MULTI-STAGE METASOMATISM IN A MANTLE-WEDGE AND EXHUMATION MÉLANGE: NEW INSIGHTS FROM THE PERIDOTITES OF THE ULTEN ZONE (EASTERN ALPS, ITALY)

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INTRODUCTION

Subduction zones in continental collisional settings are key loci where various petrogenetic processes, involving melts and fluids, promote fundamental mass exchange between the crustal portion of the subducting slab and the overhanging mantle portion, the mantle wedge. Fluids and melts released from the crustal portion can migrate into the mantle wedge and modify its chemical composition. Therefore, fluid- and melt-mediated metasomatism of mantle wedge plays a key role in mass transfer and element cycling between the Earth's reservoirs, and is of particular interest for geologists. Since the availability of orogenic mantle-wedge samples that experienced interaction with subducting crustal rocks and exhumation in a continental collisional setting is limited, the mantle wedge remains the least understood portion in the "subduction factory" (*e.g.*, Brueckner, 1998; Scambelluri *et al*., 2006). However, slices of the mantle wedge can be incorporated and reside in subducted crustal host rocks, and provide, when exposed at the surface, favorable conditions for studying the formation of the mantle and its evolution from the wedge to exhumation in the context of fluid- and/or melt-assisted interaction with subducted crustal material.

AIMS OF THE STUDY

The orogenic peridotites from the Ulten Zone (UZ) give insights into the mechanisms of crustal metasomatism at the slab-mantle interface from subduction to exhumation, and are therefore valuable samples for studying the element cycling from crust to mantle (and back) in a continental collisional setting. The aim of this PhD work was to shed more light on conditions and timing of individual melt-mediated and fluid-mediated metasomatic stages affecting the UZ peridotites during their evolution. In this context, it aimed to help unravel the origin of chemical heterogeneities in a subcontinental lithospheric mantle subjected to intense metasomatism by multiple agents, and to contribute to the understanding of the element mobility during crust-mantle interaction in an exhumation-related crust-mantle mélange.

GEOLOGICAL SETTING AND PETROLOGICAL BACKGROUND

The orogenic UZ is a pre-Alpine basement unit (*e.g.*, Martin *et al*., 1993) belonging to the Austroalpine system in the Italian Eastern Alps (Fig. 1a) and represents a fragment of the Late Paleozoic Variscan belt (Fig. 1b; Godard *et al*., 1996). It is composed of high-grade metamorphic basement rocks (garnet-kyanite paragneiss and migmatites + orthogneiss; *e.g.*, Obata & Morten, 1987; Godard *et al*., 1996; Del Moro *et al*., 1999) containing lenses (up to several hundred meters in length) of ultramafic rocks (peridotites ± pyroxenites; Fig. 1c). The peridotites display a variety of textures reflecting a transition from coarse-grained (up to few cm grain size) both garnet-bearing and garnet-free spinel peridotites to highly deformed fine-grained (0.2 mm to 1 mm grain size) garnet-amphibole peridotites and amphibole-chlorite peridotites (Obata & Morten, 1987). The wide range of petrographic characteristics has been interpreted to record the complex tectono-metamorphic history of the UZ peridotites in the course of continental subduction during the Variscan orogeny: *i*) primary coarse-grained spinel peridotites in a hot shallow supra-subduction zone mantle wedge were metasomatized due to interaction with upwelling subduction-related melts containing recycled crustal material (*e.g.*, Scambelluri *et al*., 2006); *ii*) the peridotites were brought closer to the slab-mantle interface due to corner flow, and experienced recrystallization into fine-grained garnet-amphibole peridotites due to interaction with COH-fluids derived from the crustal portion of the slab (Rampone & Morten, 2001; Scambelluri *et al*., 2006; Marocchi *et al*., 2007; Tumiati *et al*., 2007); *iii*) slices of the peridotites were incorporated into the subducted crustal rocks, and the crust-mantle mélange consisting of peridotites and crustal host rocks subsequently experienced exhumation starting at *ca.* 330 Ma (Tumiati *et al*., 2003, 2007). Since the UZ was only slightly overprinted by Alpine metamorphism, the UZ lithologies preserve pre-Alpine metamorphic signatures and assemblages (*e.g*., Godard *et al*., 1996).

