

## Data repository item 2006054

### *LITERATURE DATA USED IN FIGURE 2*

#### *Clinopyroxene from off-craton spinel peridotites entrained in intraplate volcanics*

- Bedini, R.M., Blichert-Toft, J., Boyet, M., and Albarede, F., 2004, Isotopic constraints on the cooling of the continental lithosphere: Earth and Planetary Science Letters, v. 223, p. 99-111.
- Bizimis, M., Sen, G., and Salters, V.J.M., 2004, Hf-Nd isotope decoupling in the oceanic lithosphere: constraints from spinel peridotites from Oahu, Hawaii: Earth and Planetary Science Letters, v. 217, p. 43-58.
- Neumann, E.-R., Wulff-Pedersen, E., Pearson, N.J., and Spencer, E.A., 2002, Mantle xenoliths from Tenerife (Canary Islands): Evidence for reactions between mantle peridotites and silicic carbonatite melts inducing Ca metasomatism: Journal of Petrology, v. 43, p. 825-857.
- Witt-Eickschen, G., and Kramm, U., 1997, Mantle upwelling and metasomatism beneath Central Europe: Geochemical and isotopic constraints from mantle xenoliths from the Rhön: Journal of Petrology, v. 38, p. 479-493.
- Witt-Eickschen, G., Seck, H.A., Mezger, K., Eggins, S.M., and Altherr, R., 2003, Lithospheric mantle evolution beneath the Eifel (Germany): Constraints from Sr-Nd-Pb isotopes and trace element abundances in spinel peridotite and pyroxenite xenoliths: Journal of Petrology, v. 44, p. 1077-1095.

#### *Clinopyroxene and garnet from off-craton peridotites entrained in intraplate volcanics*

- Ionov, D.A., Blichert-Toft, J., and Weis, D., 2005, Hf isotope composition and HREE variations in off-craton garnet and spinel peridotite xenoliths from central Asia: Geochimica et Cosmochimica Acta, v. 69, p. 2399-2148.

#### *Clinopyroxene and garnet from kimberlite-bourne xenoliths*

- Aulbach, S., Griffin, W.L., O'Reilly, S.Y., and McCandless, T.E., 2004, Genesis and evolution of the lithospheric mantle beneath the Buffalo Head Terrane, Alberta (Canada): Lithos, v. 77, p. 413-451.
- Bedini, R.M., Blichert-Toft, J., Boyet, M., and Albarede, F., 2004, Isotopic constraints on the cooling of the continental lithosphere: Earth and Planetary Science Letters, v. 223, p. 99-111.
- Carlson, R.W., Irving, A.J., Schulze, D.J., and Hearn Jr., B. C., 2004, Timing of Precambrian melt depletion and Phanerozoic refertilization events in the lithospheric mantle of the Wyoming Craton and adjacent Central Plains Orogen: Lithos, v. 77, p. 453-472.

## CHEMICAL SEPARATION AND MASS SPECTROMETRY TECHNIQUES FOR LU-Hf ISOTOPIC ANALYSIS

The chemical separation and mass spectrometric procedures of Bizzarro et al. (2003) and Ulfbeck et al. (2003) were used to make Lu-Hf isotope measurements. Approximately 0.1 g of hand-picked clinopyroxene was leached with 6M HCl for ca. 30 min at approximately 120°C. A relatively harsh leaching procedure was adopted as it is evident that the extremely low Hf concentrations of these mantle xenoliths make them susceptible to interaction with their host basalts. For example, whole rock analyses of northern FMC xenoliths have chondritic Zr/Hf (Lenoir et al., 2000) as compared to the markedly sub-chondritic Zr/Hf obtained by in situ methods on the clinopyroxenes (Downes et al., 2003), which suggests that the xenoliths have been infiltrated by small quantities of host basalt. After repeatedly rinsing with MQ water, the mineral separates were dried and then weighed into pre-ignited 6 mL high-purity graphite crucibles with the sample sandwiched between ~0.4 g of ultra-pure lithium metaborate flux. The sample-flux mixture was fused for ca. 7 minutes at 1100°C until completely molten and poured into 15 mL of 2M HCl doped with separate enriched  $^{180}\text{Hf}$  and  $^{176}\text{Lu}$  isotopic spikes. To facilitate complete sample digestion, the beaker was agitated in an electronic shaker and kept on a hotplate before chemical separation of Lu and Hf was performed on 30 mL Teflon columns containing AG-50Wx8 cation exchange resin. Elution of 25 mL of 2M HCl and 30 mL of 2M  $\text{HNO}_3$  removed most major and trace elements. Lu was collected in 3 mL of 4M HCl and then evaporated and fluxed with concentrated  $\text{HNO}_3$  before isotopic analysis. Hf was finally collected together with other REE and high-field-strength elements in 20 mL of 6M HCl. The Hf cut was evaporated and re-dissolved in 1 mL of 10.5M HCl for further purification on TEVA-spec chromatographic resin. To separate Ti and REE from Hf a double column pass was performed using 1.5 mL pipette-tips loaded with 100-200  $\mu\text{L}$  of TEVA-spec resin; 7 mL of 10.5M HCl was eluted to remove REE and Ti. Hf (and Zr) was then collected in three reservoirs of 2M HCl, and the Hf cut evaporated and fluxed with concentrated  $\text{HNO}_3$ . Lu and Hf isotopic ratios were determined by multiple-collector inductively coupled plasma mass spectrometry as described by Bizzarro et al. (2003) and Ulfbeck et al. (2003). Hf concentration and Lu/Hf and Hf isotope ratios were corrected for a Hf procedural blank of 100 pg. Although blank corrections to the Hf concentration, Lu/Hf ratio and Hf isotopic data in Table DR1 are sometimes relatively large, these corrections have no affect on calculated Lu-Hf model ages as the blank produces strongly correlated effects on  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$ .

