

Geological Society, London, Special Publications

**Chemical and isotopic systematics of oceanic basalts:  
implications for mantle composition and processes**

S.-s. Sun and W. F. McDonough

*Geological Society, London, Special Publications* 1989; v. 42; p. 313-345  
doi:10.1144/GSL.SP.1989.042.01.19

---

**Email alerting  
service**

[click here](#) to receive free email alerts when new articles cite this article

**Permission  
request**

[click here](#) to seek permission to re-use all or part of this article

**Subscribe**

[click here](#) to subscribe to Geological Society, London, Special Publications or the Lyell Collection

---

**Notes**

**Downloaded by**

University of Maryland on 24 March 2008

---

# Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes

S.-s. Sun & W.F. McDonough

**SUMMARY:** Trace-element data for mid-ocean ridge basalts (MORBs) and ocean island basalts (OIB) are used to formulate chemical systematics for oceanic basalts. The data suggest that the order of trace-element incompatibility in oceanic basalts is  $Cs \approx Rb \approx (Ti) \approx Ba(\approx W) > Th > U \approx Nb = Ta \approx K > La > Ce \approx Pb > Pr (\approx Mo) \approx Sr > P \approx Nd (> F) > Zr = Hf \approx Sm > Eu \approx Sn (\approx Sb) \approx Ti > Dy \approx (Li) > Ho = Y > Yb$ . This rule works in general and suggests that the overall fractionation processes operating during magma generation and evolution are relatively simple, involving no significant change in the environment of formation for MORBs and OIBs.

In detail, minor differences in element ratios correlate with the isotopic characteristics of different types of OIB components (HIMU, EM, MORB). These systematics are interpreted in terms of partial-melting conditions, variations in residual mineralogy, involvement of subducted sediment, recycling of oceanic lithosphere and processes within the low velocity zone. Niobium data indicate that the mantle sources of MORB and OIB are not exact complementary reservoirs to the continental crust. Subduction of oceanic crust or separation of refractory eclogite material from the former oceanic crust into the lower mantle appears to be required. The negative europium anomalies observed in some EM-type OIBs and the systematics of their key element ratios suggest the addition of a small amount ( $\leq 1\%$  or less) of subducted sediment to their mantle sources. However, a general lack of a crustal signature in OIBs indicates that sediment recycling has not been an important process in the convecting mantle, at least not in more recent times ( $\leq 2$  Ga). Upward migration of silica-undersaturated melts from the low velocity zone can generate an enriched reservoir in the continental and oceanic lithospheric mantle. We propose that the HIMU type (eg St Helena) OIB component can be generated in this way. This enriched mantle can be re-introduced into the convective mantle by thermal erosion of the continental lithosphere and by the recycling of the enriched oceanic lithosphere back into the mantle.

That much good ensues and that the science is greatly advanced by the collision of various theories cannot be doubted. Each party is anxious to support opinions by facts. Thus, new countries are explored and old districts re-examined; facts come to light that do not suit either party; new theories spring up; and in the end, a greater insight into the real structure of the earth's surface is obtained.

Henry Thomas De la Beche (1830)

It is now well established that chemical and isotopic heterogeneities of different scales, ranging from centimetres to thousands of kilometres, exist in the Earth's mantle. Such heterogeneities reflect variations in elemental abundance ratios generated by depletion and enrichment processes that have operated in the Earth's mantle throughout geological time.

In this paper we attempt to integrate the chemical and isotopic data from oceanic basalts in order to establish coherent relationships between isotopic compositions and the consistent (but variable) trace-element patterns observed in these basalts. These regularities are then interpreted in terms of the physical and chemical processes that have operated in the mantle.

Our discussion is preceded by an outline of

some of the major issues in the chemical evolution and geodynamics of the Earth's mantle. This is followed by some ideas on forward modelling, developed by investigating the possible consequences of major physical and chemical processes in the mantle. Finally, we discuss factors which influence the chemical and isotopic compositions of oceanic basalts.

## Major issues in the chemical evolution and geodynamics of the mantle

A first-order aim in the study of oceanic basalts is to improve our understanding of the chemical

and dynamic processes which have operated in the past and today within the Earth's mantle. To achieve this it is necessary to delineate the major issues, which requires the integration of data derived from different branches of Earth sciences. We need to do the following.

- (1) Undertake complete chemical and isotopic characterization of the Earth's primitive mantle (the silicate sphere of the Earth) and understand the timing and processes involved in core growth, and related mantle differentiation.
- (2) Characterize the behaviour of elements and the melting and extraction processes involved during magma genesis within different tectonic environments.
- (3) Delineate the processes responsible for development of ocean island basalt (OIB) source characteristics.
- (4) Document the secular variations of element abundances and their ratios in the mantle in order to understand mantle differentiation processes involved in crust formation.
- (5) Firmly establish the extent of crustal recycling in the mantle and document its effects on the chemical and isotopic evolution of the mantle.
- (6) Establish whether the chemical and isotopic characteristics shared between mid-ocean ridge basalts (MORBs) and OIBs reflect a complementary relationship with the continental crust.
- (7) Clarify the geometric and dynamic relationship between the different mantle reservoirs, and evaluate dynamic processes involved in the genesis and evolution of these reservoirs.
- (8) Determine the survival time of chemical and isotopic heterogeneities in the continental lithosphere and in the underlying convecting mantle.
- (9) Determine the fate of subducted oceanic lithosphere: is it simply recycled and re-sorbed back into the upper mantle, or is part of it transported into the lower mantle during mantle differentiation processes?

### Forward modelling of mantle differentiation and crustal formation

The combined processes of plate tectonics, mantle convection, magma generation, crustal recycling and upper and lower mantle exchange

contribute to the geochemical and isotopic evolution of mantle reservoirs. The nature of mantle convection processes through time (whole mantle or layered mantle) is critical to our understanding of the chemical and thermal evolution of the Earth.

