



PII S0016-7037(01)00856-0

## Implications of Nb/U, Th/U and Sm/Nd in plume magmas for the relationship between continental and oceanic crust formation and the development of the depleted mantle

IAN H. CAMPBELL\*

Research School of Earth Sciences, Australian National University, Canberra, ACT, 0200, Australia

(Received December 15, 2000; accepted in revised form October 22, 2001)

**Abstract**—The Nb/U and Th/U of the primitive mantle are 34 and 4.04 respectively, which compare with 9.7 and 3.96 for the continental crust. Extraction of continental crust from the mantle therefore has a profound influence on its Nb/U but little influence on its Th/U. Conversely, extraction of midocean ridge-type basalts lowers the Th/U of the mantle residue but has little influence on its Nb/U. As a consequence, variations in Th/U and Nb/U with Sm/Nd can be used to evaluate the relative importance of continental and basaltic crust extraction in the formation of the depleted (Sm/Nd enriched) mantle reservoir.

This study evaluates Nb/U, Th/U, and Sm/Nd variations in suites of komatiites, picrites, and their associated basalts, of various ages, to determine whether basalt and/or continental crust have been extracted from their source region. Emphasis is placed on komatiites and picrites because they formed at high degrees of partial melting and are expected to have Nb/U, Th/U, and Sm/Nd that are essentially the same as the mantle that melted to produce them. The results show that all of the studied suites, with the exception of the Barberton, have had both continental crust and basaltic crust extracted from their mantle source region. The high Sm/Nd of the Gorgona and Munro komatiites require the elevated ratios seen in these suites to be due primarily to extraction of basaltic crust from their source regions, whereas basaltic and continental crust extraction are of subequal importance in the source regions of the Yilgarn and Belingwe komatiites. The Sm/Nd of modern midocean ridge basalts lies above the crustal extraction curve on a plot of Sm/Nd against Nb/U, which requires the upper mantle to have had both basaltic and continental crust extracted from it.

It is suggested that the extraction of the basaltic reservoir from the mantle occurs at midocean ridges and that the basaltic crust, together with its complementary depleted mantle residue, is subducted to the core-mantle boundary. When the two components reach thermal equilibrium with their surroundings, the lighter depleted component separates from the denser basaltic component. Both are eventually returned to the upper mantle, but the lighter depleted component has a shorter residence time in the lower mantle than the denser basaltic component. If the difference in the recycling times for the basaltic and depleted components is ~1.0 to 1.5 Ga, a basaltic reservoir is created in the lower mantle, equivalent to the amount of basalt that is subducted in 1.0 to 1.5 Ga, and that reservoir is isolated from the upper mantle. It is this reservoir that is responsible for the Sm/Nd ratio of the upper mantle lying above the trend predicted by extraction of continental crust on the plot of Sm/Nd against Nb/U. Copyright © 2002 Elsevier Science Ltd

### 1. INTRODUCTION

The modern upper mantle, as sampled by midocean ridge basalts (MORBs), is depleted in incompatible elements such as U, Th, Nd, and Hf. Because these elements are present in high concentrations in the continental crust, this depletion is normally attributed to the formation of the continental crust, which is regarded as the complement to the depleted mantle (Hurley et al., 1962; Hart, 1971; DePaolo and Wasserburg, 1976; Jacobsen and Wasserburg, 1979; Hofmann, 1988). However, Nd and Hf isotope data show that the Earth's oldest rocks formed from a mantle reservoir that was already depleted in incompatible elements and that had Sm/Nd and Lu/Hf above chondritic values by 3.9 Ga (Patchett et al., 1981; Bennett et al., 1993; Vervoort et al., 1996; Blichert-Toft and Arndt, 1999). Although the extent of the increases in the Sm/Nd and Lu/Hf remain controversial, the conclusion that the Earth's oldest known rocks were extracted from a depleted mantle reservoir is widely accepted. Positive  $\epsilon_{Nd}$  and  $\epsilon_{Hf}$  values dominate analyses of samples from all locations older than 3.4 Ga, indicating the

existence of a widespread mantle reservoir with  $\epsilon_{Nd}$  values of at least +2 to +3 and  $\epsilon_{Hf}$  values of +4 to +5 by 3.9 Ga (Fig. 1).

The development of a widespread depleted mantle reservoir by 3.9 Ga appears to be inconsistent with a complementary reservoir that consists solely of continental crust. The formation of an already depleted mantle reservoir with an  $\epsilon_{Nd}$  value of +2 and an  $\epsilon_{Hf}$  value of +4 by 3.9 Ga requires the reservoir to have had a  $^{147}\text{Sm}/^{144}\text{Nd}$  of 0.23 and a  $^{176}\text{Lu}/^{177}\text{Hf}$  of 0.043 since the time of formation of the Earth at 4.5 Ga. These ratios are well above chondritic values and above those for the modern depleted mantle of 0.22 and 0.039, respectively. If the depleted mantle reservoir is due solely to the formation of the continental crust, and if it had a mass similar to that of the modern depleted reservoir, these increases in  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{176}\text{Lu}/^{177}\text{Hf}$  require the mass of the continental crust at 4.5 Ga to have been greater than the mass of the modern continental crust. The mass of the required continental crust increases dramatically if the continental crust is assumed to have started forming later at 4.0 Ga, the age of the oldest preserved continental crust, but decreases if the mass of the 4.0 to 4.5 Ga depleted mantle reservoir was less than the mass of the modern depleted mantle

---

\* ian.campbell@anu.edu.au.

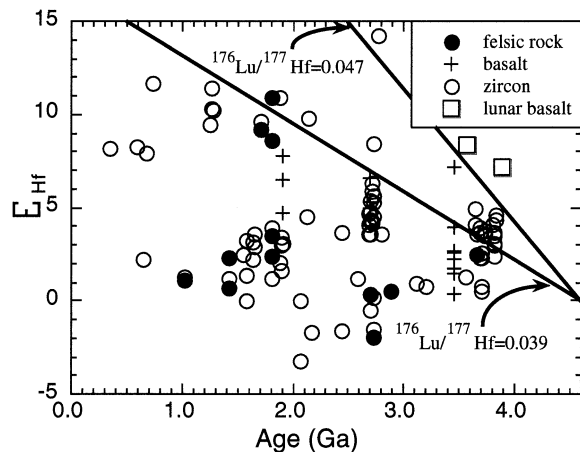


Fig. 1. A plot of  $\epsilon_{\text{Hf}}$  for basalts (crosses), felsic rocks (open circles), and zircons (filled circles) plotted against time. Lunar basalts (squares) are shown for comparison. The  $\epsilon_{\text{Hf}}$  growth lines are for  $^{176}\text{Lu}/^{177}\text{Hf}$  values of 0.039 and 0.047. Data from Patchett et al. (1981), Corfu and Noble (1992), Vervoort et al. (1996), Blichert-Toft and Arndt (1999), and Gruau et al. (1990).

reservoir, for example, if it occupied only part of the upper mantle (McCulloch and Bennett, 1994). Nevertheless, it is difficult to escape the conclusion that continental crust can only be the complementary reservoir to the depleted mantle if a substantial mass of continental crust had formed by  $\sim 4.2$  Ga. The oldest preserved continental crust is the 4.0 Ga Acasta gneiss from Canada (Bowring et al., 1989), and the only direct evidence that the continental crust may have formed before this time is provided by rare detrital zircons with ages of up to 4.4 Ga (Froude et al., 1983; Wilde et al., 2001). If an extensive reservoir of continental crust existed before 4.0 Ga, no evidence for its existence has been found in the Nd or Hf model ages of Earth's oldest sediments (Jacobsen, 1988; Stevenson and Patchett, 1990) and only tenuous evidence in the zircons extracted from them (Froude et al., 1983; Nutman, 1996; Wilde et al., 2001).

An alternative hypothesis is that oceanic crust is the complement to early Earth's depleted mantle. Nd, Sm, Lu, Hf, and other incompatible elements partition strongly into basaltic oceanic crust, leaving behind a mantle residue that is depleted in these elements and that has elevated Sm/Nd and Lu/Hf. There are two variations on this theme. The first is that the Earth's early basaltic crust was subducted into the lower mantle, where it was temporarily stored, leaving behind an upper mantle with elevated Sm/Nd and Lu/Hf (Chase and Patchett, 1988). The second is that the primitive Earth's basaltic reservoir was a stable outer shell of alkalic basalt that formed at relatively low degrees of partial melting (2 to 10%; Galer and Goldstein, 1991). These suggestions have not been well received principally because the "hidden reservoir" of high-Sm/Nd and high-Lu/Hf basaltic material is not sampled by early basalts or komatiites (Blichert-Toft and Arndt, 1999).

