

Hf isotope evidence for a hidden mantle reservoir

Martin Bizzarro*

Antonio Simonetti

Ross K. Stevenson

Jean David

Centre for Research in Isotopic Geochemistry and Geochronology (GÉOTOP), Université du Québec à Montréal, succursale Centre-ville, CP 8888, Montréal, Québec H3C 3P8, Canada

ABSTRACT

High-precision Hf isotopic analyses and U-Pb ages of carbonatites and kimberlites from Greenland and eastern North America, including Earth's oldest known carbonatite (3 Ga), indicate derivation from an enriched mantle source. This previously unidentified mantle reservoir—marked by an unradiogenic Hf isotopic composition and preserved in the deep mantle for at least 3 b.y.—may account for the mass imbalance in Earth's Hf-Nd budget. The Hf isotopic data presented here support a common mantle source region and genetic link between carbonatite and some oceanic-island basalt volcanoes.

Keywords: Hf isotopes, Archean, mantle, carbonatite, kimberlite.

INTRODUCTION

Recent Hf isotopic studies of Early Archean juvenile lithologies (Vervoort and Blichert-Toft, 1999; Amelin et al., 2000) advocate for mantle depletion early in Earth's history (>3.7 Ga). This depletion may have resulted via the extraction of sialic (Bowring and Housh, 1995), or large ion lithophile element (LILE)-enriched mafic crust (Chase and Patchett, 1988; Vervoort and Blichert-Toft, 1999). The paucity of unradiogenic Hf isotopic signatures in juvenile Early Archean rocks, indicative of derivation from an enriched mantle source, suggests that this crust was rapidly recycled back into the mantle and isolated from convective stirring. Isolation of recycled material may be achieved at deep mantle levels, such as the 660 km seismic discontinuity or the core-mantle boundary. Recycling at the 660 km discontinuity implies a layered convective regime for Earth's mantle, which is not supported by geophysical evidence (Van der Hilst et al., 1997), thus leaving the core-mantle boundary region as the most likely possibility of the two. As discussed elsewhere (Albarède et al., 2000), the exact chemical and physical nature of the bottom 1000 km of the mantle is unknown. The presence of strong seismic heterogeneity in this region of the mantle is consistent with the existence of compositionally distinct domains, possibly isolated from convective stirring (Tackley, 2000). Sampling of these deep mantle domains may occur via the production of vertically oscillating domes with narrow tubular plumes arising from their upper surfaces, as modeled by thermochemical convection experiments (Davaille, 1999). For Earth's mantle, this process occurs at low density contrasts (<1%), and provides a mechanism by which deep (recycled?) material may be involved in surface volcanic processes. Recycled material in the source region of recent oceanic volcanism, in particular for HIMU basalts (generated from mantle source with high μ - $^{238}\text{U}/^{206}\text{Pb}$ ratios), has been argued based on Pb (White and Hofmann, 1982) and Hf isotopes (Salters and White, 1998; Blichert-Toft et al., 1999). One commonly held view is that HIMU-type basalts are derived from a boundary region where subducted oceanic lithosphere has accumulated (e.g., Hofmann, 1997; Bell and Tilton, 2001). It has been proposed that the HIMU mantle component may be stored at the core-mantle boundary (Hart, 1988), and recent tomographic results indicate major upwelling from this region in at least two places (Van der Hilst et al., 1997). These are the southeast Pacific Ocean and the East African

Rift zone; the latter contains an overwhelming number of kimberlite and carbonatite complexes (Woolley, 1989). Furthermore, Nd, Pb, and Sr isotope data from carbonatites worldwide (in particular those <200 Ma) indicate similarities to oceanic-island basalts (OIBs) as previously proposed by other workers (e.g., Nelson et al., 1988), and suggest mantle mixing involving the HIMU component (Tilton and Bell, 1994). To date, the Hf isotopic systematics of carbonatites and kimberlites, and their kinship to HIMU basalts, has yet to be thoroughly investigated. To this effect, we report on the Hf, Nd, and U-Pb isotope systematics of carbonatites and kimberlites from eastern North America and Greenland in order to constrain their mantle source regions. The carbonatites at Qaqarsuk, Sarfartoq, and Tupertalik of southwestern Greenland (Larsen and Rex, 1992), and kimberlites from the Guigues pipe of eastern Canada (Heaman and Kjarsgaard, 2000) and Sarfartoq (Larsen and Rex, 1992), were intruded over a period of >2.6 b.y. (see Table 1). This provides an unparalleled opportunity to investigate the chemical evolution of their source regions.

