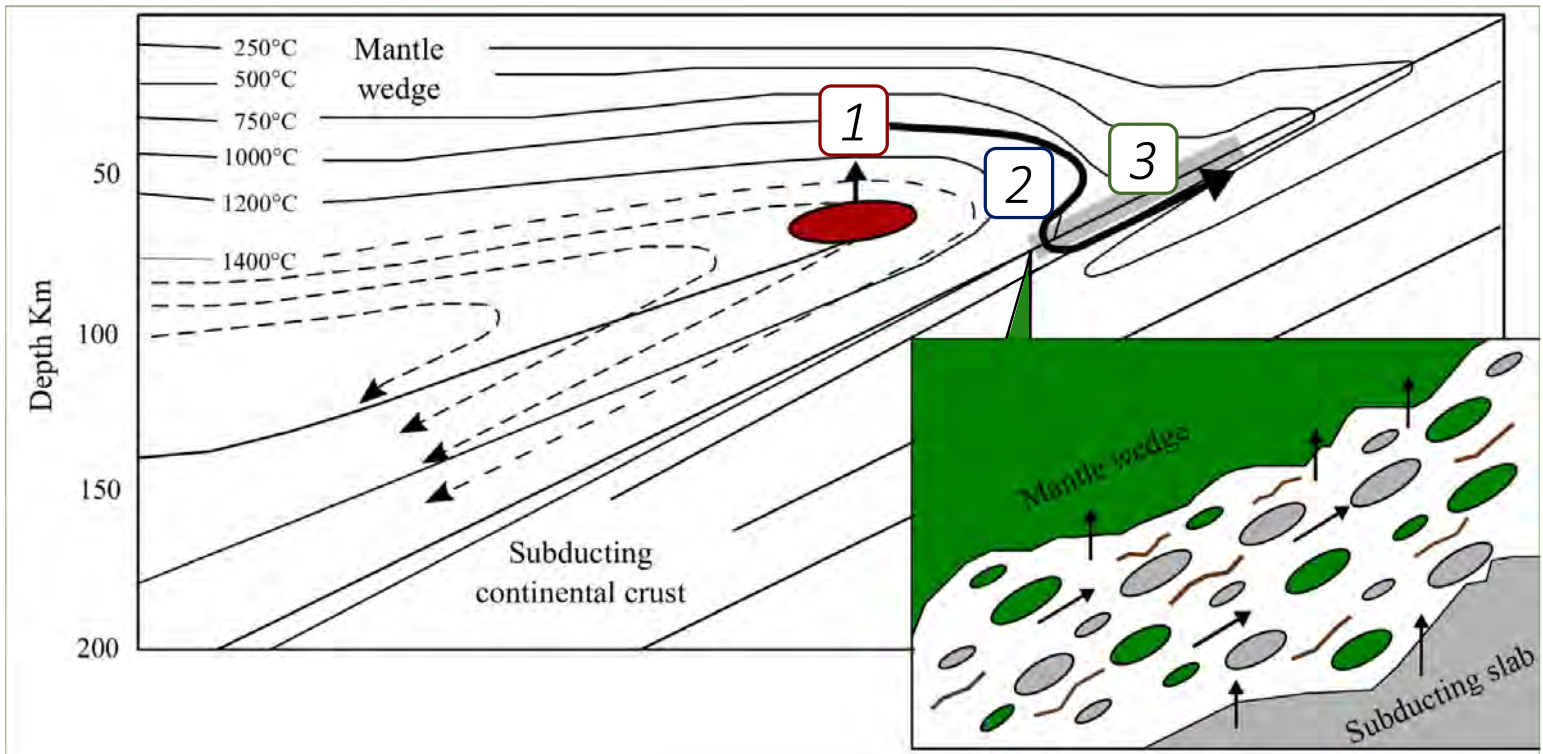


Figure3

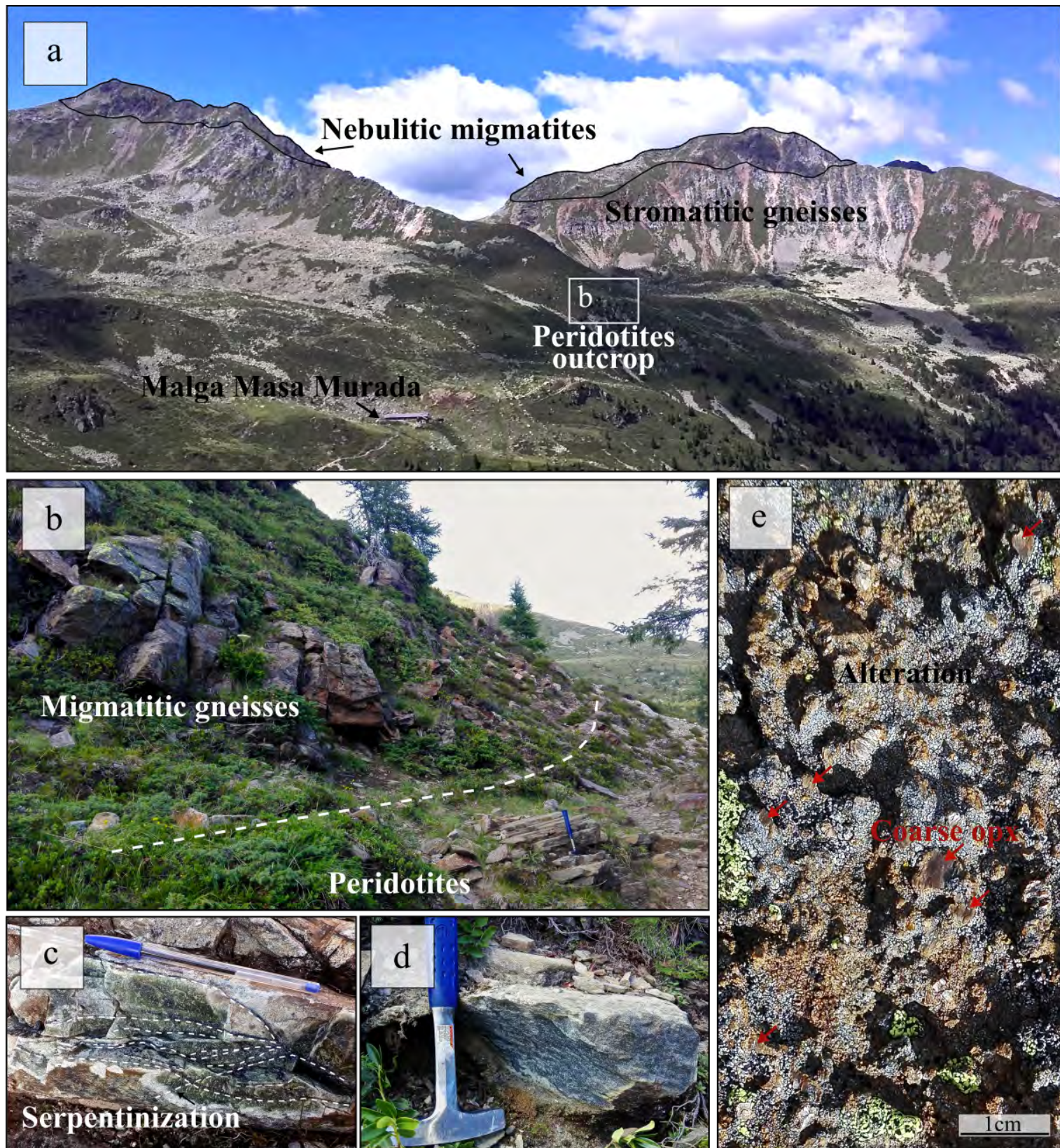


Figure4

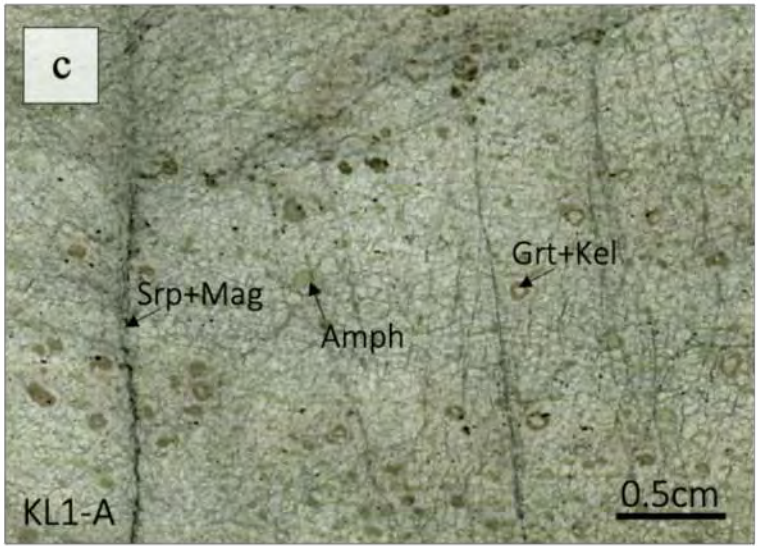
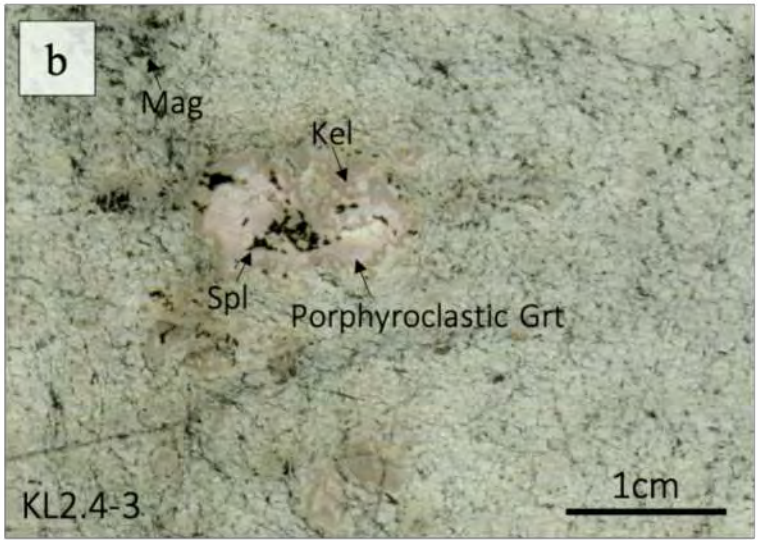
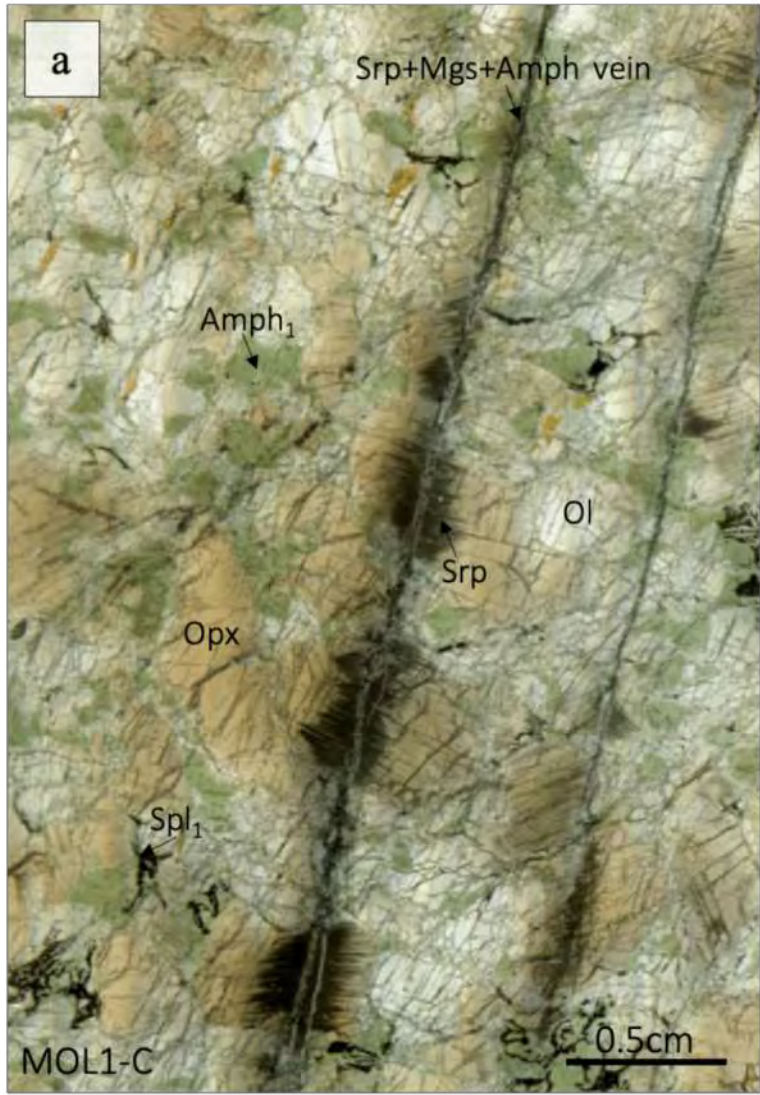


Figure 5

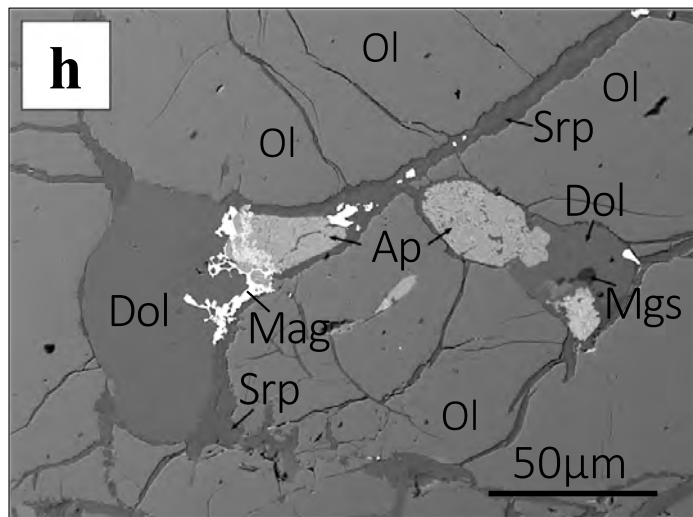