The term 'reservoir' is used here in a general sense to refer to a part of the mantle which has a particular regional chemical and isotopic composition, whereas the term 'component' specifically refers to a reservoir (or many reservoirs) in the mantle with an isotopically distinctive composition (*eg* HIMU, EM, MORB). This use of the term 'component' is similar to that in Zindler & Hart (1986).

In essence each mantle reservoir carries an identifiable chemistry and isotopic fingerprint of the specific processes and environments which have acted upon it. These compositional fingerprints reflect the responses to such factors as partial melting under different  $P$ - $T$ - $X(\text{CO}_2, \text{water rich, melts or fluids})$  conditions, sediment subduction, and recycling of oceanic crust and asthenosphere through the subduction zone environment.

### Mantle differentiation processes through time

Our understanding of mantle differentiation associated with the Earth's accretion, core formation and the early history of mantle-crust fractionation relies upon chemical and isotopic studies of Archaean to modern volcanic rocks and other planetary bodies, petrological and chemical experiments carried out under high-temperature and high-pressure conditions, and numerical modelling of the thermal evolution of the Earth.

Even if some thermal models favour the presence of upper and lower mantle convection cells at present (*eg* Richter 1985), there is no obvious reason to argue against whole-mantle convection during the early history of the Earth. It is generally assumed that the early Earth's mantle temperature was higher (*eg* 2000 °C surface potential temperature) (Richter 1985), which would favour vigorous, and probably chaotic, whole-mantle convection with possible large-scale mantle melting. Consequently, it is very likely that the lower mantle would have been involved in the formation of the earliest enriched lithosphere, resulting in an incompatible-element-depleted character, *ie* a non-primitive fractionated lower mantle. At the same time, dense early-formed severely hydrothermally altered mafic to ultramafic crust and lithospheric mantle may well have been rapidly recycled back into the convective mantle by meteorite

bombardment and lithosphere subduction. Vigorous convection in the early Earth's mantle would quickly stretch and mix this oceanic lithosphere with the convective mantle. Some of this lithosphere may have been subducted into the lower mantle. The magnitude of these activities decreased as the Earth's heat engine slowed down. Two-layer mantle convection may have eventually been initiated as a result of a density barrier imposed by temperature-dependent phase transformation at 670 km (eg Sawamoto 1987) or cumulation of refractory subducted lithosphere at the base of the upper mantle (Ringwood & Irifune 1988). However, it is possible that whole-mantle convection has continued throughout Earth's history (Gurnis & Davies 1986).

If the mantle differentiation scheme discussed above is realistic then the high  $^3\text{He}/^4\text{He}$  ratios ( $\geq 20 \times$  atmospheric) observed in some OIBs do not indicate an origin from a primordial unfractionated lower mantle. These ratios may instead result from the cooling of the outer core. Similarly, the  $^{129}\text{Xe}$  anomaly observed in some MORB samples (Allègre *et al.* 1987) is unlikely to result from the early (4.4 Ga) separation of the upper mantle from the lower mantle.

The stabilization of the Archaean continental crust was accompanied by the formation of thick refractory harzburgitic lithosphere. This subjacent mantle formed as a residual product of mantle melting. Occurrences of diamonds of Archaean age from kimberlite pipes from the Kaapvaal craton, South Africa (Kramers 1977; Richardson *et al.* 1984), suggest the early existence of Archaean continental lithosphere up to about 200 km thick. Such lithosphere could have been developed through underplating of residual mantle related to intraplate magmatic activity and/or depletion of the mantle wedge above a subduction zone.

Studies of modern island arc basalts suggest that subduction of the oceanic lithosphere, with or without associated sediment, can continuously modify the chemical, isotopic and mineralogical composition of the overlying mantle wedge. The release of fluids and hydrous silicate melts from the down-going altered oceanic crust can result in the enrichment of incompatible elements in the mantle wedge above the subduction zone. Stabilization of phlogopite in the mantle wedge provides a site for the introduced alkalis and barium (eg Wyllie & Sekine 1982) and it has been suggested that the formation of titanate minerals (such as sphene and rutile) in the subducted slab may have played an important role in the depletion of high field strength elements (eg titanium, niobium, tantalum) in

arc basalts (eg Saunders *et al.* 1980). Recycling of this mantle wedge or the overlying lithosphere could introduce subduction-zone-related chemical and isotopic characteristics into the convecting asthenosphere. For example, the recycled oceanic crust might show a positive niobium anomaly relative to lanthanum (*ie*  $\text{La}/\text{Nb} > 0.95$  (the chondritic ratio), but  $\text{La}/\text{Sm} < \text{chondrite}$ ).

The upward migration of highly incompatible-element-enriched  $\text{CO}_2$ -rich melts from the low velocity zone (LVZ) beneath the continental and oceanic lithosphere (eg kimberlites, carbonatites, nephelinites) can be a continuous or episodic process responsible for local enrichments of incompatible trace elements (eg Green 1971). Although such enrichment processes should not be limited to the Archaean and early Proterozoic, the more vigorous melting possible in the Precambrian mantle would promote such enrichment processes. This type of enrichment can be superimposed upon earlier enrichment events related to subduction zone processes. Such enriched lithospheric mantle commonly has a refractory major-element composition, reflecting residual products of earlier melting event(s) (eg Frey & Green 1974).

Recycling of the continental lithosphere by delamination (McKenzie & O'Nions 1983) or thermal erosion, and the subduction of oceanic lithosphere (Hofmann & White 1982; Ringwood 1982), introduce compositionally distinctive sources into the convecting mantle. Such material could be preserved as coherent entities through billions of years of convection. Thermal reactivation of enriched ancient continental lithosphere by plume activity or rifting may also play an important role in the generation of some continental basalts. Additionally, it may also cause thermal erosion of the continental lithosphere and incorporate it into the convecting mantle.