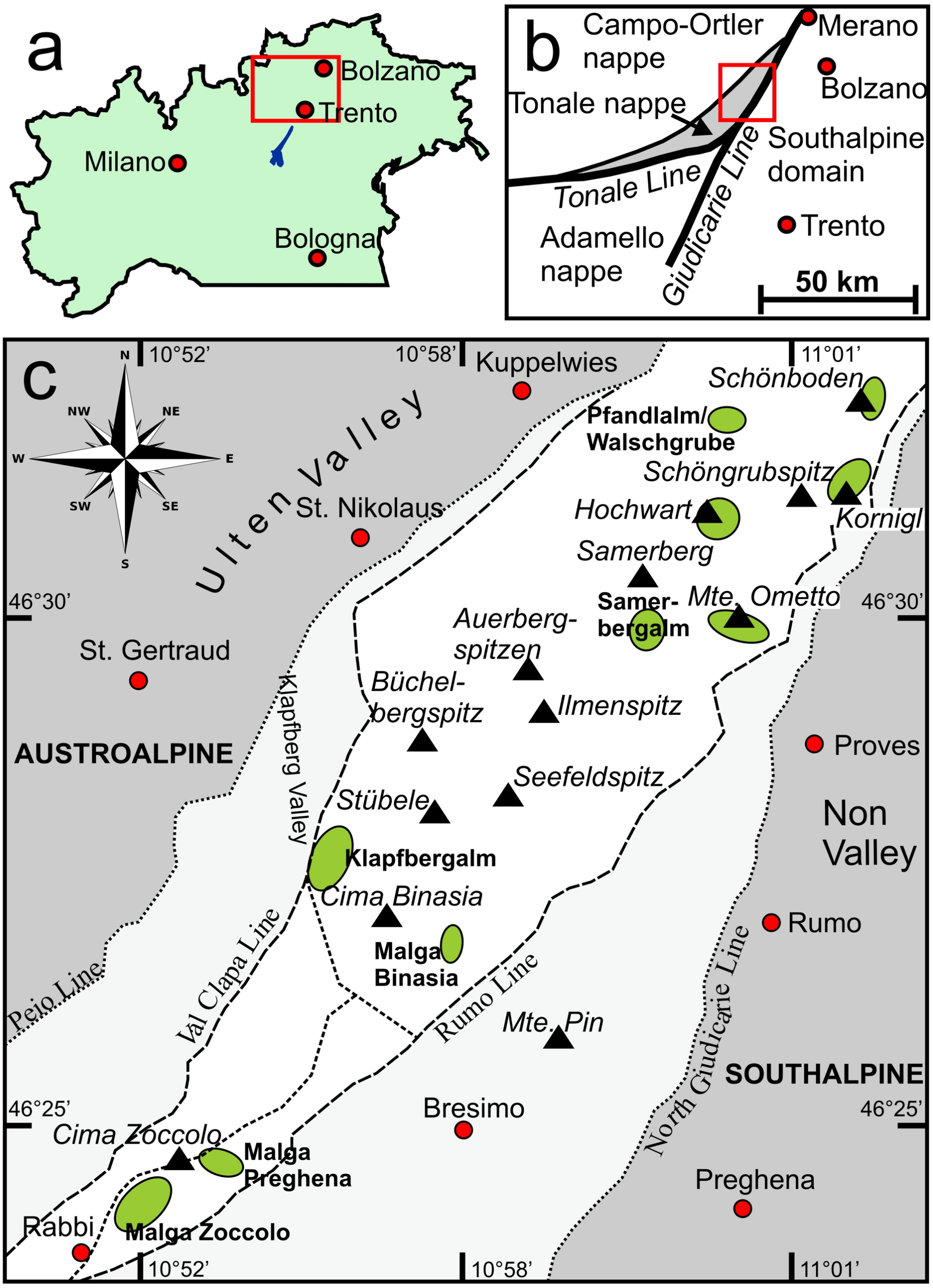

Fig. 1 - Map of the Ulten Zone (UZ). a) Location of the UZ in the Italian Eastern Alps in North Italy, as b) part of the Tonale nappe which is a fragment of the Paleozoic Variscan belt; c) White field encompasses the UZ located between the Val Clapa Line and the Rumo Line. Ellipses mark the locations of ultramafic bodies from which the majority of the peridotite samples was selected for this study.