Extraction of both continental and basaltic crust from the mantle raises the Sm/Nd and Lu/Hf of the mantle residue. As a consequence, although Nd and Hf isotopic studies of basalts, komatiites, and picrites can be used to determine whether their mantle source region has experienced long-term depletion in

incompatible elements, they cannot be used to distinguish between depletion due to extraction of continental crust and depletion due to extraction of basaltic crust. To make this distinction, two element pairs are required: one that fractionates during extraction of the continental crust but not during the extraction of basaltic crust and a second pair that fractionates during basaltic crust extraction but not during extraction of continental crust. Nb/U and Th/U have the required properties.

The application of Nb/U and Th/U to evaluate continental crust extraction is straightforward. The Nb/U and Th/U of the primitive mantle are 34 and 4.04 respectively, which compare with 9.7 and 3.96 (Sun and McDonough, 1989; Rudnick and Fountain, 1995) for the continental crust. This marked difference between the Nb/U of the mantle and continental crust and the small difference in the Th/U, means that extraction of continental crust from the mantle has a profound influence on its Nb/U (Hofmann et al., 1986) but little influence on its Th/U.

The effect of removing basaltic crust is the reverse. Nb and U have similar partition coefficients during partial melting to form MORB, but  $D^{\text{Th}} > D^{\text{U}}$ . As a consequence, basalt extraction lowers the Th/U ratio of the mantle residue but has little effect its Nb/U (Hofmann et al., 1986). Alternatively, Nb/Pr can be used as a substitute for Th/U. The Nb/Pr ratio of the continental crust is similar to the mantle, but  $D^{\text{Nb}} \gg D^{\text{Pr}}$  during basalt extraction. Plots of Nb/Pr against Nb/U should therefore discriminate between mantle that has had basalt or continental crust extracted from it. The advantage of Nb/Pr over Th/U is that the difference in the  $D$  values for Nb-Pr is much greater than for Th-U during basalt extraction. The disadvantage is that Pr is less incompatible than Th and U, so that the assumption that Nb/Pr in the melt is the same as the mantle source region is only valid at very high degrees of partial melting and in the absence of garnet.

If extraction of the continental crust changes the Nb/U of the mantle residue without changing its Th/U and extracting MOR-type basaltic crust changes its Th/U without changing its Nb/U, variations in Th/U and Nb/U with Sm/Nd can be used to show whether the Sm/Nd (and Lu/Hf) enrichment of the depleted mantle is due to extraction of basaltic or continental crust. This can be done by comparing the trends of Nb/U and Th/U against Sm/Nd for suites of picrites, komatiites, and associated basalts with calculated trends produced by extraction of continental and basaltic crust.

This study compares Nb/U, Nb/Pr, Th/U, and Sm/Nd trends, in various combinations, for komatiites, picrites, and their associated basalts, with the calculated trends produced by extracting continental and basaltic crust from the mantle. The data used in this study are from the literature and include seven Archaean komatiite-basalt localities; Tisdale Township, Munro Township (Kerrick et al., 1999a, 1999b), Lumby Lake-Steep Rock (Fan and Kerrick, 1997), the Barberton (Campbell, submitted), Norseman-Wiluna (Sylvester et al., 1997), Kostomuksha (Puchtel et al., 1998b), and Sumozero-Kenozero (Puchtel et al., 1999) greenstone belts; a Proterozoic flood basalt, the Onego plateau (Puchtel et al., 1998a); and three modern oceanic basalt suites, Iceland (Hemond et al., 1993), Réunion (Albarède et al., 1997), and Malaita islands. All are thought to be the melting products of mantle plumes; the Archaean suites because they are associated with high-temperature komatiites, Iceland and Réunion because they formed above the Iceland

and Réunion plumes respectively, and Malaita Island because it forms part of the Ontong Java Plateau, which is believed to have been produced by melting an oceanic plume head. Arguments for assigning these komatiites, picrites, and their associated basalts to mantle plumes are developed in greater detail by Campbell (submitted).

## 2. CALCULATING TRACE ELEMENT TRENDS IN THE RESIDUAL MANTLE PRODUCED BY BASALT AND CONTINENTAL CRUST EXTRACTION

### 2.1. Continental Crust Extraction

The method used to calculate the effect of continental crust extraction on trace element ratios in the residual mantle differs from the normal approach, which assumes that the continental crust was extracted from a known mass of mantle. The problem with applying this type of calculation to modern Earth is that although the mass of the modern continental crust is well known, the mass of the depleted mantle is not. For the Archaean continental crust and depleted mantle, the calculation is even more difficult because the mass of the Archaean continental crust, and how it changes with time, is poorly constrained and because the mass of the Archaean depleted mantle is unknown. Furthermore, the composition of the Archaean mantle, as sampled by Archaean komatiites and their associated basalts, is highly variable, with Sm/Nd in komatiites varying between 0.33 and 0.70 and Nb/U between 30 and 70.

An alternative approach is to consider the mantle as being made up of a series of finite elements, each with a different composition. For practical purposes, the volume of these elements is taken as the volume sampled by the individual flows that were included in this study. The effect on the Nb/U, Th/U, and Sm/Nd of the residual mantle of extracting a given fraction of material, which has the trace element concentrations of the continental crust, is then calculated. This can be done from the following equation:

$$\frac{C_r^i}{C_r^j} = \frac{C_o^i - fC_c^i}{C_o^j - fC_c^j} \quad (1)$$

where  $C_r^i/C_r^j$  is the ratio of the elements  $i$  and  $j$  in the mantle residue,  $C_o^i$  and  $C_o^j$  are their concentrations in the mantle before melting,  $C_c^i$  and  $C_c^j$  are their concentrations in the crust, and  $f$  is the fraction of crust extracted. The advantage of this type of approach is that it allows Nb/U, Th/U, and Sm/Nd fractionation trends produced in the mantle by continental crust extraction to be calculated without knowing the masses of the continental crust or depleted mantle reservoir and without specifying details of the crust forming process. In addition, the results can be readily applied to a heterogeneous mantle.

### 2.2. Basalt Extraction

Unfortunately, because the trace element concentrations of the Archaean upper mantle and MORBs are not known, the methodology used to calculate the trace element trends produced by continental crust extraction cannot be extended to basaltic crust extraction. However, because the effects of basalt extraction on the Nb/U, Nb/Pr, and Sm/Nd of the mantle residue are well known, this is not necessary for these element

pairs. The suggestion that the Th/U of the mantle is depleted by basalt extraction, however, requires justification.

The best evidence for Th/U fractionation during basalt extraction comes from uranium series disequilibrium studies of basalts. These studies have shown that both MORBs and oceanic island basalts (OIBs) have activity ratios ( $r$ ) that are normally above 1 and can be as high as 1.4. Initially, this was interpreted to indicate that the Th/U of melt was  $r$  times higher than the Th/U of the mantle source region (Allègre and Condomines, 1982). However, dynamic melting models have shown that the Th/U enrichment associated with melting can be  $<r$  by an amount that depends on the rate of upwelling of the mantle and the geometry of the melt zone (McKenzie, 1985; Williams and Gill, 1989). All that can be said with confidence from these studies is that Th was more incompatible than U during melting to form MORBs and OIBs, which requires that  $D^{Th} < D^U$  in the melt zone. This is normally interpreted to be due to the presence of garnet, which is the mineral that is most effective in fractionating Th from U during melting (Salters and Longhi, 1999). However, recent studies suggest that clinopyroxene can also have  $D^{Th} < D^U$  if melting occurs at pressures above  $\sim 1.5$  GPa (Wood et al., 1999).

If the degree of partial melting is high, so that the melt fraction,  $F$ , is much greater than  $D^{Th}$  and  $D^U$ , all of the highly incompatible elements are concentrated in the melt, and the Th/U ratio of the melt is approximately equal to the Th/U ratio of the mantle source. This is a first-order result that is true for all melting models (Williams and Gill, 1989). It is important to note that if  $D^{Th} < D^U$ , the Th/U ratio of the melt must always be greater the Th/U ratio of the source region, and the Th/U of the residue must always be less. From mass balance considerations, the increase in the Th/U of the melt can be very small at high degrees of melting, but the decrease in the Th/U ratio of the residue can be substantial, depending on the difference between  $D^{Th}$  and  $D^U$ . Details of the melting process are not important in the present context. The important points are (a) that basalt extraction lowers the Th/U of the mantle residue, especially at high melt fractions, and (b) that the melt's Th/U ratio is approximately equal to the Th/U ratio of the initial mantle if  $F \gg D^{Th}$  and  $D^U$ .