RESULTS

Table 1 lists the results for U-Pb age determinations using isotope dilution thermal ionization mass spectrometry (ID-TIMS) and Hf isotopic composition by multicollection, inductively coupled plasma-mass spectrometry (MC-ICP-MS; IsoProbe from Micromass) for baddeleyite (ZrO_2) and zircon (ZrSiO_4) from carbonatite and whole-rock kimberlite (hypabyssal facies) from Greenland and Canada. U, Pb, and Hf isotopic compositions were determined on the same baddeleyite-zircon grain or mineral fraction for both solution and laser ablation modes. Additional data tables are available in the GSA Data Repository¹.

The U-Pb data obtained for 7 baddeleyite fractions yield the precise concordia age of 3007 ± 2 Ma (Fig. 1); thus, Tupertalik is Earth's oldest known carbonatite. This age is ~300 m.y. older than any other carbonatite occurrence documented to date (Woolley, 1989). Only grains exhibiting concordant U-Pb ages (i.e., closed-system behavior) were selected for Hf isotope analyses. The occurrence of baddeleyite is restricted to mafic and alkaline magmas (Heaman and LeCheminant, 1993), and not likely inherited from the surrounding felsic crustal lithologies. The $^{176}\text{Lu}/^{177}\text{Hf}$ values for 10 zircons and 10 baddeleyites from the Tupertalik carbonatite and for 7 zircons from Sarfartoq, determined by laser ablation MC-ICP-MS, range from 0 to 0.0002 and 0.0001 to 0.0004, respectively; this results in a maximum (downward) age correction on the $^{176}\text{Hf}/^{177}\text{Hf}$ value of <20 ppm for Sarfartoq and <5 ppm for Tupertalik. These corrections are considered negligible because they are well within the internal precision of individual analyses (Table 1) and the (2σ) external reproducibility (100 ppm): present-day Hf isotopic compositions of baddeleyites and zircons were considered initial values for all carbonatite complexes.

Hf isotopic results are presented in an ϵ_{Hf} (ϵ_{Hf} is a deviation of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio from the chondritic reference value, multiplied by 10^4) versus age diagram (Fig. 2). The three kimberlite samples analyzed are characterized by Hf isotopic compositions intermediate be-

¹GSA Data Repository item 2002089, U-Pb, Lu-Hf, and Sm-Nd data tables, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA, editing@geosociety.org, or at www.geosociety.org/pubs/ft2002.htm.

*Present address: Geologisk Museum, Øster Voldgade 5-7, 1350 Copenhagen K., Denmark.