SAMPLE MATERIAL AND METHODS

Sample material

More than 150 new hand specimens of ultramafic rocks (peridotites ± pyroxenites) from outcrops across the entire UZ were collected (Fig. 1c). The peridotite samples selected for this study were classified regarding their textural type (coarse-grained *vs*. fine-grained) and their mineral facies (spinel *vs*. garnet) according to the classification by Obata & Morten (1987). The sample set comprises coarse-grained spinel peridotites with protogranular-porphyroclastic texture (Fig. 2a), some of which containing coronitic garnet (Fig. 2b), fine-grained garnet-amphibole peridotites (Fig. 2c) as well as fine-grained garnet-free peridotites (Fig. 2d) with mylonitic granoblastic-porphyroclastic textures. All samples contain amphibole in variable amounts and display alteration in variable degrees, with the strongest alteration shown by some of the fine-grained peridotites by a dense mesh of crosscutting veins consisting of serpentine and opaque minerals (Fig. 2). Garnet in the fine-grained garnet-amphibole peridotites has variable sizes, may contain spinel and often has a kelyphitic corona (Fig. 2c). Some of the fine-grained garnet-free peridotites contain subrounded aggregates of amphibole ± chlorite ± spinel, which are presumably pseudomorphs after garnet.

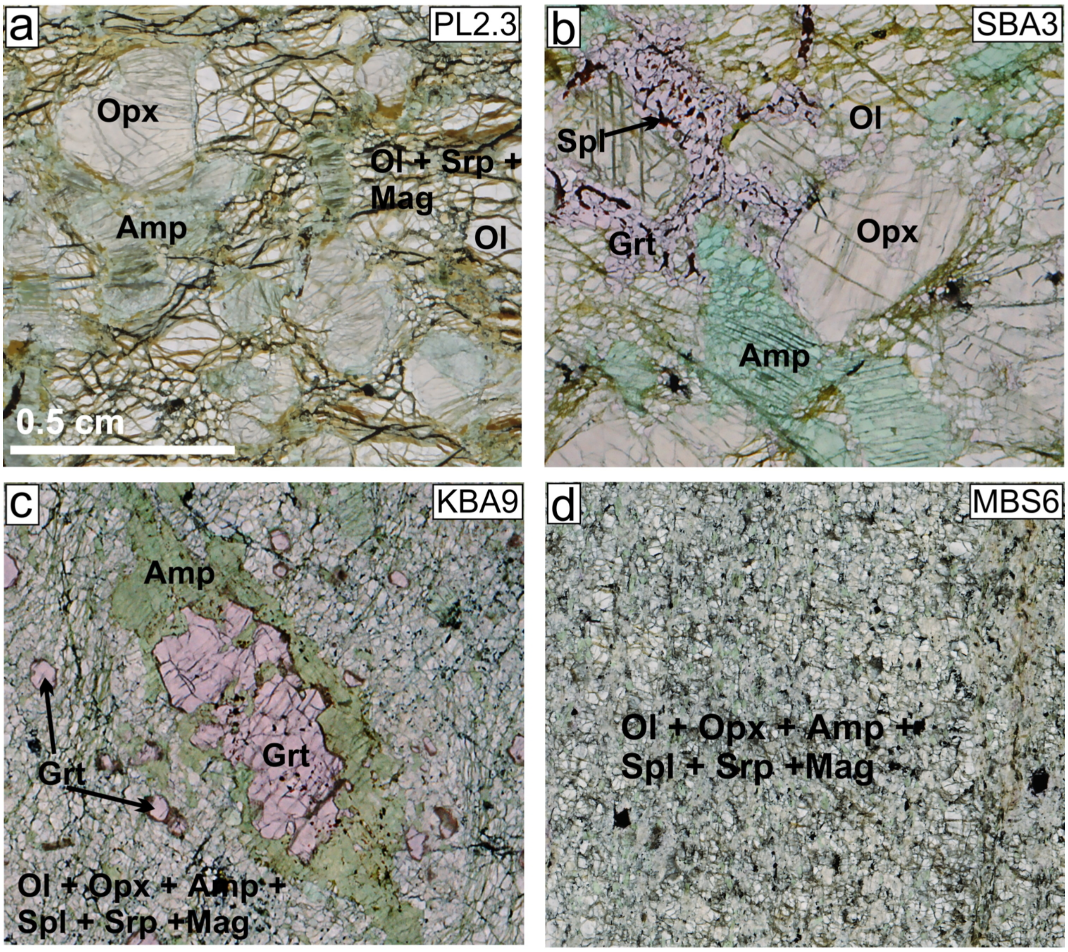

Fig. 2 - Details of thin-section scans of the UZ peridotites. a) Coarse-grained spl peridotite displaying the transition from a protogranular to a porphyroclastic texture; b) Coarse-grained peridotite showing a protogranular texture of partly fractured ol, opx and amp with anhedral coronitic grt rimming vermicular spl; c) Fine-grained grt-amp periodotites with a granoblastic-porphyroclastic texture; anhedral grt is often associated to amp; d) Fine-grained grt-free spl peridotite with an equigranular-granoblastic texture. Fine-grained peridotites display variable degrees of serpentinization, visible from the high abundance of opaque minerals which occur in serpentine veins. Kely: kelyphite, other mineral abbreviations after Whitney & Evans (2010).

Analytical methods

