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# Multi-stage sulfur and carbon mobility in fossil continental subduction zones: new insights from carbonate-bearing orogenic peridotites

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## Abstract

The volatile transfer in subduction zones and the role of sulfate as a vector for the mobilization of oxidized components from down-going slabs remain hotly debated issues. Orogenic spinel and garnet peridotite lenses from the Ulten Zone (Eastern Alps, Italy), exhumed as part of felsic metamorphic terranes in continental collision zones, bear witness to mass transfer processes in these pivotal environments.

In this study, we report a multi-method investigation of mantle sulfides coexisting with four generations of carbonates, indicating coupled sulfur and carbon mobility throughout the peridotites' metamorphic evolution as part of the Variscan subduction architecture. Detailed petrography, bulk rock measurements, *in situ* chemical and geochemical analyses of sulfides as well as Sr isotope analyses of associated clinopyroxene and amphibole are combined with the aim to constrain the origin, nature and effect of multiple C-O-H-S-bearing fluids and melts the peridotite interacted with. The first, pre-peak, metasomatic pulse (Stage 1) is represented by an H<sub>2</sub>S-CO<sub>2</sub>-bearing melt from the subduction-modified hot mantle wedge, which formed a pyroxenite layer hosting matrix pentlandite with  $\delta^{34}\text{S}$  of +2.77‰. Heavier  $\delta^{34}\text{S}$  (up to +3.43‰), radiogenic Sr ( $^{87}\text{Sr}/^{86}\text{Sr}_{\text{clinopyroxene}} > 0.7052$ ) and elevated Pb abundances recorded in coarse-grained garnet peridotite under eclogite-facies peak-conditions (Stage 2) are ascribed to interaction with isotopically heavy melts carrying recycled crustal component, permissive of, but not requiring, involvement of oxidized S species. Matrix carbonates occasionally occur in the coarse-grained peridotite. Conversely, isotopically lighter matrix pentlandite ( $\delta^{34}\text{S} = -1.62$  to +0.67‰), and radiogenic Sr in amphibole ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7056$ ) and associated dolomite (published data), from fine-grained garnet-amphibole peridotite may point to involvement of H<sub>2</sub>S-

CO<sub>2</sub>-bearing crustal fluids, which variably equilibrated with the mantle before interacting with the peridotites. Sulfide and amphibole in retrogressed spinel peridotite reveal the highest contents of fluid-mobile elements (As, Sb) and <sup>87</sup>Sr/<sup>86</sup>Sr<sub>amphibole</sub> up to 0.7074, suggesting late interaction with isotopically heavy crustal fluids at high fluid-rock ratios. The post-peak Stage 3 marks the entrapment of peridotites to form a tectonic mélange. Here, kelyphitization of garnet is catalyzed by further ingress of a S-bearing fluid ( $\delta^{34}\text{S} = -0.38\text{‰}$ ), while carbonate veining with occasional sulfides witnesses channelized fluid flow. Textural observations indicate that, during Stage 4, serpentinization of peridotite at low  $f\text{S}_2$  played an active role not only in CO<sub>2</sub> release by conversion of dolomite to calcite + brucite intergrowths, but also in local removal of <sup>32</sup>S during the final exhumation stage. Late channelized sulfur remobilization is evidenced by the serpentine + magnetite ( $\pm$  millerite  $\pm$  calcite) vein carrying > 300 ppm S.

Overall, the relatively narrow range of sulfur isotope composition ( $\delta^{34}\text{S} = -1.62$  to  $+3.76\text{‰}$ ) denotes limited interaction with isotopically heavy crustal fluids, and points to a subordinate role for subduction-derived sulfate throughout the extended evolution of UZ peridotites, first in the mantle wedge and then as part of a tectonic mélange.

## 1 Introduction

1 Sulfur (S) is a minor component in the mantle, yet it is thought to exert a key control on mantle redox  
2 conditions as well as ore-forming processes (e.g., [Tomkins and Evans, 2015](#); [Evans et al., 2017](#); [Holwell et](#)  
3 [al., 2019](#)). In xenoliths and orogenic peridotites, S is mostly stored in sulfides, such as pentlandite,  
4 pyrrhotite, chalcopyrite, monosulfide-solid-solution (mss) and intermediate-solid-solution (iss) (e.g., [Lorand](#)  
5 [et al., 2013](#); [Kiseeva et al., 2017](#); [Vaughan and Corkhill, 2017](#)). The speciation and mobility of S in  
6 subduction zones is of particular interest because magmas in convergent-margin settings have been shown to  
7 be more oxidized than those from spreading ridges (e.g., [Kelley and Cottrell, 2009](#); [Evans, 2012](#)), and with a  
8 redox budget of eight electrons, S has been invoked as a potential oxidizing agent ([Evans et al., 2017](#);  
9 [Bénard et al., 2018](#)).

10 Development of cutting-edge analytical techniques and improvement of thermodynamic modeling tools have  
11 recently led to major advances in constraining the speciation, sources and mobility of sulfur in oceanic  
12 subduction settings and associated ore deposit formation (e.g., [Schwarzenbach et al., 2018a](#), [Li et al., 2020](#);

14 [Walters et al., 2020](#)). However, major uncertainties persist for several reasons, such as (i) the lack of defined  
15 sulfide solid solution models for thermodynamic modeling; (ii) the limited control on physicochemical  
16 conditions (e.g. oxygen fugacity) determining S speciation and behavior, (iii) the lack of data from the  
17 mantle wedge, prevented by the small size of mantle sulfides, which remains a less-well known domain  
18 within the subduction factory.

19 Of note, the resultant recent research efforts produced conflicting lines of evidence for the sulfur behavior in  
20 subduction zones and for its contribution to the oxidation state of the sub-arc mantle region. Thus, exhumed  
21 mafic and ultramafic rocks from the island of Syros (Greece), interpreted as blocks detached from the  
22 lithospheric slab to form a subduction channel mélange under blueschist-facies conditions, were shown to  
23 have bulk-rock S isotopic signatures inherited from seawater alteration and overprinted by sediment-derived  
24 fluids mobilizing S along the plate interface ([Schwarzenbach et al., 2018a](#)). [Evans et al. \(2014\)](#) find complex  
25 S isotopic zoning of pyrite grains in eclogites originating as subducted oceanic crust from the Zermatt-Saas  
26 zone (Western Alps) and the Pouébo terrane (New Caledonia), which they ascribe to S loss during prograde  
27 metamorphism and sulfide growth at the earliest stage of exhumation. Similarly, [Walters et al. \(2019\)](#)  
28 describe sulfides of metasomatic origin from a global suite of exhumed high-pressure rocks, that yield a wide  
29 range of S isotopic compositions interpreted as precipitated from sulfate-bearing fluids. [Bénard et al. \(2018\)](#)  
30 [also maintain that](#) oxidized slab components have the potential to oxidate the sub-arc mantle, by  
31 documenting dissolved S<sup>6+</sup> in spinel-hosted glass inclusions in sub-arc mantle xenoliths brought to the  
32 surface by a recent volcanic activity in the Kamchatka (Russia) and West Bismarck arcs (Papua New  
33 Guinea). On the other hand, [Li et al. \(2020\)](#) show most S to be present as reduced species, and argue for  
34 limited S release in slab fluids. These constraints are based on a combination of petrographic observations,  
35 whole-rock and *in situ* S isotope measurements and thermodynamic modelling of sulfide-bearing high-  
36 pressure rocks and veins from the southwestern Tianshan (ultra-)high-pressure metamorphic belt (China).  
37 Thermodynamic modeling results of [Piccoli et al. \(2019\)](#) also support the reducing nature of dehydrated slab  
38 fluids at sub-arc depth. [Giacometti et al. \(2014\)](#) report little evidence from microtextural and *in situ* S  
39 isotopic analysis of exhumed meta-ophiolites from the Western Alps for S mobilization during  
40 metamorphism. Two-stage release of S during subduction is predicted by the thermodynamic modelling  
41 results of [Walters et al. \(2020\)](#), with a small flux of reduced S at shallow depth and elevated S fluxes from

42 deep, cold oxidized slabs via release of sulfate and sulfide species. Although [Tomkins and Evans \(2015\)](#) also  
43 predict a two-stage release process, they model anhydrite dissolution into fluids at low temperatures and the  
44 release of H<sub>2</sub>S when pyrite converts to pyrrhotite at higher temperatures.

45 Despite the importance of orogenic mantle peridotites as proxies for deep and retrograde-fluid-mediated  
46 volatile exchange between crust and mantle ([Scambelluri et al., 2010](#)), few studies have investigated the S  
47 speciation and isotopic composition of orogenic mantle rocks as an integral component of the global S cycle.

48 Orogenic spinel lherzolites in the North-Eastern Pyrénées yield negative values of  $\delta^{34}\text{S} = -3.2\text{‰}$  to represent  
49 an ancient S depletion event in the upper mantle, whereas positive values up to +3.3‰ of pyroxenite  
50 intrusions were interpreted to reflect various enriched mantle sources ([Chaussidon and Lorand, 1990](#)). The  
51 positive shift in the  $\delta^{34}\text{S}$  of sulfides up to +5.4‰ from the garnet-bearing pyroxenite in the Western Gneiss  
52 Region of Norway ([Rielli et al., 2018](#)) are ascribed to contamination from oceanic slab-derived oxidized  
53 fluids, whereas negative values down to -10.0‰ are attributed to fluids sourced from the enclosing gneisses  
54 or subducted oceanic sediments.

55 We focus on this little-explored facet of the S cycle, by investigating well-characterized orogenic spinel and  
56 garnet peridotites from the Ulten Zone (UZ) in the Eastern Alps that originated as continental mantle that  
57 became involved in continent-continent collision during the Variscan Orogeny. Displaying a diversity of  
58 compositional and mineralogical features, including several generations of hydrous and carbonate minerals,  
59 UZ peridotites have been the subject of multiple investigations, with a view to unraveling the element cycles  
60 in convergent margin settings ([Rampone and Morten, 2001](#); [Scambelluri et al., 2006](#); [Hermann et al., 2006](#);  
61 [Marocchi et al., 2009](#); [Sapienza et al., 2009](#); [Marocchi et al., 2010](#); [Scambelluri et al., 2010](#); [Marocchi et al.,](#)  
62 [2011](#); [Braga and Massonne, 2012](#); [Förster et al., 2017](#); [Ionov et al., 2017](#); [Gudelius et al., 2019](#); [Consuma et](#)  
63 [al., 2020](#); [Lo Pò et al., 2020](#)). The occurrence of sulfides in the UZ peridotites and their petrological  
64 implications have so far been overlooked as an important source of information on the behavior of S in  
65 continental subduction zones. Taking advantage of the spatial resolution and textural control afforded by *in*  
66 *situ* analyses on single sulfide grains, we use S isotopes as a sensitive tracer of the speciation and source of S  
67 in subduction zones. Additional constraints on the nature of metasomatic agents can be inferred from the  
68 variation in the trace element composition of texturally diverse pentlandite, which is known to reflect  
69 changes in the physicochemical fluid parameters (e.g., pressure, temperature, oxygen fugacity). Dehydration

70 and partial melting generally depletes the upper mantle in fluid-mobile and magmaphile elements,  
71 respectively, including the chalcophile elements As, Sb, Se, Te and Pb (Hattori et al., 2002; Hattori and  
72 Guillot, 2003). As a consequence, their enrichment in the mantle wedge is usually explained by the supply of  
73 these elements from slab-derived fluids and melts that percolate and metasomatize the overlying mantle.  
74 These variably chalcophile elements (e.g., Barnes, 2016) would be expected to follow sulfide (e.g., as HS<sup>-</sup>)  
75 mobilized in fluids and melts. *In-situ* determination of S isotopic and trace element compositions of  
76 pentlandite, combined with whole-rock analyses, *in situ* Sr isotope compositions of amphibole and  
77 clinopyroxene, and published *in situ* Sr isotope of the associated carbonates, allow to delineate a model for  
78 the formation and modification of sulfide and associated carbonates, and to discuss the potential sources and  
79 effects of C-O-H-S fluids percolating the mantle wedge during continental collision.