There are different opinions regarding the fate of the subducted oceanic lithosphere. It could have been continuously stretched and eventually well mixed back into the convective upper mantle (eg Allègre & Turcotte 1986). Alternatively, because of the density barrier at 670 km caused by phase transformations, the subducted oceanic crust and refractory harzburgite lithosphere beneath it may buckle and accumulate at the base of the upper mantle and form a boundary layer (eg Ringwood 1982; Ringwood & Irifune 1988). However, subduction of the oceanic lithosphere into the lower mantle appears to be indicated by geophysical observations (Creager & Jordan 1984). In Ringwood's model, the megalith accumulates at the base of the upper mantle and warms up

after some hundreds of millions of years. Partial melts of the former oceanic crust may fertilize the surrounding refractory harzburgite, while denser residues of former oceanic crust may sink into the lower mantle. Once thermally equilibrated, the harzburgite becomes intrinsically lighter than the surrounding and overlying mantle and ascends. These refractory peridotite diapirs are considered to give birth to mantle plumes or blobs that are enriched in incompatible elements due to equilibration with residual garnetite minerals, which are stable at depths of 400–600 km (Ringwood 1982).

#### Factors influencing chemical and isotopic characteristics of basaltic magmas

The distinctive chemical and isotopic characteristics of basalts from different tectonic environments can be attributed to the following factors:

- (1) the source characteristics, which are a function of its previous history;
- (2) the present tectonic environment of magma generation;
- (3) magma generation conditions and processes;
- (4) mixing of different mantle source regions.

As discussed earlier, core–mantle–crust differentiation and geodynamic processes have contributed to the formation of a chemically and isotopically heterogeneous mantle. Modern processes operating in the source regions produce further modifications to the chemical compositions of basalts.

In addition to the effects of source mineral composition, pressure, temperature and mineral/melt partition coefficients  $K_d$ , magma generation processes can also affect the composition of the resulting melt. Segregation of melts from a mantle diapir most probably involves mixing of migrating melts formed under different conditions (eg Oxburgh & Turcotte 1968; Hanson 1977; Langmuir *et al.*; McKenzie 1984). At present, numerical modelling of melt migration and separation is very dependent upon some basic assumptions. Detailed studies of ophiolites, alpine peridotites and ultramafic xenoliths can aid in evaluating the dynamic processes involved in melt generation and segregation (eg Nicolas 1986). If the mantle is veined as a result of melt migration and/or convective mixing of the recycled oceanic crust, low-temperature melting will selectively sample areas near these fertile veins. At higher temperatures the degree of partial melting increases, and the refractory non-veined peridotite becomes progressively more involved in melting (eg Sun & Hanson

1975a, b; Hanson 1977; Zindler *et al.* 1984). Finally, mixing of a diapiric plume with the asthenosphere and/or lithosphere through which it passes can be reflected in the erupted basalts. Hot and dense tholeiitic and picritic magmas may interact extensively with the lithosphere and crust to induce further melting. In contrast, owing to their volatile-rich character, alkali basalts rise rapidly to the Earth's surface, often carrying mantle xenoliths, and generally escape significant crustal contamination.

#### Chemical systematics of oceanic basalts

Since chemical and isotopic characteristics of basalts are governed primarily by their source character, their tectonic environment of magma generation and magma generation processes, it is logical to expect systematic compositional variations caused by these factors. Here we describe some chemical regularities observed in oceanic basalts (OIB and MORB) and relate the chemical variations in different groups of oceanic basalts to their isotope character.

#### Systematic relationships amongst incompatible trace elements

During partial melting of mantle peridotite the incompatible elements are concentrated into the magma. When two incompatible elements have identical mineral/melt  $K_d$  during partial melting their abundance ratio in the magma reflects that of their source, regardless of the degree of partial melting, *ie* their abundance ratios do not vary with increasing concentrations in the magma. In contrast, the ratios of incompatible elements having different  $K_d$  values will vary with the degree of partial melting. The more incompatible an element, the more it will be preferentially enriched in the melt. On the basis of this simple rule we can establish the degree of incompatibility of trace elements in oceanic basalts during magma generation. Obviously, in different tectonic environments with different physical conditions and mineral assemblages, the order of element incompatibility may change significantly. Thus, such an approach is very useful in evaluating the viability of possible mantle processes.

To present graphically the trace-element data of a sample for the purpose of pattern recognition it is convenient to normalize these data to

the trace-element abundances of the primitive mantle composition. This type of plot, established by Sun *et al.* (1979), has been called a 'spidergram' by Thompson *et al.* (1983) and an 'extended Coryell–Masuda diagram' by Hofmann *et al.* (1986). We prefer that the diagram be called a mantle normalizing diagram.

This method of normalization is similar to the practice of chondrite normalization for the rare earth elements. However, as Newsom *et al.* (1986) and Hofmann *et al.* (1986) have pointed out, there are potential problems in such normalization plots if the relative incompatibility of elements changes with time. They found that the Ce/Pb and Nb/U ratios observed in OIB and MORB are nearly constant,  $25 \pm 5$  and  $47 \pm 10$  respectively, but quite different from the primitive silicate mantle ratios (9 and 30), indicating that processes operating in the early history of the Earth ( $\geq 2$  Ga) caused fractionation of cerium from lead and niobium from uranium. Rubidium and caesium show a similar behaviour. Oceanic basalts have nearly constant Rb/Cs ratios of about 80, which is distinct from the primitive mantle value of  $20 \pm 10$  (McDonough *et al.* 1987). Taking these observations into account we have calculated the normalizing mantle values for lead (used in Fig. 1 and other figures of this paper) on the basis of a Ce/Pb ratio of 25 and for caesium on the basis of an Rb/Cs ratio of 80. The primitive mantle values used here are given in Table 1, with the element concentrations in C1 carbonaceous chondrites and the three different types of oceanic basalts shown for comparison.