A comprehensive petrographic study focused on the characterization of different petrographic peridotite types and on the occurrence of carbonate phases in the UZ peridotites.

Whole-rock major- and trace elements were analyzed by ICP-MS (inductively-coupled plasma mass spectrometry) and the concentrations of oxidized and reduced carbon in the UZ peridotites were analyzed by means of multiphase carbon determination with infrared spectrometry.

Analyses of the total elemental carbon concentration and whole-rock carbon-isotope composition in UZ peridotites were carried out using EA-CF-IRMS (elemental analysis continuous flow isotope ratio mass spectrometry).

A multi-isotope study on whole-rocks provided the first combined analysis of the radiogenic isotopes Nd, Sr, Hf and Pb in UZ peridotites, performed by ICP-MS after chemical extraction of the elements by multi-step column chromatography.

The occurrence of metasomatic accessory minerals (zircon and carbonates) allowed *in-situ* geochemical and geochronological analyses of zircon by means of LA-ICP-MS (Laser ablation ICP-MS) as well as analyses of the stable-isotope composition (carbon and oxygen) of carbonates, using magnetic sector IRMS after dissolution of carbonates in phosphoric acid.

RESULTS AND DISCUSSION

Whole-rock elemental and isotopic compositions constrain the evolution of orogenic mantle from wedge to exhumation

While all UZ peridotites have variable HREE compositions < DM, indicating variable degrees of partial melting, the compositional trends displayed by whole-rock major elements record refertilization in addition to a former partial melting event. Fine-grained peridotites are enriched in the most incompatible trace elements relatively to the coarse-grained peridotites, implying ingress of crust-derived aqueous fluid(s) enriched in these elements, during interaction of the wedge-derived peridotites with the crustal slab.

The protoliths of the UZ peridotites may have experienced melt depletion during the assembly of the supercontinent Rodinia in the Proterozoic, which is inferred from Hf and Nd T_{CHUR} model ages of > 1 Ga, obtained from peridotites with depleted major-element compositions and with depleted Hf- and Nd-isotope compositions.

