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Evolution of recycled crust within the mantle: constraints from the garnet pyroxenites in the mantle section of the External Ligurian ophiolites (N Apennine, Italy)

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Supplementary Material

Sample locations

GPS Coordinates of the investigated samples are N 44°38'55", E 10°4'59" (samples AM288A, AM403, AM404, AM483, AM393, Northeastern side of Monte Prinzera) and N 44°41'47", E 10°4'24" (samples BA3-W, AM353, AM387, AM397, Valceno quarry). Websterite AM393 was collected along the margin of a thick Type-C layer, close to Type-C pyroxenite AM483

Analytical Methods

Whole-rock major and trace element compositions were obtained by ICP-MS at Activation Laboratories (Ancaster, W Ontario, Canada, http://www.actlabs.com).

Trace element analyses of clinopyroxene were carried out by laser ablation inductively coupled plasma-mass spectrometry at C.N.R.-Istituto di Geoscienze e Georisorse, U.O. di Pavia. Reproducibility and accuracy of concentration values were assessed on the BCR-2g (USGS) reference glass and are mostly <7% and <10%, respectively. Further analytical details are reported in Tiepolo et al. (2003) and Montanini et al. (2012).

Sm-Nd and Lu-Hf isotope compositions were determined at the Department of Geology, Royal Holloway, University of London. All errors are 2SD and relate to the last significant digits. Elemental abundances have been determined by isotope dilution. Details of sample digestion and ion exchange chromatography were presented in Anczkiewicz et al. (2004). Elemental separation was undertaken in four column steps (details have been given by Anczkiewicz and Thirlwall, 2003). Total procedure analytical blanks for Hf and Nd were

<30 ρg. Hf isotopic analyses were carried outin static mode on a IsoProbe multicollector ICP-MS (2000 GV Instruments) using the approach of Thirlwall & Anczkiewicz (2004). Nd isotope analyses were performed using a multi-collector VG354 mass spectrometer for all samples but E181, that was analyzed by Isoprobe. All measurements were conducted on a single day to minimize correction for secular variation in static $^{176}Hf/^{177}Hf$ of JMC47. $^{147}Sm/^{144}Nd$ errors are 0.3%. Reproducibility of Aldrich Nd standard on the day of analyses was $^{143}Nd/^{144}Nd = 0.511420$ (2SD = 0.000010, n = 8). Daily variations in $^{143}Nd/^{144}Nd$ ratios were normalized to $^{143}Nd/^{144}Nd = 0.511421$. $^{176}Lu/^{177}Hf$ errors are 0.5%; JMC475 standard on a day of analyses yielded 0.282165 (2SD =0.000013, n = 7). Daily variation in $^{176}Lu/^{177}Hf$ ratios were normalized to $^{176}Lu/^{177}Hf = 0.282165$. Mass bias corrections were made using $^{146}Nd/^{144}Nd = 0.7219$ and $^{179}Hf/^{177}Hf = 0.7325$.

Trace element modeling

Calculations of melts in equilibrium with clinopyroxene of Type-C garnet clinopyroxenite AM403 and websterite BA3-W were carried out through the clinopyroxene/melt partition coefficients determined experimentally by Barth et al. (2002). Calculation of the parental liquid in equilibrium with whole-rock (garnet clinopyroxenite AM403, Table DR1) was carried out according to the procedure of Bédard (1994); assumed mineral mass fractions in the original cumulus assemblage of the garnet clinopyroxenite: cpx = 0.60, garnet = 0.40. Melting calculations were performed for an eclogite derived from a troctolite protholith (Godard et al., 2009) assuming a simple batch melting model of an eclogite assemblage composed of cpx = 70 vol%, garnet = 30 vol%. D values for garnet and clinopyroxene adopted in the melting model after Barth et al. (2002).

