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

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ABSTRACT

Carbonate-bearing wedge peridotites attest the mobilization of carbon (C) by slab fluids/melts 1 circulating in a subduction setting. In general, COH fluids are thought to derive from the 2 3 dehydration/partial melting of the crustal portions of slabs, especially during the exhumation of crust-mantle mélanges along continental subduction channels. In this study we combined textural 4 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 the HP-carbonation at peak (eclogite-facies) conditions, with formation of interstitial matrix 13 14 dolomite in textural equilibrium with hornblende to pargasite amphibole and Cl-apatite. This

dolomite exhibits relatively unradiogenic ⁸⁷Sr/⁸⁶Sr present day values of 0.70487±0.00010, 15 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 ⁸⁷Sr/⁸⁶Sr (0.7036-0.7083), reflecting both the primary composition of carbonates and the consequent 19 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

At convergent plate boundaries, the interface between subducting slab and overhanging mantle wedge represents a complex region, where a mix of slab- and wedge-derived lithologies plays a key role in the surface-to-mantle volatiles budget on Earth (Bebout and Penniston-Dorland, 2016). In 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 references therein). Accordingly, several studies highlight the importance of subducted continental 46 crust as source of metasomatic C-bearing fluids/hydrous melts reacting and enriching the 47 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-reprecipitation of carbonates at relatively shallow (P < 3 GPa) and cold ($T < 850^{\circ}$ C) 55 conditions. The UZ peridotites record the transition from mantle wedge, coarse-grained, spinelperidotite to high-pressure, fine-grained, garnet-bearing amphibole-peridotite and, finally to low-P, 56 57 low-T serpentinized 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-T59 conditions, along the complex metasomatic evolution of a paleo-mantle wedge involved in 60 continental collision. We combined microstructural observations, major elements compositions, micro-Raman analyses of carbonates and associated minerals, with in situ ⁸⁷Sr/⁸⁶Sr isotopic 61 62 composition of carbonates as a tracer for investigating the potential sources of C-bearing fluids. The choice of using elemental Sr and ⁸⁷Sr/⁸⁶Sr ratio to shed more light on C-metasomatism is based on 63

64 the fact that: (i) it is relatively abundant in the carbonates structure due to its easy substitution with Ca^{2+} ; (ii) the partition of Rb into the carbonate crystal structure is hampered because of its large 65 ionic size, and we therefore assume that carbonates may inherit the Sr isotopic composition of C-66 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).

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

The UZ petrology and metasomatic evolution is the subject of several studies well summarized in Scambelluri et al. (2010) and the sketch of Figure 2 contains the main features of an otherwise complex sequence of events. In stage 1 (Fig. 2), coarse-grained peridotites made of olivine +
enstatite + diopside + Cr-Al spinel with protogranular texture (Obata and Morten, 1987) were
percolated by hydrous basic melts from deeper lithospheric mantle before the Variscan orogeny,
leading to LREE and LILE enrichment at spinel facies conditions (1200°C and 1.3-1.6 GPa; Nimis
and Morten, 2000).

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

Stage 3 (Fig. 2) represents the retrograde evolution of the crust-mantle association, recorded by (i) kelyphitic coronas around garnet in fine-grained garnet-amphibole peridotites (Godard and Martin, 2000) and (ii) the occurrence of fine-grained spinel/chlorite-amphibole peridotite, interpreted as retrograde derivates from garnet-peridotites (Obata and Morten, 1987; Braga and Sapienza 2007; Marocchi et al., 2007). All the UZ lithotypes experienced a post-Variscan exhumation and were subjected to variable degrees of serpentinization that in some instances erased the previous texture 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 boundary. This reaction produced an orthopyroxene-rich layer and LILE-rich residual fluids 130 131 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 metasomatism, while the main metasomatic episodes were governed by slab-derived crustal fluids 133 134 equilibrating with the lithospheric mantle prior to the Variscan subduction.

Dolomite, previously found in all UZ textural types, is the main C-repository (Sapienza et al., 2009;
Förster et al., 2017; Gudelius et al., 2018). Trace elements analyses of dolomite from stage 2 and
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-reprecipitation 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 ~ 1µm. 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). Ftopaz (F), jadeite (Na₂O), orthoclase (K₂O), rutile (TiO₂), rhodonite (MnO), MgO, diopside (CaO), 153 154 chromite (Cr₂O₃), almandine (FeO), corundum (Al₂O₃), atacamite (Cl), baryte (BaO), Ni-olivine (NiO), and quartz (SiO₂) were used as standards for silicates and oxides analyses, while calcite 155 156 (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

Micro-Raman spectroscopy was performed for the identification of the serpentine phases and 160 161 calcite + brucite intergrowths at the Department of Mathematical, Physical and Computer Sciences, University of Parma. Polished thick sections and rock chips were investigated with a Horiba Jobin-162 163 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. The 473.1 nm source was selected to work in the spectra range with the maximum sensitivity of 166 the detector to enhance the OH stretching signal of the water molecules in the high wavenumber 167 range (3000-4000 cm⁻¹). The spectra were collected using the ULWD 50X objective with repeated 168 acquisition. The background subtraction of each spectrum was performed with the LabSpec® 169 170 software.

