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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_2S-CO_2-bearing melt from the subduction-modified hot mantle wedge, which formed a pyroxenite layer hosting matrix pentlandite with $\delta^{34}S$ of +2.77‰. Heavier $\delta^{34}S$ (up to +3.43‰), radiogenic Sr ($^{87}Sr/^{86}Sr_{clinopyroxene} > 0.7052$) 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 ($\delta^{34}S$ = -1.62 to +0.67‰), and radiogenic Sr in amphibole ($^{87}Sr/^{86}Sr$ = 0.7056) and associated dolomite (published data), from fine-grained garnet-amphibole peridotite may point to involvement of H_2S-

CO_2-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 $^{87}Sr/^{86}Sr_{amphibole}$ 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 ($\delta^{34}S$= -0.38‰), while carbonate veining with occasional sulfides witnesses channelized fluid flow. Textural observations indicate that, during Stage 4, serpentinization of peridotite at low fS_2 played an active role not only in CO_2 release by conversion of dolomite to calcite + brucite intergrowths, but also in local removal of ^{32}S during the final exhumation stage. Late channelized sulfur remobilization is evidenced by the serpentine + magnetite (± millerite ± calcite) vein carrying > 300 ppm S.

Overall, the relatively narrow range of sulfur isotope composition ($\delta^{34}S$= -1.62 to +3.76‰) 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

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

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

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

Of note, the resultant recent research efforts produced conflicting lines of evidence for the sulfur behavior in subduction zones and for its contribution to the oxidation state of the sub-arc mantle region. Thus, exhumed mafic and ultramafic rocks from the island of Syros (Greece), interpreted as blocks detached from the lithospheric slab to form a subduction channel mélange under blueschist-facies conditions, were shown to have bulk-rock S isotopic signatures inherited from seawater alteration and overprinted by sediment-derived fluids mobilizing S along the plate interface (Schwarzenbach et al., 2018a). Evans et al. (2014) find complex S isotopic zoning of pyrite grains in eclogites originating as subducted oceanic crust from the Zermatt-Saas zone (Western Alps) and the Pouébo terrane (New Caledonia), which they ascribe to S loss during prograde metamorphism and sulfide growth at the earliest stage of exhumation. Similarly, Walters et al. (2019) describe sulfides of metasomatic origin from a global suite of exhumed high-pressure rocks, that yield a wide range of S isotopic compositions interpreted as precipitated from sulfate-bearing fluids. Bénard et al. (2018) also maintain that oxidized slab components have the potential to the oxidate the sub-arc mantle, by documenting dissolved S^{6+} in spinel-hosted glass inclusions in sub-arc mantle xenoliths brought to the surface by a recent volcanic activity in the Kamchatka (Russia) and West Bismarck arcs (Papua New Guinea). On the other hand, Li et al. (2020) show most S to be present as reduced species, and argue for limited S release in slab fluids. These constraints are based on a combination of petrographic observations, whole-rock and *in situ* S isotope measurements and thermodynamic modelling of sulfide-bearing high-pressure rocks and veins from the southwestern Tianshan (ultra-)high-pressure metamorphic belt (China). Thermodynamic modeling results of Piccoli et al. (2019) also support the reducing nature of dehydrated slab fluids at sub-arc depth. Giacometti et al. (2014) report little evidence from microtextural and *in situ* S isotopic analysis of exhumed meta-ophiolites from the Western Alps for S mobilization during metamorphism. Two-stage release of S during subduction is predicted by the thermodynamic modelling results of Walters et al. (2020), with a small flux of reduced S at shallow depth and elevated S fluxes from deep, cold oxidized slabs via release of sulfate and sulfide species. Although Tomkins and Evans (2015) also predict a two-stage release process, they model anhydrite dissolution into fluids at low temperatures and the release of H_2S when pyrite converts to pyrrhotite at higher temperatures.

Despite the importance of orogenic mantle peridotites as proxies for deep and retrograde-fluid-mediated volatile exchange between crust and mantle (Scambelluri et al., 2010), few studies have investigated the S speciation and isotopic composition of orogenic mantle rocks as an integral component of the global S cycle. Orogenic spinel lherzolites in the North-Eastern Pyrénées yield negative values of $\delta^{34}S$ = -3.2‰ to represent an ancient S depletion event in the upper mantle, whereas positive values up to +3.3‰ of pyroxenite intrusions were interpreted to reflect various enriched mantle sources (Chaussidon and Lorand, 1990). The positive shift in the $\delta^{34}S$ of sulfides up to +5.4‰ form the garnet-bearing pyroxenite in the Western Gneiss Region of Norway (Rielli et al., 2018) are ascribed to contamination from oceanic slab-derived oxidized fluids, whereas negative values down to -10.0‰ are attributed to fluids sourced from the enclosing gneisses or subducted oceanic sediments.