## 3. RESULTS

### 3.1. Basalt Trace Element Ratios as Indicators of Source Ratios

An important assumption of this study is that the trace element ratios of the basalts that have been included in this study are, to a good approximation, the same as their mantle source region, which is true if  $F \gg D$  for both of the elements under consideration. For highly incompatible elements such as Nb, Th, and U, this is true for magmas that form at moderate to high degrees of partial melting, including tholeiites, picrites, and komatiites. However, for elements that are less incompatible, such as Pr, Nd, and Sm, this assumption is only valid for magmas that form at high degrees of partial melting. For this reason, only picrites and komatiites are considered when interpreting trace element ratios involving Pr, Nd, and Sm. Alkali basalts have been excluded from this study.

Al-depleted komatiites, which have higher Th/U and lower Sm/Nd ratios than their mantle source regions, are an important

exception. They are interpreted to form in the transition zone and to leave abundant garnet in their residue, so that the assumption that  $F \gg D^{\text{Th}}$ ,  $D^{\text{U}}$ ,  $D^{\text{Sm}}$ , and  $D^{\text{Nd}}$  is not valid for these rocks. Fortunately, they are readily distinguished from other komatiites by their high Ca/Al and low Al/Ti ratios (Sun and Nesbitt, 1978).

### 3.2. Nb/U-Nb/Th

Figures 2 and 3 are plots of Nb/U against Nb/Th for the seven Archaean komatiite-basalt localities, one Proterozoic flood basalt, and the basalts from Iceland, Réunion, and Malaita islands. Samples with constant Th/U plot on a straight line with a slope that is inversely proportional to Th/U. As argued earlier, all of the suites included in this study are thought to be the products of high degrees of partial melting in mantle plumes. Their Th/U should therefore be essentially the same as the mantle source region that melted to produce them, provided the degree of partial melting exceeds the critical level required to remove all (or most) of the garnet from the residue.

Figures 2 and 3 show a strong correlation between Nb/U and Nb/Th for most of the suites considered in this study. The variation in Th/U within suites is generally small, but there is significant variation between suites. Eight of the suites (Réunion, Malaita, Iceland, Munro, Onega, Sumozero-Kenozero, Kostomuksha, and Norseman-Wiluna) have CaO/Al<sub>2</sub>O<sub>3</sub> near 1.0, indicating that there is no significant garnet in the mantle residue of these suites and that their Th/U should be inherited from their mantle source region. The average Th/U is  $3.78 \pm 0.31$  for Réunion,  $3.87 \pm 0.23$  for Malaita,  $3.86 \pm 0.21$  for Norseman-Wiluna,  $3.38 \pm 0.27$  for Onega,  $3.41 \pm 0.57$  for Sumozero-Kenozero,  $3.05 \pm 0.14$  for Iceland,  $2.79 \pm 0.48$  for Munro, and  $2.71 \pm 0.51$  for Kostomuksha.

The standard deviation for Th/U for five of the suites is <10% of the mean, and for three suites (Iceland, Réunion, and Norseman-Wiluna) it is ~5%. However, for three other suites (Sumozero-Kenozero, Kostomuksha, and Munro), the standard deviation approaches 20%. It is not clear whether the wide range of Th/U seen in these suites is due to variations in the Th/U of the source region, U mobility during alteration, or the difficulty of analysing U at low concentrations. The average Th/U calculated from Pb isotope analyses is available for three of these suites:  $3.41 \pm 0.51$  for Sumozero-Kenozero,  $3.01 \pm 0.19$  for Kostomuksha, and  $3.4 \pm 0.3$  for Onega, which compare with  $3.41 \pm 0.57$ ,  $2.71 \pm 0.51$ , and  $3.38 \pm 0.27$ , respectively, from trace elements. With the possible exception of Kostomuksha, the Pb isotope data provide no evidence of a systematic error in the Th/U trace element analyses.

Three of the Archaean komatiite-basalt suites (Barberton, Tisdale, and Lumby Lake-Steep Rock) have CaO/Al<sub>2</sub>O<sub>3</sub> well above 1.0 and subchondritic Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>. The Barberton Al-depleted komatiites and basalts have Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> of 5.6 to 14.5 and Th/U of  $4.16 \pm 0.21$ , the Tisdale suite has Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> that are mainly between 12 and 16 and Th/U of  $4.28 \pm 0.62$ , and the Lumby Lake-Steep Rock suite has Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> that range from 3 to 15 and a Th/U of  $4.77 \pm 0.47$ . The high Th/U of these Al-depleted komatiites, which are above the primitive mantle ratio of 4.04, are attributed to the presence of residual garnet in their mantle source region following melting. In this context, it is interesting to note that the Lumby Lake-Steep Rock suite,

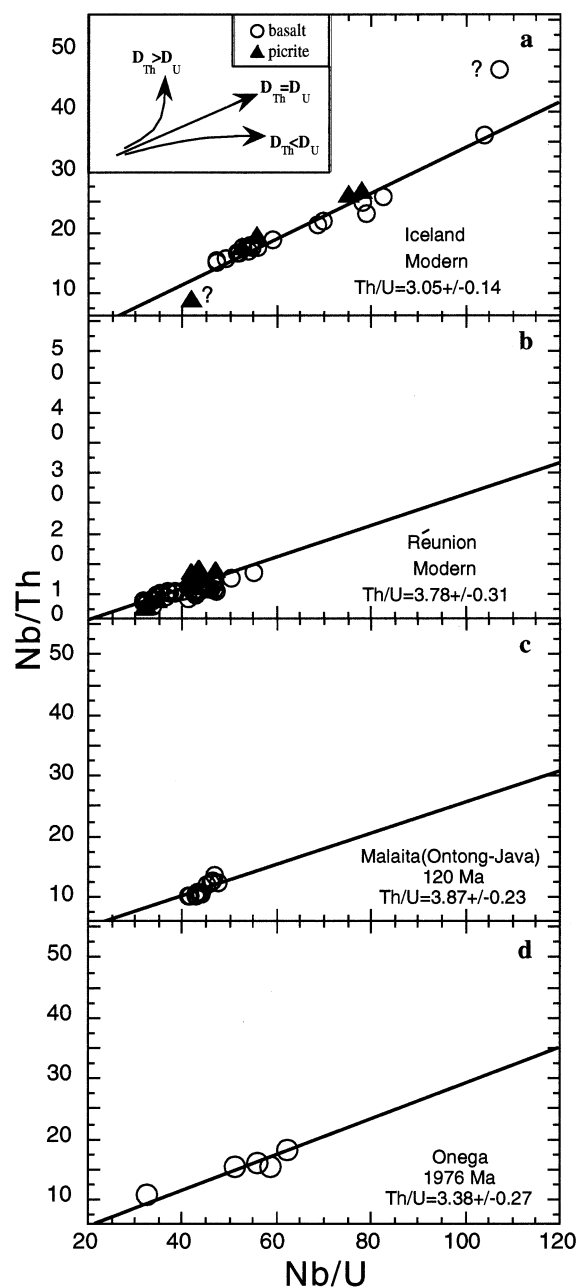


Fig. 2. Nb/Th plotted against Nb/U for modern and Proterozoic komatiites, picrites, and basalts from Ontong-Java, Iceland, Réunion, and Onega (Proterozoic). The quoted uncertainty is 1 standard deviation. Samples with an alkali index >1.0 and three samples with Th/U  $\gg 5$  have been omitted from the Réunion plot. The effect of extracting continental crust on the Th/U of the mantle residue is shown in the inset assuming  $D^{\text{Th}} > D^{\text{U}}$ ,  $D^{\text{Th}} = D^{\text{U}}$ , and  $D^{\text{Th}} < D^{\text{U}}$ . Triangles: picrites; circles: basalts. Data from Hemond et al. (1993); Campbell, Babbs, and Saunders (unpublished data); Albarède et al. (1997); and Puchtel et al. (1998a) for Iceland, Malaita, Réunion, and Onega, respectively.

which has the lowest average Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> (7.0), has the highest average Th/U.