Isotopic calculations

Nd-Hf isotopic compositions of recycled oceanic rocks were calculated assuming that their initial isotopic composition was equal to those of the MORB source at the time of recycling (2.0-0.5 Ga). $^{147}Sm/^{144}Nd$ and $^{176}Lu/^{177}Hf$ values of the MORB source were obtained assuming that present-day depleted mantle has the the isotopic composition of average present-day MORB and is derived from Bulk Earth (BE, data in Stracke et al., 2003) at 3.0 Ga. Values of parent/daughter ratios of oceanic olivine gabbro ($^{147}Sm/^{144}Nd$ =0.183, $^{176}Lu/^{177}Hf$ = 0.027) from Hart et al. (1999), average N-MORB ($^{147}Sm/^{144}Nd$ =0.203, $^{176}Lu/^{177}Hf$ = 0.028) from Stracke et al. (2003), oceanic troctolite ($^{147}Sm/^{144}Nd = 0.240$, $^{176}Lu/^{177}Hf$ =0.064) from Godard et al. (2009) and Perk et al. (2007).

Table DR1. WHOLE ROCK MAJOR AND TRACE ELEMENT ANALYSES

	Type-C garnet clinopyroxenites				Websterites				
Sample	**AM403**	**AM404**	**AM288A**	**AM483**	**AM353**	**AM397**	**AM387**	**BA3-W**	**AM393**
(wt%)									
SiO_2	47.19	46.90	47.73	46.58	42.76	49.08	48.77	47.99	46.86
TiO_2	0.14	0.26	0.18	0.20	0.46	0.45	0.25	0.28	0.36
Al_2O_3	15.81	15.45	14.31	15.19	11.73	10.80	8.11	9.94	7.18
FeO	7.19	6.71	6.15	7.14	9.91	6.17	5.79	5.43	8.26
MnO	0.14	0.12	0.13	0.13	0.21	0.17	0.14	0.16	0.15
MgO	14.44	16.09	17.83	17.26	24.75	22.99	29.86	27.92	30.76
CaO	13.68	13.20	12.56	12.42	9.64	9.57	6.54	7.86	5.45
Na_2O	1.37	1.22	1.03	1.06	0.26	0.72	0.51	0.43	0.84
K_2O	<0.01	<0.01	0.05	<0.01	0.04	0.01	0.01	<0.01	0.01
P_2O_5	0.01	0.02	0.02	<0.01	0.02	0.03	0.01	<0.01	0.02
LOI	0.38	1.55	0.35	2.44	8.53	1.81	4.84	5.18	5.05
Mg#	78.3	81.2	83.9	81.3	81.8	87.0	90.3	90.3	87.0
(ppm)									
V	167	141	119	140	245	248	159	138.5	124
Cr	909	1370	1440	1560	763	1440	2990	2230	1820
Ni	271	527	393	520	392	660	760	554	1360
Co	53	56	54	72	61	46	62	51	86
Sc	44	34	35	38	46	40	31	30	21
Sr	37	189	81	137	55	166	189	146	49
Y	5.6	6.4	5.4	7.3	18	14.6	9.6	6.7	11.5
Nb	0.3	<0.1	3.7	0.3	<0.1	0.3	0.48	0.35	0.9
Zr	7	18	18	10	18	22	9	12	16
Hf	0.109	0.5	0.36	0.3	0.7	0.6	0.5	0.435	0.5
La	0.18	0.25	0.88	0.36	0.3	0.42	0.35	0.37	0.39
Ce	0.48	1.03	3.06	1.19	1.30	1.61	1.18	1.49	1.53
Pr	0.08	0.24	-	0.20	0.19	0.31	0.19	0.26	0.29
Nd	0.48	1.59	1.98	1.13	1.80	2.00	1.38	1.88	2.11
Sm	0.23	0.65	0.52	0.38	0.90	0.95	0.67	0.78	0.82
Eu	0.18	0.30	0.25	0.24	0.42	0.39	0.28	0.33	0.34
Gd	0.47	0.88	0.69	0.66	1.80	1.73	1.11	1.13	1.32
Tb	0.12	0.17	0.13	0.14	0.40	0.37	0.24	0.22	0.26
Dy	0.86	1.12	0.91	1.04	2.80	2.68	1.57	1.28	1.75
Ho	0.20	0.24	0.20	0.24	0.60	0.63	0.35	0.25	0.39
Er	0.65	0.74	0.59	0.73	2.30	1.80	1.15	0.78	1.26
Tm	0.10	0.11	0.08	0.11	0.36	0.30	0.18	0.12	0.19
Yb	0.63	0.65	0.54	0.72	2.30	1.88	1.17	0.70	1.24
Lu	0.11	0.10	0.08	0.11	0.36	0.28	0.18	0.11	0.19
$(Ce/Sm)_N$	0.51	0.39	1.43	0.76	0.35	0.41	0.43	0.47	0.46
$(Sm/Yb)_N$	0.40	1.10	1.06	0.58	0.43	0.56	0.63	1.22	0.73
Lu_N	4.5	4.1	3.3	4.5	14.8	11.5	7.4	4.3	7.8
Eu/Eu*	1.6	1.2	1.3	1.4	1.0	0.9	1.0	1.1	1.0
Sr/Sr*	5.1	9.3	2.2	7.9	2.3	6.0	9.7	5.7	1.7