171

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

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

Laser ablation parameters consisted of a laser spot ranging from 55 μ m to 100 μ m (see Table 4), a fluence of ~10 J/cm², a laser frequency of ~10 Hz and a He flux of ~0.5 L/min. Signals were acquired in static mode with a block of 250 cycles (including laser warm-up, ~50–80 cycles of analysis and washout) and an integration time of 0.5 s. Collected *m/z* were 82Kr, 83Kr, 84Sr, 85Rb, 85.5, 86Sr, 86.5, 87Sr and 88Sr. Masses 85.5 and 86.5 were measured to check doubly charged Yb 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 argides; while mass 83 to check the presence of Er²⁺. Rb was corrected by calculating the ⁸⁷Rb 186 contribution to mass 87 by measuring the interference-free ⁸⁵Rb signal, correcting for instrumental 187 mass fractionation, and using the natural ⁸⁷Rb/⁸⁵Rb ratio. Mass bias normalization was performed 188 through exponential law and a ⁸⁸Sr/⁸⁶Sr ratio of 8.375209. The accuracy of the analyses was 189 190 checked using an in-house reference material (modern marine shell) (see Table X in Supplementary Material), which yielded a 87 Sr/ 86 Sr ratio of 0.709174 ± 0.000064 (2 σ ; n = 19), in agreement with 191 192 modern seawater (0.70917). Three analyses of a second in-house carbonate reference material vielded a 87 Sr/ 86 Sr ratio of 0.707562 ± 0.000018 (2 σ), equal to the solution reference value (0.70756 193 194 \pm 0.00003; 2 σ) (Weber et al., 2019). Data reduction was performed using a customized excel 195 spreadsheet.

196

4 Results

198 **4.1 Sample description and petrography**

Peridotite samples were collected from the Northeastern part of the UZ (Fig.s 1 and 3), from outcrops or boulders very close to the outcrops (Table 1 for sample description, location) (Fig.3). Each sample underwent weak up to very strong serpentinization that in some instances overprinted the previous textures. All the samples investigated contain carbonates such as dolomite and, locally, magnesite and calcite (see Table 1). From now on, the numbers 1 and 2 refer to first and second generation respectively of olivine, orthopyroxene, clinopyroxene and spinel.

Samples 18LP1 and MOL1-C are coarse-type spinel peridotites consisting mainly of large (1-4 mm) olivine₁, orthopyroxene₁ and spinel₁. Sample 18LP1 shows orthopyroxene₁ with undulose extinction and kink bands and they are usually surrounded by a chlorite rim with a diameter of about 150 µm. Clinopyroxene₁, exhibiting amphibole and spinel exsolutions, is associated with 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 encounters coarse crystals of orthopyroxene₁, serpentine minerals grow along orthopyroxene₁ 218 219 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 μ m) (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.

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

consisting of (i) apatite, ilmenite, pentlandite, calcite-brucite intergrowths and phlogopite; (ii) 234 235 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 keliphitic corona.

Sample KL1-A is a fine-grained garnet-amphibole peridotite with the same mineralogy of the previous samples but equigranular texture (ca. 300 μ m) (Fig. 4c). Here, intergrowths of calcite + brucite associated with relict dolomite occur in the matrix (Fig. 5f). Widespread small-sized pinkish-garnets (200-300 μ m) occur interstitially in the matrix, always exhibiting a kelyphitic corona of orthopyroxene + amphibole + clinopyroxene ± spinel. This peridotite sample shows mesh and bastite replacement textures of olivine and pyroxene respectively. This sample is also 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 μ m and commonly associated with apatite (Figs. 5h and S1b in Supplementary 258 Material).