The simplest explanation for the linear trends seen in Figures 2 and 3, which imply constant Th/U over a wide range in Nb/U, is that the Th/U of the continental crust being extracted from

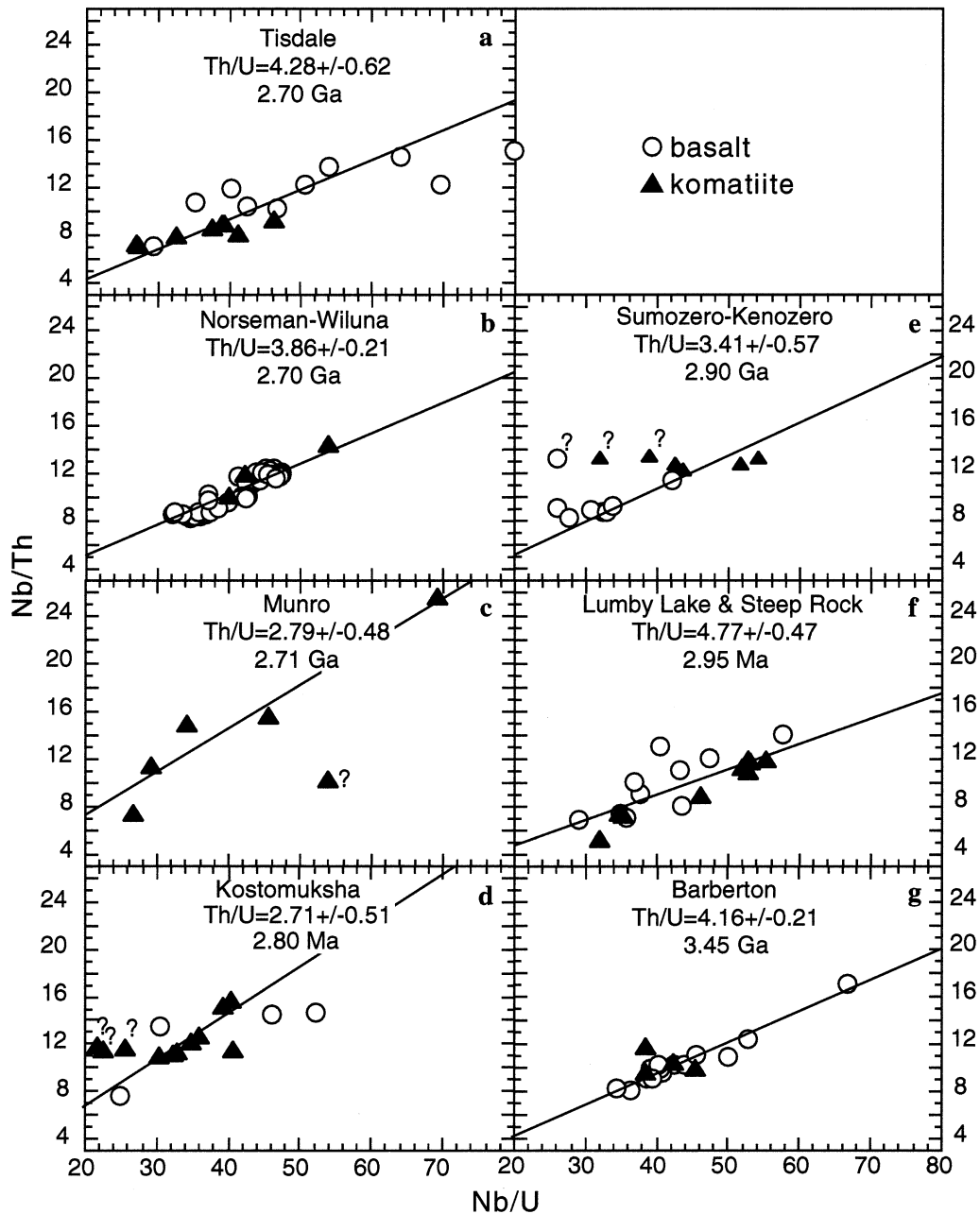


Fig. 3. Nb/Th plotted against Nb/U for Archean komatiites and basalts from Tisdale Township; Munro Township; Lumby Lake-Steep Rock; and the Norseman-Wiluna, Barberton, Sumozero-Kenozero, and Kostomuksha greenstone belts. The quoted uncertainty is 1 standard deviation. Queried data are ignored in the regression. Data for the Barberton greenstone from Campbell (submitted); for Tisdale Township and Munro Township from Kerrich et al. (1999a) and Kerrich et al. (1999b); for Lumby Lake-Steep Rock from Fan and Kerrich (1997); for the Norseman-Wiluna greenstone from Sylvester et al. (1997); for the Kostomuksha greenstone from Puchtel (1998b); and for Sumozero-Kenozero from Puchtel (1999).

the mantle is the same as that of the mantle from which it is being extracted. This requires that  $D^{\text{Th}} \sim D^{\text{U}}$  for partitioning of these elements between the continental crust and mantle. If  $D^{\text{Th}} > D^{\text{U}}$ , the basalts should lie on a curve that is concave up, whereas if  $D^{\text{Th}} < D^{\text{U}}$ , the curve should be concave down (Fig. 2 inset).

The trend of increasing Nb/U at a constant Th/U of  $3.05 \pm 0.14$ , over a wide range of Nb/U for Iceland (41 to 106), implies that  $D^{\text{Th}} \sim D^{\text{U}}$  during crustal extraction. The low Th/U suggests

that the mantle source region for these rocks also has had basaltic crust extracted from it, but it is not apparent from Figure 2 which event occurred first, basaltic or continental crust extraction. Figure 4, which is a plot of Nb/U against  $\epsilon_{\text{Nd}}$  for the Iceland basalts, shows no evidence of a correlation between  $\epsilon_{\text{Nd}}$  and Nb/U. Either the principal event that fractionated Sm from Nd in source region (basalt extraction?) occurred well before extraction of continental crust, or continental crust extraction had relatively little influence on the Sm/Nd of the residual

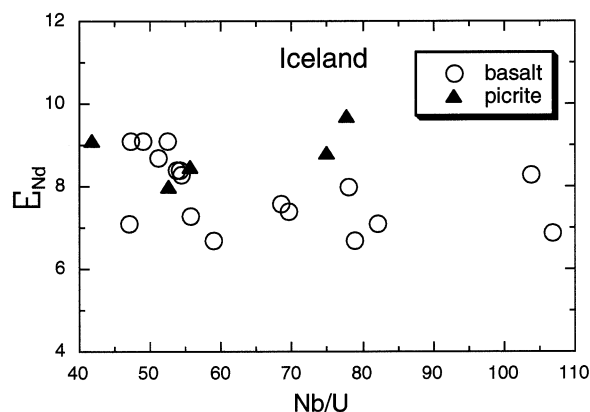


Fig. 4. A plot of  $\epsilon_{Nd}$  against Nb/U for basalts and picrites from Iceland. Data from Hemond et al. (1993).

mantle, or both. The Réunion suite has lower average Nb/U and a smaller range of values than Iceland, suggesting that its source region has had less continental crust extracted from it.

Compositional ranges of Nb/U and Nb/Th for the Archaean komatiites and basalts are similar to the oceanic suites, with one notable exception: Nb/U of the komatiites suites may fall below the mantle value of 34 (Fig. 3). This is attributed to crustal contamination, a common phenomenon in Archaean komatiites and basalts. The spread in Nb/U seen in the Archaean komatiite-basalt association is therefore probably due to a combination of variable crustal extraction from the mantle and variable amounts of crustal contamination of the erupted magmas. Unfortunately, it is not possible to distinguish between these possibilities. The addition of as little as 2% continental crust is sufficient to change the Nb/U of a komatiite from 50 to 30 (Sylvester et al., 1997). Nevertheless, all of the komatiite-basalt suites, including the 3.5 Ga Barberton greenstone samples, include one or more samples with Nb/U above 47, the average value for the modern OIB- and MORB-type mantles.

Four of the Archaean suites (Norseman-Wiluna, Sumozero-Kenozero, Munro, and Kostomuksha) show no evidence of having had garnet in their mantle residue. The Norseman-Wiluna suite has an average Th/U of  $3.86 \pm 0.21$ . Lack of variation in Th/U with increasing Nb/U within this suite again confirms that continental crust formation has little influence on the Th/U of the mantle residue. The Sumozero-Kenozero, Munro, and Kostomuksha suites have average Th/U ratios of 3.4, 2.8, and 2.7 which implies that some basalt has been removed from the source region of these suites. Their Th/U are, however, highly variable, which may indicate that basalt extraction in their source regions was heterogeneous.