We focus on this little-explored facet of the S cycle, by investigating well-characterized orogenic spinel and garnet peridotites from the Ulten Zone (UZ) in the Eastern Alps that originated as continental mantle that became involved in continent-continent collision during the Variscan Orogeny. Displaying a diversity of compositional and mineralogical features, including several generations of hydrous and carbonate minerals, UZ peridotites have been the subject of multiple investigations, with a view to unraveling the element cycles in convergent margin settings (Rampone and Morten, 2001; Scambelluri et al., 2006; Hermann et al., 2006; Marocchi et al., 2009; Sapienza et al., 2009; Marocchi et al., 2010; Scambelluri et al., 2010; Marocchi et al., 2011; Braga and Massonne, 2012; Förster et al., 2017; Ionov et al., 2017; Gudelius et al., 2019; Consuma et al., 2020; Lo Pò et al., 2020). The occurrence of sulfides in the UZ peridotites and their petrological implications have so far been overlooked as an important source of information on the behavior of S in continental subduction zones. Taking advantage of the spatial resolution and textural control afforded by *in situ* analyses on single sulfide grains, we use S isotopes as a sensitive tracer of the speciation and source of S in subduction zones. Additional constraints on the nature of metasomatic agents can be inferred from the variation in the trace element composition of texturally diverse pentlandite, which is known to reflect changes in the physicochemical fluid parameters (e.g., pressure, temperature, oxygen fugacity). Dehydration and partial melting generally depletes the upper mantle in fluid-mobile and magmaphile elements, respectively, including the chalcophile elements As, Sb, Se, Te and Pb (Hattori et al., 2002; Hattori and Guillot, 2003). As a consequence, their enrichment in the mantle wedge is usually explained by the supply of these elements from slab-derived fluids and melts that percolate and metasomatize the overlying mantle. These variably chalcophile elements (e.g., Barnes, 2016) would be expected to follow sulfide (e.g., as HS^-) mobilized in fluids and melts. *In-situ* determination of S isotopic and trace element compositions of pentlandite, combined with whole-rock analyses, *in situ* Sr isotope compositions of amphibole and clinopyroxene, and published *in situ* Sr isotope of the associated carbonates, allow to delineate a model for the formation and modification of sulfide and associated carbonates, and to discuss the potential sources and effects of C-O-H-S fluids percolating the mantle wedge during continental collision.

2. Geological setting and metasomatic history

The Ulten Zone (UZ) is a Variscan tectonic unit located in the Tonale Nappe (Eastern Alps) (Fig. 1). It is part of the metamorphic basement of the Austroalpine domain, interpreted as a constituent of Gondwana before its involvement in the Variscan collision with Laurussia (Regorda et al., 2020). In this unit, relicts of high-pressure (HP) metamorphism are preserved in lenses of ultramafic rocks (mostly garnet-bearing peridotites and eclogites) within migmatites and garnet-kyanite gneisses. The peridotites first resided in a supra-subduction zone mantle wedge at relatively high temperature (about 1200°C), followed by re-equilibration under eclogite-facies HP conditions of ~850°C and pressure of 2.2-2.7 GPa (Nimis and Morten, 2000; Braga and Sapienza, 2007), as a result of their movement toward deeper portions of the upper mantle during continental crust subduction along a relatively cold path (Fig. 2a-b). Prior to or contemporaneously with the attainment of eclogite-facies conditions, the former coarse-protogranular peridotites experienced deformation and recrystallization into fine-grained peridotites, with formation of garnet and amphibole at the expense of spinel and clinopyroxene. The post-collisional stage comprises the development of a crust-peridotite tectonic mélange, and the onset of its exhumation is estimated to begin at around 330 Ma (Tumiati et al., 2003). The three different lithologies described by Obata and Morten (1987) synthetize the different stages of peridotite evolution: (1) (pre-peak) coarse-grained protogranular spinel peridotite (CS) that transforms into a variety with coronitic garnet (CG), consisting of olivine + enstatite + diopside + Cr-Al spinel (± garnet); (2) (peak) porphyroclastic (P-FGA) to equigranular fine-grained garnet-amphibole peridotite (FGA) consisting of olivine + orthopyroxene + clinopyroxene + garnet + Ca-amphibole + spinel; and (3) (post-peak/exhumation) fine-grained spinel (chlorite-amphibole) peridotite (FSA) with olivine + orthopyroxene + Ca-amphibole + chlorite ± spinel. All the UZ peridotites were variably serpentinized as they were involved in a crust-mantle mélange along the exhumation path. The exceptional complexity of the study area results from polyphase C-O-H-metasomatism along the Variscan continent collision (i.e. peak pressure conditions and afterwards), during which inputs of metasomatic liquids percolated the overlying orogenic mantle wedge inducing the formation of hydrous and carbonate phases.

On the basis of the high modal amphibole with a strong LILE/HSFE fractionation, Rampone and Morten (2001) suggested that the metasomatic agents of the high-pressure hydrous metasomatism are fluids with a low CO_2/H_2O ratio sourced from the neighboring crustal rocks. Nevertheless, carbonate phases related to the progressive metasomatic stages are ubiquitous in Ulten Zone peridotites, the petrography of which is described in detail in Förster et al. (2017). Inclusion of dolomite in coarse spinel, itself enclosed in garnet, was ascribed as a trapped melt during the high-temperature metasomatic stage in the mantle wedge (Stage 1 in Fig. 2a-b), despite the radiating fracturing may point to a late metasomatic process (Consuma et al. 2020). Formation of interstitial dolomite with minor magnesite has been ascribed as a peak-pressure feature, while late exhumation-related serpentinization caused dolomite dissolution and formation of calcite+brucite intergrowths via the reaction $CaMg(CO_3)_2 + H_2O \rightarrow CaCO_3 + Mg(OH)_3 + CO_2$. This reaction implies CO_2 liberation from peridotites now entrapped in a crust-mantle mélange (Förster et al., 2017). Subsequent *in situ* Sr isotope measurements in the UZ carbonates have shown multiple signatures related to their textural positions (Consuma et al., 2020): relatively unradiogenic $^{87}Sr/^{86}Sr$ of ~ 0.705 of matrix dolomite formed at eclogite-facies conditions, were taken to indicate that fluid sources that had variably equilibrated with a depleted mantle reservoir mostly acted at high-pressure peak conditions. In contrast, variably radiogenic $^{87}Sr/^{86}Sr$ (0.7036 to 0.7083) was ascribed to hybridized sources (i.e. mixing of depleted mantle and crustal liquids) generated after the entrapment of peridotites into crustal rocks during the exhumation stage (Consuma et al., 2020). The occurrence of these carbonates commonly in intimate association with sulfides in different textural positions proves that metasomatic fluids and melts played a role in the mobility not only of carbon but also of sulfur in the mantle wedge and tectonic mélange, and thus opens new questions regarding their role in the global S cycle.