TABLE 1. Hf, Nd, AND U-Pb DATA

No.*	$^{176}\text{Hf}/^{177}\text{Hf}_{(0)}$	$\epsilon_{\text{Hf}(t)}$	$^{206}\text{Pb}/^{238}\text{U}$	$^{207}\text{Pb}/^{235}\text{U}$	U-Pb age†	$\epsilon_{\text{Nd}(t)}$
Solution mode						
<i>Carbonatites</i>						
Qaqarssuk 2z	0.282519 (48)	-5.11	0.0246	0.17	157	4.45
Qaqarssuk 3z	0.282637 (19)	-0.94	0.026	0.1432	165	
Qaqarssuk 4z	0.282656 (19)	-0.26	0.0263	0.1498	167	
Qaqarssuk 5z	0.282745 (06)	2.88	0.0261	0.1691	166	
Qaqarssuk 6z	0.282770 (08)	3.77	0.0263	0.1812	167	
Sarfartoq 1z	0.282493 (07)	3.35	0.0702	0.5808	604	
Sarfartoq 2z	0.282438 (07)	1.4	0.077	0.6422	621	4.21
Sarfartoq 3z	0.282520 (31)	4.31	0.0888	0.7302	590	
Sarfartoq 4z	0.282581 (27)	6.47	0.0834	0.6897	603	
Sarfartoq 6z	0.282621 (19)	7.88	0.0903	0.7441	595	
Sarfartoq 7z	0.282490 (08)	3.24	0.0937	0.7719	594	
Sarfartoq 8z	0.282476 (08)	2.75	0.0921	0.7548	584	
Tupertalik 3b	0.280788 (52)	-2.45	0.5883	18.103	3004	2.88
Tupertalik 5b	0.280742 (08)	-4.09	0.5955	18.378	3009	
Tupertalik 7b	0.280802 (10)	-1.96	0.583	17.948	3005	
Tupertalik 8b	0.280870 (11)	0.47	0.5941	18.312	3007	
Tupertalik 1z	0.280805 (12)	-1.85	0.5888	18.069	2999	
Tupertalik 2z	0.280780 (08)	-2.74	0.5847	17.778	2985	
Tupertalik 4z	0.280760 (08)	-3.45	0.5921	18.22	3004	
Tupertalik 5z	0.280846 (15)	-0.39	0.5834	17.633	2975	
Tupertalik 6z	0.280882 (12)	0.89	0.5778	17.766	3003	
<i>Kimberlites</i>						
Guigues G-3	0.282636 (22)	-1.92	N.D. [§]	N.D.	N.D.	5.23
Sarfartoq S-1	0.282467 (14)	2.43	N.D.	N.D.	N.D.	2.98
Sarfartoq S-2	0.282462 (10)	2.25	N.D.	N.D.	N.D.	3.01
Laser ablation						
<i>Carbonatites</i>						
Sarfartoq 101z	0.282430 (23)	1.12	0.0926	0.7814	609	4.21
Sarfartoq 102z	0.282527 (25)	4.55	0.0898	0.7448	610	
Sarfartoq 105z	0.282533 (25)	4.77	0.0951	0.8075	690	
Sarfartoq 106z	0.282409 (23)	0.38	0.0935	0.7626	598	
Sarfartoq 106z	0.282422 (22)	0.84	N.D.	N.D.	N.D.	
Sarfartoq 122z	0.282543 (32)	5.12	0.0955	0.8019	612	
Sarfartoq 133z	0.282492 (29)	3.31	0.0994	0.8495	706	
Tupertalik 101z	0.280856 (30)	-0.03	0.5991	18.2079	2992	2.88
Tupertalik 102z	0.280824 (22)	-1.17	N.D.	N.D.	N.D.	
Tupertalik 103z	0.280846 (29)	-0.39	0.6007	18.7191	2990	
Tupertalik 105z	0.280812 (24)	-1.6	0.6257	19.829	2983	
Tupertalik 106z	0.280769 (30)	-3.13	N.D.	N.D.	N.D.	
Tupertalik 107z	0.280870 (27)	0.47	0.5988	17.9693	2977	
Tupertalik 109z	0.280829 (22)	-0.99	0.6656	20.4002	2952	
Tupertalik 109z	0.280827 (29)	-1.07	N.D.	N.D.	N.D.	
Tupertalik 110z	0.280800 (29)	-2.03	0.6037	18.6924	2999	
Tupertalik 111z	0.280812 (30)	-1.6	0.6019	18.2484	2992	

Note: $\epsilon_{\text{Hf}(t)}$ and $\epsilon_{\text{Nd}(t)}$ values were calculated using planetary reference values of Blichert-Toft and Albarède (1997) and Jacobsen and Wasserburg (1980), respectively, and the Lu decay constant (λ) of $1.865 \times 10^{-11} \text{ yr}^{-1}$ (Scherer et al., 2001). $\epsilon_{\text{Hf}(t)}$ values were calculated using ages of 175 Ma and 600 Ma for the Guigues and Sarfartoq kimberlites, respectively. Chemical separation for Lu and Hf is after Blichert-Toft et al. (1997) and Amelin et al. (2000). Procedural blanks of <50 pg for Hf are considered negligible. Measured ratios were corrected for mass fractionation to $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$; spiked samples were corrected by iteratively solving a nonlinear equation combining the exponential fractionation law and the spike-natural mixing equation (Blichert-Toft et al., 1997). $^{176}\text{Lu}/^{177}\text{Hf}$ ratios of the G-3, S-1, and S-2 kimberlites are 0.008, 0.002, and 0.001, respectively (error of $\pm 2\%$). Repeated analysis ($n = 20$) of the JMC Hf standard yielded $^{176}\text{Hf}/^{177}\text{Hf} = 0.28216 \pm 3$, $^{178}\text{Hf}/^{177}\text{Hf} = 1.46726 \pm 15$, and $^{180}\text{Hf}/^{177}\text{Hf} = 1.88667 \pm 26$ (2σ standard deviation). Average $^{178}\text{Hf}/^{177}\text{Hf}$ and $^{180}\text{Hf}/^{177}\text{Hf}$ ratios for both solution and laser ablation runs are 1.46724 ± 14 , 1.88667 ± 27 (2σ , $n = 20$), and 1.46731 ± 13 , 1.88669 ± 32 (2σ , $n = 17$), respectively. U-Pb and Hf laser ablation protocols outlined in Machado and Simonetti (2001). Chemical procedures and isotopic analyses for Nd are after Henry et al. (1998).

*b = baddeleyite, z = zircon.

†Reported U-Pb ages (Ma) calculated using the $^{207}\text{Pb}/^{206}\text{Pb}$ value (Tupertalik and Sarfartoq carbonatites), and the $^{206}\text{Pb}/^{238}\text{U}$ result for Qaqarssuk.