Table DR2. MAJOR AND TRACE ELEMENT COMPOSITION OF CLINOPYROXENE

Rock type	***Type-C garnet clinopyroxenites***							***Websterites***					
sample	**AM288A**	**AM403**	**AM403**	**AM403**	**AM483A**	**AM483A**	**AM404**	**BA3-W**	**BA3-W**	**AM387**	**AM397**	**AM353**	**AM393**
	p-c	**p1-c**	**p1-r**	**p2-c**	**p1-c**	**p2-c**	**p-c**	**p1-c**	**p2-c**	**p-c**	**p-c**	**p-c**	**p-c**
Major elements (wt%)													
SiO_2	48.77	49.47	49.30	49.47	48.57	49.65	48.75	49.93	50.36	50.68	49.61	50.24	50.06
TiO_2	0.32	0.28	0.25	0.30	0.21	0.41	0.76	0.57	0.71	0.49	0.90	0.70	1.02
Al_2O_3	11.33	8.95	9.32	8.79	10.83	8.96	8.73	10.59	8.30	7.83	8.52	8.30	7.90
Cr_2O_3	0.32	0.21	0.31	0.58	0.10	0.31	0.40	0.33	0.46	0.87	0.43	0.34	0.36
FeO_t	5.02	5.05	4.64	5.00	5.91	5.85	5.45	3.22	3.17	3.02	3.53	3.01	3.71
MnO	0.16	0.11	0.10	0.05	0.24	0.14	0.16	0.11	0.17	0.14	0.14	0.07	0.14
MgO	12.43	12.82	12.87	12.87	12.66	13.29	12.66	15.65	13.87	14.38	13.84	13.55	13.44
CaO	20.34	21.22	21.76	21.50	20.05	20.36	22.24	19.12	21.16	21.83	22.07	21.62	20.61
Na_2O	0.90	1.06	1.05	1.03	1.02	0.97	0.92	0.78	0.94	1.13	0.92	0.92	1.49
Σ	99.59	99.17	99.60	99.58	99.58	99.94	100.07	100.30	99.14	100.37	99.96	98.75	98.74
Mg#	81.5	81.9	83.3	82.3	79.2	80.3	80.7	89.6	88.7	89.5	87.5	88.9	86.6
Trace elements (ppm)													
Sc	9.4	16.4	27.5	37.1	36.8	75.0	51.7	21.4	48.1	39.4	64.9	70.3	47.9
Ti	916	1091	1260	1453	1194	2313	3556	3012	3987	3175	4248	5165	5098
V	101.9	175	169	133	197	167	371	236	251	338	380	269	331
Cr	1304	1287	1161	2513	592	1231	2062	2540	2480	4830	1724	3108	2818
Co	24.5	47.5	24.7	28.0	31.3	31.7	33.3	14.2	19.4	22.3	20.1	27.6	28.8
Sr	78.0	9.8	5.9	6.3	5.3	8.7	7.4	33.5	21.0	55.4	10.0	18.1	63.4
Y	1.4	1.5	8.7	6.4	6.8	15.5	22.8	4.6	10.4	14.4	53.4	29.5	21.5