3. Samples, prior work and sulfide petrography

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

Ten samples encompassing coarse spinel peridotites (UN1, UN2), fine-grained garnet-amphibole peridotites (UN3, UN6, UN7, UN9, UN10, UN14) and fine-grained spinel-amphibole peridotites (UN8, UN16) were previously studied in detail for their petrography, bulk-rock and mineral major-, minor- and trace-element composition, as well as for garnet Fe speciation (Gudelius et al., 2019). The study shows that LILE, LREE and some HFSE are co-enriched and revealed significant compositional differences between sampling localities (Samerberg vs. Seefeld/Malga Masa Murada; Fig. 1), which is ascribed to different positions of the peridotite bodies relative to the slab during subduction and exhumation. Despite evidence for strong metasomatic overprint, Fe^{3+}/Fe^{2+} in garnet remains low (<0.046), and oxygen fugacities relative to the Fayalite-Magnetite-Quartz buffer ($\Delta \log fO_2$) of -2.4 to -0.32 are calculated for P=2 GPa, suggesting reducing conditions in the mantle wedge beneath the Ulten Zone (Gudelius et al., 2019). Conversely, Malaspina et al. (2009) find more oxidizing conditions (FMQ to FMQ+2 calculated at P = 3GPa) in FGA peridotites from the Malga Masa Murada and Samerberg areas. Thus, the UZ records heterogeneous redox conditions of various mantle wedge and tectonic mélange domains (Fig. 2c).

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

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

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

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

Sulfides occur as discrete monophase and subordinately as polyphase grains with different shapes (rounded grains, elongated, blocky, skeletal or irregular) and sizes (up to 150 μm). They show various stages of alteration, ranging from none, to partial or strong alteration and fracturing, as illustrated in Figure 3 and Electronic Annex B.

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

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

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

2. *Discrete sulfide inclusions (Stage 1-2):* Orthopyroxene grains, Cr-rich spinel in garnet, Cr-poor spinel in the matrix and kelyphitic corona host different types of sulfides, whereas no sulfides are found in olivine. Notably, kelyphite around spinel and garnet commonly hosts sulfides (mostly pentlandite) of exceptional dimensions (30-150 μm; Fig. 3d). They commonly occur at the edge of coarse spinel following the directions of the kelyphite growths or at the edge of the corona in contact with the peridotite matrix (e.g. pentlandite with magnetite exsolutions and cut by late chlorite flakes; pentlandite + sphalerite + native-Cu blebs associated with Cl-apatite and cut by chlorite flakes; 30 μm zoned chalcopyrite grain).
3. *Interstitial sulfides (Stage 2):* They occur at silicate grain boundaries and commonly in close spatial relationship with matrix dolomite (Fig. 3c). In the coarse-grained peridotite (CS + CG + CGn), they are usually anhedral or subhedral with rounded or elongated shape and show a grain size from 10 to 50 μm. The carbonate-free peridotite SBA2 contains only five fractured blocky monophase pentlandite grains with no alteration features. In CS and CG peridotites MOL1-C and 18LP1, interstitial sulfides occur mainly as pentlandite + millerite assemblages partially replaced by magnetite. In MOL1-C, pentlandite (partly replaced and rimmed by thin magnetite) + heazlewoodite + dolomite + serpentine assemblage is cut by chlorite flakes (Fig. 3c). In the FGA peridotites KL1-A and VM10A, pentlandite is commonly interstitial to olivine, orthopyroxene and pargasitic to hornblenditic amphibole. It is locally associated with disseminated dolomite. Nickeline blebs (Ni, As) are found within disseminated rounded pentlandite in association with Cl-apatite in FGA peridotite VM10A. It is worth noting that this peridotite is very weakly serpentinized.
4. *In carbonate veins (Stage 3)*: Pentlandite + millerite cut by late chlorite flakes (with magnetite filling the cleavage) are hosted in a vein predominantly formed by dolomite (and minor magnesite) + tremolite + serpentine that cuts the peridotite matrix 18LP1 (Fig. 3e). Monophase pentlandite also

occurs not directly within the vein but in spatial proximity with it (i.e. few μm from the vein). A nickeline bleb enclosed into pentlandite partially replaced by magnetite is documented.

5. *In matrix serpentine or serpentine vein (Stage 4):* P-FGA peridotites KL2.4-2b and KL2.4-3 show pentlandite + magnetite exsolutions contoured by chalcopyrite blebs. Exceptionally in these two samples, sphalerite can also be found included in matrix serpentine, as single phase or polyphase-assemblages (pentlandite + sphalerite + chalcocite). Matrix serpentine in FSA peridotite MM1 is dominated by pentlandite rarely replaced by millerite or heazlewoodite. Conversely, the composite serpentine + magnetite (± calcite ±dolomite) vein MM1B, crosscutting the matrix of peridotite MM1, hosts fractured elongated-to-rounded millerite in intimate association with Ni-oxide grains with sizes of ~30 and 20 μm respectively. Nickeline blebs (NiAs; 3-5 μm on average) occasionally occur within pentlandite (± magnetite) grains associated with serpentine (e.g. in peridotites MOL1-C, 18LP1 and VM10A). Pentlandite enclosed in the serpentine + magnesite + tremolite vein (peridotite MOL1-C) is pseudomorphously replaced by magnetite (Fig. 3e). Perpendicularly to this vein, serpentine + pentlandite + magnetite fills the cleavage of the host mm-sized enstatite, rarely containing small nickeline blebs.
6. *In halos, apophyses and sulfide-filled fractures (Stage 2-3-4):* Diffuse sulfide material is commonly observed in i) halos around discrete sulfide grains, ii) apophyses leading into sulfide-filled fractures and iii) sulfide in fractures apparently unconnected to discrete sulfide grains (Fig. 3f). In megacrysts, similar observations are ascribed to decrepitation of the sulfide during heating in contact with host basalt (Andersen et al., 1987), a mechanism that does not apply here. It is noteworthy that such features are observed both in fine-grained garnet amphibole peridotite and in spinel peridotite and therefore not (exclusively) related to late-stage retrogression.