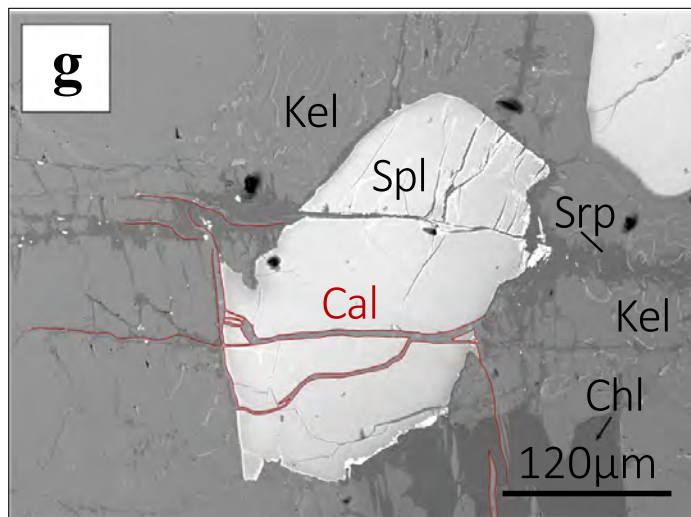
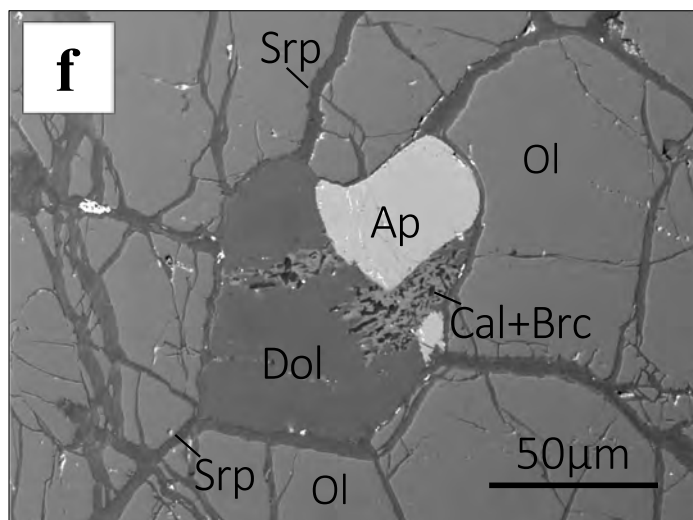
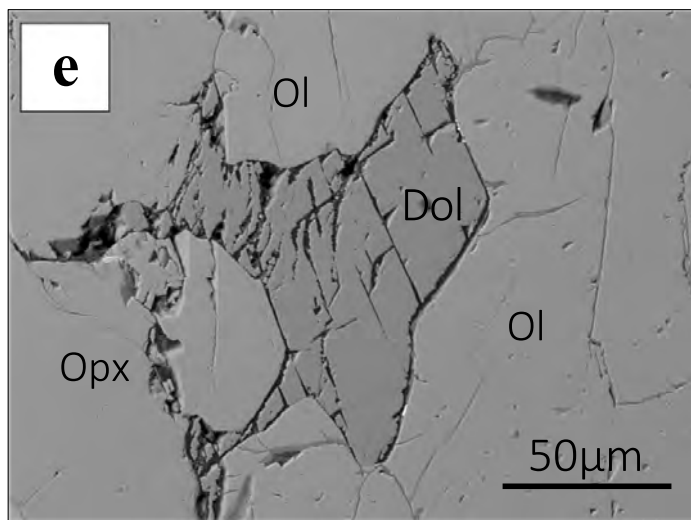
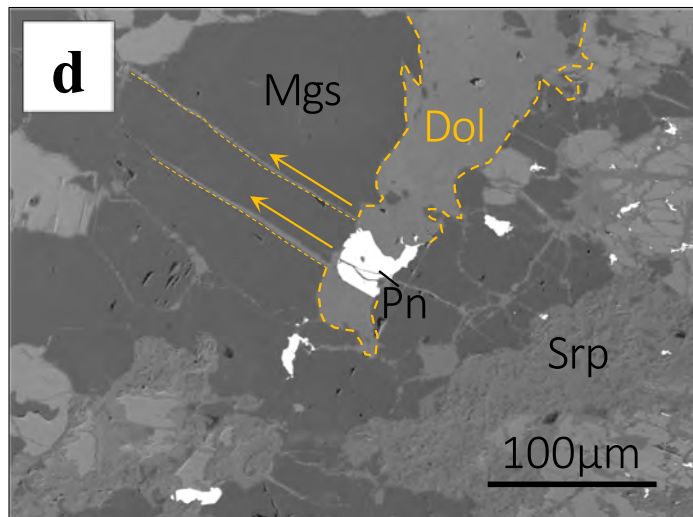
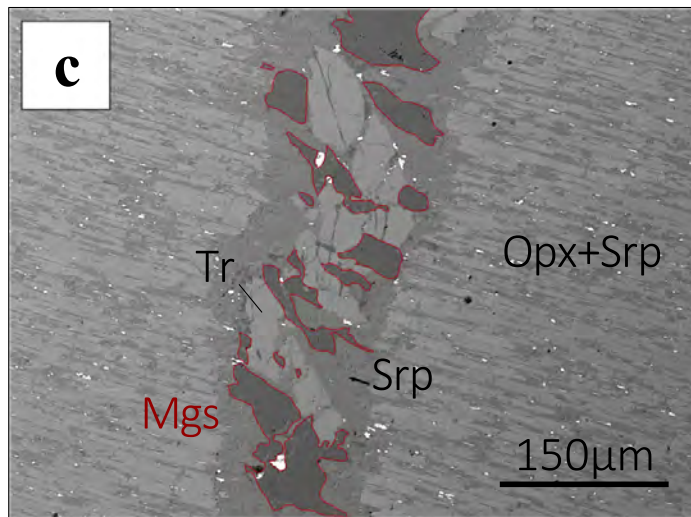
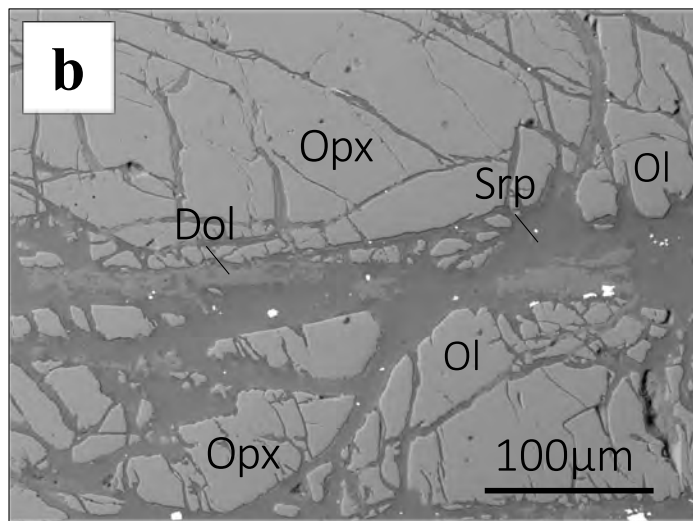
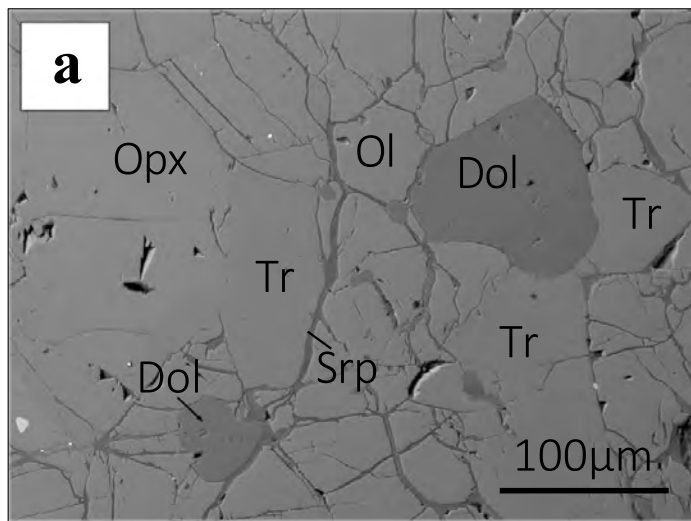