§Not determined.

tween depleted mantle (DM) and unradiogenic values ($\epsilon_{\text{Hf}} < 0$), similar to kimberlites from South Africa (Nowell et al., 1999). Zircon and baddeleyite from carbonatites have isotopic compositions extending toward unradiogenic values, except for the Sarfartoq zircons, showing signatures intermediate to bulk silicate earth (BSE) and DM. Unradiogenic Hf isotopic signatures ($\epsilon_{\text{Hf}} \sim -10$) have also been reported for concordant baddeleyites from the 2059 Ma Palaborwa carbonatite, South Africa (Fig. 2; Scherer et al., 2001). The ϵ_{Hf} compositions of

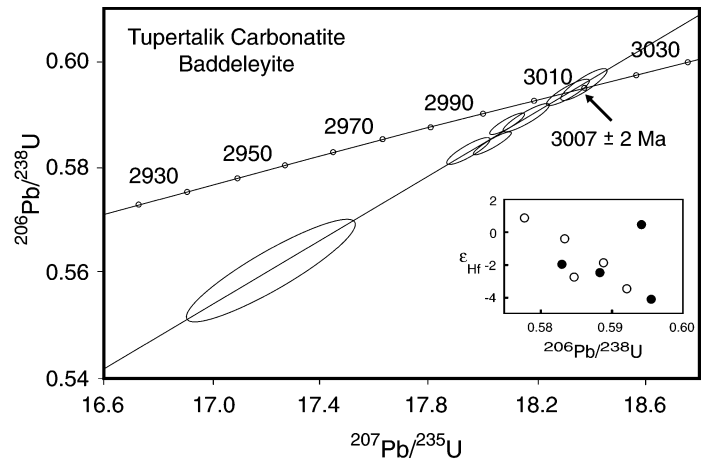


Figure 1. U-Pb concordia diagram for single baddeleyite grains from Tupertalik carbonatite. Error ellipses are 1σ and age uncertainty is quoted at 2σ level. U-Pb analyses followed isotope dilution methods outlined in Heaman and Kjarsgaard (2000) and Amelin et al. (2000). Relationship between ϵ_{Hf} and $^{206}\text{Pb}/^{238}\text{U}$ for zircon (open symbols) and baddeleyite (solid symbols) of Tupertalik carbonatite is shown in inset.

baddeleyite and zircon from the Tupertalik carbonatite exhibit a good correlation with the $^{206}\text{Pb}/^{238}\text{U}$ ratio (Fig. 1), such that the most concordant grains (high $^{206}\text{Pb}/^{238}\text{U}$) show negative ϵ_{Hf} values. In addition, the U content is not correlated to either the Hf isotopic composition or the $^{206}\text{Pb}/^{238}\text{U}$ value of the grains analyzed. This indicates that the negative ϵ_{Hf} component is not the result of a postcrystallization metamorphic disturbance, but probably represents the true isotopic signature of the melt. A combined U-Pb and Hf laser ablation (LA) MC-ICP-MS study was undertaken on zircons from the Tupertalik and Sarfartoq carbonatites. Zircons for which a concordant U-Pb age was determined by LA-MC-ICP-MS yielded a range of Hf isotopic compositions comparable to that established in solution mode (Fig. 2).

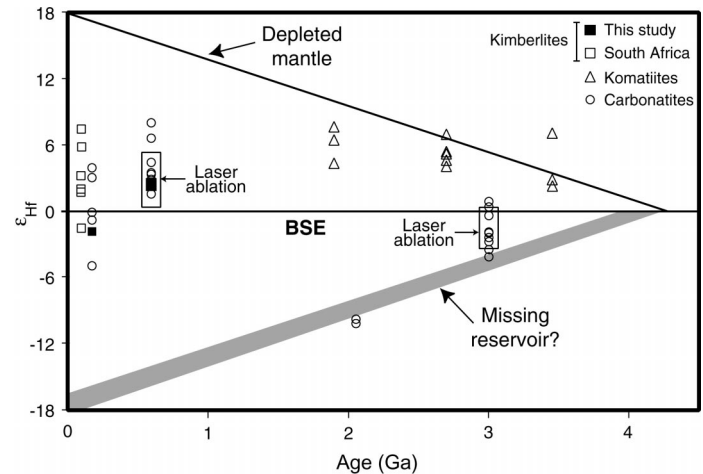


Figure 2. Hf isotope evolution diagram. Boxes outline range of Hf isotopic compositions determined by laser ablation-multicollection, inductively coupled plasma-mass spectrometry. Komatiite data are from Blichert-Toft and Arndt (1999), whereas Hf isotope values at 2.059 Ga and <90 Ma are from Scherer et al. (2001) and Nowell et al. (1999), respectively. External reproducibility (2σ), based on repeated analysis of JMC 475 standard in solution mode (Table 1 footnote), is $\sim \pm 1 \epsilon_{\text{Hf}}$ unit. Bulk silicate earth (BSE) reference line is from Blichert-Toft and Albarède (1997), and depleted mantle evolution line is modified from Vervoort and Blichert-Toft (1999). Gray band depicts evolution of enriched reservoir using $^{176}\text{Lu}/^{177}\text{Hf} \sim 0.027$ and extraction age of 4 Ga.