### 3.3. Sm/Nd-Th/U

Dupré et al. (1984) showed that there is a strong inverse correlation between Sm/Nd and Th/U in komatiites. Figure 5 shows this relationship for several komatiite suites of different age. There is also a correlation between the radiogenic  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio and Nd isotopes for modern OIBs and MORBs (Allègre et al., 1986; Hofmann, 1997), which is as strong as the well-known correlation between Sr and Nd isotopes. It shows

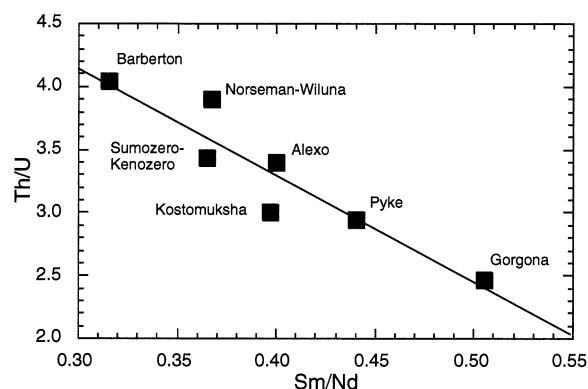


Fig. 5. A plot of Th/U against Sm/Nd for komatiites from the Barberton, Sumozero-Kenozero, Kostomuksha, and Norseman-Wiluna greenstone belts, Alexo, Pike Hill, and Gorgona. After Dupré et al. (1984), with additional data from Puchtel (1998b), Puchtel (1999), and Campbell (submitted).

that the Th/U-Sm/Nd relationship identified in the komatiites is of global significance. Whatever is responsible for Th/U fractionation in the mantle is also responsible for Sm/Nd fractionation. Dupré et al. (1984) suggested that both are produced by the formation of the continental crust. Nonetheless, because there is no significant difference between the Th/U of the continental crust and primitive mantle, and because the variations in the Nb/U seen in Figures 2 and 3 occur at constant Th/U, the only viable explanation for the inverse correlation between Th/U and Sm/Nd is that it is due to the extraction of basaltic crust. A corollary of this hypothesis is that if a basaltic mantle reservoir is the complementary component to the depleted mantle, it should have higher Th/U and lower Sm/Nd than the depleted mantle. This is an important point that will be addressed in section 4.6.

### 3.4. Nb/Pr-Nb/U

Figure 6 is a plot of Nb/U against Nb/Pr for komatiites from various localities. As discussed earlier, basalt extraction lowers the Nb/Pr of the mantle below its mean value of 2.63 without

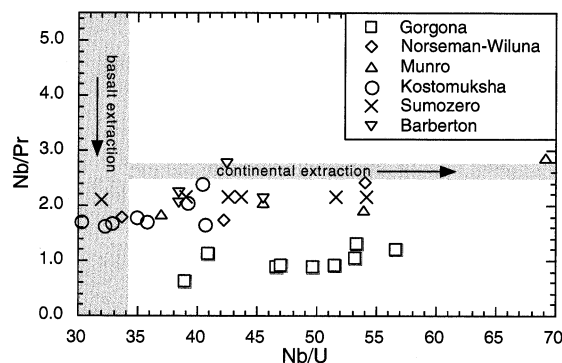


Fig. 6. A plot of Nb/Pr against Nb/U for komatiites from Munro Township (Fan and Kerrick, 1997), Barberton, Yilgarn, Gorgona (Campbell, unpublished data), Kostomuksha (Puchtel, 1998b), and Sumozero-Kenozero (Puchtel, 1999). The shaded fields are the trends produced by extraction of pure continental and basaltic crust.

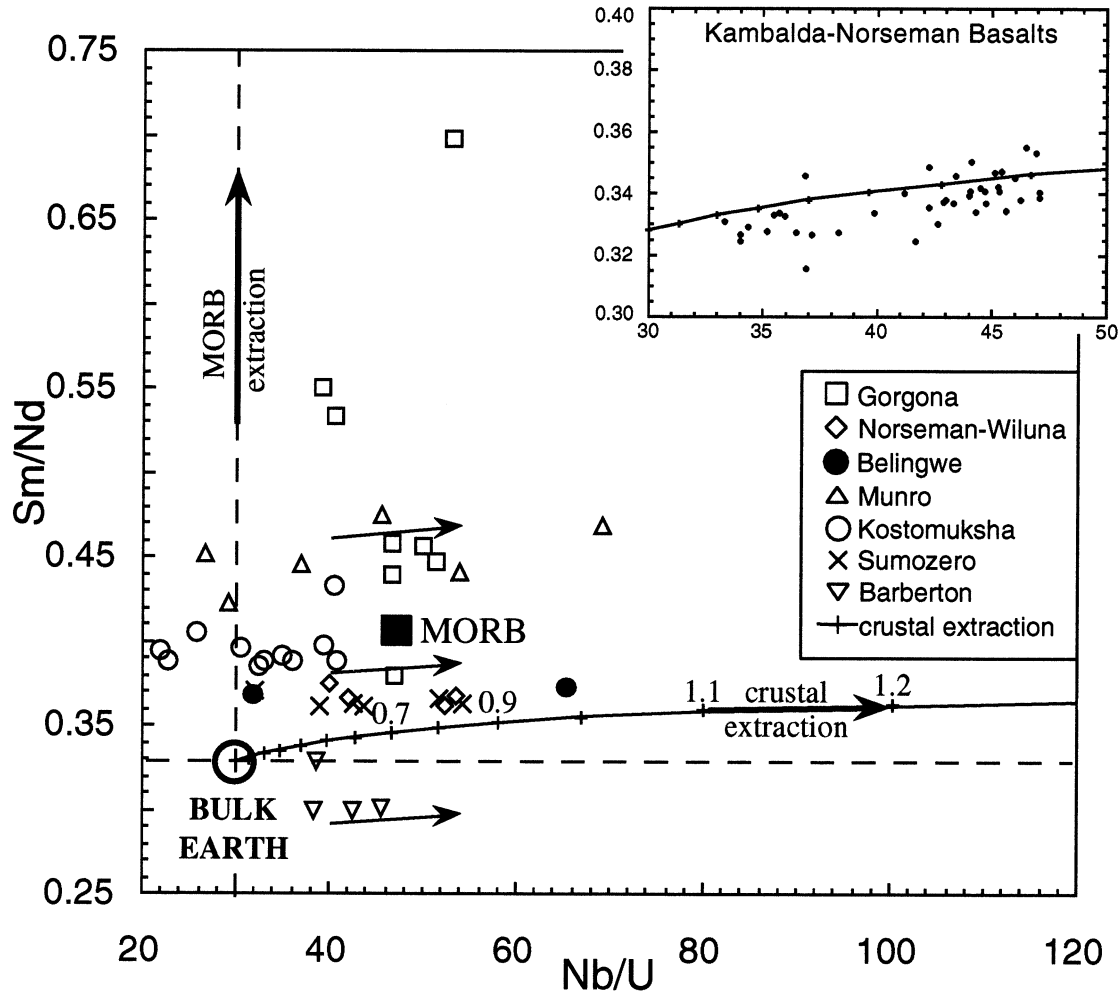


Fig. 7. A plot of Sm/Nd against Nb/U for komatiites from various locations. Also shown is the effect of extracting various fractions of continental crust on the Sm/Nd and Nb/U of the mantle residue. The Sm, Nd, Nb, and U concentrations for the mantle and crust used in the calculations are those of Sun and McDonough (1989) and Rudnick and Fountain (1995), respectively. If the crustal concentrations of Taylor and McLennan (1985) are used, the fraction of crust that must be removed from the mantle for a given increase in Nb/U or Sm/Nd almost doubles, but there is no significant change in the direction of the crustal extraction curve. The trend for basalts from the Kambalda-Norseman-Wiluna area of the Norseman-Wiluna greenstone belt are shown as an insert. Notice that the trend for the three Al-depleted Barberton komatiites lies below the crustal extraction trend. This is probably because garnet has remained in the residue following partial melting, which has resulted in the melt having a lower Sm/Nd than its mantle source region. The normal Al Barberton komatiite, 49J, plots within error of the crustal extraction curve. The tick marks on the crustal extraction curve are percentage crust extracted and are 0.1% apart. Data from Fan and Kerrich (1997), Sylvester et al. (1997), Puchtel (1998b, 1999), and Campbell (submitted).

changing its Nb/U, whereas continental crust extraction raises Nb/U without changing its Nb/Pr. Most of the komatiites plotted in Figure 6 have had both basaltic and continental crust extracted from their mantle source region. Because the assumption that the Nb/Pr of the melt is essentially the same as the mantle source region is only valid at very high degrees of partial melting and in the absence of abundant residual garnet, only normal Al komatiites have been included in Figure 6.