259 4.2 Major element compositions and micro-Raman spectroscopy

Representative major element compositions of silicate minerals and apatites are listed in Table 2 260 261 (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 Fo₈₈₋₉₀ Teph₀₋₂. Orthopyroxene is commonly En₉₀₋₉₂Fs₈₋₁₀Wo₀₋₁ with Al₂O₃ reaching values up to 2.80 wt.%. Two textural-types of spinel are recognized: a first 265 266 generation of coarse spinel₁ included in porphyroblastic garnets exhibits $Cr \# \sim 0.43$, where Cr # is 267 Cr/(Cr+Al), while the second generation of matrix smaller spinel₂ has Cr# of about 0.35. 268 *Clinopyroxene* is always diopside (En₄₆₋₄₉Fs₂₋₃Wo₄₇₋₅₀). 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* (Al₂O₃ \sim 0.25 wt.%). Considering the three amphibole-types, 271 Na₂O and Al₂O₃ contents range from 0.1 to 1.6 wt.% and from 0.25 to 16.6 wt.%, respectively. When amphibole occurs in veinlets, its composition is always tremolitic (i.e. magnesite vein with 272 273 tremolite and serpentine). Unzoned garnet is pyrope-rich (Py₅₁₋₇₀Alm₁₇₋₃₀Sps₁₋₄Grs₁₁₋₁₅) 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 was characterized by micro-Raman spectroscopy showing lizardite and mixed lizardite/chrysotile 278 279 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 Na₂O content 281 of phlogopite reaches values of 0.13 wt.%.

282 Carbonate compositions are given in the MgCO₃-CaCO₃-FeCO₃ 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_{FeCO3} of about 0.02 in all the samples. Similarly, magnesite veinlet shows high Fe content, with X_{FeCO3} of about 0.05. Calcite 285 286 (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

In situ ⁸⁷Sr/⁸⁶Sr isotope ratio analyses are listed in Table 4. Carbonates were previously chosen and 291 292 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 μ m. Calcite veins are too narrow (ca. 294 $20-30 \,\mu\text{m}$ 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 μ m, in relation to the carbonate size (see Table 4). The 297 ⁸⁷Sr/⁸⁶Sr 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.

In the coarse-type spinel peridotite *18LP1*, the dolomite vein associated with tremolite and chlorite exhibits highly variable Sr isotopic values ranging from 0.70360 ± 0.00007 to 0.70830 ± 0.00015 (n=12) (Figs. 8 and 9). Two lobate-shaped dolomite grains (spots 5, 8) shown in Figure 9 exhibit the lowest values of all UZ carbonates analyzed. In *MOL1-C* late vein dolomite cutting a magnesite vein (Fig. 5d) gives an average value of 0.71184 ± 0.00026 (n=2), representing the highest radiogenic ratio obtained by the *in-situ* Sr measurements of all Ulten carbonates-bearing peridotites 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 peridotites. In the mylonitic garnet-amphibole peridotite VM10A, the ⁸⁷Sr/⁸⁶Sr ratio of matrix 310 311 dolomite is 0.70529+0.00011 (n=4). In the same sample, a large dolomite inclusion (ca. 7 mm long) occurring in a zircon porphyroclast exhibits a 87 Sr/ 86 Sr ratio of 0.70597 ±0.00007, obtained 312 313 by analyzing a line scan along the carbonate grain. In the fine-grained garnet-amphibole peridotite *KL1-A*, the dolomite 87 Sr/ 86 Sr ratio is 0.70671 \pm 0.00021 whereas calcite (associated to brucite) 314 315 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 included in the spots analyses. However, brucite is not supposed to incorporate Sr^{2+} and we 317 318 therefore consider our data as exclusive for calcite. Average value of matrix dolomite in fine-319 grained amphibole-chlorite peridotite *MM1* is 0.70487 ± 0.00010 (n=16).

320 **5. Discussion**

Petrographic data indicate that the UZ peridotites, during their complex metasomatic history, 321 322 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

depths), in a supra-subduction setting similar to the mantle wedge sampled by harzburgite xenoliths
from the western Pacific. Given the uncertainty of 'crustal' vs 'mantle' origin of metasomatizing
fluids, the Sr concentration and isotopic signature of carbonates of the UZ peridotites may help to
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 Stage1 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). At this stage there is no petrographic evidence of carbonation. Conversely, the occurrence of lobate-347 348 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 elements composition obtained with EPMA shows that this inclusion has the same composition as 356 357 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 meltrelated process in the high-T spinel stage given by Förster et al., 2017). At peak conditions, fluids 361 362 prompted the precipitation of interstitial dolomite.