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

To sum up, in order of decreasing abundance, sulfides occur mostly interstitial to silicates and associated with matrix dolomite, enclosed in veins of serpentine and carbonates (dolomite, magnesite) and finally as inclusions (in coarse spinel and few grains in silicates), coexisting with dolomite and calcite. Interstitial pentlandite is by far the dominant sulfide phase occurring in all the UZ peridotite samples, with an average grain size of 5-150 μm, followed by heazlewoodite and millerite mostly found in association with pentlandite in serpentine and carbonate veins. Enclosed pentlandite is common in spinel as a discrete phase or PI, while pyrrhotite (± pentlandite) occurs as PI in cm-sized garnet in peridotite P10B, except for few matrix pyrrhotite grains in the "UN" sample suite. Finally, few sphalerite, chalcopyrite and chalcocite grains are hosted only in P-FGA peridotites, mostly within coarse-grained spinel and kelyphite (KL24-2b, Kl24-3, VM10A, P10B).

4. Methods

Each analytical method and specifics on quality control measures are detailed in Electronic Annex C. Samples were examined in polished thin section and slices of peridotite of 3 mm thickness by optical transmitted and reflected light using a polarized optical microscope, and by Scanning Electron Microscopy (SEM) for X-ray maps at the Department of Biological, Geological and Environmental Sciences, University of Bologna, Italy.

Bulk rock major- and minor-element compositions along with selected trace elements were acquired by X-Ray-Fluorescence, using a Phillips Magi XPRO spectrometer at Johannes Gutenberg-University Mainz. Results are shown in Table S1 in Electronic Annex D. The same instrument, and a LECO-Analyzer CS 125, were used to obtain bulk-rock S concentrations for a subset of samples (UN1-UN16) for which major- and minor-element compositions had been previously determined (Gudelius et al., 2019). Remaining S concentration measurements were carried out at Karlsruhe Institute of Technology, also using a LECO instrument. Individual results are provided in Table S2. Sulfide major- and minor-element concentrations were obtained *in situ* by EPMA, using a JEOL JXA-8100 Superprobe electron micropobe at the Institute of Mineralogy and Petrology, University of Innsbruck and a JEOL JXA-8900 at Goethe-University Frankfurt. Results and summary are shown in Table S3.

Trace-element abundances were determined *in situ* in sulfides following the procedure detailed in Aulbach et al. (2012). Measurement statistics for two separate analytical campaigns and results are given in Table S4 and S5 in Electronic Annex D. Abundances of Au cannot be quantified in a subset of samples that were Au-coated prior to analysis for multiple S isotopes, as Au may have collected in small pits and cracks in the sulfides.

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

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

5. Results

5.1 Whole rock major elements and sulfur concentration

New whole rock compositions are reported in Table S1 in Electronic Annex D and illustrated together with published data (UN series) in Figure 4. Loss On Ignition (LOI) ranges between 0.37 and 13.10 wt.%, in line with the degree of serpentinization. The highest value of 13.10 wt.% is from the serpentine vein MM1B previously hand-picked from FSA peridotite MM1. Contents of Al_2O_3 in the UZ peridotites range between 1.40 and 3.12 wt.%, while CaO ranges from 0.44 to 2.84 wt.%, TiO_2 from 0.02 to 0.11 wt.% and MgO from 37.87 to 42.79 wt.%. For comparison, primitive and depleted mantle have estimated Al_2O_3 concentrations of

4.45 and 4.28 wt.%, respectively, CaO of 3.55 and 3.50 wt.%, TiO_2 contents of 0.201 and 0.19 wt.% and MgO contents of 37.8 and 38.22 wt.%, respectively (McDonough and Sun, 1995; Salters and Stracke, 2004). Sulfur concentrations for eighteen peridotite samples are reported in Figures 4-5, and Table S2 in Electronic Annex D. Overall, the S content of the orogenic peridotites ranges from as low as a few tens to hundreds ppm, averaging 171 (±45; n=18) ppm with a median value of 169 ppm. Coarse-garnet peridotite (CG) shows an average value of 180 ± 28 ppm (n=5), fine-grained garnet amphibole peridotite (FGA) an average value of 160 ± 34 ppm (n=9) and three fine-grained spinel peridotites (FSA) have wide sulfur concentration ranging from 40 to 228 ppm. The serpentine + magnetite ± sulfide (mostly millerite) ± calcite ± dolomite vein MM1B reaches the highest value of 329 ppm S. Again for comparison, primitive and depleted mantle have S concentrations of 250 and 60-119 ppm, respectively (Alt et al., 2007; McDonough and Sun, 1995; Salters and Stracke, 2004).

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

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

Pentlandite is compositionally heterogeneous with 22.8-39.5 wt.% Fe, 28.8-37.8 wt.% Ni and below detection limit (bdl)-16.6 wt.% Co. Here, pentlandite with Ni > 36wt.% is classified as Ni-pentlandite (mostly found in serpentine vein), and that with Co > 6wt.% as Co-pentlandite (mostly found associated with carbonate veins and in FSA peridotites). Data show that pentlandite enclosed in coarse spinel included in garnet (occurring both as discrete grain and PI) and in silicates, as well as most of the matrix pentlandite grains in P-FGA and FGA peridotites and some pentlandite enclosed in kelyphitic coronas around garnet fall in the “typical” mantle sulfide range according to Wang et al. 2010 (Fig. S1 in Electronic Annex A). Conversely, the other sulfides, such as those found in the matrix of CGn peridotite SBA2 and those included in a serpentine vein show higher Co/(Fe+Ni+Cu) and Co/Ni ratio with respect to the mantle sulfides.