Figure 1 presents the primitive-mantle-normalized patterns (except for Cs and Pb) for typical N-type and E-type MORB and an oceanic alkali basalt (OIB) with  $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7035$ . The data suggest that the order of trace-element incompatibility in oceanic basalts is Cs  $\approx$  Rb ( $\approx$  Tl)  $\approx$  Ba ( $\approx$  W)  $>$  Th  $>$  U  $\approx$  Nb = Ta  $\approx$  K  $>$  La  $>$  Ce  $\approx$  Pb  $>$  Pr ( $\approx$  Mo)  $\approx$  Sr  $>$  P  $\approx$  Nd ( $>$  F)  $>$  Zr = Hf  $\approx$  Sm  $>$  Eu  $\approx$  Sn ( $\approx$  Sb)  $\approx$  Ti  $>$  Dy  $\approx$  (Li)  $>$  Ho = Y  $>$  Yb. This order is mainly based upon the depletion pattern of N-type MORB and the systematics of concentration ratios observed in E-type MORB and OIB (Sun & Hanson 1975a, 1976; Sun & Nesbitt 1977; Sun *et al.* 1979; Sun 1980; Hofmann *et al.* 1986; Newsom *et al.* 1986; Ryan & Langmuir 1987). The relative incompatibilities of these elements appear constant within oceanic basalts suggesting that the fractionation processes are simple and involve no drastic change in elemental behaviour. The systematic behaviour of some elements, eg Nb–Ta, Sr–Pr, Zr–Hf–Sm, Ti–Eu<sup>3+</sup>, Ce–Pb, Nb–U, indicate that the main control

of mineral/melt  $K_d$  for these elements during oceanic basalt genesis is the presence of residual clinopyroxene and garnet (Fujimaki *et al.* 1984; Jochum *et al.* 1986; Watson *et al.* 1987).

On the basis of these chemical systematics, when accurate analytical data are available for only a few critical trace elements (eg Y, Ti, Zr, Sr, P, Nb, K, Rb), the concentrations of other elements on this plot can be estimated quite accurately. In this respect it is somewhat surprising to observe that phosphorus and neodymium behave very similarly during MORB and OIB genesis ( $\text{P}/\text{Nd} = 74 \pm 13$ ) (McDonough *et al.* 1985), since these elements substitute into different crystal sites (phosphorus substitutes for silicon whereas neodymium substitutes for calcium). Additionally, it is suggested that large deviations from Nb/Ta = 17 and Zr/Hf = 36 in MORB and OIB are most probably due to analytical errors or contamination of niobium and tantalum from the tungsten carbide mill during sample preparation. Fractionation of Nb/Ta in island arc basalts due to residual titanates during magma generation is possible, but reliable data are needed to evaluate this possibility.

Neodymium and hafnium isotope studies of mantle-derived volcanic rocks indicate that there is a consistent behaviour between Sm–Nd and Lu–Hf throughout geological time (Patchett 1983). Since Sr  $\approx$  Pr, Pb  $\approx$  Ce and Hf  $\approx$  Sm on the mantle-normalized plot (Fig. 1) and samarium, praseodymium and cerium are close to neodymium, the mixing of different mantle components for MORB and OIB (with different mantle-normalized patterns) is expected to generate linear trends in plots of isotope ratios, eg  $^{143}\text{Nd}/^{144}\text{Nd}$  versus  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$  versus  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$ . The isotope data in the literature are consistent with this (eg Zindler *et al.* 1982; White 1985).

The chemical regularities observed in basalts can be used to obtain information on the composition of the source and the processes and mineralogy involved in magma generation. The relatively constant but low concentrations of potassium, coupled with high concentrations of niobium and lanthanum in some highly undersaturated alkali basalts, kimberlites and carbonatites, suggests that potassium in the melts could be buffered by residual amphibole, phlogopite and clinopyroxene (under very high pressure) during source enrichment processes and/or magma generation (eg Sun & Hanson 1975a; Clague & Frey 1982). Such residual potassium-bearing minerals could also cause depletions of rubidium, caesium, and barium in

TABLE 1. Element concentrations (ppm) in C1 chondrite, primitive mantle, N-type MORB, E-type MORB and ocean island basalts (OIB)

| Element | C1 chondrite <sup>a</sup> | Primitive mantle <sup>a</sup> | N-type MORB | E-type MORB | OIB   |
|---------|---------------------------|-------------------------------|-------------|-------------|-------|
| Cs      | 0.188                     | 0.032 <sup>b</sup>            | 0.0070      | 0.063       | 0.387 |
| Tl      | 0.140                     | 0.005                         | 0.0014      | 0.013       | 0.077 |
| Rb      | 2.32                      | 0.635                         | 0.56        | 5.04        | 31.0  |
| Ba      | 2.41                      | 6.989                         | 6.30        | 57          | 350   |
| W       | 0.095                     | 0.020                         | 0.010       | 0.092       | 0.560 |
| Th      | 0.029                     | 0.085                         | 0.120       | 0.60        | 4.00  |
| U       | 0.008                     | 0.021                         | 0.047       | 0.18        | 1.02  |
| Nb      | 0.246                     | 0.713                         | 2.33        | 8.30        | 48.0  |
| Ta      | 0.014                     | 0.041                         | 0.132       | 0.47        | 2.70  |
| K       | 545                       | 250                           | 600         | 2100        | 12000 |
| La      | 0.237                     | 0.687                         | 2.50        | 6.30        | 37.0  |
| Ce      | 0.612                     | 1.775                         | 7.50        | 15.0        | 80.0  |
| Pb      | 2.47                      | 0.185 <sup>b</sup>            | 0.30        | 0.60        | 3.20  |
| Pr      | 0.095                     | 0.276                         | 1.32        | 2.05        | 9.70  |
| Mo      | 0.92                      | 0.063                         | 0.31        | 0.47        | 2.40  |
| Sr      | 7.26                      | 21.1                          | 90          | 155         | 660   |
| P       | 1220                      | 95                            | 510         | 620         | 2700  |
| Nd      | 0.467                     | 1.354                         | 7.30        | 9.00        | 38.5  |
| F       | 60.7                      | 26                            | 210         | 250         | 1150  |
| Sm      | 0.153                     | 0.444                         | 2.63        | 2.60        | 10.0  |
| Zr      | 3.87                      | 11.2                          | 74          | 73          | 280   |
| Hf      | 0.1066                    | 0.309                         | 2.05        | 2.03        | 7.80  |
| Eu      | 0.058                     | 0.168                         | 1.02        | 0.91        | 3.00  |
| Sn      | 1.72                      | 0.170                         | 1.1         | 0.8         | 2.7   |
| Sb      | 0.16                      | 0.005                         | 0.01        | 0.01        | 0.03  |
| Ti      | 445                       | 1300                          | 7600        | 6000        | 17200 |
| Gd      | 0.2055                    | 0.596                         | 3.680       | 2.970       | 7.620 |
| Tb      | 0.0374                    | 0.108                         | 0.670       | 0.530       | 1.050 |
| Dy      | 0.2540                    | 0.737                         | 4.550       | 3.550       | 5.600 |
| Li      | 1.57                      | 1.60                          | 4.3         | 3.5         | 5.6   |
| Y       | 1.57                      | 4.55                          | 28          | 22          | 29    |
| Ho      | 0.0566                    | 0.164                         | 1.01        | 0.790       | 1.06  |
| Er      | 0.1655                    | 0.480                         | 2.97        | 2.31        | 2.62  |
| Tm      | 0.0255                    | 0.074                         | 0.456       | 0.356       | 0.350 |
| Yb      | 0.170                     | 0.493                         | 3.05        | 2.37        | 2.16  |
| Lu      | 0.0254                    | 0.074                         | 0.455       | 0.354       | 0.300 |