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

379the formation of carbonates in the mantle wedge. However, Sr isotope values reported380by van Geldern et al. (2006) for well-preserved Devonian brachiopod shells (Mn < 100</td>381ppm; Fe < 400 ppm and Sr > 500 ppm) range from 0.70782 to 0.70804 (during the382Emsian-Eifelian boundary and early Famennian respectively), unlikely representing the383required 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 Fig. 11. Several studies (i.e. Tumiati et al. 2003 and Scambelluri et al. 2006) highlighted 386 387 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.
- (iv) The radiogenic Sr signature of few trondhjemitic dykes and pockets described by Del
 Moro et al. (1999) are close to those reported for the matrix dolomite of the fine-grained
 mylonitic garnet-amphibole peridotite VM10A from Mt. Hochwart. Based on petrology
 and whole-rock Sr-Nd isotope geochemistry, Del Moro et al. (1999) interpreted the UZ
 trondhjemite as melts produced by fluid-assisted anatexis of a metasedimentary lower
 crust characterized by low Rb/Sr and Sr isotope ratios. Once formed, the trondhjemite
 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-crysothile + 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 prior to serpentinization (650°C \leq T \leq 700°C at P of ca. 1 GPa) and, in addition, provides a 410 411 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 from the dolomite + tremolite + chlorite vein encompasses the ⁸⁷Sr/⁸⁶Sr values measured from 413 414 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 (2 σ). 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 ⁸⁷Sr/⁸⁶Sr ratios (0.7036-0.7039; Figs. 8 and 9) of two dolomite grains in this vein. As shown in Fig. 421 422 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 $T < 600^{\circ}$ C during the retrograde path. This vein is cut by a

428 dolomite vein with the highest ⁸⁷Sr/⁸⁶Sr 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

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

443 The calcite + brucite intergrowths are the result of dolomite breakdown during interaction with aqueous fluids (Figs. 5f and 7) (Förster et al., 2017) and were found only in highly serpentinized 444 445 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 $T < 300^{\circ}$ 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).

The formation of thin calcite veins occurring in the matrix and in some instances crosscutting spinel, chlorite and phlogopite, was interpreted by Förster et al. (2017) as a consequence of the influx of serpentinizing fluids that triggered dissolution of the former dolomite and crystallization of calcite + brucite intergrowths with concomitant liberation of CO₂, following the reaction CaMg(CO₃)₂ + H₂O \rightarrow CaCO₃ + Mg(OH)₃ + CO₂. The release of CO₂ may prompt *in-situ* formation of carbonates (i.e. thin calcite veins) after C saturation was achieved.

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

462

6. Conclusion and future directions

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

The relatively unradiogenic Sr isotope ratio recorded by includion- and matrix dolomite, with some grains of a dolomite vein, does not support a simple derivation from fluids derived from the migmatite host gneisses (Fig. 11). The first stage of carbonation thus requires *HP* metasomatic fluids (i.e. at ~ 2.5 GPa and 850°C) likely unrelated to the associated crust (stromatic gneisses and 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 ($\geq 50\mu$ 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.

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- 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.

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

Fig.3: The Ulten Zone peridotites in the field. (a) Overview of the geological setting close to Malga
Masa Murada with indication of the peridotites outcrop showed in detail in (b); (c)-(d)
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 keliphytic corona and includes

637 larges 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 MgCO₃-CaCO₃-FeCO₃ 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 ⁸⁷Sr/⁸⁶Sr

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.

Fig.9: Partial sketch of a dolomite vein associated with tremolite and chlorite in sample 18LP1 with
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-

out, garnet-in curve from Tumiati et al., (2013); tremolite (Tr) + magnesite (Mgs) = enstatite (En) +

- dolomite (Dol) from Malaspina and Tumiati (2012) for $X_{CO2} = 0.5$; brucite (Brc) = periclase (Per) +
- 664 water (H₂O) 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);
- aragonite = calcite from Johannes and Puhan (1971). The HP-garnet stage and chlorite-amphibole

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

Fig.11: Strontium isotopic compositions of carbonates from the Ulten Zone peridotites in comparison with the potential sources of C-bearing fluids. MORB values taken from Salters and Stracke (2004); the Sr-isotope values of stromatic gneisses and peridotites from Tumiati et al. (2003) and the stromatic gneisses, orthogneisses and trondhjemitic intrusions from Del Moro et al. (1999) are recalculated for t=330Ma, corresponding to the inferred age of the last isotopic homogenization event. The Sr-isotope values for the brachiopod shell calcites from van Geldern et al. (2006) correspond to Early to Late Devonian (Emsian-Eifelian boundary and early Famennian). Fig.1





Figure2















(**10**) 0.7070

(**6**) 0.7054

(**4**) 0.7068

(**7**) 0.7057











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).