Figure6

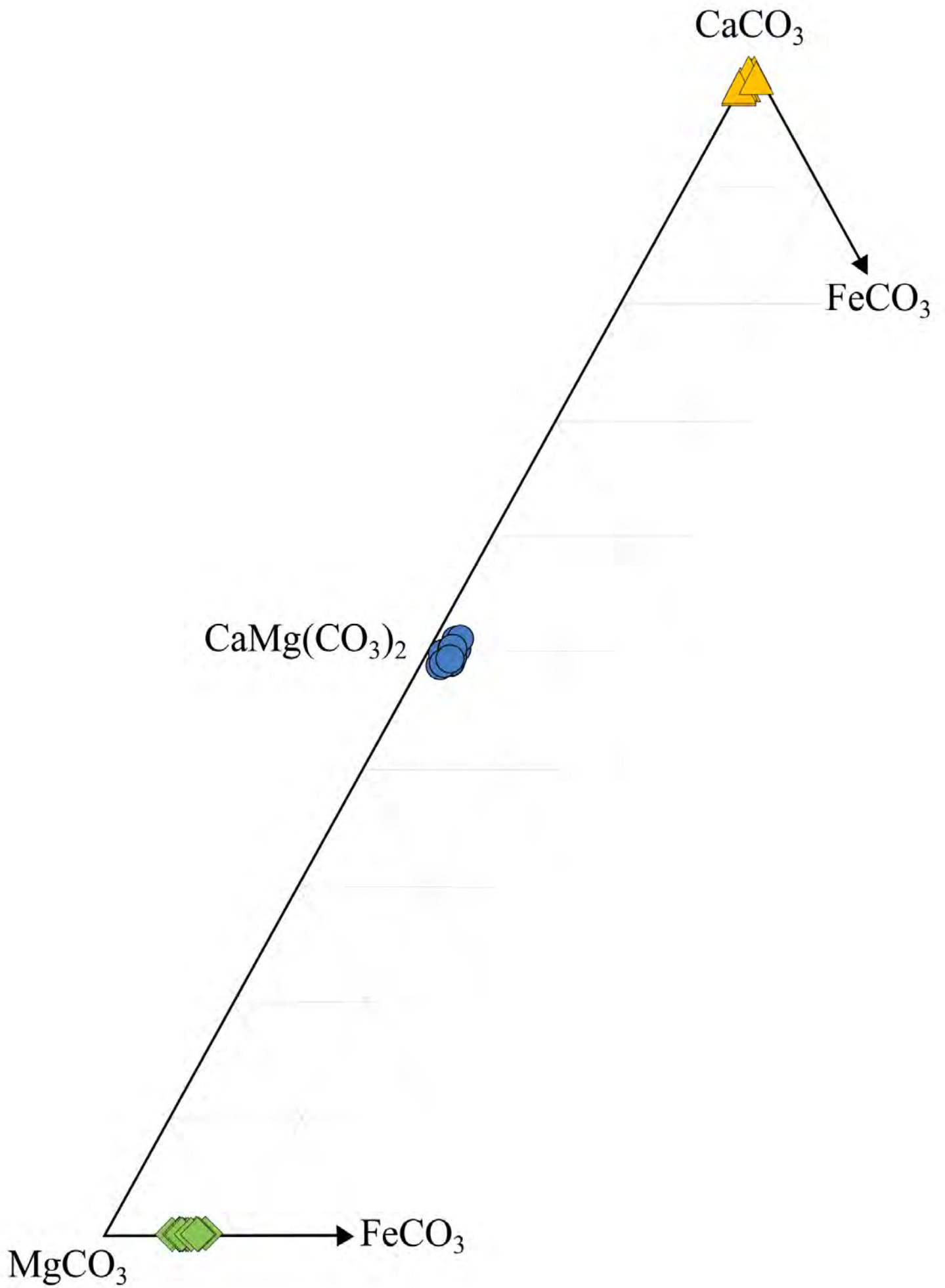


Figure7

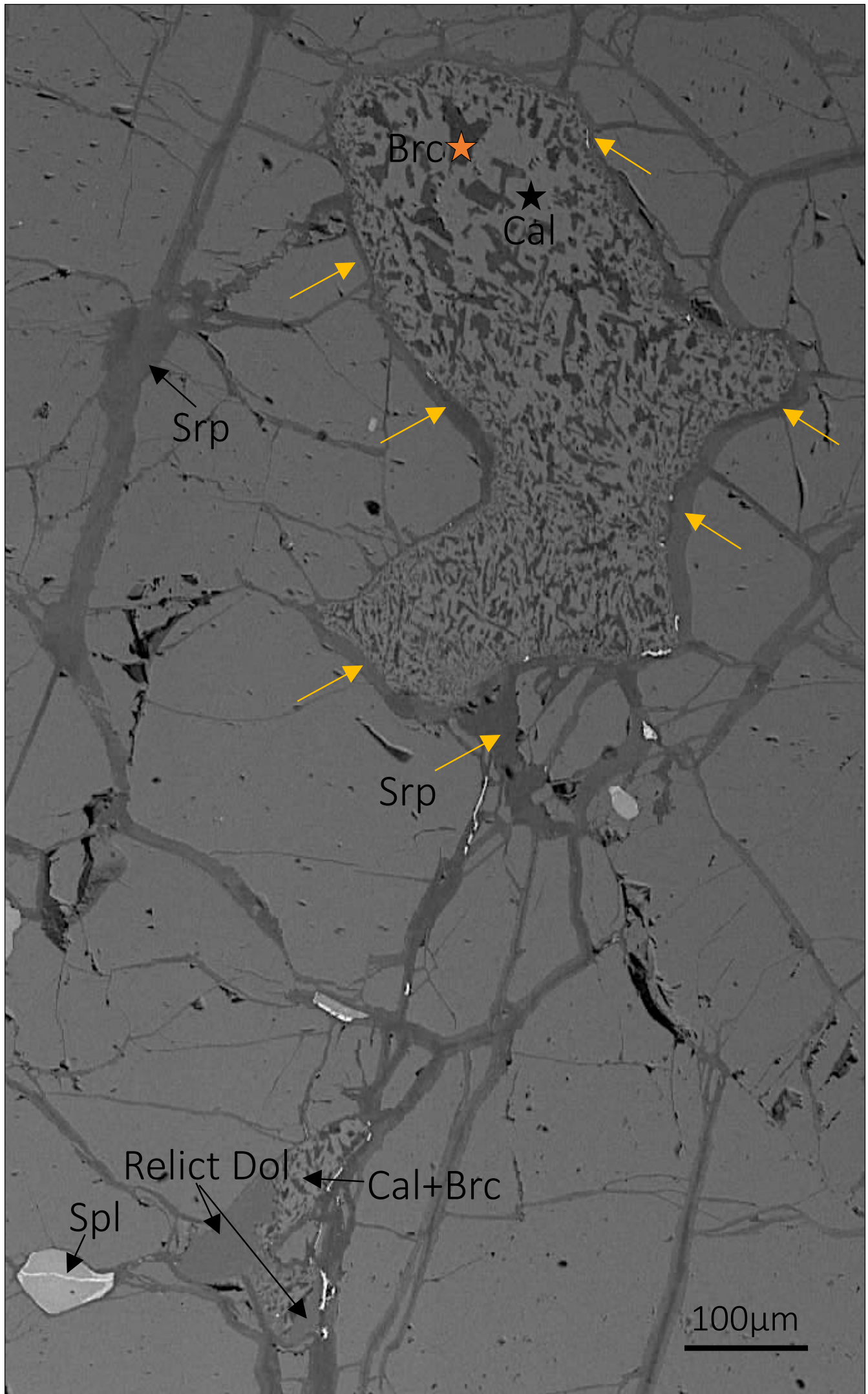


Figure 8

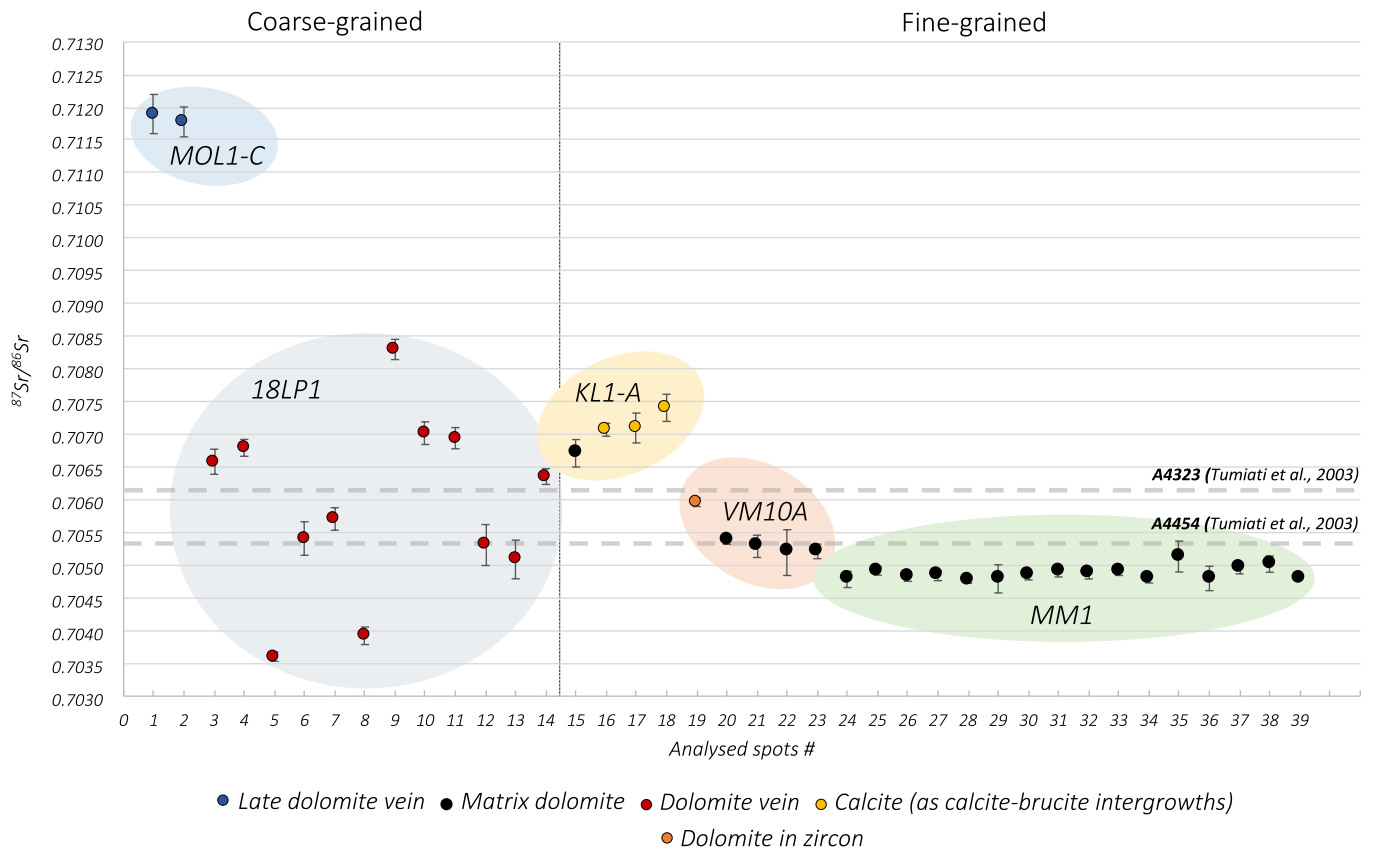


Figure9

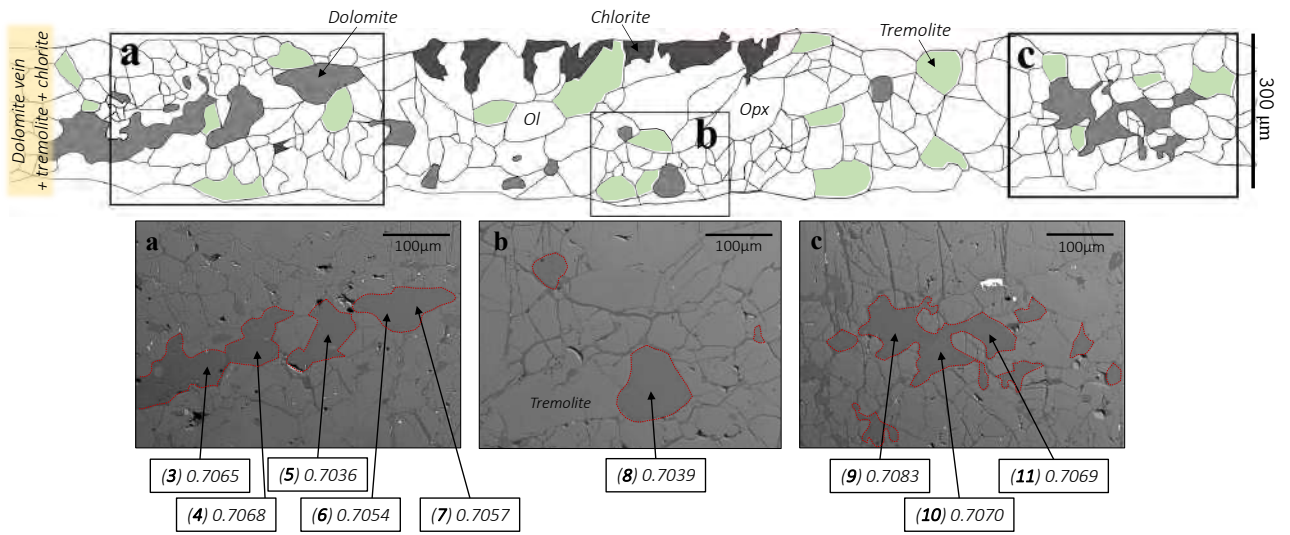


Figure10

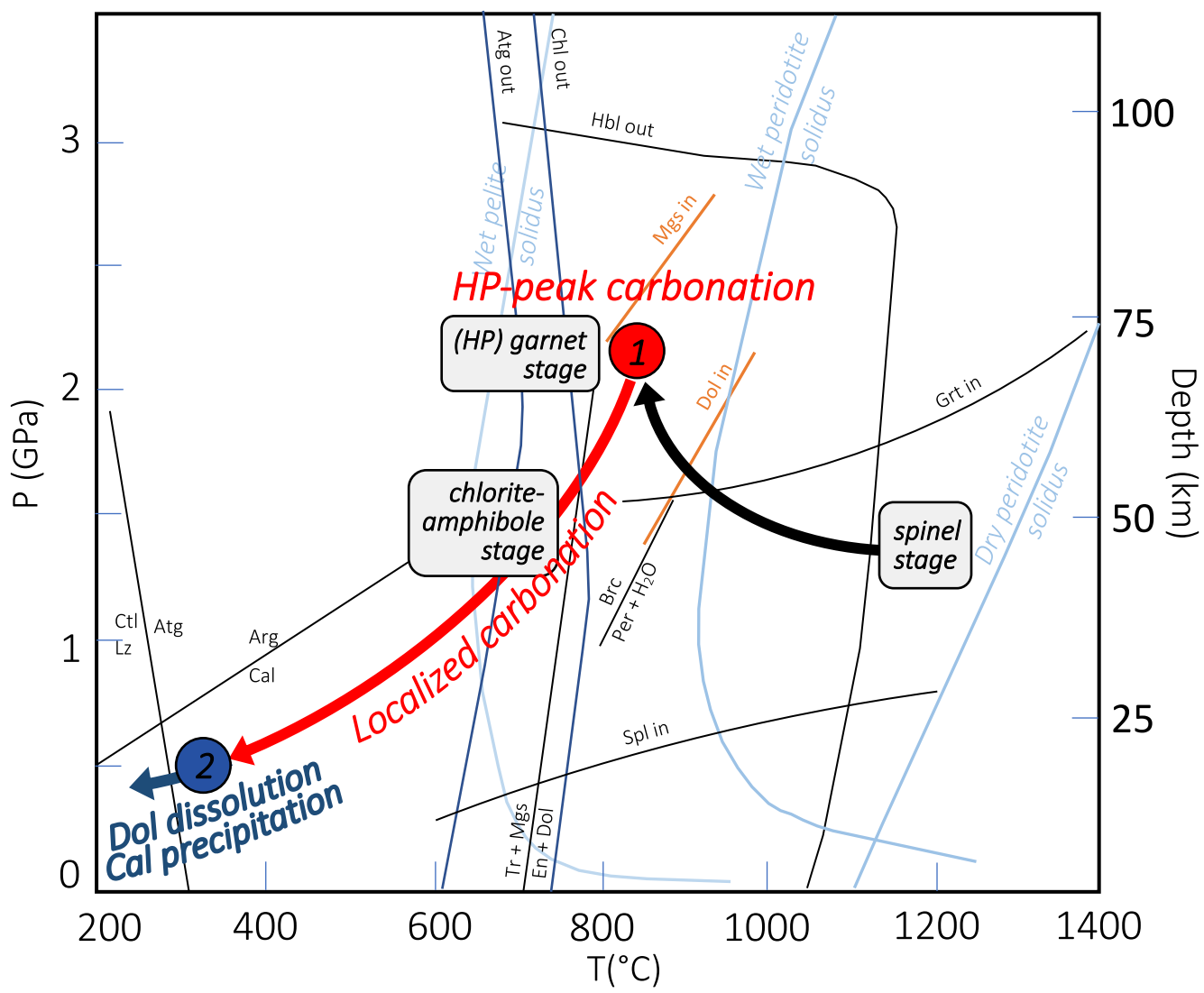
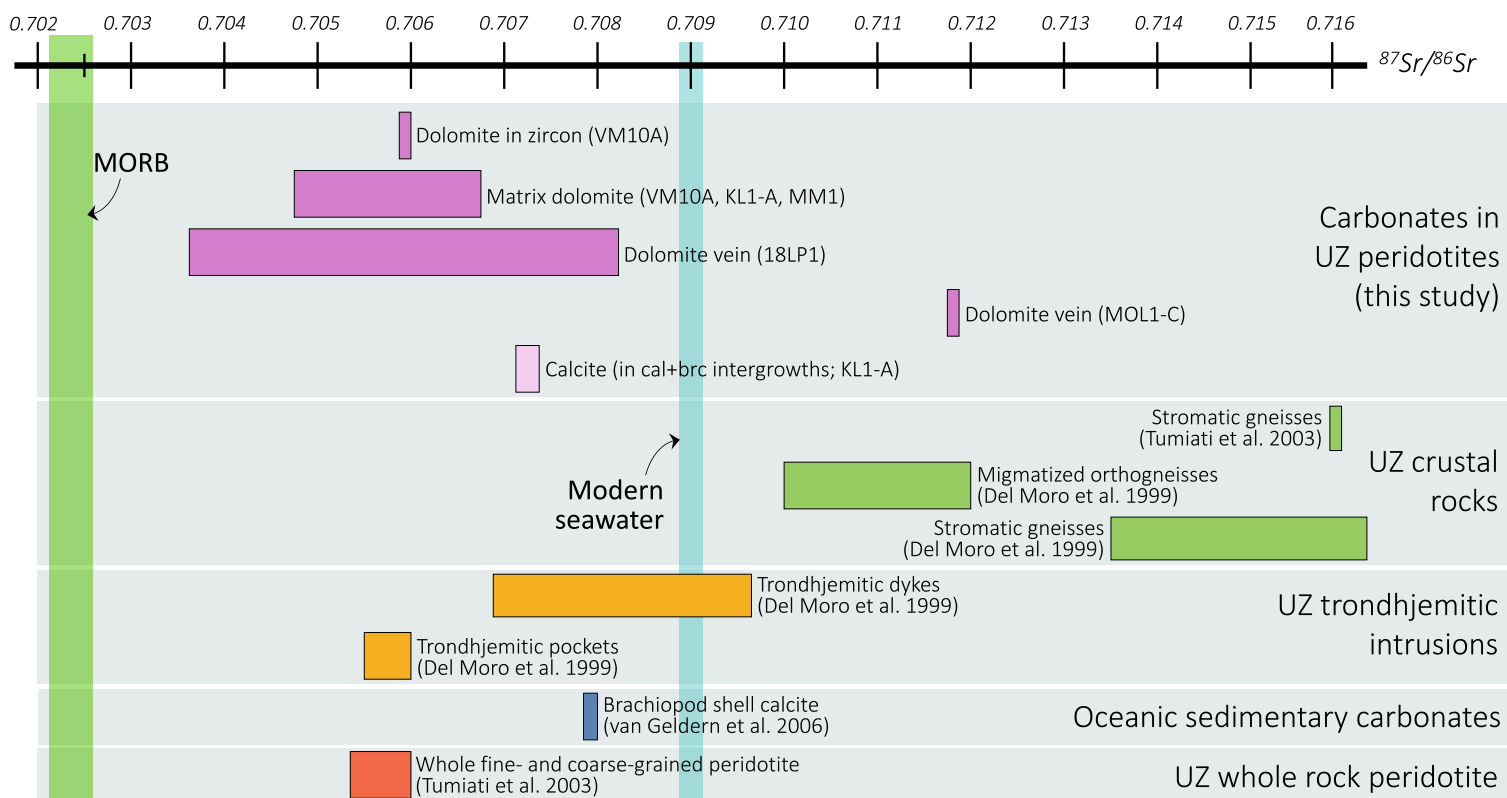


Figure11



