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Crustal fluids cause strong Lu-Hf fractionation and Li-Nd-Hf isotopic provinciality in the mantle of continental subduction zones

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ABSTRACT

Metasomatized peridotites exhumed within high-pressure terranes of continental collision zones provide unique insights into crust-mantle interaction and attendant mass-transfer, which are critical to our understanding of terrestrial element cycles. Peridotites embedded in high-grade gneisses of the Ulten Zone (Alps) record metasomatism by crustal fluids at 330 Ma and high pressure conditions (2.0 GPa, 850 °C), causing a transition from coarse-grained, garnet-bearing to fine-grained, amphibole-rich rocks. Here, we explore the effects of crustal fluids on canonically robust Lu-Hf peridotite isotope signatures in comparison with fluid-sensitive trace elements and Nd-Li isotopes. Notably, a Lu-Hf pseudo-isochron is created by a decrease in bulk-rock $^{176}\text{Lu}/^{177}\text{Hf}$ from coarse- to fine-grained peridotite demonstrably caused by HREE-loss during fluid-assisted garnet-consuming, amphibole-forming reactions, accompanied by textural changes, enrichment in fluid-mobile elements and addition of unradiogenic Nd. Thus, fluid activity can strongly alter Lu-Hf systematics of the mantle, thereby masking older crystallization ages. Despite close spatial relationships, some peridotite lenses record more intense fluid activity causing complete garnet breakdown and HFSE addition along with addition of crust-derived unradiogenic Hf, as well as distinct chromatographic LREE fractionation. We suggest that the observed geochemical and isotopic provinciality between peridotite lenses reflects different positions relative to the crustal fluid source at depth. This

interpretation is supported by Li isotopes: inferred proximal peridotites show light $\delta^7\text{Li}$ for due to strong kinetic Li isotope fractionation (2.1 to -4.7 ‰) accompanying Li enrichment, whereas distal peridotites have depleted mantle-like values.

Introduction

Earth's mantle is characterized by geochemical and isotopic heterogeneity at all scales, which reflects interaction between crustal and mantle reservoirs, mediated by subduction of compositionally diverse lithologies (e.g., Stracke, 2012). During plate convergence, the supra-subduction zone mantle becomes a repository for material that is released from the down-going plate and thereby an important archive of crust-mantle interaction and element cycles (e.g. Bodinier & Godard, 2014). Inferences about the quantity and nature of element exchange often rely on indirect methods like trace element and isotopic signatures in arc magmas (Bebout, 2013; Spandler & Pirard, 2013). However, in collision zones, continental crust can be pulled down into the mantle by oceanic slabs, detached at depth and exhumed back towards the surface, sometimes carrying tectonically trapped samples of mantle wedge peridotite (Brueckner & Medaris, 2000). This rare type of orogenic peridotite is critical for the understanding of deep-seated subduction zone processes, such as reaction of crust-derived fluids and melts with supra-subduction mantle or exhumation mechanisms (Bodinier & Godard, 2014). Radiogenic isotopes can be used as tracers and, if undisturbed, geochronometers that can help to elucidate the origin and evolution of the supra-subduction zone mantle. In contrast to Sm-Nd, the Lu-Hf system is considered relatively robust against fluid-related metasomatic overprint (e.g., Liu *et al.*, 2020), but despite sporadic reports of HFSE mobility (Woodhead *et al.*, 2001), the extent to which subduction-related fluids are capable of transporting Hf and altering the Lu-Hf isotope systematics of mantle rocks remains poorly known.

Orogenic peridotites of the Ulten Zone (N Italy) of this type are particularly interesting, as they exhibit a coupled textural and chemical transition upon variable exposure to crust-derived aqueous fluids during a HP stage within a Variscan subduction cycle (Figs. 1b, c, Fig. 2). Here, coarse-grained garnet peridotites originally derived from the hot and shallow mantle wedge were gradually transformed into fine-grained garnet-amphibole-peridotites and -pyroxenites. Amphibole-forming, garnet-consuming reactions eventually produced fine-grained spinel-amphibole peridotites without garnet (Rampone & Morten, 2001; Gudelius *et al.*, 2019). The transition from coarse- to fine-grained textures is marked by

increasing contents of fluid-mobile elements (e.g. Sr, Pb, K, LREE) accompanied by a bulk-rock decrease in HREE and Al due to garnet destabilization. Furthermore, a strong provinciality of metasomatic effects is evident: compared to Samerberg locality, samples from Seefeld and Malga Masa Murada localities (summarized as Seefeld/M) systematically display more metasomatized textures and compositions, characterized by distinctly HFSE-enriched amphibole and bulk rocks (Gudelius *et al.*, 2019).