| 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 | $\begin{array}{rl} Ol_1 &+& Opx_1 &+\\ Amph &+& Spl_1 &+\\ Cpx_1 &+& Dol &+ Chl\\ &+& Phl &+ Op \end{array}$ | Dolomite veinlet (ca. 300 μ m wide) cut by thin serpentine veins with dolomite vein included (ca. 25 μ m wide). Abundance: < 1% | Medium | Chip | x |
| MOL1-C | M.te Ometto | Sp | Coarse | $\begin{array}{l} Ol_1 + Opx_1 + \\ Amph + Spl_1 + \\ Mgs + Srp + Chl \\ + Phl + Op \end{array}$ | Magnesite vein (ca. 300 µm wide) cut by late dolomite vein (ca. 200 µm long). | Medium | Thick section | х |
| MM1 | Malga Masa Murada (as sample 300B; Morten and Obata, 1990) | Sp | Fine | $\begin{array}{l} Ol_2+Opx_2+\\ Amph+Spl_2+\\ Srp+Chl+Dol\\ +Op \end{array}$ | Matrix dolomite (50- 100 μ m; 2% of abundance); dolomite and calcite inclusions (10-50 μ m) in magnetite occurring in median line of serpentine vein. | High | Chip | x |
| KL1-A | Klapfbergal m | Gr <u>t</u> | Fine | $\begin{array}{l}Ol_2+Opx_2+\\Spl_2+Grt_2+Srp\\+Op\end{array}$ | Calcite plus brucite aggregates; matrix dolomite (ca. 50 μm). Abundance : <1 %. | High | Thick section Chip | x |
| KL2.4-2b KL2.4-3 | Klapfbergal m | Gr <u>t</u> | Porphyroblast ic | $\begin{array}{l} Ol_2+Opx_2+\\ Spl_2+Grt_2+\\ Amph+Srp+\\ Dol+Cal+Op \end{array}$ | Dolomite inclusion (ca. 70 µm) in a primary spinel,; calcite plus brucite intergrowths (< 1 %). | High | Thick section | |
| VM10A | Mt.e Hochwart | Gr | Fine | $\begin{array}{l}Ol_2+Opx_2+\\Spl_2+Grt_2\end{array}$ | Matrix dolomite (< 1 % of abundance and ca. 60 μ m of size) and a mm-sized dolomite inclusion in porphyroblastic zircon. | No | Thick section Chip | x |

Table1. Studied samples from the Ulten Zone.

Mineral abbreviation after Whitney and Evans, (2010)

| Mineral | Olivine | | | Enstatite | | | Diopside | | | Amphibo | ole | | | Formatted: Font: 6 pt |
|--------------------------------|----------------------|----------------------|----------------------|-------------------|------------------------|---------------------|-----------------|----------------------|---------------------|----------------------|------------------------------------|-----------------------|--------------------------|-----------------------|
| M-type sample | С | | F | С | | F | С | F | | C | F | С | | Formatted: Font: 6 pt |
| Generation | I | II | I | I | II | II | I | II | | | | | | Formatted: Font: 6 pt |
| Comment | m | m | m | m | m | m | m | m | Relic in amph | m | m | In mgs vein | In dol+chl+tr vein | Formatted: Font: 6 pt |
| 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 | <u>b</u> 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 | <u>b</u> 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 | <u>b</u> 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 | 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 | <u>1.00</u> 0. | 1.00 2 | <u>1.00</u> 0.997 | 1.9 <u>4</u> 37 | 1.9 <u>5</u> 4 | 1.95 <mark>3</mark> | 1.9 <u>7</u> 66 | 1.97 1 | 1.9 <u>8</u> 76 | 6.64 2 | 6.51 3 | 7.8 <u>2</u> 18 | 7.88 0 | |
| Ti | 995 | | | | + | | 0.004 | 0.002 | 0.00 <mark>3</mark> | | 0.05 <mark>-1</mark> | | | |
| Al | | | | 0.114 | | | | 0.054 | 0.044 | 1.3 <u>6</u> 58 | 2.0 <u>3</u> 26 | 1.82 <mark>2</mark> | 0.1 <u>5</u> 47 | |
| Cr | | | | 0.0 <u>1</u> 07 | 0.0 <u>1</u> 0 | 0.0 <u>1</u> 05 | 0.01 | 0.0 <u>1</u> 07 | 0.0 <u>1</u> 08 | 0. <u>10</u> 09 | 0.1 <u>9</u> 89 | 0.0 <mark>2</mark> 17 | 0.0 <u>328</u> | |
| Fe ³⁺ | 0.00 <mark>0</mark> | 0.0 <mark>0</mark> 0 | 0.000 | 0.00 0 | ÷ | 0.000 | 0.000 | 0.00 <mark>0</mark> | 0.00 <mark>0</mark> | 0.344 | 0.2 <u>8</u> 76 | 0.22 <mark>2</mark> | 0.1 <u>1</u> 07 | |
| Fe ²⁺ | 0.204 | 0. <u>20</u> 19 | 1. <u>90</u> 898 | 0.183 | 0.1 <u>9</u> 8 | 0.182 | 0.0 <u>5</u> 48 | 0.0 <u>6</u> 55 | 0.052 | 0.02 <mark>0</mark> | 0.06 <mark>1</mark> | 0.0 <u>7</u> 16 | 0.0 <u>9</u> 88 | |
| Mn | 0.00 3 | ع 0.00 | 0.003 | 0.0 <u>1</u> 06 | ⇒ 0.00 3 | 0.004 | 0.002 | 0.002 | | | | 0.014 | | |
| Mg | 1.804 | 1.79 <mark>0</mark> | 1.8 <mark>105</mark> | 1.744 | 1.744 | 1.78 <mark>2</mark> | 0.9 <u>3</u> 26 | 0.934 | 0.95 <mark>3</mark> | 4.0 <u>7</u> 66 | 3.91 <mark>4</mark> | 4.0 <u>7</u> 66 | 4.7 <u>9</u> 87 | |
| Ca | | | | 0.01 0 | 0.012 | 0.0 <u>1</u> 06 | 0.9 <u>7</u> 69 | 0.9 <mark>765</mark> | 0.95 0 | 1.8 <u>4</u> 36 | 1. <u>90</u> 89 | 1.8 <u>4</u> 36 | 1. <u>90</u> 899 | |
| Sum | 3.0 <u>1</u> 0 | 3.00 3 | 3.004 | 4.0 <u>1</u> 09 | 4.0 <u>1</u> 0 | 4.00 3 | 4.0 <u>1</u> 09 | 4.0 <u>1</u> 07 | 4.00 3 | 10.5 <u>5</u> 4 | 7 10.56 4 | 10.0 <u>1</u> 0 | 10 <u>.00</u> | |
| Mg# | 5 0.90 | 0.90 | 0.90 | 0.91 | 7 0.90 | 0.91 | 0.95 | 0.95 | 0.95 | 7 1.00 | 0.98 | 5 1.00 | 0.96 | |