Supplementary Materials - Figures

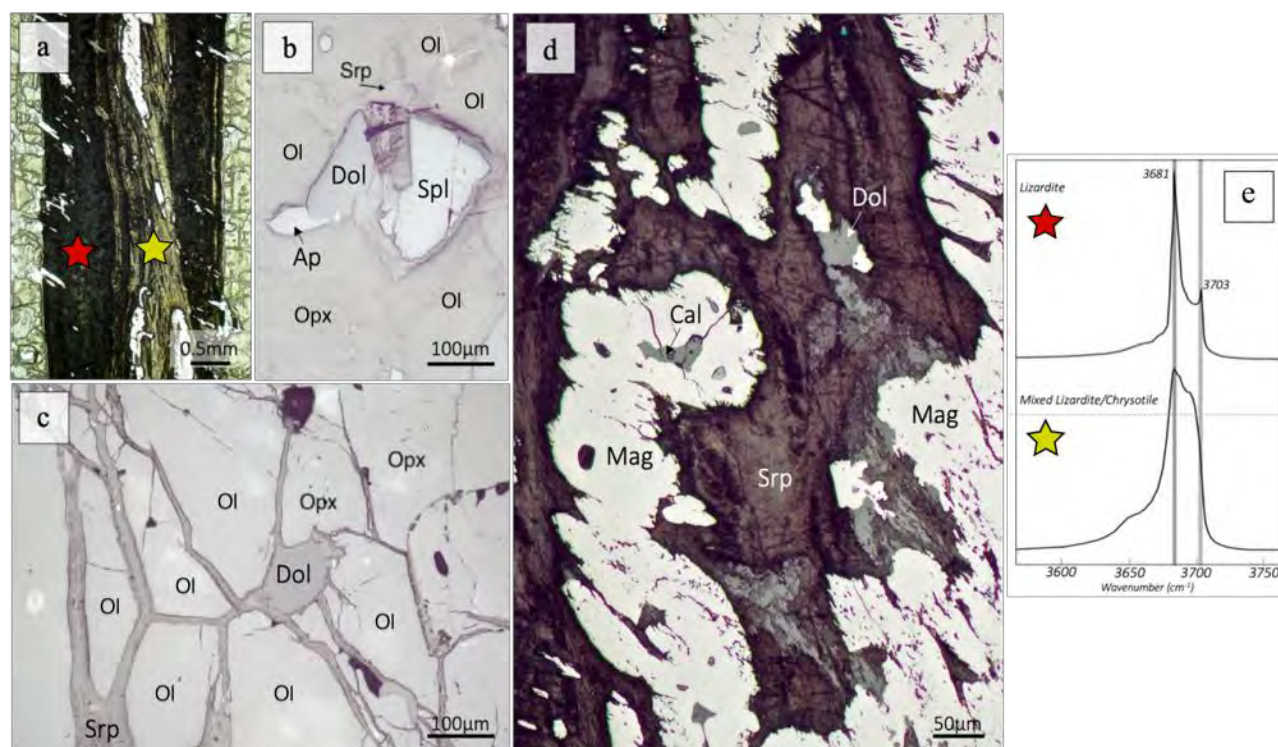


Fig. S1

(a) Zoned serpentine-rich vein cutting the MM1 fine-grained amphibole-chlorite peridotite with its constituting minerals under optical reflected light (b)-(c)-(d). (b) Matrix dolomite associated with Cl-apatite and spinel. (c) Matrix dolomite surrounded by serpentine. (d) Vein core consisting of serpentine + magnetite with calcite and dolomite included; (e) Micro-Raman spectra acquired in the OH region for a composite serpentine vein. Stars represent the analyzed spots. Mineral abbreviations after Whitney and Evans (2010).