<sup>a</sup> The compositions of C1 chondrite and primitive mantle are from McDonough & Sun (in prep.)

Values for N-type and E-type MORB and OIB are based on a literature survey and internal consistency of elemental ratios.

<sup>b</sup> For mantle-normalized diagrams, the recommended normalizing values for lead and caesium are 0.071 and 0.0079, respectively.

these magmas relative to their neighbouring elements on a mantle normalizing diagram. Decreasing ratios of Ba/Nb, K/Nb, Rb/Nb, Cs/Nb and Rb/Sr with increasing lanthanum and niobium abundances are common in alkali basalts, nephelinites and kimberlites, whereas tholeiites commonly do not show such relative depletions. This suggests that phlogopite does not play a role during tholeiitic magma generation. Moreover, since phlogopite is not an early liquidus mineral in most silica-undersaturated basaltic magmas, it acts as a residual phase during the

initial small degrees of mantle melting or during a metasomatic enrichment of the source region. If phlogopite is indeed the mineral holding back potassium, rubidium, and caesium in the source regions of silica-undersaturated nephelinites, non-micaceous kimberlites and melilitites (Sun & Hanson 1975a, b; Clague & Frey 1982), then the near constant Ba/Rb ( $\approx 12$ ) and Rb/Cs ( $\approx 80$ ) ratios observed in most OIBs requires that barium and caesium have similar phlogopite/melt  $K_d$  values relative to rubidium (Philpotts & Schnetzler 1970; Kuehner *et al.* 1981) or that

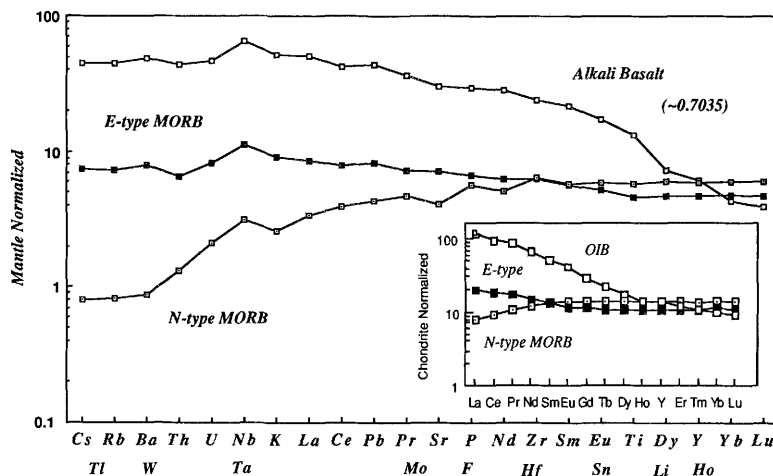


FIG. 1. Primitive mantle (modified) normalized abundance patterns for moderately to highly incompatible elements in average N-type and E-type MORB and oceanic alkali basalts with  $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7035$ . See Table 1 for normalizing values.

$K_d$  are large for barium, rubidium and caesium when phlogopite is stable. Studies of uranium disequilibrium series isotopes in OIBs indicate that 20% uranium or more has been held back in the source, assuming that thorium is perfectly incompatible (eg Oversby & Gast 1968; Newman *et al.* 1984). Therefore the variable (by more than a factor of 2) K/U ratios observed in OIBs could be due to these combined effects in addition to original source variations.

Finally, constant elemental ratios suggest that zone refining melting or the chromatographic column model of Navon & Stolper (1987) and magma chamber processes such as mixing and extensive fractionation and replenishment (as discussed by O'Hara & Mathews 1981), which could fractionate incompatible elements efficiently, are not dominant processes operating during the generation of primitive oceanic basalts.