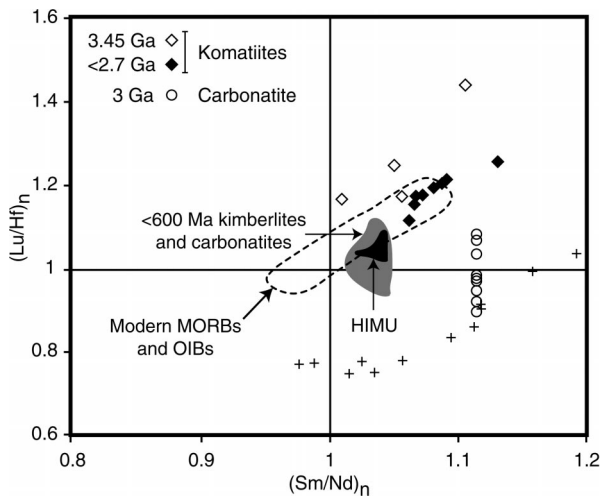


Figure 3. Time-integrated Lu/Hf vs. Sm/Nd ratios estimated for source region of komatiites, carbonatites, kimberlites, and modern mid-ocean-ridge basalts (MORBs), normalized to chondritic values (modified from Nyquist and Shih, 1992). Planetary reference values used in calculations are as in Table 1. Source for komatiite and kimberlite data is as in Figure 2, and HIMU (high μ) field is from Salters and White (1998). Nd isotope compositions for zircon and baddeleyite were assumed to be equal to initial Nd isotope compositions of their host whole-rock carbonatite because latter contains extremely high abundances of Nd (average ~250 ppm) that buffer Nd isotope composition inherited from their mantle source against possible crustal contamination. ϵ_{Nd} compositions for carbonatite and kimberlite samples represent minimum values, because their $^{147}\text{Sm}/^{144}\text{Nd}$ values are slightly lower compared to those of their mantle source region (i.e., recycled mafic component). Lower Sm/Nd values are attributed to preferential addition of Nd (and light rare earth elements), which most probably reflects presence of volatile-rich (metasomatic) agent within recycled reservoir, and low degree of partial melting. Modern MORBs and oceanic-island basalts (OIBs) array is from Albarède et al. (2000). Plus symbols show parent/daughter values for modern MORB samples (Chauvel and Blichert-Toft, 2001); these samples indicate decoupling to lower Lu/Hf ratios and may imply that similar lithospheric material has been recycled into mantle and is present in source region of kimberlite and carbonatite magmas.

DISCUSSION

The estimated compositions for the mantle sources of both <600 Ma kimberlites and carbonatites and the 3 Ga Tupertalik carbonatite are distinct from the mantle sources sampled by modern oceanic basalts, because the data are below the array formed by mid-ocean-ridge basalts (MORBs) and OIBs. Such a decoupling, also noted for HIMU basalts from St. Helena (Salters and White, 1998), indicates derivation from a reservoir with subchondritic Lu/Hf and superchondritic Sm/Nd ratios. This decoupling can be achieved during partial melting in a mid-ocean-ridge setting, because modern MORBs are characterized by subchondritic Lu/Hf and superchondritic Sm/Nd ratios. Long-term storage of such a mafic component would generate a mantle reservoir with time-integrated unradiogenic and radiogenic Hf and Nd isotopic compositions, respectively. Thus, the Sm/Nd and Lu/Hf fractionation trends observed in Figure 3 indicate that the source region for the 3 Ga Tupertalik carbonatite and younger carbonatites, kimberlites, and modern HIMU basalts, may contain a recycled mafic crustal component. The variations in Hf isotopic compositions recorded by zircon and baddeleyite crystals (Figs. 2 and 3) also suggest open-system behavior involving distinct mantle reservoirs during carbonatite formation, such as plume and subcontinental lithosphere (e.g., Bell and Simonetti,

1996; Simonetti et al., 1998). Another striking feature of Figure 3 is that the Early to Middle Archean terrestrial mantle was isotopically much more heterogeneous (in particular for Lu/Hf) than the present-day mantle sampled by MORBs and OIBs. As discussed in Albarède et al. (2000), the isotopic heterogeneity observed in the early terrestrial mantle exhibits similarities to the poorly mixed mantles of planetary bodies such as Mars and the Moon, and may represent a transient regime inherited from initial planetary differentiation. Our study thus confirms that such isotopic heterogeneity was still present as late as ca. 3 Ga, but more elusive in <2.7 Ga mantle-derived rocks.