Bizzarro, M., Baker, J.A., and Ulfbeck, D., 2003, A new digestion and chemical separation technique for rapid and highly reproducible determination of Lu/Hf and Hf isotope ratios in geological materials by MC-ICP-MS: *Geostandards Newsletters*, v. 27, p. 131-143.

Downes, H., Reichow, M.K., Mason, P.R.D., Beard, A.D., and Thirlwall, M.F., 2003, Mantle domains in the lithosphere beneath the French Massif Central: trace element and isotopic evidence from mantle clinopyroxenes: *Chemical Geology*, v. 200, p. 71-87.

Lenoir, X., Garrido, C.J., Bodinier, J.-L., and Dautria, J.M., 2000, Contrasting lithospheric mantle domains beneath the Massif Central (France) revealed by geochemistry of peridotite xenoliths: *Earth and Planetary Science Letters*, v. 181, p. 359-375.

Ulfbeck, D., Baker, J.A., Waight, T., and Krogstad, E., 2003, Rapid sample digestion by fusion and chemical separation of Hf for isotopic analysis by MC-ICPMS: *Talanta*, v. 59, p. 365-373.

### CALCULATION OF LU-HF DEPLETED MANTLE MODEL AGES

Depleted mantle model ages ( $T_{DM}$ ) were calculated using a decay constant for  $^{176}\text{Lu}$  of  $1.865 \times 10^{-11} \text{ yr}^{-1}$  (Scherer et al., 2001) and present-day depleted mantle  $^{176}\text{Hf}/^{177}\text{Hf} = 0.28328$  (Chauvel and Blichert-Toft, 2001) and  $^{176}\text{Lu}/^{177}\text{Hf} = 0.04$ . Ages calculated from replicate digestions do not always quite reproduce within calculated external uncertainties, which were estimated to be  $1.85 \times$  the internal precision of each analysis (e.g., Bizzarro et al., 2003). It is unclear whether this represents an underestimation of analytical uncertainties (an external reproducibility ca.  $2 \times$  the internal precision would yield statistically reproducible ages) or heterogeneity amongst the aliquots of digested clinopyroxene. Given the challenges of precisely measuring Lu/Hf and Hf isotope ratios on sub-ng quantities of Hf, this is unlikely to be resolved until the sensitivity of plasma-source mass spectrometers improves markedly.

Bizzarro, M., Baker, J.A., Haack, H., Ulfbeck, D., and Rosing, M., 2003, Early history of Earth's crust-mantle system inferred from hafnium isotopes in chondrites: *Nature*, v. 421, p. 931-933.

Chauvel, C., and Blichert-Toft, J., 2001, A hafnium isotope and trace element perspective on melting of the depleted mantle: *Earth and Planetary Science Letters*, v. 190, p. 137-151.

Scherer, E., Münker, C., and Mezger, K., 2001, Calibration of the Lutetium-Hafnium Clock: *Science*, v. 293, p. 683-687.

### PARTIAL MELTING CALCULATIONS

Mantle melting was modelled using the non-modal fractional melting equation of Shaw et al. (1970) to calculate source trace element concentrations in the residue with the following starting mineralogy (x) and melting proportions (p):  $ol_x = 0.534$ ,  $opx_x = 0.255$ ,  $cpx_x = 0.183$ ,  $spl_x = 0.028$ , and  $ol_p = 0.05$ ,  $opx_p = 0.25$ ,  $cpx_p = 0.65$ ,  $spl_p = 0.05$ . The starting source Lu and Hf concentrations were estimated from average clinopyroxene Lu and Hf concentrations of spinel lherzolites from the southern FMC and Pyrenean Massif ( $n = 21$ ) i.e., Lu = 0.24 ppm and Hf = 1.06 ppm and a Lu/Hf ratio similar to hypothetical primitive mantle. All Lu and Hf was assumed to reside in clinopyroxene and orthopyroxene. Partition coefficients for olivine and spinel are  $K_{D_{Lu}} = 0.0001$  and  $K_{D_{Hf}} = 0.0001$  (olivine) and  $K_{D_{Lu}} = 0.0006$  and  $K_{D_{Hf}} = 0.0006$  (spinel), respectively (Chauvel and Blichert-Toft, 2001). Orthopyroxene partition coefficients were estimated from the clinopyroxene/orthopyroxene partition coefficients of Witt-Eickschen and O'Neill (2005). The melting model is relatively insensitive to the clinopyroxene mineral/melt partition coefficient for Lu, but the clinopyroxene mineral/melt partition coefficient for Hf governs the degree of melting inferred from this model. A best-fit curve matching the available data is obtained using clinopyroxene/melt partition coefficients of  $K_{D_{Lu}} = 0.6$  and  $K_{D_{Hf}} = 0.2$  resulting in bulk partition coefficients (D) of 0.186 and 0.054 for Lu and Hf, respectively, during melting.