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

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.

| T 1 | 1 1 | <u> </u> | a . 1 |
|------------|-----|----------|-----------|
| l a | bI | e2. | Continued |
| | | | |

| Mineral | Pyrope | | Cr-Spine | 1 | | | Lizardite | | | Chlorite | | Phlogopi | te | Apatite |
|--------------------------------|--------|-------|----------|-------|--------------|-------|----------------------|--------|------------------|--------------------------|-------|---------------|-------|---------|
| M-type sample | F | | С | | F | | С | F | | С | F | С | | F |
| Generation | Ι | II | Ι | II | Ι | II | | | | | | | | |
| Comment | Р | 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 | 226 | 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 |
| P2O5 | | | | | | | | | | | | | | 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 <u>.</u> 77 | 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 <u>.</u> 03 | 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 | | 0.02 | | | | | | |
| 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 |
| Р | | | | | | | | | | | | | | 5.97 |
| Sum | 8.00 | 8.00 | 3.00 | 3.00 | 3.00 | 3.00 | 15.76 <mark>3</mark> | 15.864 | 15.6 <u>3</u> 29 | 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 | |

| Sample | 18LP1 | | | | MOL1 | -C | | | MM1 | | | | | | | VM10A | | |
|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|-----------------|-----------------|----------------------------|
| Туре | Coarse | | | | Coarse | | | | Fine | | | | | | | Fine | | |
| Mineral | Dol | | Dol | | Dol | | Mgs | | Dol | | Dol | | Dol | | Dol | Dol | | |
| Comment | Vein | | In opx | | Vein w | //mgs | Vein | | In liz | vein | Matrix | | In spl | | In mag | Matrix | | |
| 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 | Formatted: Font: Not Bold |
| 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 | Formatted: Font: Not Bold |
| MnO | 0.06 | 0.12 | 0.08 | 0.11 | 0.43 | 0.38 | 0.23 | 0.06 | 0.03 | 0.06 | 0.03 | 0 <u>.</u> ,07 | 0.02 | 0.05 | 0.27 | 0.04 | 0.00 | Formatted: Font: Not Bold |
| FeO | 1.26 | 0.15 | 1.21 | 0.10 | 1.31 | 0.39 | 5.68 | 2.10 | 1.24 | 0.07 | 1.34 | 0 <u>.</u> ,09 | 1.44 | 0.06 | 1.96 | 1.47 | 0.01 | For matter. Font. Not Bold |
| SrO | 0.01 | 0.04 | <u>bdl</u> 0.00 | 0.00 | 0.09 | 0.12 | <u>bdl</u> 0.00 | 0.00 | 0.13 | 0.11 | 0 <u>.</u> ,14 | 0 <u>.</u> ,12 | 0.20 | 0.09 | <u>bd1</u> 0.00 | 0.05 | 0.02 | Formatted: Font: Not Bold |
| 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 | Formatted: Font: Not Bold |
| Sum | 100.00 | - | 100.00 | - | 100.00 | - | 100.00 | - | 100.00 | - | 100.00 | - | 100.00 | - | 100.00 | 100.00 | - | Formatted: Font: Not Bold |
| 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 | |
| e | 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 | - | |
| 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 <u>.</u> ,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 | |