The Hf-Nd isotope systematics of modern basalts and chondrites requires an additional reservoir complementary to depleted mantle and continental crust in order to account for the accepted Hf-Nd composition of BSE (Blichert-Toft and Albarède, 1997). This missing component may consist of recycled basalts representing old oceanic crust and plateaus (Chase and Patchett, 1988; Blichert-Toft and Albarède, 1997). Assuming that this reservoir equates to the carbonatite-kimberlite source region, and formed ca. 4 Ga (Fig. 2), a $^{176}\text{Lu}/^{177}\text{Hf}$ of ~0.027 is required to generate the least radiogenic Hf composition observed at 3 Ga (i.e., 19% fractionation from the BSE value of 0.0332; Blichert-Toft and Albarède, 1997). Formation of the carbonatite and kimberlite source reservoir ca. 4 Ga is consistent with other estimates of timing of mantle differentiation (Vervoort and Blichert-Toft, 1999). Using this constraint and accepted abundances of Lu, Hf, Sm, and Nd for Earth's major geochemical reservoirs (McDonough and Sun, 1995; Rudnick and Fountain, 1995), mass-balance calculations indicate that the unradiogenic Hf component may account for 10%–15% of the total mass of silicate Earth. For depleted mantle, Hf (0.15 ppm), Lu (0.01 ppm), Nd (1 ppm), and Sm (0.2 ppm) contents were derived using batch melting equations (Albarède, 1995), partition coefficients from Hart and Dunn (1993), and assuming 10%–15% garnet-absent melting in order to yield average compositions of MORBs (McDonough and Sun, 1995). These abundances are consistent with Lu/Hf and Sm/Nd ratios accepted for depleted mantle based on Hf and Nd isotope compositions (Vervoort and Blichert-Toft, 1999). This approach results in Hf, Lu, Nd, and Sm concentrations of ~1, 0.2, 1.5, and 0.4 ppm, respectively, in the missing mantle reservoir, which represents ~10%–15% of BSE as compared to ~85%–90% for depleted mantle and 0.6% for continental crust. These concentrations are approximations because they are highly sensitive to model parameters such as partition coefficients and degree of partial melting. This calculation assumes a present-day ϵ_{Hf} ~ -17 for the enriched component, and the absence of any primitive-mantle-like reservoir, because the Hf-Nd isotope geochemistry of terrestrial basalts is inconsistent with derivation from such a component (Blichert-Toft and Albarède, 1997). The proposed model results in a present-day $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.28279 for BSE, which differs by ~75 ppm from the accepted value of 0.282772 (Blichert-Toft and Albarède, 1997). These two values, determined independently, are identical considering the uncertainties associated with both the isotopic compositions for the BSE model (Blichert-Toft and Albarède, 1997) and our calculated value (50 and 100 ppm, respectively).

Our data indicate the existence in the source region of kimberlite and carbonatite magmas, since at least 3 Ga, of a negative ϵ_{Hf} component that is decoupled from the Nd isotope systematics and divergent from either depleted- or primitive-mantle compositions. The carbonatite and kimberlite mantle source is distinct from that that generated the Archean komatiites, because these sampled a depleted mantle source ca. 3 Ga (Fig. 2). In addition, Sr and Pb isotopic data from North American carbonatites (ranging from 0.1 to 2.7 Ga) indicate derivation from a source region distinct from either primitive or MORB-like depleted mantle (Bell et al., 1982; Tilton and Bell, 1994). Alternatively, the negative ϵ_{Hf} component may also reside in the subcontinental mantle (Griffin et al., 2000). New Hf isotopic data for con-

stituent minerals from kimberlite-hosted garnet peridotite xenoliths from the Canadian Arctic (Schmidberger et al., 2002) refute this interpretation, because these analyses systematically yield positive ϵ_{Hf} signatures. Our preferred interpretation is that carbonatite-kimberlite melts are derived from an unradiogenic Hf mantle source that is at least 3 Ga. Isolation of this mantle source may have occurred in the deep mantle (core-mantle boundary region?), and may consist of recycled, fertile lithosphere related to an Early Archean mantle-depletion event (e.g., Chase and Patchett, 1988). A similar model is presented for the generation of South African group I and II kimberlites, involving plumes originating from a deep mantle source characterized by a negative ϵ_{Hf} signature (Nowell et al., 1999). Bell and Tilton (2001) also proposed carbonatite generation via plumes originating from the deep mantle (the bottom 1000 km of the mantle) involving the HIMU and EM1 (enriched-mantle 1) mantle components, corroborating the model presented here.