80

## 81 **2. Geological setting and metasomatic history**

82 The Ulten Zone (UZ) is a Variscan tectonic unit located in the Tonale Nappe (Eastern Alps) (Fig. 1). It is  
83 part of the metamorphic basement of the Austroalpine domain, interpreted as a constituent of Gondwana  
84 before its involvement in the Variscan collision with Laurussia (Regorda et al., 2020). In this unit, relicts of  
85 high-pressure (HP) metamorphism are preserved in lenses of ultramafic rocks (mostly garnet-bearing  
86 peridotites and eclogites) within migmatites and garnet-kyanite gneisses. The peridotites first resided in a  
87 supra-subduction zone mantle wedge at relatively high temperature (about 1200°C), followed by re-  
88 equilibration under eclogite-facies HP conditions of ~850°C and pressure of 2.2-2.7 GPa (Nimis and Morten,  
89 2000; Braga and Sapienza, 2007), as a result of their movement toward deeper portions of the upper mantle  
90 during continental crust subduction along a relatively cold path (Fig. 2a-b). Prior to or contemporaneously  
91 with the attainment of eclogite-facies conditions, the former coarse-protogranular peridotites experienced  
92 deformation and recrystallization into fine-grained peridotites, with formation of garnet and amphibole at the  
93 expense of spinel and clinopyroxene. The post-collisional stage comprises the development of a crust-  
94 peridotite tectonic mélange, and the onset of its exhumation is estimated to begin at around 330 Ma (Tumiati  
95 et al., 2003). The three different lithologies described by Obata and Morten (1987) synthesize the different  
96 stages of peridotite evolution: (1) (pre-peak) coarse-grained protogranular spinel peridotite (CS) that  
97 transforms into a variety with coronitic garnet (CG), consisting of olivine + enstatite + diopside + Cr-Al

98 spinel ( $\pm$  garnet); (2) (peak) porphyroclastic (P-FGA) to equigranular fine-grained garnet-amphibole  
99 peridotite (FGA) consisting of olivine + orthopyroxene + clinopyroxene + garnet + Ca-amphibole + spinel;  
100 and (3) (post-peak/exhumation) fine-grained spinel (chlorite-amphibole) peridotite (FSA) with olivine +  
101 orthopyroxene + Ca-amphibole + chlorite  $\pm$  spinel. All the UZ peridotites were variably serpentinized as they  
102 were involved in a crust-mantle *mélange* along the exhumation path. The exceptional complexity of the  
103 study area results from polyphase C-O-H-metasomatism along the Variscan continent collision (i.e. peak  
104 pressure conditions and afterwards), during which inputs of metasomatic liquids percolated the overlying  
105 orogenic mantle wedge inducing the formation of hydrous and carbonate phases.

106 On the basis of the high modal amphibole with a strong LILE/HSFE fractionation, [Rampone and Morten](#)  
107 [\(2001\)](#) suggested that the metasomatic agents of the high-pressure hydrous metasomatism are fluids with a  
108 low CO<sub>2</sub>/H<sub>2</sub>O ratio sourced from the neighboring crustal rocks. Nevertheless, carbonate phases related to the  
109 progressive metasomatic stages are ubiquitous in Ulten Zone peridotites, the petrography of which is  
110 described in detail in [Förster et al. \(2017\)](#). Inclusion of dolomite in coarse spinel, itself enclosed in garnet,  
111 was ascribed as a trapped melt during the high-temperature metasomatic stage in the mantle wedge ([Stage 1](#)  
112 [in Fig. 2a-b](#)), despite the radiating fracturing may point to a late metasomatic process ([Consuma et al. 2020](#)).

113 Formation of interstitial dolomite with minor magnesite has been ascribed as a peak-pressure feature, while  
114 late exhumation-related serpentinization caused dolomite dissolution and formation of calcite+brucite  
115 intergrowths via the reaction  $\text{CaMg}(\text{CO}_3)_2 + \text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{Mg}(\text{OH})_3 + \text{CO}_2$ . This reaction implies CO<sub>2</sub>  
116 liberation from peridotites now entrapped in a crust-mantle *mélange* ([Förster et al., 2017](#)). Subsequent *in situ*  
117 Sr isotope measurements in the UZ carbonates have shown multiple signatures related to their textural  
118 positions ([Consuma et al., 2020](#)): relatively unradiogenic <sup>87</sup>Sr/<sup>86</sup>Sr of  $\sim 0.705$  of matrix dolomite formed at  
119 eclogite-facies conditions, were taken to indicate that fluid sources that had variably equilibrated with a  
120 depleted mantle reservoir mostly acted at high-pressure peak conditions. In contrast, variably radiogenic  
121 <sup>87</sup>Sr/<sup>86</sup>Sr (0.7036 to 0.7083) was ascribed to hybridized sources (i.e. mixing of depleted mantle and crustal  
122 liquids) generated after the entrapment of peridotites into crustal rocks during the exhumation stage  
123 ([Consuma et al., 2020](#)). The occurrence of these carbonates commonly in intimate association with sulfides  
124 in different textural positions proves that metasomatic fluids and melts played a role in the mobility not only

125 of carbon but also of sulfur in the mantle wedge and tectonic mélange, and thus opens new questions  
126 regarding their role in the global S cycle.

127

### 128 **3. Samples, prior work and sulfide petrography**

129 We investigated twenty orogenic peridotite samples from different localities of the Ulten Zone (Fig. 1), as  
130 representative of different domains of the Variscan Ulten Zone mantle wedge. The selection was guided by  
131 the motivation to include specimens that are representative of the metamorphic and metasomatic stages,  
132 mineral assemblages, and presence of carbonates and sulfides.

133 Ten samples encompassing coarse spinel peridotites (UN1, UN2), fine-grained garnet-amphibole peridotites  
134 (UN3, UN6, UN7, UN9, UN10, UN14) and fine-grained spinel-amphibole peridotites (UN8, UN16) were  
135 previously studied in detail for their petrography, bulk-rock and mineral major-, minor- and trace-element  
136 composition, as well as for garnet Fe speciation (Gudelius et al., 2019). The study shows that LILE, LREE  
137 and some HFSE are co-enriched and revealed significant compositional differences between sampling  
138 localities (Samerberg vs. Seefeld/Malga Masa Murada; Fig. 1), which is ascribed to different positions of the  
139 peridotite bodies relative to the slab during subduction and exhumation. Despite evidence for strong  
140 metasomatic overprint,  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in garnet remains low ( $<0.046$ ), and oxygen fugacities relative to the  
141 Fayalite-Magnetite-Quartz buffer ( $\Delta\log f\text{O}_2$ ) of -2.4 to -0.32 are calculated for  $P=2$  GPa, suggesting reducing  
142 conditions in the mantle wedge beneath the Ulten Zone (Gudelius et al., 2019). Conversely, Malaspina et al.  
143 (2009) find more oxidizing conditions (FMQ to FMQ+2 calculated at  $P = 3$  GPa) in FGA peridotites from the  
144 Malga Masa Murada and Samerberg areas. Thus, the UZ records heterogeneous redox conditions of various  
145 mantle wedge and tectonic mélange domains (Fig. 2c).

146 A further seven samples were previously investigated by Consuma et al. (2020) (18LP1, MOL1-C, KL2.4-  
147 2b, KL2.4-3, VM10A, KL1-A, MM1), integrating petrography, *in situ* major elements, Raman analyses and  
148 *in situ* Sr isotopes of dolomite and calcite. Results show that high-pressure carbonation of the UZ peridotite  
149 led to matrix dolomite formation from fluids variably equilibrated with a depleted mantle reservoir,  
150 indicating the efficiency of the mantle wedge, as represented by UZ peridotites, in storing carbonates. During  
151 exhumation, further percolation of hybridized fluids (sourced both from mantle and associated migmatites)  
152 may have metasomatized the peridotites as part of a crust-mantle mélange, as suggested by the large range of

153  $^{87}\text{Sr}/^{86}\text{Sr}$  obtained for carbonate veins crosscutting the peridotite matrix. Dissolution of carbonates prevailed  
154 during late exhumation-related serpentinization, as testified by pseudomorphs of calcite+brucite intergrowths  
155 after dolomite first described by Förster et al. (2017).

156 The porphyroclastic fine-grained garnet-amphibole peridotite P10B was first investigated by Lo Pò et al.  
157 (2020). Based on mineral chemistry and thermodynamic modelling, they interrogate the formation of  
158 polymineralic inclusions (PI) in highly fractured cm-sized garnet. PI are proposed to crystallize as incoming  
159 saline brines flow through fractures in garnet and locally interact with it along a post-Variscan, retrograde  
160 path.

161 For the purpose of the present study, two additional peridotite samples were investigated: (i) MM1B, which  
162 represents the composite serpentine vein crosscutting the matrix of FSA peridotite MM1; and (ii) coarse-  
163 grained peridotite SBA2, the only carbonate-free sample (CGn). Classification of the samples with sulfide  
164 assemblages, salient published data and analyses performed in this study are synthesized in Table 1.

165

166 Sulfides occur as discrete monophase and subordinately as polyphase grains with different shapes (rounded  
167 grains, elongated, blocky, skeletal or irregular) and sizes (up to 150  $\mu\text{m}$ ). They show various stages of  
168 alteration, ranging from none, to partial or strong alteration and fracturing, as illustrated in Figure 3 and  
169 Electronic Annex B.

170 Six texturally distinct sulfide types are recognized linked to the different metamorphic stages of the UZ  
171 peridotites (Fig. 2d):

- 172 1. *Polycrystalline Inclusions (PI) (Stage 1-4)*: sulfide inclusions in a cm-sized garnet and in spinel  
173 included in mm-sized garnet occur as part of PI with grain size varying from 5 to 30  $\mu\text{m}$  (Fig. 3a-b).
- 174 - *Included in cm-sized garnet* (peridotite P10B): Pyrrhotite ( $\pm$  pentlandite) is solely included in garnet  
175 from this sample, whereas monophase pentlandite dominates in the matrix (Fig. 3a). PI fill a fracture  
176 crosscutting the host garnet from the rim through the core. Here, PI show a complex association of  
177 unusual minerals (amphibole + dolomite + chlorite + pentlandite + pyrrhotite + apatite +  
178 kinoshitalite + sapphirine + garnet included in amphibole; Lo Pò et al., 2020).
- 179 - *Included in spinel (enclosed in garnet)* (peridotites KL2.4-2b and KL2.4-3): They occur as  
180 assemblages of apatite + ilmenite + dolomite + pentlandite; calcite-brucite intergrowths + Cl-apatite

181 + pentlandite + ilmenite + phlogopite + chalcopyrite (Fig. 3b); calcite + ilmenite + Cl-apatite +  
182 pentlandite. Also PI of native Cu + ilmenite + Cl-apatite + amphibole occur with radiating fractures,  
183 linking the PI to the host spinel rim. Occasionally, PI (e.g. amphibole + ilmenite + sphalerite +  
184 calcite + pentlandite) occur within, but at the edge of, coarse spinel connected with the surrounding  
185 kelyphitic corona.

186 2. *Discrete sulfide inclusions (Stage 1-2)*: Orthopyroxene grains, Cr-rich spinel in garnet, Cr-poor  
187 spinel in the matrix and kelyphitic corona host different types of sulfides, whereas no sulfides are  
188 found in olivine. Notably, kelyphite around spinel and garnet commonly hosts sulfides (mostly  
189 pentlandite) of exceptional dimensions (30-150  $\mu\text{m}$ ; Fig. 3d). They commonly occur at the edge of  
190 coarse spinel following the directions of the kelyphite growths or at the edge of the corona in contact  
191 with the peridotite matrix (e.g. pentlandite with magnetite exsolutions and cut by late chlorite flakes;  
192 pentlandite + sphalerite + native-Cu blebs associated with Cl-apatite and cut by chlorite flakes;  
193 30  $\mu\text{m}$  zoned chalcopyrite grain).

194 3. *Interstitial sulfides (Stage 2)*: They occur at silicate grain boundaries and commonly in close spatial  
195 relationship with matrix dolomite (Fig. 3c). In the coarse-grained peridotite (CS + CG + CGn), they  
196 are usually anhedral or subhedral with rounded or elongated shape and show a grain size from 10 to  
197 50  $\mu\text{m}$ . The carbonate-free peridotite SBA2 contains only five fractured blocky monophase  
198 pentlandite grains with no alteration features. In CS and CG peridotites MOL1-C and 18LP1,  
199 interstitial sulfides occur mainly as pentlandite + millerite assemblages partially replaced by  
200 magnetite. In MOL1-C, pentlandite (partly replaced and rimmed by thin magnetite) + heazlewoodite  
201 + dolomite + serpentine assemblage is cut by chlorite flakes (Fig. 3c). In the FGA peridotites KL1-A  
202 and VM10A, pentlandite is commonly interstitial to olivine, orthopyroxene and pargasitic to  
203 hornblenditic amphibole. It is locally associated with disseminated dolomite. Nickeline blebs (Ni,  
204 As) are found within disseminated rounded pentlandite in association with Cl-apatite in FGA  
205 peridotite VM10A. It is worth noting that this peridotite is very weakly serpentinized.