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

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

| Table3 | Continued |
|--------|-----------|
| raucs. | Commucu. |

| Sample | KL1-A | | | | | | | KL2.4-2b | | | | | | | KL1.6 | | |
|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|---------------------------|
| Туре | Fine | | | | | | Porph-f | ine | | | | | Porph-fi | ne | fine | | |
| Mineral | Dol | | Dol | | Cal | | Dol | | Dol | | Cal | | Cal | | Dol | | |
| Comment | Matrix | | w/cal+br | c | cal+brc | | In spl | | In spl, w/ | cal+brc | cal+brc | pol.ag. | In spl (ir | n grt) | vein | | |
| n | 22 | 2σ | 6 | 2σ | 4 | 2σ | 4 | 2σ | 9 | 2σ | 2 | 2σ | 2 | 2σ | 30 | 2σ | |
| Wt% | | | | | | | | | | | | | | | | | Formatted: Font: Not Bold |
| 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 | Formatted: Font: Not Bold |
| 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 | Formatted: Font: Not Bold |
| MnO | 0.11 | 0.27 | 0.02 | 0.06 | <u>0.00bdl</u> | 0.00 | 0.05 | 0.07 | 0.02 | 0.04 | 0.03 | 0.04 | <u>bdl</u> 0.00 | 0.00 | 0.04 | 0.09 | Formatted, Font. Not Dold |
| FeO | 1.52 | 0.12 | 1.63 | 0.06 | <u>bdl</u> 0.00 | 0.00 | 1.60 | 0.08 | 1.75 | 0.46 | 1.41 | 0.33 | 0.41 | 0.15 | 1.43 | 0.18 | Formatted: Font: Not Bold |
| SrO | 0.03 | 0.07 | <u>bd1</u> 0.00 | 0.00 | 0.22 | 0.05 | 0.09 | 0.10 | 0.05 | 0.09 | 0.16 | 0.22 | <u>bd1</u> 0.00 | 0.00 | 0.02 | 0.05 | Formatted: Font: Not Bold |
| 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 | Formatted: Font: Not Bold |
| Sum | 100.00 | - | 100.00 | - | 100.00 | - | 100.00 | - | 100.00 | - | 100.00 | - | 100.00 | - | 100.00 | - | Formatted: Font: Not Pold |
| 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 | Formatted. Font. Not Bold |
| Fe ²⁺ | 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 | Formatted: Font: Not Bold |
| 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 | 100 | 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 | |
| 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 | |
| Tet | 4.00 | - | 4.00 | _ | 4.00 | _ | 4.00 | _ | 4.00 | _ | 4.00 | - | 3.93 | _ | 4.16 | _ | |
| | 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 | |