#### Modification of the 'mantle-normalized' rule and exceptions to the rule

Among OIB samples with  $\text{La} \geq 50$  ppm, decoupling and lowering of titanium, zirconium, strontium, phosphorus, potassium and thorium abundances from their corresponding rare earth elements (REEs) is common. A new set of relationships is developed for such rocks (Table 2). These features may be due to factors such as the saturation of minor minerals, changes in the residual mineral proportions (eg an increase in garnet abundance with depth), a change in mineral/melt  $K_d$ , mantle metasomatism and/or melting processes (eg if zone refining becomes important). For example, nephelinites from Oahu Island have Ti/Eu ratios less than half of that commonly observed in alkali basalts (3000 versus approximately  $6000 \pm 700$  respectively) and they are also depleted in niobium, tantalum,

TABLE 2. Generalization of primitive-mantle-normalized abundance ratios (alkali basalt with  $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7035$  to group I kimberlites)

| La (ppm)          | Nb/La     | K/La          | Sr/Pr         | Sr/Nd         | P/Nd          | Zr/Hf/Sm   | Ti/Eu         |
|-------------------|-----------|---------------|---------------|---------------|---------------|------------|---------------|
| 30                | 1.2–1.5   | 0.7–1.0       | $\approx 1.0$ | $\approx 1.0$ | 1.0           | 1.0        | $\approx 0.8$ |
| 50–100            | (1.5)–2.0 | $\approx 0.4$ | (0.8)–1.0     | $\approx 1.0$ | 1.0           | (0.7)–1.0  | $\approx 0.8$ |
| >200 <sup>a</sup> | 1.2–2.0   | $\leq 0.2$    | $\approx 0.6$ | $\leq 0.6$    | $\approx 0.5$ | $\geq 0.5$ | 0.2–0.5       |

<sup>a</sup> In general we are not sure whether at low degrees of partial melting these ratios are reflecting source mineralogy or subsequent lower-pressure fractionation effects.



zirconium and hafnium. It is very likely that these depletions are due to saturation of a titanate mineral in the source region (Clague & Frey 1982).

Furthermore, an examination of the chemical and isotopic compositions of group I and II kimberlite samples (Kramers *et al.* 1981; Smith 1983; Muramatsu 1985; Muramatsu & Wedepohl 1985; Smith *et al.* 1985) reveals that in many respects group I kimberlites are comparable with Bouvet type OIB, whereas group II kimberlites are more akin to Dupal type OIB (Le Roex 1986). However, exceptions to these general comparisons are that both groups of kimberlites have higher La/Ce ratios, lower Sr/Nd ratios and commonly show zirconium and hafnium depletions relative to samarium. These differences are most probably due to melting under very different conditions (*eg* variable clinopyroxene/garnet ratios,  $P$ - $T$  conditions and/or  $K_d$  values). Detailed study of the fine features of the mantle-normalized diagram may provide useful information regarding the relative importance of garnet and clinopyroxene, in addition to the effects of other factors. It may also give insights into the possible process of melting of stretched veins of eclogite during OIB generation.

There are several reports of tholeiites and alkali basalts that are enriched in REEs and yttrium relative to other incompatible elements (*eg* western Victoria, Australia (Frey *et al.* 1978; McDonough *et al.* 1985), Norfolk Island (Green 1978) and the Hawaiian islands (Fodor *et al.* 1987)). Some samples have negative cerium anomalies and concave-downward REE patterns with relative enrichment of the middle REEs. Recently, detailed microprobe studies by Nagashima *et al.* (1986), Fodor *et al.* (1987) and Price (1987, *pers. comm.*) have detected very small amounts of REE-rich carbonates and phosphates of secondary origin. It is therefore likely that post-magmatic alteration is responsible for REE and yttrium enrichment in these unusual samples.

#### Trace element— isotope correlations in major types of mantle sources of oceanic basalts

Combined lead, strontium and neodymium isotope studies of oceanic basalts demonstrate that the observed isotope variations in these rocks cannot be generated by a single mantle process or mixing of two kinds of mantle components with well-defined isotopic characteristics (*eg* Sun & Hanson 1975*b*; Sun 1980; Cohen & O'Nions 1982; White & Hofmann 1982; Zindler *et al.*

1982; White 1985; Hart *et al.* 1986; Zindler & Hart 1986; Allégre *et al.* 1987). Different approaches have been used to estimate the minimum number of end-members required. Zindler *et al.* (1982) suggested that on a three-dimensional plot of lead, strontium and neodymium isotopes most oceanic basalts fall on or near a mantle plane defined by average N-type MORB ( $^{206}\text{Pb}/^{204}\text{Pb} \approx 18.5$ ,  $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7029$ ,  $\epsilon_{\text{Nd}} \approx +13$ ), St Helena ( $\approx 20.8$ ,  $0.7029$ ,  $+5$ ) and Kerguelen Island ( $\approx 18.4$ ,  $0.7054$ ,  $-1$ ). White (1985) subdivided oceanic basalts into five distinct groups on isotope plots: MORB group (including Iceland, Galapagos, Easter Islands), St Helena group (including Austral, Comores, Ascension), Kerguelen group (including Gough, Tristan da Cunha), Society group (including Marquesas, Samoa, Sao Miguel) and Hawaii island group. Most Society group samples clearly fall above the mantle plane of Zindler *et al.* (1982) with higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios at the same lead and neodymium isotope ratios. Zindler & Hart (1986) used different terminology to define the characteristics of mantle end-members: DMM (depleted MORB mantle), PREMA (prevalent mantle, including Iceland, Galapagos, the Easter Islands of White's MORB group and the Hawaiian islands), HIMU (long-term high U/Pb in the source, including St Helena, Tubuai, Mangaia), EM1 (enriched mantle type 1 for the Kerguelen type) and EM2 (enriched mantle type 2 for the Society Island type). Their EM1 samples from the Walvis Ridge clearly fall below the mantle plane of Zindler *et al.* (1982) with lower  $^{87}\text{Sr}/^{86}\text{Sr}$  at the same lead and neodymium isotope ratios (Fig. 2).

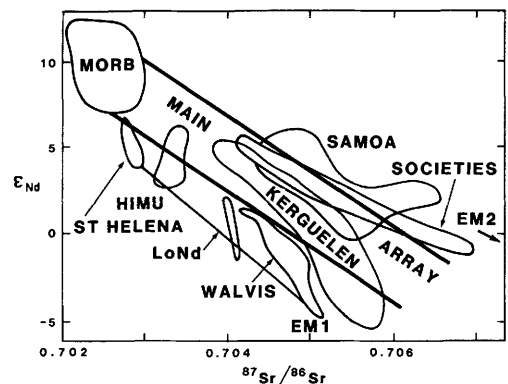


FIG. 2. Schematic diagram of the  $\epsilon_{\text{Nd}}$  versus  $^{87}\text{Sr}/^{86}\text{Sr}$  plot for OIB data to show the fields of different types of oceanic basalts and the end-member assigned by Zindler & Hart (1986). Modified from Hart *et al.* (1986).