### 3.5. Sm/Nd-Nb/U

The relative importance of continental crust and basalt extraction on the Sm/Nd of the depleted mantle can be further

evaluated by plotting Sm/Nd against Nb/U for suites of komatiites from various locations and comparing the trends with the calculated effect of removing various fractions of continental crust using Eqn. 1 (Fig. 7). The calculated trend shows that continental crust extraction has a profound influence on the Nb/U but only a small influence on the Sm/Nd. This is in marked contrast with the trend produced by basalt extraction, which has a strong influence on Sm/Nd but little or no influence on Nb/U. These differences in trend can be used to unambiguously distinguish between the effects of continental and basaltic crust extraction. The data for individual suites of Archaean komatiites lie on trend lines that are subparallel to the

crustal extraction trend but at variable Sm/Nd, whereas the younger Gorgona komatiites show marked variations in Sm/Nd but only small variations in Nb/U. All suites, with the possible exception of the Barberton Al-depleted komatiites, have had variable amounts of both continental and basaltic crust removed from their source regions. The high Sm/Nd of the Gorgona and Munro komatiites require the elevated ratios seen in these suites to be due primarily to extraction of basaltic crust from their source region, whereas basaltic and continental crust extraction are of subequal importance in the source regions to the Norseman-Wiluna and Munro komatiites. The Al-depleted Barberton komatiites have Sm/Nd below the mantle value, and this is attributed to the effect of residual garnet on the Sm/Nd. Continental crust has been extracted from their source region, but little or no basaltic crust has been extracted. This conclusion is consistent with their  $\epsilon_{Nd}$  and  $\epsilon_{Hf}$  values, which lie mainly between 0 and +1.5 and 0 and +4, respectively (Blichert-Toft and Arndt, 1999). Notice in particular that the modern upper mantle, as sampled by MORB (filled square in Fig. 7), lies well above the crustal extraction trend.

The data for the basalts from the Kambalda-Norseman area (Norseman-Wiluna greenstone belt) are also plotted in Figure 7 (inset). They fall parallel to but slightly below the crustal extraction trend. This lower than expected Sm/Nd for these basalts is attributed to a small decrease in Sm/Nd during melting.

## 4. DISCUSSION

### 4.1. Niobium in the Core

Both the upper mantle and continental crust have Nb/Ta and Nb/La that are below that for the bulk Earth, and this has led to the suggestion that the Earth has a hidden Nb enriched reservoir (Hofmann, 1988). Rudnick et al. (2000) suggested that this reservoir is former basaltic crust that has been subducted into the lower mantle. Wade and Wood (2001) argued that there is no need for a hidden reservoir because Nb is moderately siderophile at the pressure of the core-mantle boundary and that the "missing" Nb is in the core. They claimed that high-U/Pb (HIMU) basalts, which are believed to have a significant component of recycled oceanic crust in their source region, have subchondritic Nb/Ta values, which is inconsistent with Rudnick et al.'s (2000) hypothesis. On the other hand, HIMU basalts from St. Helena and the Austral Islands have superchondritic Nb/Ta and Nb/La values of 17.8 and 1.5 (Sun and McDonough, 1989; Eggins and Woodhead, unpublished data), above or well above the mantle values of 17.6 and 1.01, respectively. Furthermore, the Nb/U for the oceanic plume basalts, summarized in this study, lie between 30 and 105 (Fig. 2) and extend from the primitive mantle value, which is believed to lie between 30 and 34 (Hofmann et al., 1986; Sun and McDonough, 1989), to higher values. If significant Nb was lost to the core, oceanic basalts might be expected to include some samples with Nb/U < 30. The absence of analysed oceanic basalts with Nb/U < 30 suggests that if Nb is lost to the core, the amount is small and unlikely to affect the conclusions of this study.

### 4.2. Extraction of Basaltic Crust

It is apparent from the discussion in connection with Figures 2, 3, 5, 6, and 7 that depleted mantle has had both continental and oceanic crust extracted from it. The modern depleted upper mantle, as sampled by MORBs, has an average Nb/U of 47 (Hofmann et al., 1986). Removing enough continental crust from the mantle to raise its Nb/U to 47 increases the Sm/Nd from the primitive mantle value of 0.328 to 0.347, which compares with a value of  $\sim 0.38$  for the modern upper mantle (McCulloch and Bennett, 1994). That is, continental crust extraction can account for about one third of the increase in the Sm/Nd seen in modern MOR-type basalts. Furthermore, this discrepancy cannot be dismissed as due to the choice of Sm, Nd, Nb, and U concentrations used for the continental crust. Changing from the values of Rudnick and Fountain (1995) to those of Taylor and McLennan (1985) or Weaver and Tarney (1984) alters the fraction of continental crust that must be removed from the mantle to produce a given change in the Sm/Nd or Nb/U of the residual mantle but has little influence on the trend. Removing enough continental crust from the mantle to raise its Nb/U to 47 raises its Sm/Nd to 0.347 regardless of which set of values is used for the continental crust. This is because the incompatible trace element ratios are similar for the various estimates of the composition of the continental crust. The high Sm/Nd of MORB requires the existence of a substantial second reservoir of low-Sm/Nd material that is isolated from the upper mantle. The only realistic possibility is a basalt reservoir.

The depleted mantle, as sampled by plumes of different ages, has also had a significant component of basalt extracted from it. The average Sm/Nd is 0.36 for Sumozero-Kenozero, 0.37 for the Norseman-Wiluna and Belingwe, 0.39 for Kostomuksha, 0.40 for Alexo, 0.44 for Munro, and 0.50 for Gorgona (Fig. 7). Extraction of continental crust alone from the depleted mantle reservoir can explain less than half of the increase in Sm/Nd in the Sumozero-Kenozero, Norseman-Wiluna, and Belingwe komatiites and only a small fraction of the very high values seen in Kostomuksha, Alexo, Munro, and Gorgona. Furthermore, the difference between the measured Sm/Nd of komatiites and those predicted by continental crust extraction cannot be explained by crustal contamination of the magmas or fractionation during melting, both of which would produce a decrease in Sm/Nd in the melts compared with the mantle source region. It is clear that extraction of continental crust cannot raise the mantle's Sm/Nd to the level required for the modern or Archaean depleted mantle without also raising its Nb/U to a value well above the observed level. The formation of the depleted mantle must also involve extraction of basaltic crust.

### 4.3. Separating Basaltic Crust From Depleted Mantle

There is a problem with the basaltic complementary reservoir hypothesis that has not been addressed by either its proponents or detractors. When basaltic crust forms, a depleted harzburgite residue also develops in the underlying mantle, and it is this depleted residue that has the potential to form the depleted mantle reservoir. Only if this depleted residue becomes isolated from the basaltic crust can there be a net change in the composition of the upper mantle, and the only force



capable of producing the required separation is gravity. Separation of the basaltic crust from the underlying depleted harzburgite is unlikely to occur while the ocean lithosphere is sinking through the upper mantle because both the basaltic crust and the depleted harzburgite form part of the cold, rigid oceanic plate that remains stiff during subduction. As a consequence, the two components are inseparable on a time scale of 100 to 200 Ma (Richards and Davies, 1989), which is greater than the time required for oceanic lithosphere to sink through the upper mantle. Separation may nonetheless occur within the lower mantle when the plate reaches thermal equilibrium with its surroundings, probably at or near the core-mantle boundary. When the plate reaches the high temperatures of the lower mantle, the components of the plate become more plastic so that separation becomes possible on a time scale of several hundred million years (Christensen and Hofmann, 1994), provided there is a sufficient density difference between the former basaltic and depleted harzburgite components to drive separation. Significantly, Kesson et al. (1998) showed that the depleted harzburgite component is  $0.02 \text{ gm cm}^{-3}$  lighter than the basaltic component at core-mantle pressures. They also showed that both components of the former oceanic lithosphere are slightly lighter than unfractionated primitive mantle at lower mantle pressures, which, if correct, may imply that oceanic lithosphere cannot sink through the lower mantle. However, unfractionated mantle has never been sampled by basalts or komatiites of any age. If it exists, it cannot be an important component in the mantle, and its density is therefore irrelevant.