206 4. *In carbonate veins (Stage 3)*: Pentlandite + millerite cut by late chlorite flakes (with magnetite filling  
207 the cleavage) are hosted in a vein predominantly formed by dolomite (and minor magnesite) +  
208 tremolite + serpentine that cuts the peridotite matrix 18LP1 (Fig. 3e). Monophase pentlandite also

209 occurs not directly within the vein but in spatial proximity with it (i.e. few  $\mu\text{m}$  from the vein). A  
210 nickeline bleb enclosed into pentlandite partially replaced by magnetite is documented.

211 5. *In matrix serpentine or serpentine vein (Stage 4)*: P-FGA peridotites KL2.4-2b and KL2.4-3 show  
212 pentlandite + magnetite exsolutions contoured by chalcopyrite blebs. Exceptionally in these two  
213 samples, sphalerite can also be found included in matrix serpentine, as single phase or polyphase-  
214 assemblages (pentlandite + sphalerite + chalcocite). Matrix serpentine in FSA peridotite MM1 is  
215 dominated by pentlandite rarely replaced by millerite or heazlewoodite. Conversely, the composite  
216 serpentine + magnetite ( $\pm$  calcite  $\pm$  dolomite) vein MM1B, crosscutting the matrix of peridotite  
217 MM1, hosts fractured elongated-to-rounded millerite in intimate association with Ni-oxide grains  
218 with sizes of  $\sim 30$  and  $20 \mu\text{m}$  respectively. Nickeline blebs (NiAs;  $3\text{-}5 \mu\text{m}$  on average) occasionally  
219 occur within pentlandite ( $\pm$  magnetite) grains associated with serpentine (e.g. in peridotites MOL1-  
220 C, 18LP1 and VM10A). Pentlandite enclosed in the serpentine + magnesite + tremolite vein  
221 (peridotite MOL1-C) is pseudomorphously replaced by magnetite (Fig. 3e). Perpendicularly to this  
222 vein, serpentine + pentlandite + magnetite fills the cleavage of the host mm-sized enstatite, rarely  
223 containing small nickeline blebs.

224 6. *In halos, apophyses and sulfide-filled fractures (Stage 2-3-4)*: Diffuse sulfide material is commonly  
225 observed in i) halos around discrete sulfide grains, ii) apophyses leading into sulfide-filled fractures  
226 and iii) sulfide in fractures apparently unconnected to discrete sulfide grains (Fig. 3f). In megacrysts,  
227 similar observations are ascribed to decrepitation of the sulfide during heating in contact with host  
228 basalt (Andersen et al., 1987), a mechanism that does not apply here. It is noteworthy that such  
229 features are observed both in fine-grained garnet amphibole peridotite and in spinel peridotite and  
230 therefore not (exclusively) related to late-stage retrogression.

231 In addition to the reported textural occurrence of sulfides in peridotites, pentlandite grains interstitial to  
232 silicates are documented occurring in a pyroxenite layer found in the coarse spinel peridotite MOL1-C,  
233 which also hosts matrix dolomite. According to the Ulten Zone geodynamic scenario, these grains are related  
234 to Stage 1.

235 To sum up, in order of decreasing abundance, sulfides occur mostly interstitial to silicates and associated  
236 with matrix dolomite, enclosed in veins of serpentine and carbonates (dolomite, magnesite) and finally as

237 inclusions (in coarse spinel and few grains in silicates), coexisting with dolomite and calcite. Interstitial  
238 pentlandite is by far the dominant sulfide phase occurring in all the UZ peridotite samples, with an average  
239 grain size of 5-150  $\mu\text{m}$ , followed by heazlewoodite and millerite mostly found in association with pentlandite  
240 in serpentine and carbonate veins. Enclosed pentlandite is common in spinel as a discrete phase or PI, while  
241 pyrrhotite ( $\pm$  pentlandite) occurs as PI in cm-sized garnet in peridotite P10B, except for few matrix pyrrhotite  
242 grains in the “UN” sample suite. Finally, few sphalerite, chalcopyrite and chalcocite grains are hosted only in  
243 P-FGA peridotites, mostly within coarse-grained spinel and kelyphite (KL24-2b, KI24-3, VM10A, P10B).

244

#### 245 **4. Methods**

246 Each analytical method and specifics on quality control measures are detailed in [Electronic Annex C](#).

247 Samples were examined in polished thin section and slices of peridotite of 3 mm thickness by optical

248 transmitted and reflected light using a polarized optical microscope, and by Scanning Electron Microscopy

249 (SEM) for X-ray maps at the Department of Biological, Geological and Environmental Sciences, University

250 of Bologna, Italy.

251

252 Bulk rock major- and minor-element compositions along with selected trace elements were acquired by X-

253 Ray-Fluorescence, using a Phillips Magi XPRO spectrometer at Johannes Gutenberg-University Mainz.

254 Results are shown in [Table S1](#) in [Electronic Annex D](#). The same instrument, and a LECO-Analyzer CS 125,

255 were used to obtain bulk-rock S concentrations for a subset of samples (UN1-UN16) for which major- and

256 minor-element compositions had been previously determined ([Gudelius et al., 2019](#)). Remaining S

257 concentration measurements were carried out at Karlsruhe Institute of Technology, also using a LECO

258 instrument. Individual results are provided in [Table S2](#). Sulfide major- and minor-element concentrations

259 were obtained *in situ* by EPMA, using a JEOL JXA-8100 Superprobe electron microprobe at the Institute of

260 Mineralogy and Petrology, University of Innsbruck and a JEOL JXA-8900 at Goethe-University Frankfurt.

261 Results and summary are shown in [Table S3](#).

262

263 Trace-element abundances were determined *in situ* in sulfides following the procedure detailed in [Aulbach et](#)

264 [al. \(2012\)](#). Measurement statistics for two separate analytical campaigns and results are given in [Table S4](#)

265 [and S5 in Electronic Annex D](#). Abundances of Au cannot be quantified in a subset of samples that were Au-  
266 coated prior to analysis for multiple S isotopes, as Au may have collected in small pits and cracks in the  
267 sulfides.

268

269 The Rb-Sr isotopic composition of clinopyroxene and amphibole ([Table S6 in Electronic Annex D](#)) was  
270 obtained *in situ* by laser ablation microprobe (LAM) multi-collector inductively-coupled plasma mass  
271 spectrometry (MC-ICPMS), using a Resonetics RESolution M-50-HR laser probe linked to a  
272 ThermoFinnigan Neptune mass spectrometer at Goethe-University Frankfurt, as described in [Electronic](#)  
273 [Annex C](#).

274

275 Sulfur isotope compositions were measured *in situ* by secondary-ion mass spectrometry (SIMS) using a  
276 Cameca IMS-1280 at the Centre for Microscopy and Microanalysis (CMCA), University of Western  
277 Australia. SIMS measurements were undertaken on 30 pentlandite grains from seven peridotites and results  
278 are reported in [Table 4](#). Grains with a minimum size of 20  $\mu\text{m}$  were previously selected according to the  
279 different textural positions and association with carbonates, which track progressive metasomatic episodes  
280 during pre-peak, high-pressure-peak and retrograde conditions. All  $\delta^{34}\text{S}$  values are reported relative to  
281 Vienna Canyon Diablo Troilite – VCDT ([Ding et al., 2001](#)). Further details on the procedure are given in  
282 [LaFlamme et al. \(2016\)](#).

283

## 284 **5. Results**

### 285 **5.1 Whole rock major elements and sulfur concentration**

286 New whole rock compositions are reported in [Table S1 in Electronic Annex D](#) and illustrated together with  
287 published data (UN series) in [Figure 4](#). Loss On Ignition (LOI) ranges between 0.37 and 13.10 wt.%, in line  
288 with the degree of serpentinization. The highest value of 13.10 wt.% is from the serpentine vein MM1B  
289 previously hand-picked from FSA peridotite MM1. Contents of  $\text{Al}_2\text{O}_3$  in the UZ peridotites range between  
290 1.40 and 3.12 wt.%, while CaO ranges from 0.44 to 2.84 wt.%,  $\text{TiO}_2$  from 0.02 to 0.11 wt.% and MgO from  
291 37.87 to 42.79 wt.%. For comparison, primitive and depleted mantle have estimated  $\text{Al}_2\text{O}_3$  concentrations of

292 4.45 and 4.28 wt.%, respectively, CaO of 3.55 and 3.50 wt.%, TiO<sub>2</sub> contents of 0.201 and 0.19 wt.% and  
293 MgO contents of 37.8 and 38.22 wt.%, respectively (McDonough and Sun, 1995; Salters and Stracke, 2004).  
294 Sulfur concentrations for eighteen peridotite samples are reported in Figures 4-5, and Table S2 in Electronic  
295 Annex D. Overall, the S content of the orogenic peridotites ranges from as low as a few tens to hundreds  
296 ppm, averaging 171 ( $\pm 45$ ; n=18) ppm with a median value of 169 ppm.

297 Coarse-garnet peridotite (CG) shows an average value of  $180 \pm 28$  ppm (n=5), fine-grained garnet amphibole  
298 peridotite (FGA) an average value of  $160 \pm 34$  ppm (n=9) and three fine-grained spinel peridotites (FSA)  
299 have wide sulfur concentration ranging from 40 to 228 ppm. The serpentine + magnetite  $\pm$  sulfide (mostly  
300 millerite)  $\pm$  calcite  $\pm$  dolomite vein MM1B reaches the highest value of 329 ppm S. Again for comparison,  
301 primitive and depleted mantle have S concentrations of 250 and 60-119 ppm, respectively (Alt et al., 2007;  
302 McDonough and Sun, 1995; Salters and Stracke, 2004).

## 303

### 304 5.2 Sulfide major element composition and low-pressure re-equilibration

305 The dataset comprises 295 sulfide grains analyzed for their major element compositions (Fig. S1 in  
306 Electronic Annex A and Table S3 in Electronic Annex D); Table 2 reports the average major element  
307 concentrations for pentlandite grains according to their different textural positions while Electronic Annex B  
308 shows Backscatter-Electron (BSE) images for all analyzed sulfides in UN series samples.

309

310 Pentlandite is compositionally heterogeneous with 22.8-39.5 wt.% Fe, 28.8-37.8 wt.% Ni and below  
311 detection limit (bdl)-16.6 wt.% Co. Here, pentlandite with Ni > 36wt.% is classified as Ni-pentlandite  
312 (mostly found in serpentine vein), and that with Co > 6wt.% as Co-pentlandite (mostly found associated with  
313 carbonate veins and in FSA peridotites). Data show that pentlandite enclosed in coarse spinel included in  
314 garnet (occurring both as discrete grain and PI) and in silicates, as well as most of the matrix pentlandite  
315 grains in P-FGA and FGA peridotites and some pentlandite enclosed in kelyphitic coronas around garnet fall  
316 in the “typical” mantle sulfide range according to Wang et al. 2010 (Fig. S1 in Electronic Annex A).

317 Conversely, the other sulfides, such as those found in the matrix of CGn peridotite SBA2 and those included  
318 in a serpentine vein show higher Co/(Fe+Ni+Cu) and Co/Ni ratio with respect to the mantle sulfides.

319 The Ni/(Ni+Fe) ratio of pentlandite averages 0.46 ( $\pm 0.05$ ), ranging from 0.34 to 0.59, except for three Ni-  
320 pentlandite grains with ratios  $>0.60$ . In CGn peridotite SBA2, pentlandite shows a relatively high Co-  
321 content, with an average of 1.89 wt.% (n=10). The Co-content increases in FSA peridotites MM1 and vein  
322 MM1B with an average of 5.6 wt.% (n=7), while the highest value (Co = 16.6 wt.%) is reached in few  
323 pentlandite grains enclosed in the dolomite vein of peridotite 18LP1. Millerite and heazlewoodite ( $\pm$   
324 pentlandite) with Ni  $> 63.6$  wt.% are the dominant phases in peridotite MM1 and vein MM1B. Cu-enriched  
325 pentlandite is found in grains enclosed in kelyphitic coronas around garnet, with Cu concentration from bdl-  
326 2.6 wt.%. Nickel and Fe in pentlandite occurring in peridotites 18LP1, MM1 and MM1B are positively  
327 correlated; conversely, a negative correlation is shown for pentlandite in fine, prophyroclastic, garnet-  
328 amphibole peridotites (Fig. S1). The overall occurrence of pentlandite in the studied peridotites is consistent  
329 with the typical sulfide component of orogenic mantle (Alard et al., 2000), and the measured Ni/(Ni+Fe)  
330 ratio of about 0.46 ( $\pm 0.05$ ) is also similar to those found in mantle xenoliths (e.g., Szabó and Bodnar, 1995;  
331 Guo et al., 1999; Aulbach et al., 2019).