A Sm-Nd isochron age of 409 ± 38 Ma may constrain the timing of isotopic re-equilibration after the Proterozoic partial melting event at the time of the onset of the Variscan orogeny, as the result of interaction of the hot mantle wedge with subduction-related metasomatic liquids. Although some of the coarse-grained peridotites retain largely undisturbed isotopic compositions, the generally highly variable isotopic compositions displayed by the UZ peridotites imply multi-stage disturbance of the radiogenic isotope systems: fine-grained hydrated peridotites show relatively low Hf and Nd isotopic ratios (Fig. 3) testifying to the fluid-mediated addition of unradiogenic Hf and Nd by interaction with crust-derived fluids enriched in the most incompatible trace elements (such as LREE and LILE), and resulting in decoupling of the Lu-Hf and Sm-Nd isotopic systems. While some coarse-grained samples have unradiogenic Nd compositions but retain depleted Hf compositions, other coarse-grained samples show both depleted Hf and Nd compositions. Accordingly, addition of radiogenic Sr in the majority of the UZ peridotites is attributed to crustal input due to the crust-mantle coupling (Fig. 3). Coupled behavior of Sr and Hf (Fig. 3b) indicates coupled addition of radiogenic Sr and unradiogenic Hf during retrogression, indicating that subduction-related crustal fluids marked by radiogenic Sr compositions are capable of mobilizing HFSE. All UZ peridotites display radiogenic Pb isotopic compositions with a signature of mixed recycled crustal components in the mantle source.

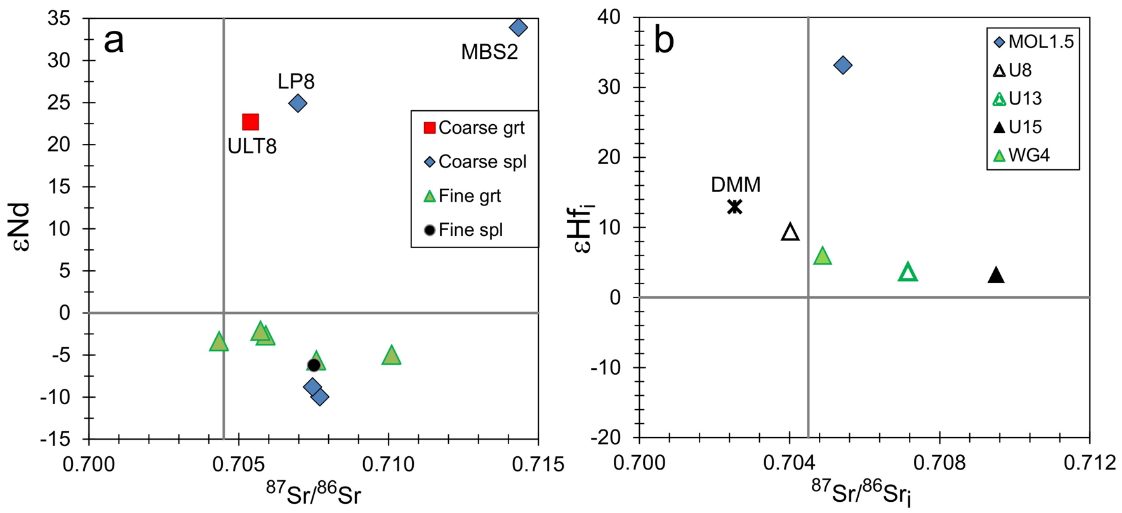

Fig. 3 - Covariation plots of whole-rock isotope compositions. a) εNd *vs.* $^{87}Sr/^{86}Sr$ and b) εHf_i *vs.* $^{87}Sr/^{86}Sr_i$. Sample MOL1.5 is a coarse-grained spinel peridotite, the samples marked with triangles are fine-grained garnet-amphibole peridotites. DMM composition from Workman & Hart (2005). The initial composition of DMM was back-calculated at 330 Ma, the time of the main event of crustal metasomatism suggested by Tumiati *et al.* (2003).

Zircon geochronology and geochemistry provide insights into metasomatic processes in a crust-mantle mélange

The study of U-Pb geochronology and trace element characteristics of zircon in peridotites and crust-peridotite contact rocks reveals valuable information on the timing and conditions of fluid-peridotite interactions during the retrograde evolution of the UZ crust-mantle mélange. The occurrence of zircon together with elevated whole-rock HFSE concentrations (inclusive average whole-rock Zr concentrations) in fine-grained (garnet-) amphibole-bearing peridotites relative to the coarse-grained peridotites clearly indicate zircon formation induced by addition of Zr during crustal metasomatism, and imply that crust-derived aqueous fluids were able to mobilize HFSE.