In this study, we present the first Lu-Hf dataset for the Ulten Zone peridotites with the aim to explore how metasomatic crust-derived fluids affect mantle Lu-Hf signatures. Along with textural constraints, we monitor the crustal imprint by using fluid-sensitive trace elements as well as new Nd, O and Li isotope data. These data not only demonstrate that fluid-assisted garnet break-down can produce a Lu-Hf pseudo-isochron but also show that the geochemical provinciality reported in Gudelius *et al.* (2019) extends to multiple radiogenic and stable isotope compositions. This highlights the need to investigate multiple peridotite bodies in a given orogenic setting to gauge the full extent and variability of crust-mantle interactions in convergent margins. Bulk-rock Lu-Hf, Sm-Nd and Li isotope compositions were obtained by multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) after wet chemical separation (see analytical methods and data tables in GSA Data Repository).

Fluid-assisted Lu-Hf fractionation of garnet peridotites

All investigated samples form an array in the Lu-Hf isochron diagram, where Hf isotope compositions become successively more unradiogenic from coarse- to fine-grained peridotites, excluding only one highly radiogenic, possibly more ancient peridotite (Fig. 3a). Calculated to the age of HP metasomatism by crustal fluids (330 Ma; Tumiati *et al.*, 2003), peridotites essentially display a decrease in $^{176}\text{Lu}/^{177}\text{Hf}$ at constant $^{176}\text{Hf}/^{177}\text{Hf}$ concomitant with transition from coarse- to fine-grained textures. Only the least-metasomatized coarse-grained sample has retained initial $^{176}\text{Lu}/^{177}\text{Hf}$ which is higher than the average depleted mantle value. Together with their similarly high $^{147}\text{Sm}/^{144}\text{Nd}$, this agrees with previous studies suggesting that the Ulten peridotites experienced partial melting before 330 Ma (Scambelluri *et al.*, 2006; Ionov *et al.*, 2017).

The decrease in $^{176}\text{Lu}/^{177}\text{Hf}$ coincides with gradual Lu removal from peridotites along with a shift in modal mineralogy consistent with destabilization of HREE-rich garnet during fluid-assisted garnet-consuming, amphibole-forming reactions, with high initial partial

pressures of H₂O during the HP stage (Rampone & Morten, 2001; Gudelius *et al.*, 2019). As newly formed amphibole did not fully accommodate HREE formerly stored in garnet, HREE were possibly scavenged by aqueous fluids via complexation with ligands such as Cl⁻, F⁻ or OH⁻ (Zack & John, 2007; Tropper *et al.*, 2013; Lo Pò *et al.*, 2020) causing net loss of Lu from bulk rocks. The anti-correlation of ¹⁷⁶Lu/¹⁷⁷Hf with fluid-sensitive trace elements (e.g. Sr/Y in Fig. 4c) as well as with increasing input of unradiogenic, i.e. crust-derived Nd (Figs. 3b, 4d) indicates that the amount of Lu removed is controlled by the intensity of metasomatism (i.e. fluid/rock ratio) by crust-derived, LILE-enriched fluids. In Ulten Zone peridotites, this caused significant Lu/Hf fractionation and a striking time-integrated shift in ¹⁷⁶Hf/¹⁷⁷Hf, from initially DM-like to significantly less radiogenic values. Thus, some ¹⁷⁶Hf/¹⁷⁷Hf variability seen in orogenic peridotites but also arc magmas might relate to single- or multi-stage fluid activity close to subducting slabs.