332 Pyrrhotite shows homogeneous chemical compositions, with a sulfur content of about 50.40 at.% ( $\pm 0.19$ ).  
333 The Ni content is always below detection limit. Minor Cu-sulfides are represented by few tiny blebs (max.  
334 5  $\mu\text{m}$ ) of chalcopyrite and chalcocite, except for one chalcopyrite grain of 30  $\mu\text{m}$  size found enclosed in  
335 kelyphite. The metal/S ratio of chalcopyrite averages 0.97 ( $\pm 0.01$ ). Only two chalcocite grains were found in  
336 sample KL2.4-2b.

337 The high-temperature precursors of the UZ sulfides can be revealed by comparing their major chemical  
338 compositions to experimentally determined phase relations at various temperatures in the ternary diagram S-  
339 Fe-(Ni+Co) in at.% (Fig. S2a in Electronic Annex A). This indicates that minor pyrrhotite and dominant  
340 pentlandite could be derived from re-equilibration of mss to low temperature (T). In addition, in the ternary  
341 system  $\text{Fe}_9\text{S}_8$ - $\text{Ni}_9\text{S}_8$ - $\text{Co}_9\text{S}_8$ , experimental studies have shown that the pentlandite composition is  
342 temperature-dependent (Kaneda et al., 1986) and can reflect the condition under which it forms (e.g., Lorand  
343 and Grégoire, 2006; LaFlamme et al., 2016). Most of the investigated pentlandite grains plot within the  
344 entire field of stability for T of 200°C and 300°C (Fig. S2b), which are consistent with low-T assemblages  
345 ( $\leq 300^\circ\text{C}$ ) re-equilibrated from high-T-(mono)sulfides, whereby higher Co content shifts the stability field

346 for pentlandite formation to higher T (c. 300° C). Pentlandite can also originate by crystallization from  
347 metasomatic Ni-Cu-rich sulfide melts with high metal/S ratios (Lorand et al., 2013).

348

### 349 **5.3 Sulfide trace element concentrations**

350 Trace elements were measured in pentlandite and pyrrhotite from the UN suite samples, peridotite P10B, and  
351 from pentlandite previously measured by SIMS. A few millerite grains were also analyzed.

352 Pyrrhotite from PI in garnet shows Ni concentrations ranging from 119 to 8332 ppm, Cu from 22 to 569  
353 ppm, Zn from 0.96 to 7.41 ppm, As from 0 to 30 ppm, Se from 2 to 24 ppm, Ag from 0.08 to 0.70 ppm, Sb  
354 from 0.07 to 0.82 ppm, Te from bdl to 1.3 ppm, Pb from 1.7 to 22.6 ppm and Bi from 0.2 to 1.1 ppm.

355 Median values are reported in Table 3 and illustrated in Figure 6, while for the full trace-element dataset the  
356 reader is referred to Table S5 in Electronic Annex D.

357 Siderophile and chalcophile element concentrations in pentlandite span a large range of values. Arsenic is the  
358 most abundant trace element, ranging from 1 to 1213 ppm (median 514 ppm; n=86). Abundances of Zn  
359 range from bdl to 535 ppm, maintaining low concentrations in matrix pentlandite from peridotite P10B (bdl-  
360 1.73 ppm). Selenium and Te are always present in detectable abundances, ranging from 12 to 211 ppm  
361 (median=81 ppm; n= 86) and from 1 to 89 ppm (median=14 ppm; n=80) respectively, while Ag ranges from  
362 bdl to 51.67 ppm (median = 1 ppm; n=86). Concentrations of Sb are usually low (from bdl to 40 ppm;  
363 median 1 ppm; n=80), except for few matrix pentlandite grains in FSA peridotites UN8 and UN16, and when  
364 in association with a dolomite vein or enclosed in a serpentine vein of peridotite MOL1-C (here Sb values  
365 are always > 13 ppm). By contrast, matrix pentlandite from P-FGA peridotite P10B varies from 0.07 to 0.28  
366 ppm and the pentlandite in PI in spinel shows Sb concentration of 7.1 ppm. Pb is from 0.9 to 1730 ppm  
367 (median=9 ppm; n=80) and Bi from 0.1 to 15.6 ppm (median=1 ppm; n=80).

368

### 369 **5.4 SIMS Sulfur isotope compositions of pentlandite**

370 Since the textural context of the sulfides provides crucial information on the stage during which S was  
371 potentially added or removed (Fig. 2d), *in situ* acquisition of S isotopic composition of sulfides is  
372 indispensable. Only a few grains showed a suitable size and composition (close to matrix-matched standards)  
373 for SIMS analysis. Results are listed in Table 4 and shown in Figure 7.

374 In the coarse-grained spinel peridotite MOL1-C, a pyroxenite layer hosts a pentlandite grain with values of  
375  $+2.77 \pm 0.37\text{‰}$  (n=2).

376 Matrix pentlandite in the only carbonate-free sample (SBA2), a coarse-grained garnet peridotite, consistently  
377 shows relatively heavy  $\delta^{34}\text{S}$ , with an average of  $+2.71 \pm 0.43\text{‰}$  (n=14). Except for one grain showing  $+0.74$   
378  $\pm 0.41\text{‰}$ , the other grains are  $\geq 1.52 \pm 0.45\text{‰}$ , reaching a maximum value of  $+3.54 \pm 0.35\text{‰}$ . There is no  
379 significant intra-grain isotope variability.

380 The CG peridotite 18LP1 contains a dolomite vein with pentlandite showing the highest Co values. Given  
381 the restricted range of Co imposed by the sulfide standard to be measured by SIMS, only few grains could be  
382 analyzed, yielding an average value of  $+0.80 \pm 0.40\text{‰}$  (n=4) for pentlandite enclosed or locally associated  
383 with the dolomite vein, while pentlandite included in coarse spinel gives  $\delta^{34}\text{S} = -0.18 \pm 0.45\text{‰}$ .

384 Pentlandite grains exhibit a wide isotopic range when occurring in serpentine + magnesite + tremolite vein,  
385 with  $\delta^{34}\text{S}$  values spanning between  $-0.29 \pm 0.34\text{‰}$  and  $+3.76 \pm 0.36\text{‰}$ . These two extreme values were  
386 measured in the same serpentine-enclosed pentlandite grain. Matrix pentlandite associated with dolomite  
387 (Fig. 3c) averages  $+3.11 \pm 0.38\text{‰}$  (n = 6).

388 The Mann-Whitney U Test (Electronic Annex C) reveals a significant difference between the  $\delta^{34}\text{S}$  values of  
389 pentlandite within the fine-grained and the coarse-grained peridotite lithotypes, at a level of significance of  
390 1% ( $p < 0.00001$ ). The isotopic values of pentlandite in the fine-grained peridotite are significantly lighter  
391 than those in the coarse-grained peridotite.

392 The single pentlandite in PI in coarse spinel (in turn included in garnet) exhibits  $\delta^{34}\text{S} = +0.46 \pm 0.34\text{‰}$ . Two  
393 matrix pentlandite grains in the fine-grained peridotite KL1-A, which are intimately associated with matrix  
394 dolomite, show values of  $-1.62 \pm 0.42\text{‰}$  and  $-1.14 \pm 0.39\text{‰}$  respectively. Matrix pentlandite in sample  
395 KL2.4-3 averages  $+0.31 \pm 0.34\text{‰}$  (n=3) with little intra-grain isotope variability. Within the same peridotite,  
396 a pentlandite grain found in kelyphite around spinel and cut by a chlorite flake averages  $-0.38 \pm 0.31\text{‰}$   
397 (n=3). In peridotite VM10A, matrix pentlandite  $\delta^{34}\text{S}$  ranges from  $-1.32 \pm 0.40\text{‰}$  to  $+0.67 \pm 0.40\text{‰}$  with an  
398 average of  $-0.21 \pm 0.41\text{‰}$  (n=12).

399 Overall, the S isotope compositions obtained for the UZ pentlandite grains range between  $-1.62 \pm 0.42\text{‰}$  and  
400  $+3.76 \pm 0.36\text{‰}$ . Matrix pentlandite from fine-grained peridotites is isotopically light, with an average of

401  $\delta^{34}\text{S} = -0.11 \pm 0.39\%$  (n=15), ranging from  $-1.62 \pm 0.42\%$  to  $+0.67 \pm 0.40\%$ . Conversely, matrix pentlandite  
402 from coarse-grained peridotites is isotopically heavy, with an average  $\delta^{34}\text{S} = +2.48\% \pm 0.41\%$  ( $1\sigma$ , n=25)  
403 and ranging between  $+0.41 \pm 0.42\%$  to  $+3.76\% \pm 0.36\%$ . For comparison,  $\delta^{34}\text{S}$  of the depleted mantle is  
404 estimated at  $-1.28 \pm 0.33\%$  (Labidi et al. 2013).

405

## 406 5.5 In situ Sr isotope of clinopyroxene and amphibole

407 Laser ablation MC-ICP-MS analyses were performed on 15 clinopyroxene grains from 5 UZ peridotite  
408 samples (total of 25 analyses; Table S6 in Electronic Annex D) (Fig. 8). Clinopyroxene in the two fine-  
409 grained garnet-amphibole peridotites P10B and VM10A sampled from Mt. Hochwart (Fig. 1) show an  
410 average measured  $^{87}\text{Sr}/^{86}\text{Sr}$  value of  $0.70538 \pm 0.000076$  ( $1\sigma$ , n = 11). The porphyroclastic garnet-amphibole  
411 peridotite sample KL2.4-2b from Klappfbergalm (Fig. 1) shows similar  $^{87}\text{Sr}/^{86}\text{Sr}$  with  $0.70535 \pm 0.00012$  ( $1\sigma$ ,  
412 n = 4). Clinopyroxene grains from the two coarse-grained peridotite samples UN1 and UN2 from Samerberg  
413 area (Fig. 1) show similarly radiogenic values of  $0.70544 \pm 0.00015$  and  $0.7055 \pm 0.0020$ . The lower  
414 standard deviations obtained for clinopyroxene in fine-grained amphibole peridotite compared to coarse  
415 protogranular peridotites (using the same method in the same laboratory) suggests a greater degree of  
416 isotopic homogenization of the former, which were subjected to recrystallization and retrogression.

417

418 Furthermore, 23 amphibole grains from 8 samples were analyzed for *in situ* Sr isotope compositions (n=41  
419 analyses; Table S6). Measured  $^{87}\text{Sr}/^{86}\text{Sr}$  of amphibole in the P-FGA peridotites UN3, UN6 (from Samerberg)  
420 and UN7 (from Seefeld) averages  $0.70548 \pm 0.00006$  ( $1\sigma$ , n = 15), while peridotite UN10 from Seefeld  
421 shows more radiogenic values of  $0.70597 \pm 0.00009$  (n = 4), and the most radiogenic value is found in  
422 peridotite UN14 from Malga Masa Murada with  $0.70705 \pm 0.00006$  (n = 6). The FSA peridotites UN8 and  
423 UN16, from Seefeld and Malga Masa Murada respectively, exhibit  $^{87}\text{Sr}/^{86}\text{Sr}$  of  $0.70679 \pm 0.00008$  (n = 5)  
424 and  $0.70779 \pm 0.00011$  (n = 6), respectively. For comparison, the primitive and depleted mantle have  
425 estimated  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.7045 and 0.7026, respectively (Workman and Hart, 2005). Whereas the low  $^{87}\text{Rb}/^{86}\text{Sr}$   
426 ratio of the clinopyroxenes (average 0.02) imply that initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (at 330 Ma; Tumiati et al. 2003)  
427 are not much different from the measured ones, this is not the case for amphiboles with an average  $^{87}\text{Rb}/^{86}\text{Sr}$

428 ratio of 0.14 (Table S6). For the purpose of the following discussion, the initial values will be used for both  
429 clinopyroxene and amphibole.