Zircons in fine-grained garnet-amphibole peridotite and in a phlogopite-rich rock from the peridotite-crust contact zone yield an age of *ca.* 333 Ma, which reflects the time of formation of the crust-mantle contact zones at low-T (and P) conditions prevailing during late-stage exhumation. At this stage, the peridotites were incorporated in the crustal host rocks and were subjected to crustal metasomatism by aqueous fluids liberated after leucosome crystallization at low pressures and temperatures (*ca.* 600-700°C, from Ti-in-zircon thermometry). These fluids were able to transport HFSE from the crustal rocks to the peridotites, and interaction with HFSE-enriched fluids at this stage may also account for the elevated HFSE concentrations in fine-grained hydrated peridotites relatively to coarse-grained peridotites which could largely escape hydration.

Younger rims on zircon display a Triassic age of 236 ± 8.0 Ma, testifying to resetting of the U-Pb system, possibly due to fluid-rock interaction during late serpentinization accompanying post-Variscan exhumation stages.

Carbonates in peridotites, combined carbon concentrations, and stable-isotope geochemistry give insights into the carbon cycle during crust-mantle interaction

The UZ peridotites contain different carbonate minerals (dolomite, magnesite, calcite) in various textural sites (Fig. 4; Förster *et al.*, 2017). The occurrence of different carbonate phases can be linked to individual stages in the peridotite evolution, indicating multi-stage carbonation and exhumation-related dolomite breakdown (Förster *et al.*, 2017):

An early generation of dolomite, formed in the high-temperature spinel-stability field in the mantle, is evidenced by dolomite inclusions in primary spinel surrounded by garnet (Fig. 4a). The liquids responsible for the formation of these dolomite inclusions could be mafic carbonated melts produced in deeper parts of the subduction zone.

Dolomite is the major carbonate phase in little-serpentinized fine-grained garnet-amphibole peridotites (Fig. 4b) and formed simultaneously with amphibole and apatite from crust-derived COH-fluids (a H_2O-CO_2-mixed aqueous fluid) released from the crustal portion of the subducting continental slab. The euhedral discrete dolomite grains are often associated with (and occasionally included in) garnet, amphibole, apatite and olivine (Fig. 4b). This indicates that crust-derived aqueous fluids can transport carbon from the slab to the associated mantle portion. However, the efficiency of such fluids to carry crust-derived carbon deeper inside the mantle wedge remains unconstrained.

Serpentinized fine-grained garnet-amphibole peridotites contain intergrowths of calcite and brucite (Fig. 4c), that form as products of serpentinization-induced dedolomitization according to the chemical reaction $CaMg(CO_3)_2 + H_2O \rightarrow CaCO_3 + Mg(OH)_2 + CO_2$. The fate of the dissolved carbon species released into the migrating serpentinizing fluid remains matter of debate, however, it may have precipitated carbonates in veins and veinlets at appropriate P-T-X conditions, as observed ubiquitously in both fine-grained garnet-free and garnet-bearing peridotites, as well as in coarse-grained garnet-free peridotites. However, ongoing ingress of crustal carbon-bearing fluids, likely during exhumation of the peridotites, is documented by the local occurrence of magnesite and calcite in veins crosscutting the peridotite matrix and of retrograde magnesite (Fig. 4d).