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

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

The high-temperature precursors of the UZ sulfides can be revealed by comparing their major chemical compositions to experimentally determined phase relations at various temperatures in the ternary diagram S-Fe-(Ni+Co) in at.% (Fig. S2a in Electronic Annex A). This indicates that minor pyrrhotite and dominant pentlandite could be derived from re-equilibration of mss to low temperature (T). In addition, in the ternary system Fe_9S_8–Ni_9S_8–Co_9S_8, experimental studies have shown that the pentlandite composition is temperature-dependent (Kaneda et al., 1986) and can reflect the condition under which it forms (e.g., Lorand and Grégoire, 2006; LaFlamme et al., 2016). Most of the investigated pentlandite grains plot within the entire field of stability for T of 200°C and 300°C (Fig. S2b), which are consistent with low-T assemblages (≤ 300°C) re-equilibrated from high-T-(mono)sulfides, whereby higher Co content shifts the stability field for pentlandite formation to higher T (c. 300° C). Pentlandite can also originate by crystallization from metasomatic Ni-Cu-rich sulfide melts with high metal/S ratios (Lorand et al., 2013).

5.3 Sulfide trace element concentrations

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

Pyrrhotite from PI in garnet shows Ni concentrations ranging from 119 to 8332 ppm, Cu from 22 to 569 ppm, Zn from 0.96 to 7.41ppm, As from 0 to 30 ppm, Se from 2 to 24 ppm, Ag from 0.08 to 0.70 ppm, Sb 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. Median values are reported in Table 3 and illustrated in Figure 6, while for the full trace-element dataset the reader is referred to Table S5 in Electronic Annex D.

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

5.4 SIMS Sulfur isotope compositions of pentlandite

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

In the coarse-grained spinel peridotite MOL1-C, a pyroxenite layer hosts a pentlandite grain with values of +2.77 ± 0.37‰ (n=2).

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

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

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

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

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

Overall, the S isotope compositions obtained for the UZ pentlandite grains range between -1.62 ± 0.42‰ and +3.76 ± 0.36‰. Matrix pentlandite from fine-grained peridotites is isotopically light, with an average of

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

5.5 In situ Sr isotope of clinopyroxene and amphibole

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

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

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

6. Discussion

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

Few studies have systematically examined the combined geochemical and isotopic signature of sulfides from orogenic mantle domains as a probe to investigate the nature of high-pressure and exhumation processes in collisional settings. The full set of metasomatic and re-equilibration processes affecting the UZ peridotites throughout their evolution dictates their sulfide mineralogy as well as their chemical and sulfur isotope compositions. As these processes may produce sulfur isotopic fractionations, the effects of high-temperature processes and low-temperature re-equilibration of the sulfide assemblage on δ^{34}S have to be considered before attempting any interpretation on the relationships between sulfur isotope signatures and source/s. Pentlandite is not stable at the mantle conditions experienced by UZ peridotites during their multi-stage evolution (Fig. 2a-b). It either formed together with minor amounts of pyrrhotite, now in part replaced by magnetite, from a high-temperature monosulfide precursor (Fig. S2), or precipitated directly from a metasomatic metal-rich fluid (Lorand and Grégoire, 2006; Lorand et al., 2013; Giuliani et al., 2016). Prior modeling has demonstrated that the S isotopic fractionation between pentlandite and a precursor monosulfide solid solution (mss) is limited to 0.7 ‰ for equal proportions of pentlandite and mss and low temperature of pentlandite formation (300°C; Giuliani et al., 2016). Given the dominance of pentlandite in the low-temperature assemblages in UZ peridotites, it is argued that the δ^{34}S signature of pentlandite largely reflects that of its high-temperature precursor. Furthermore, since the pH of fluids does not induce significant isotope fractionation at the metamorphic conditions of subduction zones (Giacometti et al., 2014), the measured δ^{34}S of pentlandite is considered broadly representative of the bulk rock that interacted with various S-bearing metasomatic fluids or melts.. The sulfur isotope composition is not modified by high-pressure prograde metamorphism of subducted rocks (Evans et al., 2014; Li et al. 2021), and the S isotopic fractionation between solid sulfide and sulfide melt or H_2S in reduced fluids is negligible (Ohmoto and Rye, 1979; Li and Liu, 2006; Marini et al., 2011). Instead, significant fractionation occurs between oxidized and reduced S species (up to 4-5‰) even at mantle temperatures (i.e. T > 900°C; Ohmoto and Rye, 1979). During the

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

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

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

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

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

The sulfur isotope composition of sub-continental lithospheric mantle (SCLM), which stabilizes by extraction of variable degrees of partial melt (e.g., Griffin et al., 2004), remains poorly constrained and has been mostly addressed in studies of sulfide inclusions in diamonds from mantle xenoliths, giving a $\delta^{34}S$ range between -4‰ and + 6‰ (Chaussidon et al., 1987; Farquhar, 2002; Thomassot et al., 2009). In the Ulten Zone, during high-temperature pre-peak conditions (Stage 1), the coarse-grained protogranular peridotites containing the assemblage olivine + enstatite + diopside + Cr-Al spinel reside in the continental lithospheric mantle and equilibrate at 1200°C and 1.3-1.6 GPa (Nimis and Morten, 2000). Their study may therefore provide insights into mantle wedge evolution before its entrainment into the Variscan subduction architecture. Samples in this study appear to fall along a curved array with respect to bulk-rock TiO_2 and Al_2O_3, both of which are moderately incompatible (Fig.4). Such arrays result from partial melt extraction. In accord with Ionov et al. (2017) and Gudelius et al. (2019), major element compositions indicate mostly ~15-25% of melt extraction (Fig. 4a), although this is a minimum estimate if refertilization occurred (Gudelius et al., 2019). At such melt fractions, sulfide would have been exhausted, depending on oxygen fugacity and S concentration (Keays, 1995; Mungall et al., 2006). For example, for Al_2O_3 contents of 2-2.3 wt.% recorded in some UZ peridotites (Fig. 4a), less than 100 ppm S would be expected to remain in the mantle for fractional melt extraction at 3 GPa and an oxygen fugacity of FMQ-2 (Aulbach et al., 2016). If melt extraction occurred at lower pressure, then S concentrations in the residue would be even lower, given increasing S solubility in silicate melt at sulfide saturation with decreasing pressure (Mavrogenes and O'Neill, 1999). In this light, the UZ peridotites containing >100 ppm S (Table S2, Electronic Annex D) almost certainly experienced S addition. Furthermore, sulfidation of peridotite has been shown to cause Fe-Ni zoning in olivine (Papike et al., 1995; Bataleva et al., 2016). Although such zoning is not observed in the UZ olivine (Gudelius et al., 2019; Consuma et al., 2020), higher NiO contents in olivine are observed in S-poor peridotites relative to olivine from S-rich peridotites, consistent with Ni extraction from olivine during metasomatic sulfide addition (Fig. 4c).