ACKNOWLEDGMENTS

Supported by a Natural Sciences and Engineering Research Council of Canada grant (to Stevenson) and a Graduate Research Grant from the Geological Society of America (to Bizzarro). Bizzarro acknowledges "Fonds de recherche sur la nature et les technologies" for a Ph.D. scholarship. Francis Albarède and Clément Gariépy informally reviewed an earlier version of this manuscript. Constructive reviews from J. Blichert-Toft, J. Patchett, and K. Bell improved the quality of this manuscript.

REFERENCES CITED

- Albarède, F., 1995, Introduction to geochemical modeling: Cambridge, Cambridge University Press, 543 p.
- Albarède, F., Blichert-Toft, J., Vervoort, J.D., Gleason, J.G., and Rosing, M., 2000, Hf-Nd evidence for a transient dynamic regime in early terrestrial mantle: *Nature*, v. 404, p. 488–490.
- Amelin, Y., Lee, D.-C., and Halliday, A.N., 2000, Early-middle Archean crustal evolution deduced from Lu-Hf and U-Pb isotopic studies of single grain zircons: *Geochimica et Cosmochimica Acta*, v. 64, p. 4205–4225.
- Bell, K., and Simonetti, A., 1996, Carbonatite magmatism and plume activity: Implications from the Nd, Pb and Sr isotope systematics of Oldoinyo Lengai: *Journal of Petrology*, v. 37, p. 1321–1339.
- Bell, K., and Tilton, G.R., 2001, Nd, Pb and Sr isotopic compositions of East African carbonatites: Evidence for mantle mixing and plume inhomogeneity: *Journal of Petrology*, v. 42, p. 1927–1945.
- Bell, K., Blenkinsop, J., Cole, T.J.S., and Menagh, D.P., 1982, Evidence from Sr isotopes for long-lived heterogeneities in the upper mantle: *Nature*, v. 298, p. 251–253.
- Blichert-Toft, J., and Albarède, F., 1997, The Lu-Hf isotope geochemistry of chondrites and the evolution of the mantle-crust system: *Earth and Planetary Science Letters*, v. 148, p. 243–258.
- Blichert-Toft, J., and Arndt, N.T., 1999, Hf isotope compositions of komatiites: *Earth and Planetary Science Letters*, v. 171, p. 439–451.
- Blichert-Toft, J., Chauvel, C., and Albarède, F., 1997, Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS: *Contributions to Mineralogy and Petrology*, v. 127, p. 248–260.
- Blichert-Toft, J., Frey, F.A., and Albarède, F., 1999, Hf isotope evidence for pelagic sediments in the source of Hawaiian basalts: *Science*, v. 285, p. 879–882.
- Bowring, S.A., and Housh, T., 1995, The Earth's early evolution: *Science*, v. 269, p. 1535–1540.
- Chase, C.G., and Patchett, P.J., 1988, Stored mafic/ultramafic crust and early Archean mantle depletion: *Earth and Planetary Science Letters*, v. 91, p. 66–72.
- 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.
- Davaille, A., 1999, Simultaneous generation of hotspots and superswells by convection in a heterogeneous planetary mantle: *Nature*, v. 402, p. 756–760.
- Griffin, W.L., Pearson, N.J., Belousova, E., Jackson, S.E., van Achterbergh, E., O'Reilly, S.Y., and Shee, S.R., 2000, The Hf isotope composition of cratonic mantle: LAM-MC-ICPMS analysis of zircon megacrysts in kimberlites: *Geochimica et Cosmochimica Acta*, v. 64, p. 133–147.
- Hart, S.R., 1988, Heterogeneous mantle domains: Signature, genesis and mixing chronologies: *Earth and Planetary Science Letters*, v. 90, p. 273–296.
- Hart, S.R., and Dunn, T., 1993, Experimental clinopyroxene-melt partitioning of 24 trace elements: *Contributions to Mineralogy and Petrology*, v. 113, p. 1–8.
- Heaman, L.M., and Kjarsgaard, B., 2000, Timing of eastern North American kimberlite magmatism: Continental extension of the Great Meteor hotspot track?: *Earth and Planetary Science Letters*, v. 178, p. 253–268.
- Heaman, L.M., and LeCheminant, A.N., 1993, Paragenesis and U-Pb systematics of baddeleyite (ZrO₂): *Chemical Geology*, v. 110, p. 95–126.