Coupled vs. decoupled Hf-Nd isotope enrichment

Metasomatism by aqueous fluids did not only alter parent/daughter ratios but also Hf and Nd isotope compositions of the investigated orogenic peridotites. While weakly metasomatized lenses (Samerberg), have retained common depleted mantle ¹⁷⁶Hf/¹⁷⁷Hf during metasomatism at 330 Ma, more metasomatized peridotite lenses (Seefeld/M) form a parallel trend distinctly offset to more unradiogenic values by about 12 ε_{Hf} units. This enrichment is accompanied by generally higher contents of Hf and other HFSE (Fig. 4 e,f). Assuming that all Ulten peridotites originate from a compositionally similar mantle protolith (Ionov *et al.*, 2017), this suggests metasomatic addition of Hf with unradiogenic ¹⁷⁶Hf/¹⁷⁷Hf by aqueous fluids derived from a crustal source. This is direct evidence for effective Hf transport by crust-derived fluids in subduction zone settings, supporting previous indications derived from arc lavas (Woodhead *et al.*, 2001). Though commonly considered fluid-immobile (Kessel *et al.*, 2005), mobilization of HFSE can be facilitated by formation of alkali-HFSE-silicate complexes in fluids with high Na/Al, at high temperatures and pressures (e.g. Wilke *et al.* (2012)) as well as by fluids with high F⁻ and Cl⁻ contents (Tanis *et al.*, 2016). All of these effects likely hold true for metasomatic fluids at Ulten, as suggested by Cl-bearing polymineralic inclusion assemblages in peridotite minerals (Lo Pò *et al.*, 2020). Addition of Hf caused further decrease in ¹⁷⁶Lu/¹⁷⁷Hf at 330 Ma along with Lu removal due to garnet breakdown. Eventually, garnet-consuming, amphibole-forming reactions and HFSE-addition resulted in strongly enriched samples with no or only few garnet remnants and abundant

HFSE-rich amphibole (Gudelius *et al.*, 2019). In combination, highly metasomatized samples experienced metasomatic addition of both unradiogenic Hf and Nd and form a closely scattered group on the mantle array in the ϵHf_i vs. ϵNd_i diagram (Fig. 3c). This supports the notion that this linear array reflects coupled behavior of Lu-Hf and Sm-Nd systems, however not only during magmatic processes or bulk mixing between depleted mantle and crustal components (Blichert-Toft & Albarède, 1997; Guarnieri *et al.*, 2012; Xiong *et al.*, 2014) but also during intense metasomatism by crustal fluids.

In contrast, peridotites from weakly metasomatized lenses (Samerberg) display distinctly decoupled Hf and Nd isotopes. Only the least-metasomatized coarse-grained peridotite lies on the mantle array on a radiogenic, MORB-like position, demonstrating that it remained largely undisturbed during crustal metasomatism (Tumiati *et al.*, 2003). All other samples deviate from the mantle array, as previously observed for other orogenic peridotites, such as Lherz (Le Roux *et al.*, 2009), Shenglikou (N Qaidam) (Xiong *et al.*, 2014; 2015) or Lanzo (Guarnieri *et al.*, 2012). Our study shows that such patterns can be generated during fluid-related addition of Nd from an unradiogenic crustal source while retaining relatively pristine Hf.

Isotopic provinciality of the mantle near continental slabs

The observed metasomatic effects of crust-derived aqueous fluids on Lu-Hf isotopes are highly different despite the investigated peridotite lenses display close present spatial relationships within the Ulten Zone. This might reflect entrapment of mantle wedge domains originally having a different proximity to the crustal fluid source or the slab-mantle interface (Bebout, 2013). In this concept, more proximal peridotites (Seefeld/M) were strongly metasomatized (high fluid/rock) accompanied by growth of abundant HFSE-rich amphibole, while distal peridotites (Samerberg) were weakly metasomatized (low fluid/rock) by residual Hf-poor fluids only causing Lu/Hf decrease due to garnet breakdown. A different proximity to the fluid source is also indicated by distinct LREE patterns consistent with chromatographic fractionation, causing steep LREE_N ($\text{La}_N/\text{Ce}_N > 1.5$) for distal and flat LREE_N ($\text{La}_N/\text{Ce}_N \sim 1.0$) for proximal peridotites (Ionov *et al.* (2017) and references therein).

Notably, proximal peridotites (Seefeld/M) not only display distinct Hf and Nd isotope compositions, but also characteristic Li isotope fractionation marked by lower $\delta^7\text{Li}$ values and generally higher Li contents compared to distal peridotites which are similar to average DM. Similar patterns were previously reported for other orogenic peridotites (e.g. Horoman: Lai *et al.* (2015)) and are possibly caused by metasomatic input rather than scavenging of Li by

dehydration fluids (Marschall & Tang, 2020). The observed $\delta^7\text{Li}$ pattern can be explained by fast Li diffusion and attendant kinetic isotope fractionation. Lithium is highly fluid-mobile and fast-diffusing in most mantle minerals, so infiltration of a Li-rich fluid into peridotite should generate a chemical potential gradient driving diffusion of Li from the fluid into the constituting minerals of the host peridotite (Aulbach & Rudnick, 2009; Marschall & Tang, 2020). During such metasomatism, low $\delta^7\text{Li}$ values can be temporarily generated due to the higher diffusivity of ^6Li compared to ^7Li in peridotite minerals (Aulbach & Rudnick, 2009; Marschall & Tang, 2020). This imprint is preserved if the Li influx is short-lived and/or the chemical gradient disappears before full isotopic equilibration. With regard to the Ulten Zone, this provides strong support of our model calling for different fluid/rock regimes to account for the striking Lu-Hf and Sm-Nd isotopic provinciality, which can be also resolved using highly fluid-sensitive Li isotope signatures.

