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

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SUPPLEMENTARY MATERIAL 1: ANALYTICAL METHODS

Specimens of eleven peridotites and pyroxenites from the Ulten Zone were cut into representative blocks and were processed as whole rock powders with an agate mill after the abrasion of surfaces to remove metal contamination from the saw. All laboratory work was performed inside a class 100 clean room equipped with metal-free, laminar-flow fume hoods. Additionally, all acids used in this study were double distilled and diluted using ultra-pure water (*MilliQ*) with a resistivity ≥18 MΩ. All analyses were performed in the Geoscience Institute at Goethe-University, Frankfurt.

Whole rock Lu-Hf and Sm-Nd isotope analysis

The samples from the Ulten Zone, replicates of BIR-1 and UB-N standards and full procedural blanks were digested in screwtop Teflon-beakers by using a mixture of 1ml 14M HNO_3, 3ml 28M HF and 100-500 µl 10M $HClO_4$ (100 µl $HClO_4$ per 50 mg sample). Before digestion, the samples were spiked with ^{176}Lu-^{180}Hf and ^{149}Sm-^{150}Nd tracers. The separation of Lu, Hf, Sm and Nd was performed using a three-step column chromatography using analytical protocols of Münker *et al.* (2001), Pin & Zalduegui (1997) with modification according to Lazarov *et al.* (2009).

The purified samples of Lu, Hf, Sm and Nd were analyzed separately using multi collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS). For analysis, a *Neptune* (*Thermo-Finnigan*) mass spectrometer was used. All analyses were performed by using an *Aridus II* (*Cetac*) spray chamber. Repeated measurement of the acid blank (2% HNO_3) resulted in detection limits (bg + 3×σ_{bg}) of: 2-216 ppt Hf, 2-30 ppt Lu, 12-35 ppt Nd and 6 ppt Sm. Full procedural blanks were: 0.02 ppb Hf, 0.1 ppb Lu, 0.01 ppb Nd and 0.06 ppb Sm. Because these background levels are insignificant compared to the sample concentrations, no correction was applied. Replicate analysis of standard materials yielded the following isotope ratios: ^{176}Hf/^{177}Hf of 0.283241 ± 0.000018 (2σ; n = 4) for BIR-1 (Bizzarro *et al.* (2003): ^{176}Hf/^{177}Hf = 0.283252 - 0.283281); ^{176}Hf/^{177}Hf of 0.283245 ± 0.000032 (2σ; n

=) for UB-N; $^{143}Nd/^{144}Nd$ of 0.513076 ± 0.000022 (2σ; n = 4) for BIR-1 (Pin *et al.* (2014): $^{143}Nd/^{144}Nd$ = 0.513074 - 0.513080) and $^{143}Nd/^{144}Nd$ of 0.512925 ± 0.000020 (2σ; n = 2) for UB-N (Pin & Zalduegui (1997): $^{143}Nd/^{144}Nd$ = 0.512925 - 0.512926).

Whole rock Li isotope analysis

About 50 mg of the whole rock powders were digested at 170 °C on hotplate in screwtop Teflon beakers using a mixture of 1 ml of 6M HNO_3 and 1 ml 28M HF. Purification of Li was performed using the analytical protocol described by Seitz *et al.* (2004). Lithium isotope ratios were obtained by MC-ICP-MS using the *Neptune* (*Thermo-Finnigan*) equipped with an *Aridus* (*Cetac*) spray chamber. The measurement was carried out by standard-sampling bracketing method using a 10 ppb L-SVEC (NIST) standard solution, which also was used to determine Li concentrations. For each sample solution, 3-4 analyses were performed and averaged. Analysis of standard materials yielded the following values: JB-2: δ^7Li = 4.2 ‰ ± 0.8 ‰ (1σ; n = 6); 8 ppm Li; UB-N: δ^7Li = -2.7 ‰ ± 0.4 ‰ (1σ; n = 6); 24.5 ppm Li ($\delta^7Li = [(^7Li/^6Li)_{sample}/(^7Li/^6Li)_{L\text{-}SVEC\ standard} - 1] \times 1000$). These results are in accordance with previously reported values compiled in the GeoReM database (Jochum *et al.*, 2005): JB-2: δ^7Li = 3.6 to 5.7 ‰; 7.2 to 8.9 ppm Li; UB-N: δ^7Li = -3 to -1.8 ‰; 20.6 to 32 ppm Li.

