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

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

3
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14
15 **ABSTRACT**

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

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

36

37

38 **Introduction**

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

59 Orogenic peridotites of the Ulten Zone (N Italy) of this type are particularly
60 interesting, as they exhibit a coupled textural and chemical transition upon variable exposure
61 to crust-derived aqueous fluids during a HP stage within a Variscan subduction cycle (Figs.
62 1b, c, Fig. 2). Here, coarse-grained garnet peridotites originally derived from the hot and
63 shallow mantle wedge were gradually transformed into fine-grained garnet-amphibole-
64 peridotites and -pyroxenites. Amphibole-forming, garnet-consuming reactions eventually
65 produced fine-grained spinel-amphibole peridotites without garnet (Rampone & Morten,
66 2001; Gudelius *et al.*, 2019). The transition from coarse- to fine-grained textures is marked by

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

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

85
86

87 **Fluid-assisted Lu-Hf fractionation of garnet peridotites**

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

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

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

113

114

115 **Coupled vs. decoupled Hf-Nd isotope enrichment**

116 Metasomatism by aqueous fluids did not only alter parent/daughter ratios but also Hf
117 and Nd isotope compositions of the investigated orogenic peridotites. While weakly
118 metasomatized lenses (Samerberg), have retained common depleted mantle ¹⁷⁶Hf/¹⁷⁷Hf during
119 metasomatism at 330 Ma, more metasomatized peridotite lenses (Seefeld/M) form a parallel
120 trend distinctly offset to more unradiogenic values by about 12 εHf units. This enrichment is
121 accompanied by generally higher contents of Hf and other HFSE (Fig. 4 e,f). Assuming that
122 all Ulten peridotites originate from a compositionally similar mantle protolith (Ionov *et al.*,
123 2017), this suggests metasomatic addition of Hf with unradiogenic ¹⁷⁶Hf/¹⁷⁷Hf by aqueous
124 fluids derived from a crustal source. This is direct evidence for effective Hf transport by crust-
125 derived fluids in subduction zone settings, supporting previous indications derived from arc
126 lavas (Woodhead *et al.*, 2001). Though commonly considered fluid-immobile (Kessel *et al.*,
127 2005), mobilization of HFSE can be facilitated by formation of alkali-HFSE-silicate
128 complexes in fluids with high Na/Al, at high temperatures and pressures (e.g. Wilke *et al.*
129 (2012)) as well as by fluids with high F⁻ and Cl⁻ contents (Tanis *et al.*, 2016). All of these
130 effects likely hold true for metasomatic fluids at Ulten, as suggested by Cl-bearing
131 polymineralic inclusion assemblages in peridotite minerals (Lo Pò *et al.*, 2020). Addition of
132 Hf caused further decrease in ¹⁷⁶Lu/¹⁷⁷Hf at 330 Ma along with Lu removal due to garnet
133 breakdown. Eventually, garnet-consuming, amphibole-forming reactions and HFSE-addition
134 resulted in strongly enriched samples with no or only few garnet remnants and abundant

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

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

151

152 **Isotopic provinciality of the mantle near continental slabs**

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

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

169 dehydration fluids (Marschall & Tang, 2020). The observed $\delta^7\text{Li}$ pattern can be explained by
170 fast Li diffusion and attendant kinetic isotope fractionation. Lithium is highly fluid-mobile
171 and fast-diffusing in most mantle minerals, so infiltration of a Li-rich fluid into peridotite
172 should generate a chemical potential gradient driving diffusion of Li from the fluid into the
173 constituting minerals of the host peridotite (Aulbach & Rudnick, 2009; Marschall & Tang,
174 2020). During such metasomatism, low $\delta^7\text{Li}$ values can be temporarily generated due to the
175 higher diffusivity of ^6Li compared to ^7Li in peridotite minerals (Aulbach & Rudnick, 2009;
176 Marschall & Tang, 2020). This imprint is preserved if the Li influx is short-lived and/or the
177 chemical gradient disappears before full isotopic equilibration. With regard to the Ulten Zone,
178 this provides strong support of our model calling for different fluid/rock regimes to account
179 for the striking Lu-Hf and Sm-Nd isotopic provinciality, which can be also resolved using
180 highly fluid-sensitive Li isotope signatures.

181

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185 of Rumo municipality for assistance with access to the sampling sites.

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

194

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

203

204 **Fig. 3** (a) Lu-Hf isochron diagram illustrating gradual decrease in $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$
205 during transition from coarse- to fine-grained peridotites. Note correlation parallel to 330 Ma
206 (age of fluid-related metasomatism: Tumiati *et al.*, 2003) and more unradiogenic trend for
207 Seefeld/M locality caused by Lu loss due to garnet destabilization and metasomatic Hf
208 addition. The more radiogenic outlier likely reflects a more ancient mantle domain. (b) Sm-
209 Nd isotopes record decrease in $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ from coarse- to fine-grained
210 peridotites reflecting addition of crustal Nd (Ulten Crust: Tumiati *et al.* (2003) and references
211 therein). (c) Hf and Nd isotope ratios at 330 Ma (expressed as $\square\text{Hf}$ and $\square\text{Nd}$, i.e. the per
212 10,000 deviation from chondrite after Bouvier *et al.*, 2008). Note decoupling due to
213 differential efficiency of fluids to transport Hf vs. Nd (Samerberg). N Qaidam: Xiong *et al.*
214 (2014; 2015); Lanzo: Guarnieri *et al.* (2012); Lherz: Le Roux *et al.* (2009). For calculation,
215 $\lambda^{176}\text{Lu}$ and $\lambda^{147}\text{Sm}$ values were taken from Söderlund *et al.* (2004) and Villa *et al.* (2020),
216 respectively. Error bars are twofold standard errors (within-run).

217

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

220 decrease in $^{176}\text{Lu}/^{177}\text{Hf}$ at the transition from coarse- to fine-grained peridotite is caused
221 exclusively by Lu loss due to garnet-consuming, amphibole-forming reactions (Rampone &
222 Morten, 2001; Gudelius *et al.*, 2019) or by additional Hf addition (Seefeld/M). This consistent
223 with a shift in modal mineralogy (b) and accompanied by a gradual crustal imprint as indicated
224 by successive LILE-enrichment and addition of unradiogenic Nd from a crustal source (c, d).
225 In contrast to Samerberg, peridotites from Seefeld/M locality record addition of unradiogenic
226 (crustal) Hf (e) and other HFSE (f) and also display distinct LREE fractionation patterns and
227 low $\delta^7\text{Li}$ indicative for chromatographic effects at a closer proximity to the fluid source (g, h).
228 The provinciality of metasomatic effects on Lu/Hf isotope systematics is suggested to be a
229 function of the crust-mantle distance in continental subduction zones. Trace element data of
230 Gudelius *et al.* (2019); DM values of Blichert-Toft & Puchtel (2010), Workman & Hart (2005),
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232

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