430

## 431 **6. Discussion**

### 432 **6.1 Fractionation of sulfur isotopes during high-temperature processes and late-stage re-equilibration**

433 Few studies have systematically examined the combined geochemical and isotopic signature of sulfides from  
434 orogenic mantle domains as a probe to investigate the nature of high-pressure and exhumation processes in  
435 collisional settings. The full set of metasomatic and re-equilibration processes affecting the UZ peridotites  
436 throughout their evolution dictates their sulfide mineralogy as well as their chemical and sulfur isotope  
437 compositions. As these processes may produce sulfur isotopic fractionations, the effects of high-temperature  
438 processes and low-temperature re-equilibration of the sulfide assemblage on  $\delta^{34}\text{S}$  have to be considered  
439 before attempting any interpretation on the relationships between sulfur isotope signatures and source/s.  
440 Pentlandite is not stable at the mantle conditions experienced by UZ peridotites during their multi-stage  
441 evolution (Fig. 2a-b). It either formed together with minor amounts of pyrrhotite, now in part replaced by  
442 magnetite, from a high-temperature monosulfide precursor (Fig. S2), or precipitated directly from a  
443 metasomatic metal-rich fluid (Lorand and Grégoire, 2006; Lorand et al., 2013; Giuliani et al., 2016). Prior  
444 modeling has demonstrated that the S isotopic fractionation between pentlandite and a precursor monosulfide  
445 solid solution (mss) is limited to 0.7 ‰ for equal proportions of pentlandite and mss and low temperature of  
446 pentlandite formation (300°C; Giuliani et al., 2016). Given the dominance of pentlandite in the low-  
447 temperature assemblages in UZ peridotites, it is argued that the  $\delta^{34}\text{S}$  signature of pentlandite largely reflects  
448 that of its high-temperature precursor. Furthermore, since the pH of fluids does not induce significant isotope  
449 fractionation at the metamorphic conditions of subduction zones (Giacometti et al., 2014), the measured  $\delta^{34}\text{S}$   
450 of pentlandite is considered broadly representative of the bulk rock that interacted with various S-bearing  
451 metasomatic fluids or melts.. The sulfur isotope composition is not modified by high-pressure prograde  
452 metamorphism of subducted rocks (Evans et al., 2014; Li et al. 2021), and the S isotopic fractionation  
453 between solid sulfide and sulfide melt or H<sub>2</sub>S in reduced fluids is negligible (Ohmoto and Rye, 1979; Li and  
454 Liu, 2006; Marini et al., 2011). Instead, significant fractionation occurs between oxidized and reduced S  
455 species (up to 4-5‰) even at mantle temperatures (i.e. T > 900°C; Ohmoto and Rye, 1979). During the

456 Variscan subduction and consequent exhumation, the precursor sulfide to pentlandite may have interacted  
457 with, or precipitated from, fluids or melts containing oxidized or reduced S species.

458 Sulfate is recycled with sediments and altered oceanic crust (Alt and Shanks, 2006; Schwarzenbach et al.,  
459 2018b), and it usually preserves a positive S isotope signature close to the seawater composition (Alt et al.,  
460 1995; Alt and Shanks, 2001, Li et al., 2021). The timing and mechanisms of sulfate-to-sulfide reduction  
461 remain poorly constrained, since so far no sulfate grains have been found in equilibrium with mineral  
462 assemblages of HP-UHP subducted metamorphic rocks (Li et al. 2021 and references therein). Of note, Li et  
463 al. (2021) measure heavy  $\delta^{34}\text{S}$  signature (+25‰) for pyrite in veins from subducted HP metamorphic rocks  
464 from the Southwestern Tianshan HP-UHP metamorphic belt (northwestern China), which exceptionally  
465 documents that the seawater sulfate-derived  $\delta^{34}\text{S}$  signature may be retained at great depths (i.e. 70 km depth).  
466 The authors suggest that reduction of sulfate to sulfide may have occurred during pre-subduction  
467 hydrothermal alteration or contemporaneous with subduction at fore-arc depths, implying that no isotope  
468 fractionation occurred (Li et al., 2021). On the other hand, a fractionation value of ~20‰ between dissolved  
469 sulfate and pyrite precipitation was modeled for fluid migration throughout the slab-mantle interface at  
470 300°C, reaching up to 120‰ depending on distance from the source, pathway and amount of pyrite  
471 precipitation (Walters et al., 2019).

472 In the UZ peridotites, the high oxygen fugacity of FMQ to FMQ+2 estimated by Malaspina et al. (2009) at  
473 3GPa approach conditions where significant proportions of oxidized S would be present (Jugo et al., 2010).  
474 However, the oxygen fugacity conditions recorded by the UZ peridotites investigated in this study (<FMQ at  
475 2 GPa; Gudelius et al. 2019) are far too reducing to allow the presence of significant amounts of sulfate.  
476 Moreover, despite the restricted range of S isotope values in the UZ peridotite, we observe a clear distinction  
477 among the lithotypes and textural occurrences. We therefore propose that multiple melt-and-fluid/rock  
478 interactions occurred along and after the Variscan Orogeny, and we discuss the nature of the fluid sources in  
479 Section 6.4.2. Although Rielli et al. (2018) obtained a much larger range of  $\delta^{34}\text{S}$  (-10.0 to +5.4‰), it is worth  
480 noting that their sample suite is composed of pyroxenite and websterite lenses in garnetite and amphibole  
481 layers in pyroxenite within the main peridotite bodies from the Western Gneiss Region (Norway), whereas  
482 no sulfide grain was found within the matrix of the only peridotite sample in their study. Consequently, there

483 are no sulfur isotope compositions of garnet peridotite available in the literature to make a strong comparison  
484 with the data presented in our study.

485

## 486 **6.2 Near-quantitative sulfide extraction during SCLM stabilization and addition during refertilization**

487 The sulfur isotope composition of sub-continental lithospheric mantle (SCLM), which stabilizes by  
488 extraction of variable degrees of partial melt (e.g., [Griffin et al., 2004](#)), remains poorly constrained and has  
489 been mostly addressed in studies of sulfide inclusions in diamonds from mantle xenoliths, giving a  $\delta^{34}\text{S}$   
490 range between -4‰ and + 6‰ ([Chaussidon et al., 1987](#); [Farquhar, 2002](#); [Thomassot et al., 2009](#)). In the  
491 Ulten Zone, during high-temperature pre-peak conditions (Stage 1), the coarse-grained protogranular  
492 peridotites containing the assemblage olivine + enstatite + diopside + Cr-Al spinel reside in the continental  
493 lithospheric mantle and equilibrate at 1200°C and 1.3-1.6 GPa ([Nimis and Morten, 2000](#)). Their study may  
494 therefore provide insights into mantle wedge evolution before its entrainment into the Variscan subduction  
495 architecture. Samples in this study appear to fall along a curved array with respect to bulk-rock  $\text{TiO}_2$  and  
496  $\text{Al}_2\text{O}_3$ , both of which are moderately incompatible (Fig.4). Such arrays result from partial melt extraction.  
497 In accord with [Ionov et al. \(2017\)](#) and [Gudelius et al. \(2019\)](#), major element compositions indicate mostly  
498 ~15-25% of melt extraction (Fig. 4a), although this is a minimum estimate if refertilization occurred  
499 ([Gudelius et al., 2019](#)). At such melt fractions, sulfide would have been exhausted, depending on oxygen  
500 fugacity and S concentration ([Keays, 1995](#); [Mungall et al., 2006](#)). For example, for  $\text{Al}_2\text{O}_3$  contents of 2-2.3  
501 wt.% recorded in some UZ peridotites (Fig. 4a), less than 100 ppm S would be expected to remain in the  
502 mantle for fractional melt extraction at 3 GPa and an oxygen fugacity of FMQ-2 ([Aulbach et al., 2016](#)). If  
503 melt extraction occurred at lower pressure, then S concentrations in the residue would be even lower, given  
504 increasing S solubility in silicate melt at sulfide saturation with decreasing pressure ([Mavrogenes and](#)  
505 [O'Neill, 1999](#)). In this light, the UZ peridotites containing >100 ppm S ([Table S2, Electronic Annex D](#))  
506 almost certainly experienced S addition. Furthermore, sulfidation of peridotite has been shown to cause Fe-  
507 Ni zoning in olivine ([Papike et al., 1995](#); [Bataleva et al., 2016](#)). Although such zoning is not observed in the  
508 UZ olivine ([Gudelius et al., 2019](#); [Consuma et al., 2020](#)), higher NiO contents in olivine are observed in S-  
509 poor peridotites relative to olivine from S-rich peridotites, consistent with Ni extraction from olivine during  
510 metasomatic sulfide addition (Fig. 4c).

511 Hereafter, for each metamorphic stage, we discuss (i) the process and related metasomatic agents that may  
512 have modified the sulfide component throughout the evolution of peridotites; (ii) the relevant conditions (P-  
513 T-fO<sub>2</sub>-fS<sub>2</sub>) that may have exerted a major control on the nature of sulfides and their mobility with respect to  
514 the melt/fluid phase; (iii) the textural relationship of sulfides with the coexisting carbonates and hydrous  
515 minerals. We conclude with the potential implications that our findings may have for the understanding of  
516 the global sulfur cycle.

517

### 518 **6.3 Pre-collision mantle metasomatism (Stage 1)**

519 Stage 1 is represented by rare coarse spinel peridotites containing pyroxenite layers (Nimis and Morten,  
520 2000), with only one sample available for this study (MOL1-C). During this stage, percolation of a hydrous  
521 basic melt induces an enrichment of the lithospheric mantle in LREE, LILE and Li at spinel-facies  
522 conditions (Nimis and Morten, 2000; Scambelluri et al., 2006). Precipitation of this melt prompts the  
523 formation of sulfide-bearing pyroxenite layers within the peridotite. The  $\delta^{34}\text{S}$  signature ( $+2.77 \pm 0.37\%$ ;  
524  $n=2$ ) of matrix pentlandite in pyroxenites is heavier than that estimated for continental lithospheric mantle  
525 ( $+1.35 \pm 0.25 \%$ ; Fiorentini et al., 2018), and similar to the  $\delta^{34}\text{S}$  signature (up to  $+5.4\%$ ) of sulfides  
526 contained in pyroxenite lenses within peridotite bodies from the Western Gneiss Region (Rielli et al., 2017).  
527 Similarly, pentlandite associated with dolomite in the surrounding peridotite matrix is also isotopically heavy  
528 ( $+3.11 \pm 0.38\%$ ;  $n = 6$ ) (Table 4).

529 Euhedral inclusions of dolomite in primary spinel within porphyroclastic garnet from coarse-grained UZ  
530 peridotite, may represent relics that testify to the percolation of carbon-bearing liquids prior to Stage 2 garnet  
531 growth (Förster et al., 2017). The aforementioned petrographic and isotopic evidence indicate the presence  
532 of (possibly subduction-related) isotopically heavy S in the source of the melts involved in Stage 1  
533 metasomatism. Temperature and oxygen fugacity are the main factors that dictate the solubility and  
534 speciation of sulfur in silicate melts (Clemente et al. 2004; Jugo et al. 2010; Jégo and Dasgupta, 2014; Canil  
535 and Fellows, 2017). Experimental data on the sulfide vs. sulfate stability in basaltic and sediment glasses  
536 (Jugo et al., 2010; Canil and Fellows, 2017) suggest that the melt is saturated in sulfide (S<sup>2-</sup>) rather than in  
537 sulfate (S<sup>6+</sup>) at oxygen fugacity lower than around the Fayalite-Magnetite-Quartz (FMQ) buffer. In this light,  
538 the relatively reducing nature (<FMQ; Gudelius et al., 2019) of the investigated samples is suggested to also

539 indicate a system dominated by reduced S species. Additionally, the overall lack of identifiable reduced  
540 carbon species (i.e. graphite or disordered carbonaceous material; e.g., Vitale Brovarone et al., 2020) in the  
541 UZ peridotites requires carbon to be present mostly as carbonate (CO<sub>2</sub>). We speculate that any S added from  
542 melt leaving a lithospheric mantle source would have involved an H<sub>2</sub>S-CO<sub>2</sub>-bearing agent, consistent with  
543 suggestions that mantle fluids are H<sub>2</sub>S-dominated (Eggler and Lorand, 1993).

## 544

### 545 **6.4 High-pressure (garnet) metamorphism and recrystallization (Stage 2)**

#### 546 *6.4.1 Coarse-grained vs Fine-grained peridotite*

547 With the onset of the Variscan Orogeny, the corner flow initiated by continental subduction dragged the UZ  
548 peridotites deeper into the lithospheric mantle towards the slab-wedge interface, causing their textural  
549 transition from coarse protogranular to porphyroclastic and finally fine equigranular. The peak conditions  
550 were attained at ~850°C and 2.2-2.7 GPa (Nimis and Morten, 2000; Braga and Sapienza, 2007). At this  
551 stage, the UZ peridotites still resided in the mantle wedge (Scambelluri et al., 2006), where matrix  
552 pentlandite coexisted along with high-pressure matrix phases, such as recrystallized olivine and pyroxenes,  
553 pargasitic to hornblenditic amphibole, garnet, and dolomite. Thus, the S isotopic composition of pentlandite  
554 may reflect peak-garnet conditions with superposed local interaction with retrograde fluids. The Mann-  
555 Whitney U Test allows to distinguish two populations of matrix sulfides with respect to δ<sup>34</sup>S: one from fine-  
556 grained peridotite (δ<sup>34</sup>S = -0.11‰ ± 0.39; 1σ, n=15) and one from the coarse counterpart (δ<sup>34</sup>S = +2.35‰ ±  
557 0.43‰; 1σ, n=18). Thus, despite the limited range of measured sulfur isotope ratios for the entire data set (-  
558 1.62 to +3.76 ‰), differences in the source of sulfur for texturally diverse sulfides are detected. Moreover,  
559 some coupling between the δ<sup>34</sup>S signature of pentlandite and trace elements becomes evident when not only  
560 the textural positions (Fig. 9), but also the different sampling localities are considered. This suggests some  
561 provinciality with respect the nature of metasomatism (see Fig. S3 in Electronic Annex A), as previously  
562 recognized based on lithophile elements (Gudelius et al., 2019).