SUPPLEMENTARY MATERIAL 2: ISOTOPIC DATA

Bulk rock Lu-Hf, Sm-Nd, and Li isotope systematics for peridotites and pyroxenites of the Ulten Zone

Sample	wt (g)	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$	2σ	εHf[a,b]	$εHf_{330}$[c]	Lu (ppm)	Hf (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	2σ	εNd[a,b]	$εNd_{330}$[c]	Sm (ppm)	Nd (ppm)	$δ^7Li$[d]	Li
coarse-grained spinel-peridotites with coronitic garnet																	
UN1	0.21	0.11651	0.28379	0.000080	35.9	17.6	0.047	0.058	0.10622	0.51269	0.000009	1.01	4.76	0.243	1.389	7.2	5.5
UN2	0.20	0.16225	0.28393	0.000130	41.1	12.8	0.066	0.059	0.36272	0.51345	0.000022	15.9	8.9	0.139	0.232	1.7	1.4
fine-grained garnet-amphibole peridotites																	
UN3	0.21	0.05903	0.28462	0.000156	65.3	59.7	0.024	0.053	0.08149	0.51253	0.000014	-2.11	2.75	0.187	1.386	1.7	1.7
UN6	0.20	0.08838	0.28351	0.000122	26.2	14.1	0.034	0.055	0.09497	0.51254	0.000010	-1.82	2.46	0.249	1.583	1.0	1.7
UN7	0.21	0.07648	0.28355	0.000043	27.4	17.9	0.031	0.053	0.09270	0.51253	0.000007	-2.21	2.17	0.231	1.504	2.7	2.8
UN9	0.10	0.07130	0.28306	0.000055	10.3	1.9	0.035	0.076	0.11703	0.51251	0.000012	-2.45	0.91	0.194	1.003	-1.5	3.0
UN14	0.05	0.01850	0.28278	0.000025	0.2	3.5	0.040	0.305	0.11942	0.51256	0.000007	-1.61	1.64	0.477	2.416	-3.7	3.6
fine-grained spinel-amphibole peridotites																	
UN8	0.10	0.01238	0.28271	0.000036	-2.3	2.3	0.016	0.173	0.12234	0.51250	0.000010	-2.66	0.47	0.346	1.708	-2.8	3.8
UN16	0.24	na	na	na	na	na	na	na	0.08834	0.51232	0.000009	-6.26	-1.70	0.109	0.745	2.1	4.6
fine-grained garnet-amphibole pyroxenites																	
UN10	0.06	0.03986	0.28295	0.000023	6.2	4.8	0.110	0.380	0.10939	0.51251	0.000011	-2.47	1.21	1.101	6.085	-4.2	3.2
UN11	0.06	0.04715	0.28308	0.000019	10.8	7.8	0.120	0.338	0.11072	0.51250	0.000007	-2.67	0.95	0.970	5.298	0.3	2.9
Standards																	
BIR-1	0.05	0.06099	0.28324	0.000018	16.6		0.250	0.582	0.26961	0.51308	0.000022	8.55		1.051	2.356		
UB-N	0.10	0.05432	0.28325	0.000032	16.7		0.047	0.120	0.21211	0.51293	0.000020	5.60		0.205	0.584	-2.7	24.5
JB-2																4.2	8.0

2σ = twofold absolute standard error, na = not available, wt = weight of digested sample powder.

[a] per 10,000 deviation from chondritic mantle (present-day)

[b] Chondritic mantle (CHUR) of Bouvier *et al.* (2008)

[c] εHf and εNd values at 330 Ma, the age of the HP stage of the Ulten Zone (Tumiati *et al.*, 2003). $λ^{176}Lu=1.876 * 10^{-11}$ (Söderlund *et al.*, 2004); $λ^{147}Sm=6.524 * 10^{-12}$ (Villa *et al.*, 2020)

[d] $δ^7Li$ indicates per 1,000 deviation of $^7Li/^6Li$ from L-SVEC standard

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