Hereafter, for each metamorphic stage, we discuss (i) the process and related metasomatic agents that may have modified the sulfide component throughout the evolution of peridotites; (ii) the relevant conditions (P-T-fO_2-fS_2) that may have exerted a major control on the nature of sulfides and their mobility with respect to the melt/fluid phase; (iii) the textural relationship of sulfides with the coexisting carbonates and hydrous minerals. We conclude with the potential implications that our findings may have for the understanding of the global sulfur cycle.

6.3 Pre-collision mantle metasomatism (Stage 1)

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

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

indicate a system dominated by reduced S species. Additionally, the overall lack of identifiable reduced carbon species (i.e. graphite or disordered carbonaceous material; e.g., Vitale Brovarone et al., 2020) in the UZ peridotites requires carbon to be present mostly as carbonate (CO_2). We speculate that any S added from melt leaving a lithospheric mantle source would have involved an H_2S-CO_2-bearing agent, consistent with suggestions that mantle fluids are H_2S-dominated (Eggler and Lorand, 1993).

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

6.4.1 Coarse-grained vs Fine-grained peridotite

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

Coarse-grained garnet peridotite. The positive $\delta^{34}S$ values obtained for a population of matrix pentlandite in the coarse-grained garnet peridotites are distinct from the proposed depleted mantle range of $\delta^{34}S$ of -1.28 ± 0.33‰ (Labidi et al. 2013), from the suggested mantle wedge composition of 0‰ (Li et al. 2020), and from the proposed composition of continental lithospheric mantle (+1.35 ± 0.25 ‰; Fiorentini et al., 2018). Combined with elevated S abundances (≥166 ppm; Table 1), the measured isotope values require addition of isotopically heavy S, either from an enriched mantle source as recognized by Ionov et al. (1992) or involving processes inducing heavy S isotope enrichment, such as fractionation of isotopically light sulfide (Walters et al., 2019). The initial Sr isotopic composition of clinopyroxene in two coarse-grained peridotites ($^{87}Sr/^{86}Sr$=0.70509-0.70538; Table 1) is more radiogenic than that of the primitive or depleted mantle (0.7045 and 0.7026, respectively; Workman and Hart, 2005), and also indicates that the enrichment in radiogenic Sr pre-dates the entrapment of peridotites into the tectonic mélange. Indeed, coarse-grained UZ peridotites show evidence for interaction with crust-derived silicic melts (Gudelius et al., 2019). Figure 9 shows that the isotopically heavy $\delta^{34}S$ signature of pentlandite in coarse peridotites is coupled with with elevated Pb concentrations, but not with similarly elevated abundances of other fluid-mobile elements, such as As and Sb, which may again point to a continental crustal contaminant carried by a melt rather than a fluid. Indeed, for sulfide- rather than sulfate-saturated sediment-derived melts, Sb will be depleted in the melt relative to As and Pb (Canil and Fellows, 2017), which corresponds to the systematics observed for sulfide in the coarse-grained peridotite (Fig. 9).

Fine-grained garnet-amphibole peridotite. Following the interpretation of Obata and Morten (1987), the fine-grained lithotypes record re-crystallization of the coarse-grained peridotites during downward movement into the deeper portion of the supra-subduction mantle. Compared to coarse-grained peridotites, the average sulfur isotope composition of matrix pentlandite from fine-grained peridotites is distinctly lower ($\delta^{34}S$= -0.11‰ ± 0.39; 1σ, n=15), with few grains within the DM value of $\delta^{34}S$ = -1.28 ± 0.33‰ (Labidi et al. 2013), as shown in Figure 7. Although the relationship between coarse- and fine-grained peridotites remains unclear, the latter clearly document interaction with crust-derived hydrous fluids based on elevated contents of fluid-mobile lithophile elements (Gudelius et al., 2019). This may be borne out by sulfide compositions, where contents of the fluid-mobile elements As and Sb, which are highly soluble in aqueous fluids (Jochum and Verma, 1996), are slightly more elevated in fine-grained than in coarse-grained peridotites (Fig. 9). In addition, Se and Te abundances are markedly higher in fine-grained peridotites, and, as strongly chalcophile elements (e.g., Barnes, 2016), might be expected to follow the sulfide anion. Thus, formation from reduced and slightly isotopically heavy (with respect to DM) reduced S species is inferred during this stage. At > 30km reduced S species carrying As(-1), Sb and Te may be sourced from the subducted slab and dissolved in hot aqueous fluids (Hattori and Guillot, 2007), where they dominate over oxidized species and are efficiently mobilized (Li et al., 2020).