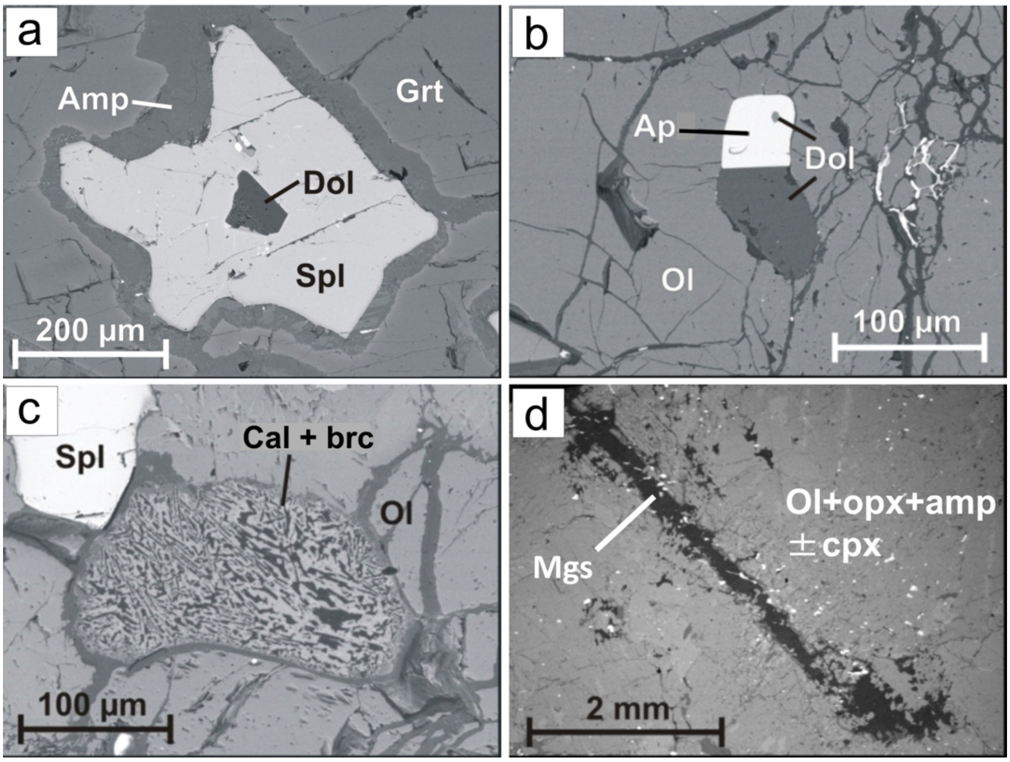

Fig. 4 - Back-scattered electron images of sections of (a-c) fine-grained garnet-amphibole peridotites showing: a) an inclusion of euhedral dolomite in spinel surrounded by garnet; b) a discrete dolomite grain in the matrix of little-serpentinized peridotite associated with apatite, and a dolomite inclusion in apatite; c) an intergrowth of calcite and brucite located with the serpentine mesh texture in serpentinized peridotite; d) a distinct magnesite vein with frayed grain boundaries associated with serpentine crosscutting the matrix of coarse-grained peridotite.

In addition to carbon in carbonates (concentration of oxidized carbon from 0.0014 to 0.1810 wt.%), all UZ peridotites contain reduced carbon (0.0164 to 0.1240 wt.%) and the whole-rock total carbon concentration ranges from 0.0130 to 0.2800 wt.% (Fig. 5a). The generally light carbon isotopic composition in whole rocks

(Fig. 5a) suggests that the carbon was sourced in the crustal host rocks, implying the capability of mantle wedge-derived rocks to store crust-derived carbon.

During tectonic uplift and exhumation in the crust-peridotite mélange to crustal levels, some portions of peridotites possibly interacted with fluids sourced from different adjacent lithologies residing at crustal levels. This is mirrored by highly variable stable-isotope compositions of carbonates (Fig. 5b), which distinguish the UZ in a northeastern (NE) domain with more negative $\delta^{13}C$ (from -16.8‰ to -5.7‰) and a southwestern (SW) domain with carbonates displaying less negative $\delta^{13}C$ (from -11.1‰ to -0.03‰), indicating that the fluids carried different carbon-isotope signatures. Importantly, retrograde magnesite is observed in peridotites from the NE domain only, which also contain higher carbon concentrations (up to 0.181 wt.% oxidized carbon) than peridotites from the SW domain. However, the release of a carbon species due to dedolomitization testifies to decarbonation at the serpentinization stage during exhumation and shows that carbon, which was once transported to deeper levels in the subduction zone, can be ultimately brought back to crustal levels. This suggests that subduction zones in continental collisional settings are not only responsible for carbon transport to mantle depths and for carbon introduction into the mantle, but contribute also to the return of carbon from mantle depths to the crust.