Chauvel, C., and Blichert-Toft, J., 2001, A hafnium isotope and trace element perspective on melting of the depleted mantle: *Earth and Planetary Science Letters*, v. 190, p. 137-151.

Shaw, D.M., 1970, Trace element fractionation during anatexis: *Geochimica et Cosmochimica Acta*, v. 34, p. 237-243.

Witt-Eickschen, G., and O'Neill, S.C., 2005, The effect of temperature on the equilibrium distribution of trace elements between clinopyroxene, orthopyroxene, olivine and spinel in upper mantle peridotite: *Chemical Geology*, v. 221, p. 65-101.

TABLE DR1. Lu-Hf CONCENTRATION AND ISOTOPE DATA FOR CLINOPYROXENE FROM FRENCH MASSIF CENTRAL PERIDOTITES

	Lu (ppm)	Hf (ppm)	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$ ( $\pm 2$ se)	$\epsilon\text{Hf}$	$T_{\text{DM}}$ Myr	$\epsilon\text{Nd}$	Pb (ppm)	$\text{Al}_2\text{O}_3$ (wt%)	$\text{Na}_2\text{O}$ (wt%)	Mg#	Cr#
<b>northern French Massif Central</b>												
<i>spinel lherzolite</i>												
Mb 4	0.1370	0.02742	0.7088	0.28749 $\pm$ 10	+166.8	336 $\pm$ 15	+16.0	0.497	4.23	0.87	91.69	11.71
Mb 4	0.1329	0.02431	0.7758	0.28871 $\pm$ 27	+210.0	394 $\pm$ 36						
Mb 4	0.1323	0.02929	0.6406	0.28740 $\pm$ 11	+163.7	367 $\pm$ 18						
Mb 4 weighted mean age						353						
Mb 47	0.1323	0.02151	0.8724	0.28856 $\pm$ 18	+204.7	339 $\pm$ 21	+91.2	0.335	3.83	0.65	92.09	11.83
Mb 47	0.1389	0.02183	0.9024	0.28922 $\pm$ 10	+228.0	368 $\pm$ 12						
Mb 47 weighted mean age						361						
<i>spinel harzburgite</i>												
Mb 50	0.1279	0.03063	0.5924	0.28735 $\pm$ 61	+161.9	395 $\pm$ 107	+18.1	0.242	4.47	0.62	91.83	9.76
Mb 50	0.1275	0.03462	0.5222	0.286676 $\pm$ 69	+138.1	376 $\pm$ 14						
Mb 50 weighted mean age						377						
Ph 1	0.08900	0.004554	2.778	0.29929 $\pm$ 51	+584.1	313 $\pm$ 18	+2.1	0.050	4.17	0.68	93.35	14.14
Ph 2	0.1010	0.001339	10.83	0.3559 $\pm$ 19	+2586.1	360 $\pm$ 18	+3.3	0.048	2.95	0.54	93.69	14.48
Fr 9	0.07170	0.06793	0.1496	0.283892 $\pm$ 59	+39.6	298 $\pm$ 53						
<b>southern French Massif Central</b>												
<i>spinel lherzolite</i>												
Rp 91-8	0.2642	1.169	0.03209	0.283236 $\pm$ 12	+16.4		+13.1	0.096	5.86	1.72	91.60	7.70
<i>spinel harzburgite</i>												
Rp 87-1	0.1605	1.091	0.02089	0.283086 $\pm$ 8	+11.1		+7.6	0.111	3.51	1.15	91.30	13.80
<b>standard data</b>												
BHVO-2 (n = 6)	0.2767 $\pm$ 36	4.475 $\pm$ 32	0.008777 $\pm$ 92	0.283102 $\pm$ 13	+11.7							

Note:  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios are reported relative to 0.282160 for JMC475 and errors are 2 se internal errors.  $\epsilon\text{Hf}$  and  $\epsilon\text{Nd}$  are calculated as the part per 10,000 deviation from present-day chondrite values of 0.282772 (Blichert-Toft and Albarède, 1997) and 0.512638 (Jacobsen and Wasserburg, 1980), respectively. For description of analytical methods and the calculation of depleted mantle model ages ( $T_{\text{DM}}$ ) ( $\pm 2$  sd) see GSA Data Repository<sup>1</sup>. Pb and major element data are taken from Downes et al. (2003) and Zangana et al. (1997). Mg# and Cr# are clinopyroxene Mg and Cr numbers (i.e., 100 x atomic Mg/[Mg+Fe] and Cr/[Cr+Al]). Errors on BHVO-2 standard are the 2 sd external reproducibility of replicate digestions.