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

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

The early stages of the Ulten Zone continental subduction were characterized by a continental crust possibly still attached to a mature oceanic slab (Ranalli et al. 2005). In this light, possible sources capable to furnish sulfur to the mantle wedge are subducted altered oceanic crust, overlying metasediments, metaserpentinites and enclosing gneisses. The low fO_2 recorded in the investigated UZ peridotites (Fig.2c) does not preclude that isotopically heavy sulfide with $\delta^{34}S$ up to +3.76 ‰ formed by reduction of oxidized S species under appropriate conditions. Oxidized S could derive from seawater-altered oceanic lithosphere, which records a large range of $\delta^{34}S$ values (-50 to +20 ‰) in seafloor hydrothermal sedimentary pyrite, but with a predominantly negative isotopic signature (Canfield & Farquhar, 2009). In contrast, sulfates in serpentinite and metabasic rocks from Syros, as analogs of subducted lithosphere, record dominantly heavier $\delta^{34}S$ of +15.7 to +20.8‰ and +3.5 to +20.1‰, respectively (Schwarzenbach et al., 2018a). In exhumed high-pressure rocks, metasomatic sulfides with a much larger range of $\delta^{34}S$ (-21.7 to +13.9‰) than in UZ peridotites were ascribed to the combined effects of isotope fractionations due to sulfate reduction and fluid evolution due to precipitation of isotopically light sulfide (Walters et al., 2019). Li et al. (2021) collate a comprehensive dataset of sulfides from worldwide HP-UHP metamorphic terranes. Combined with new data, they find a $\delta^{34}S$ signature of -33 to -6‰ in metasediments, $\delta^{34}S$ of -4 to +4‰ in metabasite/metagabbros, and $\delta^{34}S$ of +2 to +18‰ in HP serpentinites.

Given the mélange setting of Ulten Zone peridotites, the continental crust may also be a source of isotopically heavy S, either by direct formation from H_2S if the lighter value applies, or by sulfate reduction if the heavier value applies.

The availability of both S and Sr isotopic data in this study allow some constraints to be placed on the sources and amount of contaminant involved in the formation of sulfides and associated clinopyroxene or amphibole (Fig.10). The S isotopic composition of the garnet-kyanite gneisses of continental crust enclosing the UZ peridotites is unknown, but metapelites metamorphosed under amphibolite-facies conditions from the Kinzigite Formation of the Ivrea Zone ($\delta^{34}S$ values of +3.6‰ to +10.1‰; Fiorentini et al., 2018) may represent reasonable analogues that can be used to model mixing with the depleted mantle. This is because these metapelites are of a similar age and composition as the UZ gneisses, and, moreover, have S concentrations (600 ± 10 ppm, n=12; Bargossi et al., 2003) similar to those employed in the mixing model. Figure 10 shows the binary mixing between a depleted mantle (DM) reservoir with plausible slab-derived sources in a closed system (full dataset in Electronic Annex C). The sample scatter reflects the variability of the S and Sr concentrations and isotopic composition of melts/fluids and their evolution between leaving the source and their interaction with the Ulten Zone peridotites. Results show that <<10% of a continental crust component with $\delta^{34}S$ values +10.1‰ and 600ppm of S are required to explain the S-Sr isotopic composition of UZ fine-grained peridotite during Stage 2. Concentrations of several 100 ppm S may be expected for a crustal melt, and of several 1000 ppm S for a fluid equilibrated with crustal rock (Electronic Annex C). Conversely, in accordance with trace element composition and with the lack of carbonates, the outlier CGn peridotite SBA2 points to a liquid carrying isotopically heavy S, which percolated the mantle wedge in the Samerberg Area, and which can be explained by invoking a third S source derived from isotopically heavy, but less radiogenic serpentinite (Fig. 10). In this scenario, formation of isotopically heavy sulfide by reduction of sulfate, accompanied by isotopic fractionation of several ‰ at the estimated conditions of 850°C (cf., Ohmoto and Rye, 1979) is not required, nor is it precluded by the data.

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

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

On the basis of mineral assemblages and textural relationships, it is suggested that the pentlandite-hosting dolomite vein formed prior to serpentinization at T = 650°C-700°C and P = 1GPa (Consuma et al. 2020). Along this vein, enclosed pentlandite associated with millerite exhibits δ^{34}S = +1.13 ± 0.38‰, which is somewhat heavier than the values of pentlandite in kelyphite and interstitial to silicates. Furthermore, a distinct fluid source is otherwise required to explain the lower δ^{34}S of 0.68 ± 0.40‰ (n=3) for matrix pentlandite spatially close to the dolomite vein, found in peridotite sample 18LP1. The heterogeneity of the measured *in situ* Sr isotopes of this dolomite vein ($^{87}Sr/^{86}Sr$=0.7035-0.7085) was interpreted to reflect retrograde hybridized C-fluids channelized into the peridotites during exhumation, when the crust-peridotite mélange was already formed (Consuma et al. 2020). Coupled S and Sr isotopic ratios related to dolomite veining during early exhumation (in coarse peridotite 18LP1) and even more so in serpentinite + magnesite vein MOL1 -C suggest higher degrees of contamination from a continental crustal source (Fig.10). High Se and Te contents, together with intermediate to high Sb and As concentrations, suggest that this was a hydrous fluid carrying HS^- as the dominant S species.

6.6 Serpentinization and local effect of fluid-rock interactions on S content and isotope composition (Stage 4)

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

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

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

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

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

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

Nevertheless, the $\delta^{34}S$ (+0.46 ± 0.34‰) of pentlandite in PI is only moderately heavier than the suggested depleted mantle with $\delta^{34}S$ of -1.28 ± 0.33‰ (Labidi et al., 2013). The PI assemblages (see Section 3; Fig. 3b) may point to the involvement late, C-S-bearing saline, possibly seawater-derived agents, as previously suggested (Lo Pò et al., 2020). Indeed, saline, oxidizing, sulphate-bearing brines have been implicated in sulfide dissolution in subduction mélanges (Schwarzenbach et al., 2018a), corresponding to the tectonic setting where UZ peridotites were serpentinized. Experimental studies performed by Bataleva et al. (2018) reveal that interaction of olivine with sulfate and C-bearing brines may induce mantle sulfide and carbonate formation via the reaction olivine + anhydrite + C → diopside + S_0 + CO_2, followed by olivine sulfidation. If so, the relatively low $\delta^{34}S$ of PI sulfide requires a low-T origin when the isotopic fractionation would be largest. For examples, Walters et al. (2019) model fractionations of some 20‰ for pyrite precipitation from sulfate at 300 °C. Pentlandite in the PI has also moderate to high contents of the fluid-mobile elements Sb and As, but low Se and Te compared to other samples (Fig. 6). This may indicate limited addition of Se and Te by saline media where concentrations may be low due to limited availability of the HS^- ligand, with which chalcophile elements could complex.