#### 4.4. Origin of the Modern Depleted Upper Mantle

The separation of the former basaltic and depleted harzburgite components at the bottom of the mantle leads to some interesting possibilities. One is that the hotter and compositionally lighter harzburgite returns to the upper mantle before the cooler and compositionally denser basaltic component. Two factors may contribute to the faster return of the harzburgite component: its lower density and its greater thickness. It is the second of these factors that is the more important. The thickness of the depleted harzburgite layer is a factor of 10 greater than that of the basaltic layer, and in the Stokes buoyancy equation, the length scale term is squared, whereas the density term is raised to the first power. As a consequence, the thicker, lighter harzburgite component can be expected to return to the upper mantle faster than the much thinner, denser basaltic component. In this scenario, the mantle consists of former basalt and depleted mantle mixed in varying proportions, and the difference between the chemistry of the MORB and OIB sources is due to the former having less basaltic crust and more depleted harzburgite than the latter.

The simplest explanation for the putative buildup of former basaltic crust in the lower mantle is that the modern mantle has evolved to a steady state, with the basaltic component in subducted slabs having a longer residence time in the lower mantle than lighter depleted harzburgite. If it is assumed that MORB production rates have not changed over the last 1.0 Ga or so and that the average residence time of former basaltic crust in the lower mantle is  $\sim 1.0$  to  $1.5$  Ga longer than depleted harzburgite, the excess mass of basaltic crust in the lower mantle is approximately  $8$  to  $12 \times 10^{25}$  gm, or 4 to 6 times the

mass of the continental crust. If the basaltic crust has the same Sm and Nd concentrations as MORB, it would contain about twice as much of these elements as the continental crust. It is suggested that it is this reservoir of former basaltic crust in the lower mantle that is responsible for the Sm/Nd of the upper mantle lying well above the trend predicted by extraction of continental crust on plots of Sm/Nd against Nb/U.

Alternatively, the slow rate of return of former basaltic crust compared with depleted harzburgite may result in a net buildup of the basaltic component in the lower mantle through time. In this context, it is interesting to note that the present mass flux for subduction of oceanic lithosphere is  $3 \times 10^{10}$  gm/s, compared with  $7 \times 10^9$  gm/s in plumes (Sleep, 1990; Hill et al., 1992). That is, only one quarter as much material ascends in plumes as is subducted into the mantle, leaving ample scope for a buildup of former basaltic material in the lower mantle. The lower mantle seismic anomaly observed by van der Hilst and Kárason (1999) may result from this accumulation.

#### 4.5. Why High Sm/Nd Ratios Are Confined to Komatiites

Samples with Sm/Nd above 0.40 are confined to the Alexo, Munro, and Gorgona komatiites. If the interpretation that these very high values are due mainly to removal of basalt for their mantle source region is correct, the suites with the highest Sm/Nd have had the most basalt extracted from their source, which will make them the most refractory. If the modern MORB source consists of a mixture of former basalt and depleted harzburgite, as suggested in section 4.4, it is only the low solidus basaltic and least depleted harzburgite that will melt at MORs. It is suggested that high Sm/Nd are confined to komatiites because they form by melting in plumes that are hot enough to melt more refractory mantle. If refractory mantle with a Sm/Nd above 0.40 is an important component in the modern upper mantle, it is likely that it cannot be sampled by MORBs because it is too refractory to melt at the lower temperatures found at MORs. It is therefore possible that estimates of the Sm/Nd of the upper mantle based on Sm-Nd isotopic studies of MORBs underestimate the average Sm/Nd of the upper mantle.

#### 4.6. Other Implications for Mantle Geochemistry

The basalt-recycling hypothesis may provide answers to two puzzling features of mantle geochemistry. First, if the depleted harzburgite component of subducted slabs is recycled faster than the basaltic component, Archaean plumes should contain depleted mantle. The spent plumes, including the residue from partial melting at the top of the mantle, may then be mixed into the upper mantle to contribute to Earth's early depleted upper mantle. This prediction can be tested from the isotopic characteristics of Archaean komatiites, which, because of their high liquidus temperature, are interpreted to be the melting products of Archaean plumes. Archaean komatiites invariably have positive  $\epsilon_{\text{Nd}}$  and  $\epsilon_{\text{HF}}$ , indicating that they originated from a depleted mantle source (Campbell and Griffiths, 1993).

Second, if the time scale for recycling of the cooler, denser basaltic component is greater than that of the depleted harzburgite component, the basaltic component should be absent from early plumes. If basalt is an essential component of enriched or

OIB-type plumes (Hofmann and White, 1982), alkalic basalts should be absent from Earth's early volcanic rocks. OIB-type magmas are rare in Archaean plumes, become important in Proterozoic plumes, and dominate modern plume volcanic rocks, which is consistent with this hypothesis.

Finally, modern OIBs have a Th/U of 3.0 to 3.8, compared with 2.5 for MORBs. This difference is consistent with the interpretation that OIB-type magmas are derived from plumes that include a significant component entrained from the basaltic reservoir. If the reduction in the Th/U of the upper mantle is due to extraction of basalt, it follows that the basaltic reservoir should have a higher Th/U and lower Sm/Nd than the depleted mantle and that OIBs, which come from a basalt enriched source, should have a higher Th/U and lower  $\epsilon_{Nd}$  than MORBs.

*Acknowledgments*—I wish to thank Vickie Bennett, Geoff Davies, Chris Hawkesworth, Al Hofmann, and Sue Kesson for reviewing the manuscript and Charlotte Allen and Kay Provins for assisting with its preparation.