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Fig. 1 (a) (a) Simplified geological map of the Ulten Zone with sampling locations Seefeld, Samerberg and Malga Masa Murada. (b) P-T evolution of the Ulten Zone peridotites, characterized by (1) hot and shallow mantle wedge conditions (spinel stability field), (2) HP metasomatism by crust-derived aqueous fluids in the garnet stability field, followed by (3) exhumation. Green dashed lines indicate estimates for the P-T-evolution of the Ulten Zone crust (modified from Gudelius *et al.* (2019) and references therein). Mineral abbreviations: grt = garnet, spl = spinel, dol = dolomite, hbl = hornblende, mgs = magnesite, sil = sillimanite, ky = kyanite.

Fig. 2 (a-c) Representative photomicrographs (top) and BSE images (base) illustrating the main textural transformation of the Ulten Zone peridotites from (a) coarse-grained garnet peridotites (note absence of kelyphite) to (b) fine-grained garnet-amphibole peridotite with kelyphitic garnet to (c) fine-grained spinel-amphibole peridotites. Modal metasomatism during the HP stage (stage 2 in Fig. 1b) by crust-derived fluids caused garnet-consuming/ amphibole-forming reactions ($\text{Grt} + \text{Cpx} + \text{Opx} + \text{H}_2\text{O} \rightarrow \text{Amp} + \text{Ol}$) along with enrichment in fluid-mobile elements (Rampone & Morten, 2001; Gudelius *et al.*, 2019), as qualitatively indicated with fading colored bars at the bottom. Mineral abbreviations as in Fig. 1.

Fig. 3 (a) Lu-Hf isochron diagram illustrating gradual decrease in $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ during transition from coarse- to fine-grained peridotites. Note correlation parallel to 330 Ma (age of fluid-related metasomatism: Tumati *et al.*, 2003) and more unradiogenic trend for Seefeld/M locality caused by Lu loss due to garnet destabilization and metasomatic Hf addition. The more radiogenic outlier likely reflects a more ancient mantle domain. (b) Sm-Nd isotopes record decrease in $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ from coarse- to fine-grained peridotites reflecting addition of crustal Nd (Ulten Crust: Tumati *et al.* (2003) and references therein). (c) Hf and Nd isotope ratios at 330 Ma (expressed as δHf and δNd , i.e. the per 10,000 deviation from chondrite after Bouvier *et al.*, 2008). Note decoupling due to differential efficiency of fluids to transport Hf vs. Nd (Samerberg). N Qaidam: Xiong *et al.* (2014; 2015); Lanzo: Guarnieri *et al.* (2012); Lherz: Le Roux *et al.* (2009). For calculation, $\lambda^{176}\text{Lu}$ and $\lambda^{147}\text{Sm}$ values were taken from Söderlund *et al.* (2004) and Villa *et al.* (2020), respectively. Error bars are twofold standard errors (within-run).

Fig. 4 Effects of metasomatism by crustal fluids on Lu-Hf systematics of peridotites, causing (a-b) fluid-assisted Lu/Hf fractionation and (c-h) a distinct Hf isotopic provinciality. (a) Gradual

decrease in $^{176}\text{Lu}/^{177}\text{Hf}$ at the transition from coarse- to fine-grained peridotite is caused exclusively by Lu loss due to garnet-consuming, amphibole-forming reactions (Rampone & Morten, 2001; Gudelius *et al.*, 2019) or by additional Hf addition (Seefeld/M). This consistent with a shift in modal mineralogy (b) and accompanied by a gradual crustal imprint as indicated by successive LILE-enrichment and addition of unradiogenic Nd from a crustal source (c, d). In contrast to Samerberg, peridotites from Seefeld/M locality record addition of unradiogenic (crustal) Hf (e) and other HFSE (f) and also display distinct LREE fractionation patterns and low $\delta^7\text{Li}$ indicative for chromatographic effects at a closer proximity to the fluid source (g, h). The provinciality of metasomatic effects on Lu/Hf isotope systematics is suggested to be a function of the crust-mantle distance in continental subduction zones. Trace element data of Gudelius *et al.* (2019); DM values of Blichert-Toft & Puchtel (2010), Workman & Hart (2005), and Tang *et al.* (2007).

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