Different mantle processes have been proposed for the generation of the different isotope groups and end-members. Since isotope variation is a function of parent/daughter abundance ratio and isolation time, the same mantle process operating at different times and with different degrees of elemental fractionation will result in variable but coherent lead, strontium and neodymium isotopic compositions. Consequently, the 'end-members' (or components) proposed by Zindler & Hart (1986) would not be expected to have fixed isotopic compositions.

It is not surprising to find that the different mantle processes responsible for generating a variety of *isotope* groups also create distinct *chemical* signatures. Therefore the variations in the mantle-normalized patterns for different mantle components may reflect the effects of the different processes and environments, as with isotopic data. A comparison of Nb/Pb, Ce/Pb, Nb/U, K/U, K/Nb and Rb/Cs ratios, ratios which encompass elements considered to behave similarly during generation of oceanic basalts, for different OIB end-members is presented in Table 3. The contrast between samples of the HIMU (or St Helena) and EM (or Gough) type is quite clear and there are consistent differences, especially for Nb/Pb and Ce/Pb ratios, in other OIB samples. Ratios involving potassium may be affected by the retention of potassium (rubidium, barium and caesium) in

potassium-bearing residual minerals, as discussed earlier.

In Fig. 3 a representative HIMU-type sample (St Helena: 2882) and an EM-type sample (Gough island: G111) (Table 4) are used to illustrate the differences in mantle-normalized patterns for these two types of mantle source. These patterns are considered representative of their respective types on the basis of these plus other high quality data having good consistency with other samples from the same islands. This statement is also supported by data of critical element ratios presented in Table 3. The HIMU-type mantle with low  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7027–0.7030) and very radiogenic  $^{206}\text{Pb}/^{204}\text{Pb}$  ( $\geq 21$ ) is characterized by a low Rb/Sr ratio (0.01–0.03) and a high  $^{238}\text{U}/^{204}\text{Pb}$  ratio ( $\geq 30$ ); such mantle materials tend to have low K/U and K/Nb ratios (related to potassium, rubidium and barium depletions). The mantle-normalized patterns of HIMU-type mantle (St Helena) display a continuous decrease in the abundances of the elements niobium to caesium, similar to typical MORB. In contrast, for EM-type OIB with  $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.7040$  and lower  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios than St Helena type mantle ( $< 18.6$  for EM1, 18.6–19.7 for EM2), the mantle-normalized pattern shows increased abundances of elements more incompatible than niobium (Cs, Rb, Ba, Th, U, K) and lead compared with the St Helena type. Because these two patterns

TABLE 3. Contrasts of some element ratios observed in N-type MORB and HIMU-type and EM-type ocean island basalts

|                                     | Nb/Pb | Ce/Pb        | Nb/U      | K/U                 | K/Nb  | Rb/Cs | Nb/Th |
|-------------------------------------|-------|--------------|-----------|---------------------|-------|-------|-------|
| <i>N-type MORB 0.7025</i>           |       |              |           |                     |       |       |       |
| MORB                                | 7.5   | 25           | 50        | 12700               | 260   | 80    | 20    |
| <i>HIMU (St Helena) type 0.7029</i> |       |              |           |                     |       |       |       |
| St Helena                           | 23    | 33           | 48        | 8000                | 180   | 100   | 13.3  |
| Rurutu                              | 18    | $\approx 30$ | —         | 7000                | 180   | —     | 12.5  |
| Mangaia                             | 18    | 29           | —         | 6000                | 160   | —     | 10    |
| Dunedin                             | 20    | $\approx 30$ | $\sim 45$ | 7000                | 170   | —     | 17    |
| Ua Pou (th)                         | 19    | 38           | 43        | 8000                | 180   | —     | 13    |
| <i>EM-type OIB 0.705–0.706</i>      |       |              |           |                     |       |       |       |
| Gough                               | 10.4  | 20           | 43        | 18000               | 430   | 70    | 9.3   |
| Kerguelen                           | 8.5   | 14.5         | 43        | (8000) <sup>a</sup> | 270   | —     | 11.5  |
| Aitutaki                            | 8.3   | 16           | —         | (5600)              | (170) | —     | 6.3   |
| Upolu                               | 12.1  | 31           | —         | (9700)              | (200) | —     | —     |
| Tutuila                             | 12.2  | $\approx 25$ | —         | (8300)              | (250) | —     | 9.1   |
| Tristan                             | 15.9  | 24           | 41        | 11500               | 270   | 85    | 9.1   |
| Sao Miguel                          | —     | —            | 40        | 13700               | 340   | 90    | 9.2   |

<sup>a</sup> Low K/La suggesting potassium has been held back? Data sources: Sun & Hanson (1975a); White *et al.* (1979); Hofmann & White (1983); Hofmann *et al.* (1986); Newsom *et al.* (1986); Palacz & Saunders (1986); Weaver *et al.* (1986); this paper.

(Fig. 3) have similar REE abundances, the two distinctive patterns from caesium to niobium cannot be due solely to different degrees of partial melting. Moreover, such OIBs often have barium spikes and high La/Nb ratios (sometimes higher than the chondritic ratio). This latter point is illustrated in Fig. 4 which shows a linear correlation between Ba/Nb and La/Nb among OIBs (Weaver *et al.* 1986). These two ratios also correlate with  $^{87}\text{Sr}/^{86}\text{Sr}$  in general. 'Exceptions' are known for other EM-type samples (*eg* group I kimberlites and Tutuila), which have  $\text{Ba}/\text{Nb} \leq 8$  and  $\text{La}/\text{Nb} \leq 0.8$ , and such differences most probably reflect the multiple origins of EM-type source regions. However, we note that a general trend of low  $^{87}\text{Sr}/^{86}\text{Sr}$ , La/Nb and Ba/Nb to high  $^{87}\text{Sr}/^{86}\text{Sr}$ , La/Nb and Ba/Nb exists.