| Sample and mineral | # | Microstructure | ⁸⁸ Sr (V) | ⁸⁷ Rb/ ⁸⁶ Sr | ⁸⁷ Sr/ ⁸⁶ 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 | <u><0.0001</u> | 0.70830 | 0.00015 | 100 |
| Dolomite | 10 | Vein | 1.6 | < 0.0001 | 0.70702 | 0.00017 | 100 |
| Dolomite | 11 | Vein | <u>1.3</u> | < 0.0001 | 0.70694 | 0.00016 | 100 |
| Dolomite | 8 | Vein | <u>2.4</u> | <u><0.0001</u> | 0.70392 | 0.00013 | 90 |
| Dolomite | 7 | Vein | <u>1.2</u> | <u><0.0001</u> | 0.70571 | 0.00017 | 90 |
| Dolomite | 6 | Vein | <u>0.8</u> | <u>0.0001</u> | 0.70541 | 0.00026 | 65 |
| Dolomite | 5 <u>*</u> | Vein | <u>3.0</u> | <u><0.0001</u> | 0.70360 | 0.00007 | 65 |
| Dolomite | 4 | Vein | <u>1.2</u> | <u>0.0003</u> | 0.70680 | 0.00013 | 65 |
| Dolomite | 3 <u>*</u> | Vein | <u>1.5</u> | <u>0.0001</u> | 0.70658 | 0.00019 | 100 |
| Dolomite | 12 | Vein | <u>0.5</u> | <u><0.0001</u> | 0.70531 | 0.00031 | 100 |
| Dolomite | 13 | Vein | <u>0.7</u> | <u>0.0001</u> | 0.70509 | 0.00030 | 100 |
| Dolomite | 14 * + | Vein | <u>1.6</u> | <u><0.0001</u> | 0.70636 | 0.00012 | 100 |
| VM10A | | | | | | | |
| Dolomite | 23 * | Matrix | <u>3.4</u> | <u><0.0001</u> | 0.70521 | 0.00011 | 65 |
| Dolomite | 22 <u>*</u> | Matrix | <u>1.2</u> | <u><0.0001</u> | 0.70519 | 0.00035 | 65 |
| Dolomite | 20* | Matrix | <u>3.4</u> | <u><0.0001</u> | 0.70539 | 0.00006 | 65 |
| Dolomite | 21* | Matrix | <u>1.6</u> | <u><0.0001</u> | 0.70529 | 0.00017 | 55 |
| Dolomite | 19^{+} | In zircon | <u>1.3</u> | <u>0.0011</u> | 0.70597 | 0.00007 | 55 |
| KL1-A | | | | | | | |
| Dolomite | 15 | Matrix | <u>1.2</u> | <u>0.0004</u> | 0.70671 | 0.00021 | 65 |
| Calcite | 16 | In cal+brc | <u>2.4</u> | <u><0.0001</u> | 0.70707 | 0.00021 | 65 |
| Calcite | 17 | In cal+brc | <u>08</u> | <u><0.0001</u> | 0.70709 | 0.00023 | 65 |
| Calcite | 18 | In cal+brc | <u>1.1</u> | <u><0.0001</u> | 0.70741 | 0.00009 | 65 |
| MM1 | | | | | | | |
| Dolomite | 24 | Matrix | <u>4.7</u> | <u><0.0001</u> | 0.70486 | 0.00007 | 65 |
| Dolomite | 25* | Matrix | <u>4.4</u> | <u><0.0001</u> | 0.70489 | 0.00005 | 65 |
| Dolomite | 26 | Matrix | <u>4.6</u> | <u><0.0001</u> | 0.70478 | 0.00005 | 65 |
| Dolomite | 27 | Matrix | <u>4.5</u> | <u><0.0001</u> | 0.70490 | 0.00008 | 65 |
| Dolomite | 28 | Matrix | <u>2.4</u> | <u><0.0001</u> | 0.70502 | 0.00012 | 65 |
| Dolomite | 29 | Matrix | <u>3.3</u> | <u><0.0001</u> | 0.70495 | 0.00008 | 65 |
| Dolomite | 30 | Matrix | <u>3.8</u> | 0.0002 | 0.70491 | 0.00006 | 65 |
| Dolomite | 31 | Matrix | $\frac{2.0}{2.7}$ | 0.0005 | 0.70478 | 0.00012 | 65 |
| Dolomite | 32 <u>*</u> | Matrix | 2.7 | <u>0.0004</u> | 0.70484 | 0.00008 | 65 |
| Dolomite | 33 | Matrix | <u>4.8</u> | <u><0.0001</u> | 0.70481 | 0.00005 | 65 |
| Dolomite | 34 <u>*</u> | Matrix | <u>1.3</u> | <u><0.0001</u> | 0.70479 | 0.00022 | 65 |
| Dolomite | 35 | Matrix | <u>4.2</u> | <u><0.0001</u> | 0.70477 | 0.00005 | 65 |
| Dolomite | 36 27* | Matrix | <u>2.9</u> | 0.0005 | 0.70484 | 0.00007 | 65 |
| Liolomite | 3/ ~ | Matrix | 1./ | 0.0007 | 0.70513 | 0.00024 | 65 |
| | 20 | N | 1.5 | 0.0004 | 0.70400 | 0.00010 | <i></i> |

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

Table4. ⁸⁷Sr/⁸⁶Sr isotope ratio measured with LA-MC-ICP-MS for selected carbonates in Ulten Zone peridotites. (+) <u>A</u>analyses were collected along lines <u>using the same spot size for spot</u> 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

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| Table I. Maj | or elements co | mpositions (w | t%) of olivine. | Formula bas | sed on 4 oxyc |
|--------------------------------|----------------|---------------|-----------------|-------------|---------------|
| Anions | Δ | 4 | Д | Д | Δ |
| Cations | 3 | 3 | 3 | 3 | 3 |
| cations | 5 | 5 | 5 | 5 | 5 |
| 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 |
| TiO2 | bdl | bdl | bdl | bdl | bdl |
| Cr_2O_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 Ti Al | 0.99 | 0.99 | 0.99 | 0.99 | 0.99 |
| 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 . $\overline{N^{\circ}Mg, \Lambda}$