Zr	4.37	3.2	5.5	5.9	2.7	13.4	24.8	12.8	21.6	24.7	45.9	50.1	44.9
Nb	0.65	0.12	0.27	0.14	0.13	0.12	0.07	0.05	0.09	0.08	0.23	0.04	0.08
La	2.62	0.49	0.58	0.67	0.46	0.48	0.52	0.51	0.70	0.93	0.73	1.14	1.31
Ce	8.77	1.59	1.93	2.08	1.25	1.91	3.03	2.12	3.55	3.27	4.00	5.96	6.48
Pr	1.32	0.25	0.31	0.26	0.19	0.33	0.70	0.44	0.73	0.66	0.87	1.28	1.10
Nd	4.55	1.11	1.43	1.19	0.98	1.90	4.65	2.76	4.91	4.21	5.58	7.56	6.13
Sm	0.54	0.33	0.51	0.61	0.52	1.12	1.67	1.03	1.63	1.86	2.58	3.12	2.51
Eu	0.28	0.19	0.39	0.31	0.28	0.55	0.61	0.56	0.69	0.61	1.21	1.20	1.21
Gd	0.38	0.35	0.87	0.84	0.84	1.49	2.36	1.35	2.07	2.84	5.00	3.95	3.24
Tb	0.05	0.05	0.17	0.18	0.13	0.33	0.49	< 0.26	0.37	0.5	1.18	0.74	0.53
Dy	0.29	0.34	1.40	1.14	1.10	2.34	3.62	1.11	2.33	3.01	8.12	5.59	4.21
Ho	0.06	0.06	0.31	0.25	0.24	0.55	0.88	0.21	0.45	0.59	2.05	1.22	0.93
Er	0.11	0.16	0.85	0.77	0.81	1.58	2.82	0.58	1.23	1.82	5.90	3.67	2.59
Tm	0.02	0.02	0.15	0.10	0.12	0.23	0.43	0.08	0.16	0.25	0.98	0.50	0.34
Yb	0.15	0.12	1.09	0.80	0.82	1.59	3.09	0.39	1.17	1.68	7.36	3.45	2.44
Lu	0.03	0.03	0.14	0.10	0.12	0.23	0.40	0.04	0.15	0.26	1.08	0.42	0.34
Hf	0.130	0.17	0.21	0.38	0.09	0.65	0.93	0.42	0.76	0.85	1.38	1.97	1.54
Pb	0.069	0.036	0.041	0.045	0.045	0.035	0.044	0.086	0.060	0.107	0.063	0.060	-
Th	0.082	0.026	0.036	0.004	0.008	0.009	0.006	0.014	0.022	0.028	0.040	0.028	-
U	0.035	0.004	0.007	0.013	0.006	0.011	0.005	0.003	0.009	0.013	0.023	0.003	-
Eu/Eu*	1.76	1.72	1.78	1.30	1.28	1.29	0.94	1.45	1.14	0.80	1.01	1.04	1.29
$(Ce/Sm)_N$	3.92	1.17	0.92	0.83	0.59	0.41	0.44	0.50	0.53	0.43	0.38	0.46	0.63
$(Ce/Yb)_N$	16.13	3.57	0.48	0.70	0.41	0.32	0.26	1.46	0.82	0.52	0.15	0.46	0.71
$(Gd/Yb)_N$	2.14	2.41	0.66	0.87	0.86	0.77	0.63	2.87	1.47	1.40	0.56	0.95	1.10
Yb_N	0.90	0.74	6.71	4.90	5.02	9.78	19.02	2.40	7.17	10.34	45.29	21.23	15.00