563

564 *Coarse-grained garnet peridotite.* The positive δ<sup>34</sup>S values obtained for a population of matrix pentlandite in  
565 the coarse-grained garnet peridotites are distinct from the proposed depleted mantle range of δ<sup>34</sup>S of -1.28 ±  
566 0.33‰ (Labidi et al. 2013), from the suggested mantle wedge composition of 0‰ (Li et al. 2020), and from

567 the proposed composition of continental lithospheric mantle ( $+1.35 \pm 0.25 \text{ ‰}$ ; Fiorentini et al., 2018).  
568 Combined with elevated S abundances ( $\geq 166 \text{ ppm}$ ; Table 1), the measured isotope values require addition of  
569 isotopically heavy S, either from an enriched mantle source as recognized by Ionov et al. (1992) or involving  
570 processes inducing heavy S isotope enrichment, such as fractionation of isotopically light sulfide (Walters et  
571 al., 2019). The initial Sr isotopic composition of clinopyroxene in two coarse-grained peridotites  
572 ( $^{87}\text{Sr}/^{86}\text{Sr}=0.70509\text{-}0.70538$ ; Table 1) is more radiogenic than that of the primitive or depleted mantle  
573 ( $0.7045$  and  $0.7026$ , respectively; Workman and Hart, 2005), and also indicates that the enrichment in  
574 radiogenic Sr pre-dates the entrapment of peridotites into the tectonic mélange. Indeed, coarse-grained UZ  
575 peridotites show evidence for interaction with crust-derived silicic melts (Gudelius et al., 2019).  
576 Figure 9 shows that the isotopically heavy  $\delta^{34}\text{S}$  signature of pentlandite in coarse peridotites is coupled with  
577 with elevated Pb concentrations, but not with similarly elevated abundances of other fluid-mobile elements,  
578 such as As and Sb, which may again point to a continental crustal contaminant carried by a melt rather than a  
579 fluid. Indeed, for sulfide- rather than sulfate-saturated sediment-derived melts, Sb will be depleted in the  
580 melt relative to As and Pb (Canil and Fellows, 2017), which corresponds to the systematics observed for  
581 sulfide in the coarse-grained peridotite (Fig. 9).  
582  
583 *Fine-grained garnet-amphibole peridotite.* Following the interpretation of Obata and Morten (1987), the  
584 fine-grained lithotypes record re-crystallization of the coarse-grained peridotites during downward  
585 movement into the deeper portion of the supra-subduction mantle. Compared to coarse-grained peridotites,  
586 the average sulfur isotope composition of matrix pentlandite from fine-grained peridotites is distinctly lower  
587 ( $\delta^{34}\text{S} = -0.11\text{ ‰} \pm 0.39$ ;  $1\sigma$ ,  $n=15$ ), with few grains within the DM value of  $\delta^{34}\text{S} = -1.28 \pm 0.33\text{ ‰}$  (Labidi et  
588 al. 2013), as shown in Figure 7. Although the relationship between coarse- and fine-grained peridotites  
589 remains unclear, the latter clearly document interaction with crust-derived hydrous fluids based on elevated  
590 contents of fluid-mobile lithophile elements (Gudelius et al., 2019). This may be borne out by sulfide  
591 compositions, where contents of the fluid-mobile elements As and Sb, which are highly soluble in aqueous  
592 fluids (Jochum and Verma, 1996), are slightly more elevated in fine-grained than in coarse-grained  
593 peridotites (Fig. 9). In addition, Se and Te abundances are markedly higher in fine-grained peridotites, and,  
594 as strongly chalcophile elements (e.g., Barnes, 2016), might be expected to follow the sulfide anion. Thus,

595 formation from reduced and slightly isotopically heavy (with respect to DM) reduced S species is inferred  
596 during this stage. At > 30km reduced S species carrying As(-1), Sb and Te may be sourced from the  
597 subducted slab and dissolved in hot aqueous fluids (Hattori and Guillot, 2007), where they dominate over  
598 oxidized species and are efficiently mobilized (Li et al., 2020).

599 Initial  $^{87}\text{Sr}/^{86}\text{Sr}$  of matrix amphibole from high-pressure fine-grained peridotites is elevated, ranging from  
600  $0.705334 \pm 0.00006$  to  $0.70691 \pm 0.00006$ , again pointing to the addition of an isotopically evolved crustal  
601 component, either from the surrounding gneisses or from seawater-altered slab components (considering that  
602 the  $^{87}\text{Sr}/^{86}\text{Sr}$  of seawater at 330Ma was equal to 0.7078; Peterman et al., 1970). Variable equilibration of the  
603 resultant fluids with unradiogenic mantle material prior to metasomatizing the UZ peridotites can explain the  
604 variable  $^{87}\text{Sr}/^{86}\text{Sr}$  signature. This was previously invoked to explain relatively unradiogenic *in situ*  $^{87}\text{Sr}/^{86}\text{Sr}$   
605 values of  $\sim 0.705$  of matrix dolomite formed under eclogite-facies conditions (Consuma et al. 2020). The  
606 heterogeneous nature of Stage 2 metasomatism is also reflected in the S concentration of fine-grained  
607 peridotites, which encompasses the entire range of 40 to 288 ppm in this study. This suggests local variations  
608 in terms of S concentration and/or degrees of S saturation levels due to multiple fluid infiltration, causing  
609 only minor sulfide addition in some (e.g., peridotite UN-3 with a sulfide mode of 0.02 wt%) and abundant  
610 sulfide addition in other samples (e.g., peridotite UN-14 with sulfide mode of 0.09 wt%). Interestingly, the  
611 aforementioned peridotites were sampled from Samerberg and Malga Masa Murada, which also respectively  
612 show lower and higher levels of lithophile fluid-mobile element enrichment, suggestive of more and less  
613 distal positions relative to the source of the metasomatic fluids (Gudelius et al., 2019).

614

#### 615 6.4.2. Stage 2: The sources of Ulten Zone metasomatic agents

616 The early stages of the Ulten Zone continental subduction were characterized by a continental crust possibly  
617 still attached to a mature oceanic slab (Ranalli et al. 2005). In this light, possible sources capable to furnish  
618 sulfur to the mantle wedge are subducted altered oceanic crust, overlying metasediments, metaserpentinites  
619 and enclosing gneisses. The low  $f\text{O}_2$  recorded in the investigated UZ peridotites (Fig.2c) does not preclude  
620 that isotopically heavy sulfide with  $\delta^{34}\text{S}$  up to +3.76 ‰ formed by reduction of oxidized S species under  
621 appropriate conditions. Oxidized S could derive from seawater-altered oceanic lithosphere, which records a  
622 large range of  $\delta^{34}\text{S}$  values (-50 to +20 ‰) in seafloor hydrothermal sedimentary pyrite, but with a

623 predominantly negative isotopic signature (Canfield & Farquhar, 2009). In contrast, sulfates in serpentinite  
624 and metabasic rocks from Syros, as analogs of subducted lithosphere, record dominantly heavier  $\delta^{34}\text{S}$  of  
625 +15.7 to +20.8‰ and +3.5 to +20.1‰, respectively (Schwarzenbach et al., 2018a). In exhumed high-  
626 pressure rocks, metasomatic sulfides with a much larger range of  $\delta^{34}\text{S}$  (-21.7 to +13.9‰) than in UZ  
627 peridotites were ascribed to the combined effects of isotope fractionations due to sulfate reduction and fluid  
628 evolution due to precipitation of isotopically light sulfide (Walters et al., 2019). Li et al. (2021) collate a  
629 comprehensive dataset of sulfides from worldwide HP-UHP metamorphic terranes. Combined with new  
630 data, they find a  $\delta^{34}\text{S}$  signature of -33 to -6‰ in metasediments,  $\delta^{34}\text{S}$  of -4 to +4‰ in  
631 metabasite/metagabbros, and  $\delta^{34}\text{S}$  of +2 to +18‰ in HP serpentinites.

632 Given the mélangé setting of Ulten Zone peridotites, the continental crust may also be a source of  
633 isotopically heavy S, either by direct formation from  $\text{H}_2\text{S}$  if the lighter value applies, or by sulfate reduction  
634 if the heavier value applies.

635 The availability of both S and Sr isotopic data in this study allow some constraints to be placed on the  
636 sources and amount of contaminant involved in the formation of sulfides and associated clinopyroxene or  
637 amphibole (Fig.10). The S isotopic composition of the garnet-kyanite gneisses of continental crust enclosing  
638 the UZ peridotites is unknown, but metapelites metamorphosed under amphibolite-facies conditions from the  
639 Kinzigite Formation of the Ivrea Zone ( $\delta^{34}\text{S}$  values of +3.6‰ to +10.1‰; Fiorentini et al., 2018) may  
640 represent reasonable analogues that can be used to model mixing with the depleted mantle. This is because  
641 these metapelites are of a similar age and composition as the UZ gneisses, and, moreover, have S  
642 concentrations ( $600 \pm 10$  ppm,  $n=12$ ; Bargossi et al., 2003) similar to those employed in the mixing model.

643 Figure 10 shows the binary mixing between a depleted mantle (DM) reservoir with plausible slab-derived  
644 sources in a closed system (full dataset in Electronic Annex C). The sample scatter reflects the variability of  
645 the S and Sr concentrations and isotopic composition of melts/fluids and their evolution between leaving the  
646 source and their interaction with the Ulten Zone peridotites. Results show that  $\ll 10\%$  of a continental crust  
647 component with  $\delta^{34}\text{S}$  values +10.1‰ and 600ppm of S are required to explain the S-Sr isotopic composition  
648 of UZ fine-grained peridotite during Stage 2. Concentrations of several 100 ppm S may be expected for a  
649 crustal melt, and of several 1000 ppm S for a fluid equilibrated with crustal rock (Electronic Annex C).

650 Conversely, in accordance with trace element composition and with the lack of carbonates, the outlier CGn

651 peridotite SBA2 points to a liquid carrying isotopically heavy S, which percolated the mantle wedge in the  
652 Samerberg Area, and which can be explained by invoking a third S source derived from isotopically heavy,  
653 but less radiogenic serpentinite (Fig. 10). In this scenario, formation of isotopically heavy sulfide by  
654 reduction of sulfate, accompanied by isotopic fractionation of several ‰ at the estimated conditions of  
655 850°C (cf., Ohmoto and Rye, 1979) is not required, nor is it precluded by the data.

656

### 657 **6.5 Exhumation of crust-mantle mélange and retrogression (Stage 3)**

658 Shortly after the attainment of peak-P conditions, UZ peridotites became part of a crust-mantle mélange  
659 (Scambelluri et al., 2006), where they were exposed to infiltration of channelized C-O-H fluids and late  
660 serpentinization along a fast exhumation path in the late Carboniferous (Ranalli et al. 2005; Consuma et al.  
661 2020), with conditions of 650-700 °C and P ranging between 2.2 and 1 GPa (Fig. 2a,b). Two types of  
662 sulfides represent this stage and are interpreted as retrograde: (1) sulfide grains in retrograde kelyphitic  
663 coronas around garnet, and (2) those included and associated with a dolomite + tremolite + chlorite vein.  
664 Late pyrite in retrograde coronas reported in few studies has been interpreted as a result of late influx of S-  
665 rich fluids which were produced deeper in the slab (c.f., Evans et al., 2014; Giacometti et al., 2014), possibly  
666 involving redox reactions (Walters et al., 2019). Similarly, the presence of pentlandite in garnet coronas of  
667 UZ peridotites suggests that partial kelyphitization was catalyzed by ingress of a S-bearing fluid. Corona-  
668 associated pentlandite averages  $\delta^{34}\text{S}$  of  $-0.38\text{‰}$  ( $1\sigma$ ,  $n=3$ ), with negligible intra-grain variability. This grain  
669 is also cut by a late chlorite flake, whose cleavage is filled with magnetite, suggesting its formation above the  
670 chlorite-out reaction (i.e. at  $\sim 750\text{-}800^\circ\text{C}$  and P of 1.7 GPa), that is, somewhat warmer than the conditions  
671 inferred earlier (650-700°C; Consuma et al. 2020). No carbonates occur in these retrograde coronas. Low Pb,  
672 As and Sb contents (Fig. 9) suggest kelyphitization at low fluid-rock ratios, consistent with incomplete  
673 garnet breakdown.