*Associate editor:* M. A. Menzies

## REFERENCES

- Albarède F., Luais B., Fitton G., Semet M., Kaminski E., Upton B. G. J., Bachelery P., and Cheminee J.-L. (1997) The geochemical regimes of Piton de la Fournaise volcano (Réunion) during the last 530,000 years. *J. Petrol.* **38**, 171–201.
- Allègre C. J. and Condomines M. (1982) Basalt genesis and mantle structure studied through Th isotopic geochemistry. *Nature* **299**, 21–24.
- Allègre C. J., Dupré B., and Lewin E. (1986) Thorium/uranium ratio of the Earth. *Chem. Geol.* **56**, 219–227.
- Bennett V. C., Nutman A. P., and McCulloch M. T. (1993) Nd isotopic evidence for transient, highly depleted mantle reservoirs in the early history of the Earth. *Earth Planet. Sci. Lett.* **119**, 299–317.
- Blichert-Toft J. and Arndt N. T. (1999) Hf isotope composition of komatiites. *Earth Planet. Sci. Lett.* **171**, 439–451.
- Bowring S. A., Williams I. S., and Compston W. (1989) 3.96 Ga gneiss from the Slave Province, NW Territories, Canada. *Geology* **17**, 971–975.
- Campbell I. H. (submitted) Evidence of early crustal extraction from the 3.5 Ga Barberton mantle from Ub/U and Nb/Th ratios in basalts.
- Campbell I. H. and Griffiths R. W. (1993) The evolution of the mantle's chemical structure. *Lithos* **30**, 389–399.
- Chase C. G. and Patchett P. J. (1988) Stored mafic/ultramafic crust and early Archaean mantle depletion. *Earth Planet. Sci. Lett.* **91**, 66–72.
- Christensen U. R. and Hofmann A. W. (1994) Segregation of subducted oceanic crust in the convecting mantle. *J. Geophys. Res.* **99**, 19867–19884.
- Corfu F. and Noble S. R. (1992) Genesis of the southern Abitibi greenstone belt, Superior Province, Canada: Evidence from zircon Hf isotope analyses using a single filament technique. *Geochim. Cosmochim. Acta* **56**, 2081–2097.
- DePaolo D. J. and Wasserburg G. J. (1976) Inferences about magma sources and mantle structure from variations of  $^{143}\text{Nd}/^{144}\text{Nd}$ . *Geophys. Res. Lett.* **3**, 743–746.
- Dupré B., Chauvel C., and Arndt N. T. (1984) Pb and Nd isotopic study of the two Archaean komatiitic flows from Alexo, Ontario. *Geochim. Cosmochim. Acta* **48**, 1965–1972.
- Fan J. and Kerrick R. (1997) Geochemical characteristics of aluminum depleted and undepleted komatiites and HREE-enriched low-Ti tholeiites, western Abitibi greenstone belt: A heterogeneous mantle plume-convergent margin environment. *Geochim. Cosmochim. Acta* **61**, 4723–4744.
- Froude D. O., Ireland T. R., Kinny P. D., Williams I. S., Compston W., Williams I. R., and Myers J. S. (1983) Ion microprobe identification of 4100–4200 Myr-old terrestrial zircons. *Nature* **304**, 616–618.
- Galer S. J. G. and Goldstein S. C. (1991) Early mantle differentiation and its thermal consequences. *Geochim. Cosmochim. Acta* **55**, 227–239.
- Gruau G., Chauvel C., Arndt N. T., and Cornichet J. (1990) Aluminum depletion in komatiites and garnet fractionation in the early Archaean mantle: Hafnium isotope constraints. *Geochim. Cosmochim. Acta* **54**, 3095–3101.
- Hart S. R. (1971) K, Rb, Sc, Sr and Ba contents and Sr isotope ratios of ocean floor basalts. *Phil. Trans. R. Soc. London, Ser. A* **26**, 573–587.
- Hemond C. H., Arndt N. T., Lichtenstein U., and Hofman A. W. (1993) The heterogeneous Iceland plume: Nd-Sr-O isotopes and trace element constraints. *J. Geophys. Res.* **98**, 15833–15850.
- Hill R. I., Campbell I. H., Davies G. F., and Griffiths R. W. (1992) Mantle plumes and continental tectonics. *Science* **256**, 186–193.
- Hofmann A. W. (1988) Chemical differentiation of the Earth: The relationship between mantle, continental crust and oceanic crust. *Earth Planet. Sci. Lett.* **90**, 297–314.
- Hofmann A. W. (1997) Mantle geochemistry: The message from oceanic volcanism. *Nature* **385**, 219–228.
- Hofmann A. W. and White W. M. (1982) Mantle plumes from ancient oceanic crust. *Earth Planet. Sci. Lett.* **57**, 421–436.
- Hofmann A. W., Jochum K. P., Seufert M., and White W. M. (1986) Nb and Pb in oceanic basalts; new constraints on mantle evolution. *Earth Planet. Sci. Lett.* **79**, 33–45.
- Hurley P. H., Hughes H., Faure G., Fairbairn H. W., and Pinson W. H. (1962) Radiogenic strontium-87 model for continent formation. *J. Geophys. Res.* **69**, 5315–5334.
- Jacobsen S. B. (1988) Isotopic constraints on crustal growth and recycling. *Earth Planet. Sci. Lett.* **90**, 315–329.
- Jacobsen S. B. and Wasserburg G. J. (1979) The mean age of mantle and crustal reservoirs. *J. Geophys. Res.* **84**, 7411–7427.
- Kerrick R., Polat A., Wyman D., and Hollings P. (1999a) Trace element systematics of Mg- to Fe-tholeiitic basalt suites of the Superior Province: Implications for Archaean mantle reservoirs and greenstone belt genesis. *Lithos* **46**, 163–187.
- Kerrick R., Wyman D., Hollings P., and Polat A. (1999b) Variability of Nb/U and Th/La in 3.0 to 2.7 Ga Superior Province ocean plateau basalts: Implications for the timing of continental growth and lithosphere recycling. *Earth Planet. Sci. Lett.* **168**, 101–115.
- Kesson S. E., Fitz Gerald J. D., and Shelley J. M. (1998) Mineralogy and dynamics of a pyrolite lower mantle. *Nature* **93**, 252–255.
- McCulloch M. T. and Bennett V. C. (1994) Progressive growth of the Earth's continental crust and depleted mantle: Geochemical constraints. *Geochim. Cosmochim. Acta* **58**, 4714–4738.
- McKenzie D. (1985)  $^{230}\text{Th}$ - $^{238}\text{U}$  disequilibrium and the melting processes beneath ridge axes. *Earth Planet. Sci. Lett.* **72**, 149–157.
- Nutman A. P. (1996) Recycling or growth of the continental crust before 3500 million years ago—What does the detrital zircon record tell us? *Ann. Report, Australian National University*, 129–130.
- Patchett P. J., Kouvo O., Hedge C. E., and Tatsumoto M. (1981) Evolution of continental crust and mantle heterogeneity: Evidence from Hf isotopes. *Contrib. Mineral. Petrol.* **78**, 279–297.
- Puchtel I. S., Arndt N. T., Hofmann A. W., Haase K. M., Kröner A., Kulikov V. S., Kilikova V. V., Garbe-Schönberg C.-D., and Nemchin A. A. (1998a) Petrology of mafic lavas within the Onega plateau, central Karelia: Evidence for 2.0 Ga plume-related continental crustal growth in the Baltic Shield. *Contrib. Mineral. Petrol.* **130**, 134–153.
- Puchtel I. S., Hofmann A. W., Mezger K., Jochum K. P., Shchipansky A. A., and Samsonov A. V. (1998b) Oceanic plateau model for continental crustal growth in the Archaean: A case study from the Kostomuksha greenstone belt, NW Baltic Shield. *Earth Planet. Sci. Lett.* **155**, 57–74.
- Puchtel I. S., Hofmann A. W., Yu V., Amelin C.-D., Garbe-Schönberg C.-D., Samsonov A. V., and Shchipansky A. A. (1999) Combined mantle plume-island arc model for the formation of the 2.9 Ga Sumozero-Kenozero greenstone belt, SE Baltic Shield: Isotope and trace element constraints. *Geochim. Cosmochim. Acta* **63**, 3579–3595.
- Richards M. A. and Davies G. F. (1989) On the separation of relatively buoyant components from subducted lithosphere. *Geophys. Res. Lett.* **16**, 831–834.
- Rudnick R. I. and Fountain D. M. (1995) Nature and composition of the

- continental crust: A lower crustal perspective. *Rev. Geophysics*. **33**, 267–310.
- Rudnick R. L., Barth M., Horn I., and McDonough W. F. (2000) Rutile-bearing refractory eclogites: Missing link between continents and depleted mantle. *Science* **287**, 278–281.
- Salters V. J. M. and Longhi J. (1999) Trace element partitioning during the initial stages of melting beneath mid-ocean ridges. *Earth Planet. Sci. Lett.* **166**, 15–30.
- Sleep N. H. (1990) Hotspots and mantle plumes: Some phenomenology. *J. Geophys. Res.* **95**, 6715–6736.
- Stevenson R. K. and Patchett P. J. (1990) Implications for the evolution of continental crust from Hf isotope systematics of Archaean detrital zircons. *Geochim. Cosmochim. Acta* **54**, 1683–1697.
- Sun S.-S. and McDonough W. F. (1989) Chemical and isotopic systematics of oceanic basalts; implications for mantle composition and processes. *Magma Ocean Basins* **42**, 313–345.
- Sun S.-S. and Nesbitt R. W. (1978) Petrogenesis of Archaean ultrabasic and basic volcanics: Evidence from rare earth elements. *Contrib. Mineral. Petrol.* **65**, 301–325.
- Sylvester P. J., Campbell I. H., and Bowyer D. A. (1997) Niobium/uranium evidence for early formation of the continental crust. *Science* **275**, 521–523.
- Tatsumoto M. (1978) Composition of lead in oceanic basalts and its implication to mantle evolution. *Earth Planet. Sci. Lett.* **38**, 63–87.
- Taylor S. R. and McLennan S. M. (1985) *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific Publications, Oxford, UK.
- van der Hilst R. D. and Kárason H. (1999) Compositional heterogeneity in the bottom 1000 kilometers of Earth's mantle: Towards a hybrid convection model. *Science* **283**, 1885–1888.
- Vervoort J. D., Patchett P. J., Gehrels G. E., and Nutman A. P. (1996) Constraints on early Earth differentiation from hafnium and neodymium isotopes. *Nature* **379**, 624–627.
- Wade J. and Wood B. J. (2001) The Earth's "missing" niobium may be in the core. *Nature* **409**, 75–78.
- Weaver B. L. and Tarney J. (1984) Empirical approach to estimating the composition of the continental crust. *Nature* **310**, 575–577.
- Wilde S. A., Valley J. W., Peck W. H., and Graham C. M. (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* **409**, 175–178.
- Williams R. W. and Gill J. B. (1989) Effects of partial melting on the uranium decay series. *Geochim. Cosmochim. Acta* **53**, 1607–1619.
- Wood B. J., Blundy J. D., and Robinson J. A. (1999) The role of clinopyroxene in generating U-series disequilibrium during mantle melting. *Geochim. Cosmochim. Acta* **63**, 1613–1620.