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

To conclude, together with the possible involvement of oxidizing H_2S-poor saline fluids in the formation of PI, serpentinization appears to be associated with highly localized processes. These may involve sulfide dissolution in S-undersaturated oxidizing saline fluids, perhaps sourced from metasediments (Schwarzenbach et al., 2018a), sulfide precipitation when such fluids reach S saturation, and removal of isotopically light S in reducing hydrous fluids, such as those associated with dehydration of oceanic mantle (Piccoli et al., 2019).

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

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

(1) The Variscan lithospheric mantle was initially depleted and sulfide-poor, and subsequently inherited a sulfur component during an early stage, when hot, H_2S-bearing melts leaving a subduction-modified source invaded the overlying spinel-facies peridotite in the mantle wedge, leading to precipitation of sulfide-bearing pyroxenite with $\delta^{34}S_{pentlandite}$ of +2.77 ‰. A reported dolomite inclusion in coarse spinel indicates carbonate mobility at this early stage.

(2) Under peak eclogite-facies conditions, heterogeneous melt and fluid sources variably enriched in carbon, isotopically heavy sulfur and radiogenic Sr were involved: (i) the positive shifts of $\delta^{34}S$ (up to +3.43‰) from typical mantle values, and radiogenic $^{87}Sr/^{86}Sr_{clinopyroxene} > 0.7053$ suggest that, at high-pressure conditions, coarse-grained garnet peridotites interacted with ^{34}S- and Pb-enriched crustal melts prior to their becoming part of a crust-mantle mélange. Matrix carbonate is usually rare in the coarse peridotite. (ii) The hydrous fluids interacting with mantle rocks during recrystallization and deformation from coarse- to fine-grained peridotites added radiogenic Sr ($^{87}Sr/^{86}Sr_{amphibole} \sim 0.7061$, this study) and had a heterogeneous effect on the bulk S content (58 to 288 ppm S), as S was variably added or removed. The presence of dolomite with $^{87}Sr/^{86}Sr \sim 0.705$ (Consuma et al., 2020) suggests that carbon was also mobilized at this stage. Given Sr isotopic evidence for a crustal fluid source, the low $\delta^{34}S$ (-1.62 to +0.67‰) compared to the coarse peridotites is suggested to reflect involvement of a sulfide- rather than sulfate-bearing fluid. The observed S-

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

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

(4) Exhumation-related serpentinization in the crust-mantle mélange had a markedly heterogeneous effect on sulfur isotopes. Pentlandite grains enclosed in a serpentine + magnesite vein crosscutting the coarse-grained peridotite matrix, and texturally cut buy a late dolomite vein with $^{87}Sr/^{86}Sr$ 0.711 (Consuma et al. 2020), show a broad range of $\delta^{34}S$ between -0.29 and +3.76‰. Furthermore, the presence of magnetite as pseudomorphs after pentlandite indicates local desulfurization with inferred preferential loss of ^{32}S, whereas the S concentration of 300 ppm in a cm-sized vein of serpentine + magnetite ± millerite ± calcite crosscutting the fine spinel peridotite indicates sulfur pathways during late exhumation stages. The presence of pentlandite as part of polycrystalline inclusions in spinel associated with calcite + brucite intergrowths indicates that local desulfurization may have been coupled with dissolution of the associated dolomite and subsequent release of CO_2.

The recorded oxidation state of the studied peridotites likely precludes stabilization of sulfate, but is permissive of carbonate as opposed to graphite stability, as confirmed by petrographic observations. The close association of sulfides and carbonates at all stages of mantle wedge evolution indicates that peak metamorphic pervasive fluids and melts, and channelized fluids generated during late exhumation, may serve as pathways for coupled sulfur and carbon transport under the investigated conditions. This indicates that these volatiles should be considered together in a discussion of mantle wedge redox evolution. Despite evidence for long-lasting and polyphase metasomatic processes involving slab-derived C-O-H-S fluids and melts (Fig.11), the measured S isotope values of the UZ pentlandite display a narrow range ($\delta^{34}S = -1.62 \pm 0.42$‰ to $+3.76 \pm 0.36$‰), which suggests that reduction of sulfate (S^{6+}) to sulfide species (S^{2-}) had a limited role throughout the Ulten Zone peridotite metamorphic evolution. Importantly, this study provides petrographic and geochemical evidence in support of a dominantly reduced nature of slab-derived sulfurbearing subduction liquids in the orogenic mantle wedge under high-pressure conditions and during subsequent exhumation within the tectonic mélange, suggesting that S is not the dominant agent causing oxidation of the mantle wedge in this setting.

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Electronic Annexes A, B, C, D.

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Figure captions
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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_{CO2} =0.5; brucite (Brc) = periclase (Per) + water (H_2O) 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 Puhan (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 Cannaò 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^- (~FMQ and maximum FMQ<+0.2, respectively) and as $H_2SO_4^{2-}$ (~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_2 (wt%) as a function of Al_2O_3 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_2 contents at a given Al_2O_3 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^2 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 ($\delta^{34}S = -1.28 \pm 0.25‰$) and Labidi et al., (2014) ($\delta^{34}S = -1.40 \pm 0.50‰$). **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 $\delta^{34}S$ 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. $\delta^{34}S$ in pentlandite (this study) vs. $^{87}Sr/^{86}Sr$ 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 $\delta^{34}S$ signature may reflect percolation by reduced, H_2S-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 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.