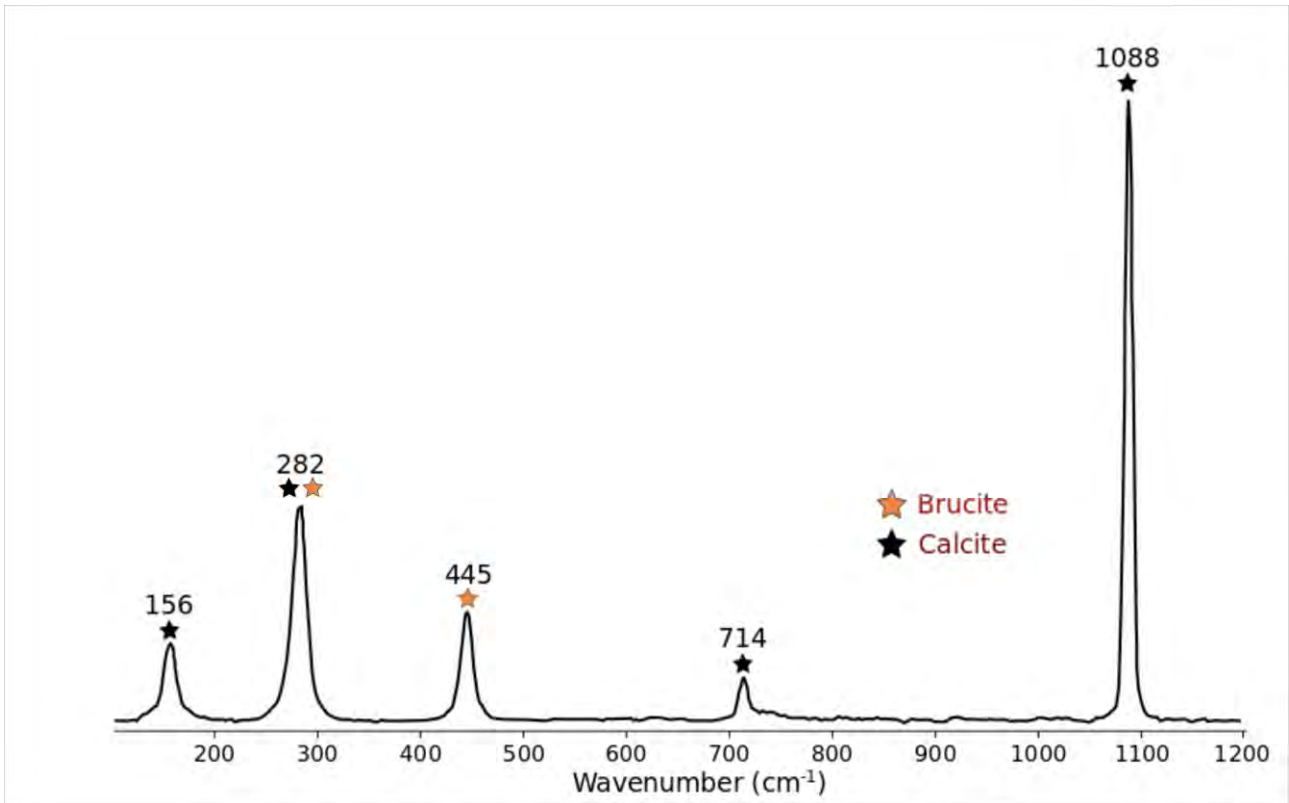


Fig. S2
Micro-Raman spectrum of analyzed calcite and brucite.

Table1. Studied samples from the Ulten Zone.

Sample	Locality	Facies	Texture	Main Assemblage	Carbonates	Serpentinization Grade	Section type	In situ Sr
18LP1	Cima Binasia nearby Lavazze river (as sample LP6; Ionov et al., 2017)	Sp	Coarse	Ol ₁ + Opx ₁ + Amph + Spl ₁ + Cpx ₁ + Dol + Chl + Phl + Op	Dolomite veinlet (ca. 300 μm wide) cut by thin serpentine veins with dolomite vein included (ca. 25 μm wide). Abundance: < 1%	Medium	Chip	X
MOL1-C	M.te Ometto	Sp	Coarse	Ol ₁ + Opx ₁ + Amph + Spl ₁ + Mgs + Srp + Chl + Phl + Op	Magnesite vein (ca. 300 μm wide) cut by late dolomite vein (ca. 200 μm long).	Medium	Thick section	X
MM1	Malga Masa Murada (as sample 300B; Morten and Obata, 1990)	Sp	Fine	Ol ₂ + Opx ₂ + Amph + Spl ₂ + Srp + Chl + Dol + Op	Matrix dolomite (50-100 μm; 2% of abundance); dolomite and calcite inclusions (10-50 μm) in magnetite occurring in median line of serpentine vein.	High	Chip	X
KL1-A	Klapfbergalm	Gr ₁	Fine	Ol ₂ + Opx ₂ + Spl ₂ + Grt ₂ + Srp + Op	Calcite plus brucite aggregates; matrix dolomite (ca. 50 μm). Abundance : <1 %.	High	Thick section Chip	X
KL2.4-2b KL2.4-3	Klapfbergalm	Gr ₁	Porphyroblastic	Ol ₂ + Opx ₂ + Spl ₂ + Grt ₂ + Amph + Srp + Dol + Cal + Op	Dolomite inclusion (ca. 70 μm) in a primary spinel; calcite plus brucite intergrowths (< 1 %).	High	Thick section	
VM10A	Mt.e Hochwart	Gr	Fine	Ol ₂ + Opx ₂ + Spl ₂ + Grt ₂	Matrix dolomite (< 1 % of abundance and ca. 60 μm of size) and a mm-sized dolomite inclusion in porphyroblastic zircon.	No	Thick section Chip	X

Mineral abbreviation after Whitney and Evans, (2010)

Table 2. Main representative major elements compositions of minerals measured by EPM.

Mineral	Olivine			Enstatite			Diopside			Amphibole			
	C		F	C		F	C		F	C		F	C
	I	II	I	I	II	II	I	II	I	II	I	II	I
Comment	m	m	m	m	m	m	m	m	Relic in amph	m	m	In mgs vein	In dol+chl+tr vein
SiO ₂	40.89	40.92	40.80	55.96	56.30	56.94	53.84	54.33	54.00	46.76	45.51	57.26	57.43
Al ₂ O ₃	bdl	bdl	bdl	2.80	2.51	1.40	1.41	1.27	1.01	10.88	12.01	1.32	0.91
MgO	49.72	49.04	49.23	33.80	33.84	34.61	17.01	17.22	17.47	19.20	18.33	23.20	23.40
CaO	bdl	bdl	bdl	0.27	0.32	0.18	24.78	24.83	24.23	12.06	12.37	12.86	12.92
K ₂ O	bdl	bdl	bdl	bdl	bdl	0.01	bdl	bdl	bdl	0.15	0.55	bdl	bdl
TiO ₂	bdl	bdl	bdl	bdl	bdl	bdl	0.05	bdl	0.12	0.21	0.48	bdl	bdl
FeO	9.57	9.51	9.37	6.33	6.40	6.29	1.56	1.81	1.70	3.07	2.81	2.09	1.70
MnO	0.14	0.15	0.12	0.19	0.11	0.15	0.07	0.06	bdl	bdl	bdl	0.10	bdl
Cr ₂ O ₃	bdl	bdl	bdl	0.26	0.17	0.18	0.38	0.25	0.29	0.85	1.67	0.16	0.26
Na ₂ O	bdl	bdl	bdl	bdl	bdl	bdl	0.22	0.22	0.23	2.39	1.95	0.37	0.19
NiO	0.41	0.37	0.40	bdl	0.11	0.02	bdl	bdl	bdl	bdl	bdl	0.06	0.07
Sum	100.7 2	100.06	99.95	99.70	99.81	99.76	99.58	100.18	99.05	95.57	95.68	97.36	96.95
Si	1.000 995	1.002	1.000 997	1.9437	1.954 7	1.953	1.9766	1.974	1.9876	6.642	6.513	7.8248	7.880
Ti							0.004	0.002	0.003		0.054		
Al				0.114				0.054	0.044	1.3658	2.0326	1.822	0.1547
Cr				0.0107	0.010 5	0.0105	0.014	0.0107	0.0108	0.1009 5	0.1989	0.0217	0.0328
Fe ³⁺	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000	0.344	0.2876	0.222	0.1107
Fe ²⁺	0.204 95	0.2049 5	1.90898	0.183	0.198 5	0.182	0.0548	0.0655	0.052	0.020	0.064	0.0716	0.0988
Mn	0.003	0.003	0.003	0.0106	0.003	0.004	0.002	0.002				0.014	
Mg	1.804	1.790	1.8105	1.744	1.744	1.782	0.9326	0.934	0.953	4.0766	3.914	4.0766	4.7987
Ca				0.010	0.012	0.0106	0.9769	0.9765	0.950	1.8436	1.9089 7	1.8436	1.90899
Sum	3.010 5	3.003	3.004	4.0109	4.010 7	4.003	4.0109	4.0107	4.003	10.554 7	10.564	10.010 5	10.00
Mg#	0.90	0.90	0.90	0.91	0.90	0.91	0.95	0.95	0.95	1.00	0.98	1.00	0.96