674 On the basis of mineral assemblages and textural relationships, it is suggested that the pentlandite-hosting  
675 dolomite vein formed prior to serpentinization at  $T = 650^\circ\text{C}\text{-}700^\circ\text{C}$  and  $P = 1\text{GPa}$  (Consuma et al. 2020).  
676 Along this vein, enclosed pentlandite associated with millerite exhibits  $\delta^{34}\text{S} = +1.13 \pm 0.38\text{‰}$ , which is  
677 somewhat heavier than the values of pentlandite in kelyphite and interstitial to silicates. Furthermore, a  
678 distinct fluid source is otherwise required to explain the lower  $\delta^{34}\text{S}$  of  $0.68 \pm 0.40\text{‰}$  ( $n=3$ ) for matrix

679 pentlandite spatially close to the dolomite vein, found in peridotite sample 18LP1. The heterogeneity of the  
680 measured *in situ* Sr isotopes of this dolomite vein ( $^{87}\text{Sr}/^{86}\text{Sr}=0.7035\text{-}0.7085$ ) was interpreted to reflect  
681 retrograde hybridized C-fluids channelized into the peridotites during exhumation, when the crust-peridotite  
682 mélange was already formed (Consuma et al. 2020). Coupled S and Sr isotopic ratios related to dolomite  
683 veining during early exhumation (in coarse peridotite 18LP1) and even more so in serpentinite + magnesite  
684 vein MOL1 -C suggest higher degrees of contamination from a continental crustal source (Fig.10). High Se  
685 and Te contents, together with intermediate to high Sb and As concentrations, suggest that this was a  
686 hydrous fluid carrying  $\text{HS}^-$  as the dominant S species.

687

## 688 **6.6 Serpentinization and local effect of fluid-rock interactions on S content and isotope composition**

### 689 **(Stage 4)**

690 The latest stage recording metasomatic modification of UZ peridotites is the serpentinization that occurred  
691 over a span of temperatures (<600°C to 300°C) along a slow and cooling exhumation path during the  
692 Permian-Triassic (300-205Ma; Ranalli et al. 2005; Consuma et al. 2020).

693 The high-T phase of Stage 4 is characterized by veining of serpentine + magnesite + tremolite crosscutting  
694 the coarse spinel peridotite MOL1-C, an assemblage which indicates a temperature of formation of < 600°C  
695 on the retrograde path (Consuma et al. 2020). Pentlandite grains enclosed in this vein locally show textural  
696 alteration features, including (i) magnetite pseudomorphs after pentlandite and (ii) association with  
697 heazlewoodite grains. The pentlandite ± heazlewoodite ± magnetite assemblages documented here and  
698 previously studied in kimberlite-borne mantle xenoliths from the Kaapvaal craton (Giuliani et al. 2016;  
699 Lorand and Grégoire, 2006), could originate from partial desulfidation of the low-T sulfide assemblage  
700 during serpentinization, which is a common feature of mantle peridotites (e.g. Lorand, 1989).

701 Desulfurization of pentlandite to awaruite (not observed in the UZ peridotite) and/or heazlewoodite  
702 represents the lowest S fugacity for a sulfide assemblage (see Fig. 8 in Lorand and Grégoire, 2006).

703 Furthermore, the relatively wide S isotopic range of these pentlandite grains ( $\delta^{34}\text{S} = -0.29$  to  $+3.76\text{‰}$ ) attests  
704 to the strongly heterogeneous effect of serpentinization on the S isotope signature, and reflects minimal  
705 isotopic homogenization at the vein scale. Importantly, this vein is texturally cut by late dolomite vein with  
706 highly radiogenic Sr ( $^{87}\text{Sr}/^{86}\text{Sr} > 0.7118$ ; Table 1).

707 The low-T phase of Stage 4 is characterized by dolomite dissolution via serpentinization and formation of  
708 pseudomorphs of calcite + brucite intergrowths, found in several fine-grained garnet-amphibole peridotite  
709 (Förster et al., 2017; Consuma et al. 2020; Gudelius et al., 2019; this study), and by the composite serpentine  
710 vein MM1B hosting magnetite + millerite with minor calcite and dolomite.

711 Several PI included in coarse spinel are intimately associated with calcite + brucite intergrowths and  
712 decrepitation features (i.e. radiating fractures; Fig. 3), and therefore represent Stage 4 processes.

713 Nevertheless, the  $\delta^{34}\text{S}$  ( $+0.46 \pm 0.34\text{‰}$ ) of pentlandite in PI is only moderately heavier than the suggested  
714 depleted mantle with  $\delta^{34}\text{S}$  of  $-1.28 \pm 0.33\text{‰}$  (Labidi et al., 2013). The PI assemblages (see Section 3; Fig. 3b)  
715 may point to the involvement late, C-S-bearing saline, possibly seawater-derived agents, as previously  
716 suggested (Lo Pò et al., 2020). Indeed, saline, oxidizing, sulphate-bearing brines have been implicated in  
717 sulfide dissolution in subduction mélanges (Schwarzenbach et al., 2018a), corresponding to the tectonic  
718 setting where UZ peridotites were serpentinized. Experimental studies performed by Bataleva et al. (2018)  
719 reveal that interaction of olivine with sulfate and C-bearing brines may induce mantle sulfide and carbonate  
720 formation via the reaction  $\text{olivine} + \text{anhydrite} + \text{C} \rightarrow \text{diopside} + \text{S}_0 + \text{CO}_2$ , followed by olivine sulfidation. If  
721 so, the relatively low  $\delta^{34}\text{S}$  of PI sulfide requires a low-T origin when the isotopic fractionation would be  
722 largest. For examples, Walters et al. (2019) model fractionations of some 20‰ for pyrite precipitation from  
723 sulfate at 300 °C. Pentlandite in the PI has also moderate to high contents of the fluid-mobile elements Sb  
724 and As, but low Se and Te compared to other samples (Fig. 6). This may indicate limited addition of Se and  
725 Te by saline media where concentrations may be low due to limited availability of the  $\text{HS}^-$  ligand, with  
726 which chalcophile elements could complex.

727 Last, in contrast to textural evidences for desulfurization and dedolomitization, high bulk S contents (> 300  
728 ppm) and high As and Sb concentrations in sulfides from the serpentine vein (Fig. 9) indicates channelized  
729 S-enriched fluid infiltration during Stage 4 (in the form of millerite grains) near the area of Malga Masa  
730 Murada.

731 To conclude, together with the possible involvement of oxidizing  $\text{H}_2\text{S}$ -poor saline fluids in the formation of  
732 PI, serpentinization appears to be associated with highly localized processes. These may involve sulfide  
733 dissolution in S-undersaturated oxidizing saline fluids, perhaps sourced from metasediments  
734 (Schwarzenbach et al., 2018a), sulfide precipitation when such fluids reach S saturation, and removal of

735 isotopically light S in reducing hydrous fluids, such as those associated with dehydration of oceanic mantle  
736 (Piccoli et al., 2019).

737

## 738 **7. Conclusions and implications for coupled sulfur-carbon cycling during continent collision**

739 We provide a new perspective of sulfur and carbon mobility in continental subduction zones from the view  
740 point of the previously poorly studied mantle wedge. A first-order observation is the intimate association  
741 between carbonates and sulfides, which occur in different textural positions related to the multi-metamorphic  
742 evolution of the Ulten Zone orogenic peridotite, as summarized in the conceptual sketch of Figure 11. Using  
743 detailed petrography with bulk-rock as well as high-resolution chemical and isotopic analyses of sulfides and  
744 associated metasomatic minerals (amphibole, clinopyroxene, carbonates), we demonstrate that the high-  
745 pressure orogenic mantle domain from the Variscan Ulten Zone repeatedly interacted with multiple  
746 metasomatic agents variably enriched in sulfur and carbon.

747 (1) The Variscan lithospheric mantle was initially depleted and sulfide-poor, and subsequently  
748 inherited a sulfur component during an early stage, when hot, H<sub>2</sub>S-bearing melts leaving a subduction-  
749 modified source invaded the overlying spinel-facies peridotite in the mantle wedge, leading to precipitation  
750 of sulfide-bearing pyroxenite with  $\delta^{34}\text{S}_{\text{peridotite}}$  of +2.77 ‰. A reported dolomite inclusion in coarse spinel  
751 indicates carbonate mobility at this early stage.

752 (2) Under peak eclogite-facies conditions, heterogeneous melt and fluid sources variably enriched in  
753 carbon, isotopically heavy sulfur and radiogenic Sr were involved: (i) the positive shifts of  $\delta^{34}\text{S}$  (up to  
754 +3.43‰) from typical mantle values, and radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}_{\text{clinopyroxene}} > 0.7053$  suggest that, at high-  
755 pressure conditions, coarse-grained garnet peridotites interacted with <sup>34</sup>S- and Pb-enriched crustal melts prior  
756 to their becoming part of a crust-mantle mélange. Matrix carbonate is usually rare in the coarse peridotite.

757 (ii) The hydrous fluids interacting with mantle rocks during recrystallization and deformation from coarse- to  
758 fine-grained peridotites added radiogenic Sr ( $^{87}\text{Sr}/^{86}\text{Sr}_{\text{amphibole}} \sim 0.7061$ , this study) and had a heterogeneous  
759 effect on the bulk S content (58 to 288 ppm S), as S was variably added or removed. The presence of  
760 dolomite with  $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.705$  (Consuma et al., 2020) suggests that carbon was also mobilized at this stage.  
761 Given Sr isotopic evidence for a crustal fluid source, the low  $\delta^{34}\text{S}$  (-1.62 to +0.67‰) compared to the coarse  
762 peridotites is suggested to reflect involvement of a sulfide- rather than sulfate-bearing fluid. The observed S-

763 Sr isotopic relationship in the fine-grained peridotite can be satisfied if a depleted mantle source is  
764 contaminated by <<10% of radiogenic and isotopically heavy fluids sourced from the neighboring garnet-  
765 kyanite paragneisses, with minor contribution of less radiogenic metaserpentinite-derived fluid.

766 (3) Shortly after peak conditions the crust-mantle mélange interacted with hybridized fluids, leading  
767 to formation of a dolomite veinlet with heterogeneous Sr isotope values ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7036$  to  $0.7083$ ;  
768 [Consuma et al., 2020](#)), which is intimately associated with (mostly) Co-pentlandite and pentlandite with  $\delta^{34}\text{S}$   
769 close to 0‰.

770 (4) Exhumation-related serpentinization in the crust-mantle mélange had a markedly heterogeneous  
771 effect on sulfur isotopes. Pentlandite grains enclosed in a serpentine + magnesite vein crosscutting the  
772 coarse-grained peridotite matrix, and texturally cut by a late dolomite vein with  $^{87}\text{Sr}/^{86}\text{Sr}$  0.711 ([Consuma et](#)  
773 [al. 2020](#)), show a broad range of  $\delta^{34}\text{S}$  between -0.29 and +3.76‰. Furthermore, the presence of magnetite as  
774 pseudomorphs after pentlandite indicates local desulfurization with inferred preferential loss of  $^{32}\text{S}$ , whereas  
775 the S concentration of 300 ppm in a cm-sized vein of serpentine + magnetite  $\pm$  millerite  $\pm$  calcite crosscutting  
776 the fine spinel peridotite indicates sulfur pathways during late exhumation stages. The presence of  
777 pentlandite as part of polycrystalline inclusions in spinel associated with calcite + brucite intergrowths  
778 indicates that local desulfurization may have been coupled with dissolution of the associated dolomite and  
779 subsequent release of  $\text{CO}_2$ .