- Henry, P., Stevenson, R.K., and Gariépy, C., 1998, Late Archean mantle composition and crustal growth: *Geochimica et Cosmochimica Acta*, v. 62, p. 143–157.
- Hofmann, A., 1997, Mantle geochemistry: The message from oceanic volcanism: *Nature*, v. 385, p. 219–229.
- Jacobsen, S.B., and Wasserburg, G.J., 1980, Sm-Nd isotopic evolution of chondrites: *Earth and Planetary Science Letters*, v. 50, p. 139–155.
- Larsen, L.M., and Rex, D.C., 1992, A review of the 2500 Ma span of alkaline-ultramafic, potassic and carbonatitic magmatism in West Greenland: *Lithos*, v. 28, p. 367–402.
- Machado, N., and Simonetti, A., 2001, U-Pb dating and Hf isotopic composition of zircon by laser-ablation MC-ICP-MS, in Sylvester, P., ed., *Laser-ablation-ICPMS in the Earth sciences: Principles and applications*: St. John's, Newfoundland, Mineralogical Association of Canada, p. 121–146.
- McDonough, W.F., and Sun, S.-S., 1995, The composition of the Earth: *Chemical Geology*, v. 120, p. 223–253.
- Nelson, D.R., Chivas, A.R., Chappell, B.W., and McCulloch, M.T., 1988, Geochemical and isotopic systematics in carbonatites and implication for the evolution of ocean-island sources: *Geochimica et Cosmochimica Acta*, v. 52, p. 1–17.
- Nowell, G.M., Pearson, D.G., Kempton, P.D., Noble, S.R., and Smith, C.B., 1999, The origins of kimberlites: A Hf isotope perspective, in Gurney, J.J., et al., eds., *Proceedings of the VIIth International Kimberlite Conference, Volume 2*: Cape Town, South Africa, Red Roof Design, p. 616–624.
- Nyquist, L.E., and Shih, C.-Y., 1992, The isotopic record of lunar volcanism: *Geochimica et Cosmochimica Acta*, v. 62, p. 525–544.
- Rudnick, R.L., and Fountain, D.M., 1995, Nature and composition of the continental crust: A lower crustal perspective: *Reviews of Geophysics*, v. 33, p. 267–309.
- Salter, V.J.M., and White, W.M., 1998, Hf isotope constraints on mantle evolution: *Chemical Geology*, v. 145, p. 447–460.
- Scherer, E., Münker, C., and Mezger, K., 2001, Calibrating the Lu-Hf clock: *Science*, v. 293, p. 683–686.
- Schmidberger, S.S., Simonetti, A., Francis, D., and Gariépy, C., 2002, Probing Archean lithosphere using the Lu-Hf isotope systematics of peridotite xenoliths from Somerset Island kimberlites, Canada: *Earth and Planetary Science Letters*, v. 197, p. 245–259.
- Simonetti, A., Goldstein, S.L., Schmidberger, S.S., and Viladkar, S.G., 1998, Geochemical and Nd, Pb, and Sr isotope data from Deccan alkaline complexes—Inferences for mantle sources and plume-lithosphere interaction: *Journal of Petrology*, v. 39, p. 1847–1864.
- Tackley, P.J., 2000, Mantle convection and plate tectonics: Towards an integrated physical and chemical theory: *Science*, v. 288, p. 2002–2007.
- Tilton, G.R., and Bell, K., 1994, Sr-Nd-Pb isotope relationships in late Archean carbonatites and alkaline complexes: Applications to the geochemical evolution of the mantle: *Geochimica et Cosmochimica Acta*, v. 58, p. 3145–3154.
- Van der Hilst, R.D., Widiyantoro, S., and Engdahl, E.R., 1997, Evidence for deep mantle circulation from global tomography: *Nature*, v. 386, p. 578–583.
- Vervoort, J., and Blichert-Toft, J., 1999, Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time: *Geochimica et Cosmochimica Acta*, v. 63, p. 533–556.
- White, W.M., and Hofmann, A.W., 1982, Sr and Nd isotope geochemistry of oceanic basalts and mantle evolution: *Nature*, v. 296, p. 821–825.
- Woolley, A.R., 1989, Spatial and temporal distribution of carbonatites, in Bell, K., ed., *Carbonatites: Genesis and evolution*: London, Unwin Hyman, p. 15–37.

Manuscript received January 31, 2002

Revised manuscript received April 30, 2002

Manuscript accepted May 2, 2002

Printed in USA