Olivine, enstatite and diopside generations are labeled I and II based on their composition and texture (see text for details); *C* coarse grained; *F* fine grained; *m* mineral in the matrix; *P* porphyroclast; *In P-grt* included in a porphyroblastic garnet; *mesh* mesh structure; *Bdl* below detection limit.

Formatted: Font: 6 pt

Formatted: Font: 6 pt

Formatted: Font: 6 pt

Formatted: Font: 6 pt

Table2. Continued

Mineral M-type sample Generation Comment	Pyrope		Cr-Spinel				Lizardite			Chlorite		Phlogopite		Apatite
	F		C		F		C	F		C	F	C	F	
	I	II	I	II	I	II								
	P	m	m	m	In P- grt	m	vein	mesh	vein	In dol+chl+tr vein	m	m	m	m
SiO ₂	41.98	41.82	bdl	0.08	bdl	0.052	41.25	40.02	42.05	30.38	29.85	40.19	37.04	bdl
Al ₂ O ₃	22.6	22.12	45.43	26.47	30.67	37.73	0.34	0.49	0.13	19.08	20.04	14.63	15.07	-
MgO	19.03	18.63	16.13	8.95	9.46	13.93	40.41	39.89	39.53	31.65	32.16	25.53	28.32	bdl
CaO	5.38	5.63	-	-	-	-	bdl	bdl	bdl	0.04	bdl	bdl	bdl	53.45
K ₂ O	-	-	-	-	-	-	bdl	bdl	bdl	-	Bdl	8.35	5.22	-
TiO ₂	bdl	bdl	-	-	0.17	bdl	bdl	bdl	bdl	0.06	0.03	0.21	0.13	-
FeO	9.25	9.70	14.80	24.76	21.24	16.33	2.90	3.72	2.02	2.55	2.22	3.45	5.03	0.41
MnO	0.47	0.63	0.21	0.48	0.49	0.29	bdl	0.12	bdl	bdl	bdl	bdl	0.05	bdl
Cr ₂ O ₃	1.44	1.45	23.09	37.02	35.76	31.01	bdl	bdl	bdl	1.39	1.06	0.76	1.14	-
Na ₂ O	-	-	-	-	-	-	bdl	bdl	bdl	bdl	bdl	0.13	0.04	bdl
NiO	-	-	0.10	-	bdl	bdl	bdl	-	bdl	0.15	0.17	0.17	0.53	-
Cl	-	-	-	-	-	-	-	0.06	0.06	-	-	-	-	5.57
P ₂ O ₅														39.57
Sum	100.27	99.73	99.80	97.85	97.86	99.35	84.94	84.43	83.83	85.42	85.60	93.45	92.57	99.21
Si	2.99	3.01	0.00	0.00	0.00	0.00	6.23	6.13	6.38	2.92	2.85	2.87	2.67	
Ti				0.00	0.00	0.00				0.00	0.00	0.01	0.01	
Al(IV)	0.01	0.00					1.577	1.87	1.62	2.08	2.15	2.13	2.33	
Al(VI)	1.90	1.87	1.48	0.99	1.12	1.29				0.08	0.11	0.21		
Cr	0.08	0.08	0.51	0.93	0.87	0.71				0.11	0.08	0.503	0.106	
Fe ³⁺	0.02	0.05	0.00	0.00	0.00	0.00								
Fe ²⁺	0.53	0.54	0.34	0.66	0.55	0.40	0.04	0.05	0.03	0.20	0.18	0.21	0.30	0.06
Mn	0.03	0.04	0.00	0.01	0.01	0.01								
Mg	2.02	1.99	0.67	0.43	0.44	0.60	9.09	9.10	8.94	4.53	4.58	2.72	3.04	
Ca	0.41	0.44								0.00	0.00			10.18
Cl								0.016	0.01					1.68
P														5.97
Sum	8.00	8.00	3.00	3.00	3.00	3.00	15.763	15.864	15.6329	9.95	10.00	7.90	7.93	17.90
Mg#	0.79	0.78	0.66	0.43	0.44	0.60	0.96	0.95	0.97	0.96	0.96	0.96	0.90	

Table3. Representative EPMA analyses of carbonate minerals. Values reported in wt.%. CO₂ reported to 100 for elements recalculations.

Sample	18LP1				MOL1-C				MM1				VM10A				
Type	Coarse				Coarse				Fine				Fine				
Mineral	Dol		Dol		Dol		Mgs		Dol		Dol		Dol		Dol		
Comment	Vein		In opx		Vein w/mgs		Vein		In liz vein		Matrix		In spl		In mag		
n	16	2σ	2	2σ	7	2σ	23	2σ	11	2σ	24	2σ	8	2σ	1	42	2σ
MgO	20.65	0.26	20.79	0.09	20.48	0.16	42.45	1.61	20.36	0.45	20.30	0.27	20.06	0.35	20.58	20.29	0.15
CaO	29.58	0.27	29.61	0.12	29.18	0.48	0.18	0.04	29.47	0.10	29.26	0.32	29.19	0.29	29.87	29.42	0.33
MnO	0.06	0.12	0.08	0.11	0.43	0.38	0.23	0.06	0.03	0.06	0.03	0.07	0.02	0.05	0.27	0.04	0.00
FeO	1.26	0.15	1.21	0.10	1.31	0.39	5.68	2.10	1.24	0.07	1.34	0.09	1.44	0.06	1.96	1.47	0.01
SrO	0.01	0.04	bdl 0.00	0.00	0.09	0.12	bdl 0.00	0.00	0.13	0.11	0.14	0.12	0.20	0.09	bdl 0.00	0.05	0.02
CO ₂	48.44	0.27	48.33	0.22	48.51	0.39	51.46	0.71	48.76	0.34	48.92	0.35	49.11	0.41	47.32	48.73	0.12
Sum	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	100.00	-
Mg	0.97	0.01	0.97	0.00	0.96	0.01	1.85	0.05	0.96	0.01	0.96	0.01	0.96	0.01	0.95	0.96	0.01
Fe ²⁺	0.03	0.00	0.03	0.00	0.03	0.01	0.14	0.05	0.03	0.00	0.04	0.00	0.04	0.00	0.05	0.04	0.00
Mn	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Ca	1.00	0.01	0.99	0.00	0.99	0.02	0.01	0.00	1.00	0.01	1.00	0.01	1.00	0.01	0.99	1.00	0.01
Sr	0.00	0.00	0.00	0.00	bdl		bdl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	2.00	0.00	2.00	0.00	2.00	0.00	2.00	0.00	2.00	0.00	2.00	0.00	2.00	0.00	2.00	2.00	0.00
Tot	4.00	-	4.00	-	4.00	-	4.00	-	4.00	-	4.00	-	4.00	-	4.00	4.00	-
CaCO ₃	49.84	0.46	49.73	0.01	49.38	0.86	0.28	0.06	50.07	0.54	49.89	0.51	50.03	0.58	49.58	49.99	0.53
MgCO ₃	48.41	0.47	48.58	0.01	48.23	0.48	92.47	2.73	48.12	0.64	48.16	0.54	47.83	0.54	47.53	47.97	0.57
MnCO ₃	0.08	0.15	0.10	0.14	0.58	0.50	0.28	0.08	0.04	0.08	0.05	0.09	0.03	0.07	0.35	0.05	0.00
FeCO ₃	1.66	0.20	1.58	0.14	1.73	0.51	6.96	2.66	1.64	0.10	1.78	0.11	1.92	0.08	2.54	1.95	0.02
SrCO ₃	0.01	0.04	0.00	0.00	0.08	0.11	0.00	0.00	0.12	0.10	0.12	0.11	0.18	0.08	0.00	0.05	0.03
Mg/(Mg+Ca)	0.49	0.00	0.49	0.00	0.49	0.01	1.00	0.00	0.49	0.01	0.49	0.01	0.49	0.01	0.49	0.49	0.01

bdl Below detection limit, *w/cal+brc* associated with *cal+brc* intergrowths

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Table3. Continued.