780 The recorded oxidation state of the studied peridotites likely precludes stabilization of sulfate, but is  
781 permissive of carbonate as opposed to graphite stability, as confirmed by petrographic observations. The  
782 close association of sulfides and carbonates at all stages of mantle wedge evolution indicates that peak  
783 metamorphic pervasive fluids and melts, and channelized fluids generated during late exhumation, may serve  
784 as pathways for coupled sulfur and carbon transport under the investigated conditions. This indicates that  
785 these volatiles should be considered together in a discussion of mantle wedge redox evolution. Despite  
786 evidence for long-lasting and polyphase metasomatic processes involving slab-derived C-O-H-S fluids and  
787 melts ([Fig.11](#)), the measured S isotope values of the UZ pentlandite display a narrow range ( $\delta^{34}\text{S} = -1.62 \pm$   
788  $0.42\%$  to  $+3.76 \pm 0.36\%$ ), which suggests that reduction of sulfate ( $\text{S}^{6+}$ ) to sulfide species ( $\text{S}^{2-}$ ) had a limited  
789 role throughout the Ulten Zone peridotite metamorphic evolution. Importantly, this study provides  
790 petrographic and geochemical evidence in support of a dominantly reduced nature of slab-derived sulfur-

791 bearing subduction liquids in the orogenic mantle wedge under high-pressure conditions and during  
792 subsequent exhumation within the tectonic mélangé, suggesting that S is not the dominant agent causing  
793 oxidation of the mantle wedge in this setting.

794

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810

## 811 **Electronic Annexes A, B, C, D.**

812

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## Figure captions

### Preference color: online only

**Figure 1** (a) Geological sketch map of the central and Eastern Alps modified after [Langone et al. \(2011\)](#). (b) Geological-structural map of the Ulten Zone modified after [Tumiati et al. \(2003\)](#) and [Consuma et al. \(2020\)](#). The reader is referred to [Consuma et al. \(2020\)](#) and ([Gudelius et al., 2019](#)) for the exact location of the samples.

**Figure 2.** (a-b) Pressure (P)-Temperature (T) diagram modified after [Consuma et al. \(2020\)](#) showing the pressure-temperature evolution of the Ulten Zone peridotites, with respect to various metasomatic stages and phase relations for COH-bearing species. The experimentally determined melting curves of sulfur, pyrrhotite, Mss and decomposition of pyrite are taken from [Brazhkin et al. \(1999\)](#), [Zhang et al. \(2015\)](#) and [Bataleva et al. \(2018\)](#). Dolomite-in, magnesite-in, dolomite-out, garnet-in curves from [Tumiati et al. \(2013\)](#); tremolite (Tr) + magnesite (Mgs) = enstatite (En) + dolomite (Dol) are from [Malaspina and Tumiati \(2012\)](#) for  $X_{\text{CO}_2}=0.5$ ; brucite (Brc) = periclase (Per) + water (H<sub>2</sub>O) from [Schramke et al. \(1982\)](#). Antigorite-out curve and chlorite-out curve from ([Fumagalli and Poli, 2005](#)). Antigorite (Atg) = chrysotile (Ctl) / lizardite (Liz) are from [Evans et al. \(1976\)](#); aragonite (Arg) = calcite (Cal) from [Johannes and Puhon \(1971\)](#). P-T conditions of Stage 2 are taken from [Nimis and Morten \(2000\)](#) and [Sapienza et al. \(2009\)](#). **Sulf**—sulfide, **Po**—pyrrhotite, **Py**—pyrite, **Mss**—monosulfide solid solution.

(c) Ranges and average values of oxygen fugacity relative to the fayalite–magnetite–quartz buffer (FMQ) for the Ulten Zone peridotites for various pressures (GPa), as well as CHO speciation, modified from Cannò and Malaspina (2018) and Gudelius et al. (2019). Note the offset to higher  $fO_2$  obtained by Malaspina et al. (2009), who, using the same method, obtained higher  $Fe^{3+}/\Sigma Fe$  in garnet from their samples. Fields denote  $fO_2$  where most S in basalt glass (Jugo et al., 2010) and in sediment glass (Canil and Fellows, 2017) is present as  $HS^-$  ( $\sim FMQ$  and maximum  $FMQ < +0.2$ , respectively) and as  $H_2SO_4^{2-}$  ( $\sim FMQ + 2$  and minimum  $FMQ > +0.2$ , respectively), with mixed species at intermediate  $fO_2$  in the basalt.

(d) Table showing the presence of rock-forming minerals, hydrous minerals, carbonates and sulfides as linked to distinct metamorphic stages (1-4) of the Ulten Zone peridotites. Grain size is qualitatively indicated for spinel, orthopyroxene, clinopyroxene and garnet. *In situ* Sr isotope compositions are reported for clinopyroxene, amphibole (this study) and for dolomite, calcite (Consuma et al., 2020). S isotope compositions of pentlandite measured by SIMS (this study) are also shown. **HT**—high temperature, **HP**—high pressure, **grt**—garnet.

**Figure 3.** Photomicrographs, back-scattered electron images, and color maps illustrating the textural settings of sulfides in Ulten Zone peridotites. (a) Scan image of thin section P10B with stars indicating locations of polyphase inclusions (PI) in garnet and matrix pentlandite (modified after Lo Pò et al. 2020) along with a BSE image of a PI and relative color mapping showing major element compositions of Po + Pn. (b) Coarse spinel enclosing PI. Note calcite + brucite intergrowths associated with pentlandite (KL24-2b). PI in spinel with ilmenite + chlorite + apatite + pentlandite (KL24-3); (c) matrix pentlandite in intimate association with dolomite (MOL1-C) and in close relationship with dolomite (VM10A). (d) kelyphite corona enclosing pentlandite cut by a chlorite flake and magnetite string; (e) dolomite vein (+ magnesite) enclosing pentlandite + millerite cut by chlorite flake (18LP1); magnesite + serpentine + tremolite vein enclosing pentlandite partially replaced by magnetite pseudomorphs (MOL1-C); (f) halos and apophyses around pentlandite (UN3) and pentlandite-fracture fillings (UN14).

**Figure 4.** (a) FeO and (b) TiO<sub>2</sub> (wt%) as a function of Al<sub>2</sub>O<sub>3</sub> of whole-rock peridotite analyses from the Ulten Zone investigated in this study (data in Table S3, Obata and Morten, 1987, Ionov et al. 2017 and Gudelius et al., 2019). Shown for comparison in (a) are residues from batch melting at 2, 4 and 6 GPa (stippled blue lines) and from polybaric fractional melting of primitive mantle (**PM**—yellow star) at 2-0, 3-0, 5-1 and 7-2 GPa (thick red lines), as well as contours of % melt extracted (orange lines) (from Herzberg, 2004). Shown for comparison in (b) are paths for polybaric fractional melting of PM at 1.5-0.5 and 2.5-0.5 GPa. Low TiO<sub>2</sub> contents at a given Al<sub>2</sub>O<sub>3</sub> in the UZ peridotites compared to the model suggest formation from a more depleted source. (c) NiO (wt.%) content of olivine grains vs bulk S concentration (ppm). Values of NiO taken from Gudelius et al. (2019) and Consuma et al. (2020). Correlation fitting lines and respective R<sup>2</sup> values are reported.

**Figure 5.** Sulfur contents (in ppm S) in UZ peridotites (this study) compared to those in different mantle and crustal reservoirs (references in panel).

**Figure 6.** Primitive-mantle normalized trace element compositions of pentlandite and pyrrhotite (primitive mantle of McDonough and Sun, 1995). For simplicity, only medians for coarse and fine peridotites, and for different textural positions are reported. Element order corresponds to decreasing compatibility during partial melting of primitive mantle (from Aulbach et al., 2012). Shown for comparison in (a) is range of abundances in pyrrhotite included in eclogitic diamond and obtained using the same method employed in this study (Aulbach et al., 2012). Shown for comparison in (c) is the range of matrix pentlandite compositions shown in (b). **CS**—Coarse-

grained spinel peridotite, **CGn**—Carbonate-free coarse-grained garnet peridotite, **CG**—Coarse-grained garnet/spinel with coronitic garnet peridotite, **(P)FGA**—Porphyroclastic and non-porphyroclastic fine-grained garnet amphibole peridotite, **FSA**—Fine-grained spinel (chlorite-amphibole) peridotite. **Po**—pyrrhotite, **Pn**—pentlandite.

**Figure 7.** (a) Sulfur isotope variations of this study compared to those in different reservoirs (Giuliani et al., 2016, and references therein), in high-pressure rocks reported in Li et al. (2020, and references therein), in slab fluids estimated by Walters et al. (2019) and Li et al. (2020), pelagic sediments from Schwarzenbach et al. (2018) and Li et al. 2020, and in sulfides (green line) and sulfates (orange line) from altered oceanic lithosphere and serpentinite (Schwarzenbach et al., 2018a,b, Li et al. 2020); (b) Histograms showing the sulfur isotope compositions in pentlandite in various textural settings measured by SIMS (this study). The yellow box corresponds to the depleted mantle value range, following Labidi et al. 2013 ( $\delta^{34}\text{S} = -1.28 \pm 0.25\%$ ) and Labidi et al., (2014) ( $\delta^{34}\text{S} = -1.40 \pm 0.50\%$ ). **CS**—Coarse-grained spinel peridotite, **CGn**—Carbonate-free coarse-grained garnet peridotite, **CG**—Coarse-grained garnet/spinel with coronitic garnet peridotite, **(P)FGA**—Porphyroclastic plus non-porphyroclastic fine-grained garnet amphibole peridotite, **FSA**—Fine-grained spinel (chlorite-amphibole) peridotite. **PI**—polycrystalline inclusions. **VCDT**—Vienna Canyon Diablo Troilite standard.

**Figure 8.** *In situ* Sr isotope ratios of (a) amphibole and clinopyroxene compared to As concentrations in the associated pentlandite. Values are reported as total averages for the different lithotypes. **CS**—Coarse-grained spinel peridotite, **CG**—Coarse-grained garnet/spinel with coronitic garnet peridotite, **(P)FGA**—Porphyroclastic and non-porphyroclastic fine-grained garnet amphibole peridotite, **FSA**—Fine-grained spinel (chlorite-amphibole) peridotite. (b) *In situ* Sr isotope compositions of clinopyroxene vs S isotope of pentlandite (this study) and vs *in situ* Sr isotope compositions of carbonates (Consuma et al. 2020). The small number of data points is due to the rare occurrence of clinopyroxene combined with the typically small grain size of clinopyroxene and carbonates, which precludes laser ablation sampling of large enough volumes for statistically meaningful Sr isotope analysis. Further limitations are imposed by the requirement of using matrix-matched sulfide grains for SIMS analyses.

**Figure 9.** Trace element concentrations (Co, Se, Te, Pb, Sb, As) versus  $\delta^{34}\text{S}$  measured in pentlandite in the Ulten Zone peridotites distinguished by textural positions. When significant, correlation fitting lines and respective  $R^2$  are reported. **CS**—Coarse-grained spinel peridotite, **CGn**—Carbonate-free coarse-grained garnet peridotite, **CG**—Coarse-grained garnet/spinel with coronitic garnet peridotite, **(P)FGA**—Porphyroclastic and non-porphyroclastic fine-grained garnet amphibole peridotite, **FSA**—Fine-grained spinel (chlorite-amphibole) peridotite. **Po**—pyrrhotite, **Pn**—pentlandite.

**Figure 10.**  $\delta^{34}\text{S}$  in pentlandite (this study) vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  in coexisting carbonate, clinopyroxene and amphibole (this study and Consuma et al., 2020). Note that MOL1-C refers to the carbonates (+serpentine)-bearing vein crosscutting the coarse spinel peridotite of Figure 3e. Mixing trends between depleted mantle (DM) source and possible slab-derived melt and fluid sources. The continental crustal component may be a melt or a fluid with variable S concentrations as shown. A single Sr concentration (130 ppm) is assumed for the purpose of modeling, since in our study the Sr concentration in fluid and melt is estimated to vary less than two-fold. Light grey area and individual data for glasses dredged on the South Atlantic ridge from Labidi et al. (2013). Input data with references, as well as the effect of varying Sr concentration on the curvature of the mixing lines, are reported in Electronic Annex C.

**Figure 11.** Conceptual model of the metamorphic stages of the Ulten Zone peridotites, see discussion for details. **Stage 1**— Only a small residual sulfur component would have remained after ca. 15-25% of melt extraction. Concentrations of 170-210 ppm S with a heavy  $\delta^{34}\text{S}$  signature may reflect percolation by reduced,  $\text{H}_2\text{S}$ -bearing hydrous basic melts from the subduction-modified deeper lithospheric mantle. **Stage 2**—At peak (garnet) conditions, when UZ peridotites still reside in the mantle wedge, sulfur is introduced into peridotites from heterogeneous melt and fluid sources, which variably equilibrated with the depleted mantle and possibly mixed with de-serpentinization fluids. **Stage 3**— The supra-depleted mantle S isotope signature again require addition of heavy sulfur. **Stage 4**—Sulfur and  $\text{CO}_2$  are variously released from the mantle-crust mélange during late-stage serpentinization, while high S concentrations ( $>300$  ppm) in a serpentine vein suggest efficient mobilization in channelized fluids.