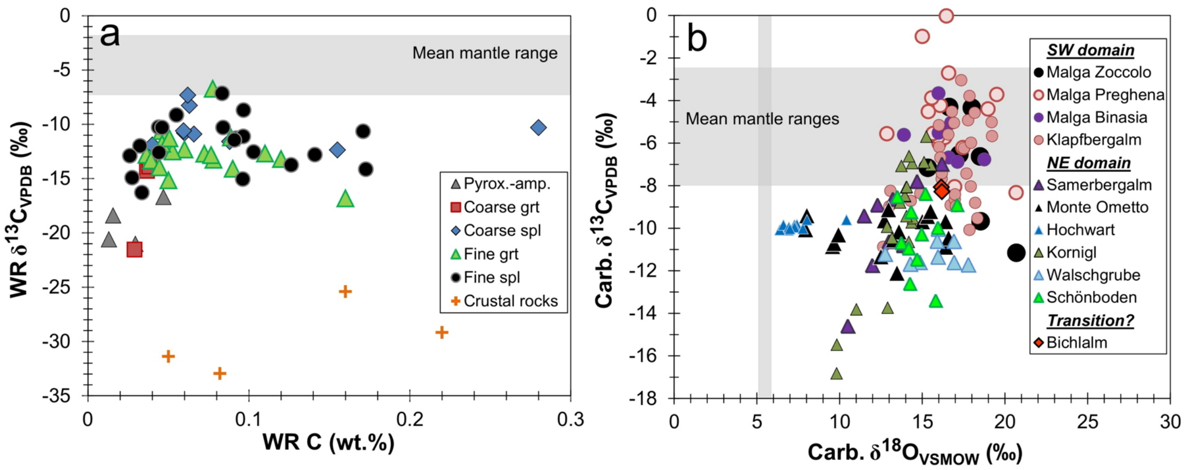

Fig. 5 - a) $\delta^{13}C$ and the total carbon concentration in whole rocks (WR) classified by the petrographic type of peridotite regarding the texture (coarse-grained *vs.* fine-grained) and facies (garnet (grt) *vs.* spinel (spl)). Pyroxenitic amphibolized samples are not classified as peridotites and are shown separately (pyrox.-amp.). The total carbon concentration and the carbon isotopic composition of the UZ peridotites are largely independent on the petrographic type. UZ crustal rocks (gneisses and migmatites) are shown for comparison. b) $\delta^{13}C$ and $\delta^{18}O$ for carbonates in UZ peridotites grouped according to the peridotite sample locality in the UZ. See text for explanation. Mean mantle ranges for $\delta^{13}C$ from -8‰ to -2.5‰ (Shirey *et al.*, 2013) and for $\delta^{18}O$ ca. +5.5‰ ±0.4‰ (Mattey *et al.*, 1994).

CONCLUSIONS

The results of this integrated study obtained by petrographic, elemental and isotopic analyses, provide new insights into the multi-stage evolution of the UZ peridotites, including melt-mediated and fluid-mediated metasomatic processes, and ultimately contribute to the understanding of the geodynamics and mass transfer in a continental collisional setting. The main findings can be summarized as follows.

i) During their evolution from the mantle wedge to exhumation, the UZ peridotites experienced multiple depletion and refertilization events. Crust-mantle coupling occurred on the retrograde exhumation path of peridotites and UZ crustal rocks at *ca*. 333 Ma. The interaction of peridotites with crustal slab-derived aqueous fluids capable of mobilizing HFSE is reflected by the formation of zircon and the decoupling of radiogenic isotope systems.

ii) The UZ peridotites were subjected to interaction with multiple carbon-bearing fluids, mirrored by the occurrence of different carbonate phases in various textural sites and highly variable carbon-isotope compositions. The occurrence of carbonates and variable carbon concentrations in UZ peridotites show that carbon can be transported from crustal rocks to mantle depths in continental settings, and that mantle-wedge peridotites can act as carbon traps.

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