Sample	KL1-A						KL2.4-2b						KL2.4-3		KL1.6	
Type	Fine						Porph-fine						Porph-fine		fine	
Mineral	Dol		Dol		Cal		Dol		Dol		Cal		Cal		Dol	
Comment	Matrix		w/cal+brc		cal+brc		In spl		In spl, w/cal+brc		cal+brc pol.ag.		In spl (in grt)		vein	
n	22	2σ	6	2σ	4	2σ	4	2σ	9	2σ	2	2σ	2	2σ	30	2σ
Wt%																
MgO	20.51	0.23	20.05	0.08	0.33	0.30	20.01	0.30	20.13	1.20	0.38	0.11	0.00	0.00	19.58	0.44
CaO	29.30	0.20	28.97	0.22	54.33	0.37	29.17	0.16	29.82	1.40	49.48	0.43	57.19	0.08	29.74	0.32
MnO	0.11	0.27	0.02	0.06	0.00 bdl	0.00	0.05	0.07	0.02	0.04	0.03	0.04	bdl 0.00	0.00	0.04	0.09
FeO	1.52	0.12	1.63	0.06	bdl 0.00	0.00	1.60	0.08	1.75	0.46	1.41	0.33	0.41	0.15	1.43	0.18
SrO	0.03	0.07	bdl 0.00	0.00	0.22	0.05	0.09	0.10	0.05	0.09	0.16	0.22	bdl 0.00	0.00	0.02	0.05
CO ₂	48.53	0.26	49.33	0.22	45.12	0.09	49.08	0.27	48.24	2.22	48.53	0.15	42.40	0.23	49.20	0.50
Sum	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-
Mg	0.97	0.01	0.96	0.01	0.02	0.02	0.95	0.01	0.95	0.03	0.02	0.01	0.00	0.00	1.09	0.54
Fe³⁺	0.04	0.00	0.04	0.00	0.00	0.00	0.04	0.00	0.05	0.01	0.04	0.01	0.01	0.00	0.04	0.02
Mn	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.99	0.00	1.00	0.00	1.98	0.02	1.00	0.01	1.01	0.04	1.93	0.01	1.84	0.02	1.18	0.55
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	2.00	0.00	2.00	0.00	2.00	0.00	2.00	0.00	2.00	0.00	2.00	0.00	2.07	0.01	1.84	0.55
Tot	4.00	-	4.00	-	4.00	-	4.00	-	4.00	-	4.00	-	3.93	-	4.16	-
CaCO ₃	49.55	0.22	49.82	0.25	98.93	0.77	49.99	0.45	50.36	1.77	96.59	0.66	99.44	0.20	51.15	0.61
MgCO ₃	48.27	0.39	47.96	0.27	0.85	0.76	47.72	0.46	47.27	1.50	1.04	0.31	000	0.00	46.86	0.68
MnCO ₃	0.15	0.37	0.03	0.08	0.00	0.00	0.07	0.10	0.02	0.05	0.04	0.06	000	0.00	0.05	0.12
FeCO ₃	2.00	0.15	2.18	0.08	0.00	0.00	2.14	0.10	2.29	0.54	2.15	0.51	0.56	0.20	1.92	0.25
SrCO ₃	0.02	0.06	0.00	0.00	0.22	0.05	0.08	0.10	0.05	0.08	0.16	0.23	0.00	0.00	0.02	0.05
Mg/(Mg+Ca)	0.49	0.00	0.49	0.00	0.01	0.01	0.49	0.00	0.48	0.02	0.01	0.00	0.00	0.00	0.48	0.01

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Formatted: Font: Not Bold

Table4. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ isotope ratio measured with by LA-MC-ICP-MS for selected carbonates in Ulten Zone peridotites.

Sample and mineral	#	Microstructure	^{88}Sr (V)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	2se	Spot Size (μm)
MOL1-C							
Dolomite	1	Vein	0.8	<0.0001	0.71189	0.00030	65
Dolomite	2	Vein	1.3	0.0002	0.71178	0.00023	65
18LP1							
Dolomite	9	Vein	1.4	<0.0001	0.70830	0.00015	100
Dolomite	10	Vein	1.6	<0.0001	0.70702	0.00017	100
Dolomite	11	Vein	1.3	<0.0001	0.70694	0.00016	100
Dolomite	8	Vein	2.4	<0.0001	0.70392	0.00013	90
Dolomite	7	Vein	1.2	<0.0001	0.70571	0.00017	90
Dolomite	6	Vein	0.8	0.0001	0.70541	0.00026	65
Dolomite	5*	Vein	3.0	<0.0001	0.70360	0.00007	65
Dolomite	4	Vein	1.2	0.0003	0.70680	0.00013	65
Dolomite	3*	Vein	1.5	0.0001	0.70658	0.00019	100
Dolomite	12	Vein	0.5	<0.0001	0.70531	0.00031	100
Dolomite	13	Vein	0.7	0.0001	0.70509	0.00030	100
Dolomite	14**	Vein	1.6	<0.0001	0.70636	0.00012	100
VM10A							
Dolomite	23*	Matrix	3.4	<0.0001	0.70521	0.00011	65
Dolomite	22*	Matrix	1.2	<0.0001	0.70519	0.00035	65
Dolomite	20*	Matrix	3.4	<0.0001	0.70539	0.00006	65
Dolomite	21*	Matrix	1.6	<0.0001	0.70529	0.00017	55
Dolomite	19 ⁺	In zircon	1.3	0.0011	0.70597	0.00007	55
KL1-A							
Dolomite	15	Matrix	1.2	0.0004	0.70671	0.00021	65
Calcite	16	In cal+brc	2.4	<0.0001	0.70707	0.00021	65
Calcite	17	In cal+brc	0.8	<0.0001	0.70709	0.00023	65
Calcite	18	In cal+brc	1.1	<0.0001	0.70741	0.00009	65
MM1							
Dolomite	24	Matrix	4.7	<0.0001	0.70486	0.00007	65
Dolomite	25*	Matrix	4.4	<0.0001	0.70489	0.00005	65
Dolomite	26	Matrix	4.6	<0.0001	0.70478	0.00005	65
Dolomite	27	Matrix	4.5	<0.0001	0.70490	0.00008	65
Dolomite	28	Matrix	2.4	<0.0001	0.70502	0.00012	65
Dolomite	29	Matrix	3.3	<0.0001	0.70495	0.00008	65
Dolomite	30	Matrix	3.8	0.0002	0.70491	0.00006	65
Dolomite	31	Matrix	2.0	0.0005	0.70478	0.00012	65
Dolomite	32*	Matrix	2.7	0.0004	0.70484	0.00008	65
Dolomite	33	Matrix	4.8	<0.0001	0.70481	0.00005	65
Dolomite	34*	Matrix	1.3	<0.0001	0.70479	0.00022	65
Dolomite	35	Matrix	4.2	<0.0001	0.70477	0.00005	65
Dolomite	36	Matrix	2.9	0.0005	0.70484	0.00007	65
Dolomite	37*	Matrix	1.7	0.0007	0.70513	0.00024	65
Dolomite	38	Matrix	1.5	0.0004	0.70480	0.00019	65
Dolomite	39	Matrix	3.6	<0.0001	0.70479	0.00006	65

Table4. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio measured with LA-MC-ICP-MS for selected carbonates in Ulten Zone peridotites. (+) Analyses were collected along lines using the same spot size for spot analyses (i.e. 55 μm).

-Sr (ppm) concentrations were recalculated from EPMA analyses. b.d.l. is below detection limit. For () samples, Sr and Rb concentrations were analyzed in LA-ICP-MS. Rb concentration is below detection limit if <0.0046 ppm. n.a. not analysed; cal+brc calcite + brucite intergrowths.

Formatted: Superscript

Formatted: Superscript

Formatted Table

Formatted: Centered

Formatted: English (United States)

Formatted: English (United States)

Table I. Major elements compositions (wt%) of olivine. Formula based on 4 oxyg

Anions	4	4	4	4	4
Cations	3	3	3	3	3
Rock type	F	F	F	F	F
Sample	MM1	MM1	MM1	MM1	MM1
Text. Pos.	m	m	m	m	m
Elemento	MM1_ol1	MM1_ol2	MM1_ol3	MM1_ol5	MM1_ol6
MgO	50.1	49.24	49.54	49.89	49.92
Al ₂ O ₃	bdl	bdl	bdl	bdl	bdl
SiO ₂	40.85	40.53	40.66	40.56	40.53
TiO ₂	bdl	bdl	bdl	bdl	bdl
Cr ₂ O ₃	bdl	bdl	bdl	bdl	bdl
MnO	0.16	0.12	0.12	0.12	0.18
FeO	9.54	9.65	9.52	9.42	9.30
NiO	0.36	0.42	0.34	0.35	0.34
Sum	101.01	100.02	100.18	100.34	100.26
Si	0.99	0.99	0.99	0.99	0.99
Ti					
Al					
Cr					
Fe ²⁺	0.19	0.20	0.19	0.19	0.19
Ni	0.01	0.01	0.01	0.01	0.01
Mn	0.00	0.00	0.00	0.00	0.00
Mg	1.81	1.80	1.81	1.82	1.82
Sum	3.01	3.01	3.01	3.01	3.01
Fo	90.20	89.98	90.16	90.31	90.38
Fa	9.64	9.90	9.72	9.57	9.44
Teph	0.16	0.12	0.12	0.12	0.18
N° Mg	90.35	90.09	90.16	90.42	90.54

F: fine-grained; C: coarse-grained; P: porphyroclastic texture; m: matrix . N° Mg, N