p = porphyroclast, c = core

Table DR3. Nd-Hf ISOTOPE COMPOSITION

Sample		Sm (ppm)	Nd (ppm)	$^{147}Sm/144Nd$	$^{143}Nd/^{144}Nd$	$\varepsilon_{Nd(0)}$	$\varepsilon_{Nd(220)}$
AM403	grt clinopyroxenite	0.399	0.212	1.1380	0.513471 ± 4	+ 16.3	+ 12.8
BA3-W	websterite	0.688	1.698	0.2450	0.513030 ± 4	+ 7.7	+ 6.3
		Lu (ppm)	Hf (ppm)	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$	$\varepsilon_{Hf(0)}$	$\varepsilon_{Hf(220)}$
AM403	grt clinopyroxenite	0.101	0.109	0.1300	0.284080 ± 30	+ 46.3	+ 32.2
BA3-W	websterite	0.101	0.435	0.0327	0.282995 ± 9	+ 7.9	+ 8.0

All errors are 2SE and relate to the last significant digits

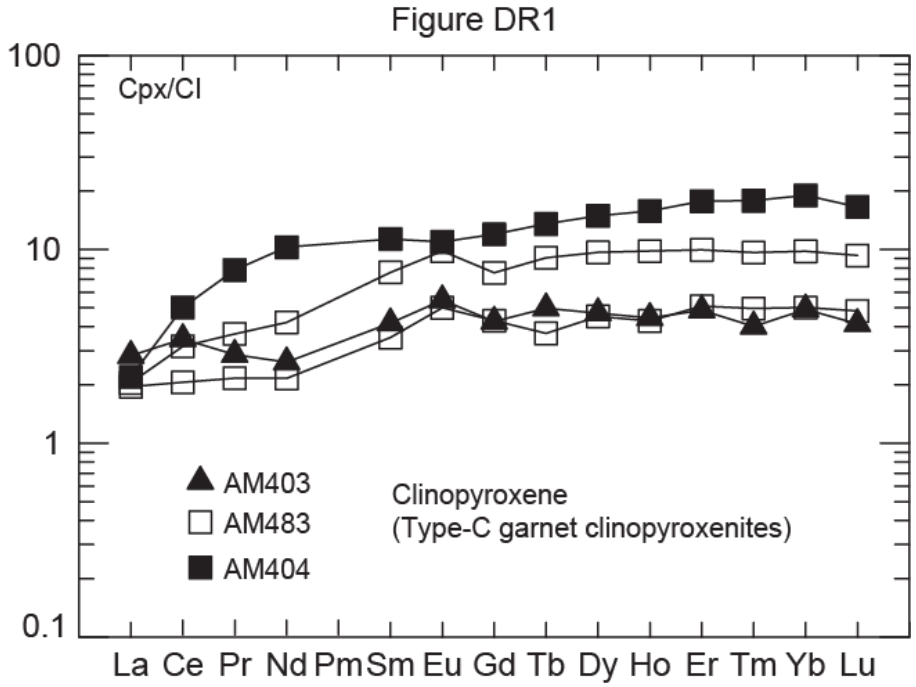

Figure DR1. Chondrite-normalized rare earth element (REE) patterns for re-equilibrated clinopyroxenes after garnet breakdown in Type-C garnet clinopyroxenites.

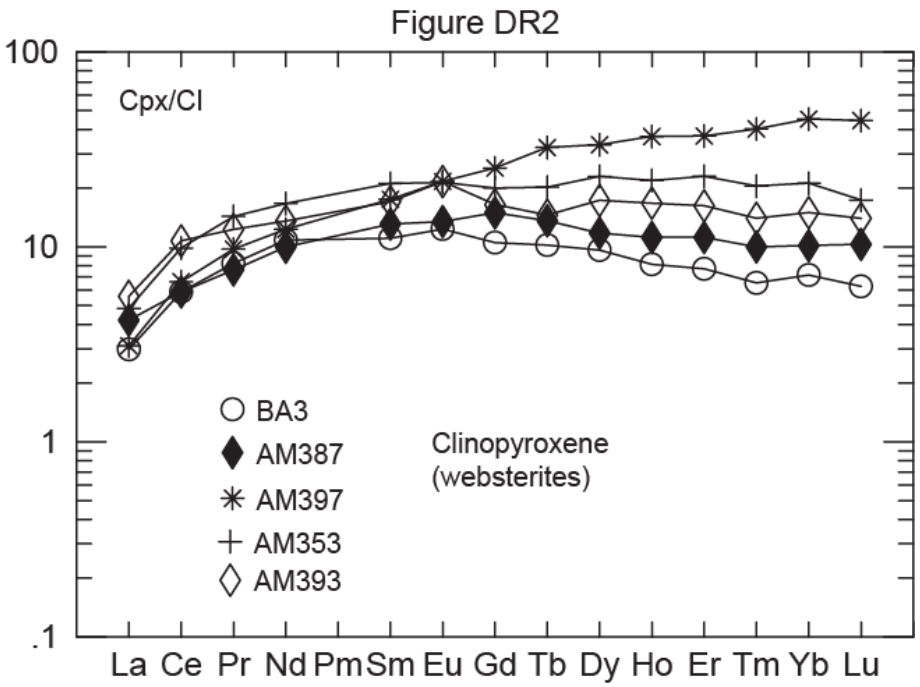

Figure DR2. Chondrite-normalized rare earth element (REE) patterns for re-equilibrated clinopyroxenes after garnet breakdown in websterites.

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