Lamproites from western Australia (Jaques *et al.* 1988) may also represent extremely enriched EM2 type. They have a highly fractionated mantle-normalized pattern (Fig. 5), especially from niobium to rubidium. These samples have low strontium and phosphorus abundances, a negative europium anomaly of up to 20% and high lead and zirconium abundances (similar to some western US minettes; Alibert *et al.* 1986), possibly reflecting a sedimentary component added to their source (*eg* Thompson *et al.* 1984). Often, but not always, they have depletions of niobium relative to lanthanum.

## The generation of different mantle types and the niobium issue

OIBs with high  $\text{K}_2\text{O}$  ( $\geq 2\%$ ) do not always have low U/Pb ( $\mu$ ) values ( $\leq 16$ ) but it is generally true that OIBs with low  $\text{K}_2\text{O}$  ( $\approx 1\%$ ) always

have high  $\mu$  values ( $\geq 20$ ). This correlation must be related to the source character and partial-melting conditions. Several mechanisms have been proposed to generate the isotopic and chemical characteristics of different types of OIB mantle sources. The HIMU and low  $^{87}\text{Sr}/^{86}\text{Sr}$  character St Helena-type OIBs have been attributed to the recycling of altered oceanic crust into the OIB source region (*eg* Zindler *et al.* 1982; Palacz & Saunders 1986), mantle enrichment through melt migration from the LVZ into oceanic and continental lithosphere (*eg* Sun 1980; Hart *et al.* 1986) or derivation of OIBs from the lower mantle which has lost lead by continuous core formation (*eg* Vidal & Dosso 1978). However, Newsom *et al.* (1986) showed that St Helena basalts have the same molybdenum (highly chalcophile) to praseodymium (highly lithophile) abundance ratios as MORBs and other OIBs, effectively arguing against continuous core formation. The EM-type character is generally considered to be related to processes associated with convergent margins, such as the recycling of sediments with oceanic crust (*eg* Hawkesworth *et al.* 1979; Cohen & O'Nions 1982; White 1985; Weaver *et al.* 1986). The formation of these OIB sources from remobilization or delamination of metasomatized enriched continental lithosphere has also been proposed (*eg* Richardson *et al.* 1982; McKenzie & O'Nions 1983; Hawkesworth *et al.* 1986).

Multiple origins for EM-type mantle is likely, including superposition of different processes. Menzies (1983) suggested that EM1 could be related to enrichment by the introduction of  $\text{CO}_2$ -rich silicate melt (*eg* kimberlite, nephelinite) whereas the high Rb/Sr,  $^{87}\text{Sr}/^{86}\text{Sr}$  character of EM2 is similar to some modern island arc basalts (*eg* White 1985). Hart (1984) and Zindler

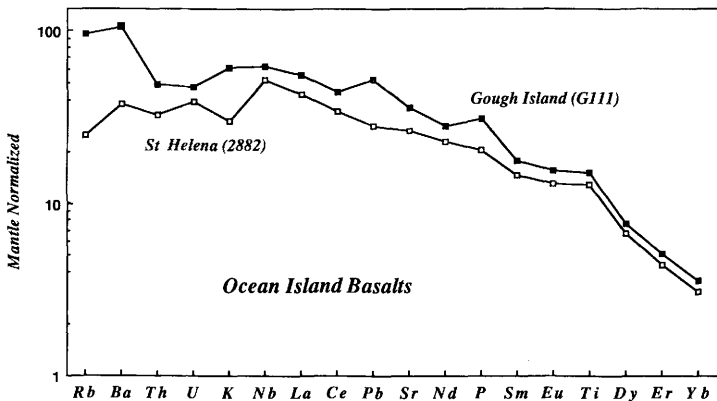


Fig. 3. A comparison of the mantle-normalized patterns of basalts from St Helena (2882), with a low  $^{87}\text{Sr}/^{86}\text{Sr}$ , and Gough Island (G 111), with a high  $^{87}\text{Sr}/^{86}\text{Sr}$ . See Table 1 for normalizing values. Data from Table 3.

TABLE 4. Chemical and isotopic composition of selected basalts

|                                      | St Helena<br>2882 | Gough<br>G 111 | Chain 43°–45°N MAR |          |
|--------------------------------------|-------------------|----------------|--------------------|----------|
|                                      |                   |                | 104–16             | 104–18   |
| <i>Major elements (wt%)</i>          |                   |                |                    |          |
| SiO <sub>2</sub>                     | 45.50             | 47.73          | 50.53              | 48.85    |
| TiO <sub>2</sub>                     | 2.80              | 3.30           | 1.35               | 1.12     |
| Al <sub>2</sub> O <sub>3</sub>       | 13.54             | 15.53          | 14.88              | 16.10    |
| FeO                                  | 11.10             | 10.67          | 9.39               | 7.84     |
| MnO                                  | 0.11              | 0.14           | 0.18               | 0.16     |
| MgO                                  | 10.40             | 8.37           | 8.22               | 9.22     |
| CaO                                  | 10.69             | 8.71           | 10.99              | 12.31    |
| Na <sub>2</sub> O                    | 2.52              | 2.89           | 2.60               | 2.42     |
| K <sub>2</sub> O                     | 0.84              | 1.70           | 0.34               | 0.48     |
| P <sub>2</sub> O <sub>5</sub>        | 0.43              | 0.66           | 0.13               | 0.15     |
| Total                                | 97.73             | 99.70          | 98.61              | 98.65    |
| <i>Trace elements (ppm)</i>          |                   |                |                    |          |
| Rb                                   | 16.1              | 62.0           | 4.1                | 7.8      |
| Sr                                   | 581               | 792            | 104                | 185      |
| Ba                                   | 275               | 760            | 41                 | 84       |
| Nb                                   | 38.5              | 46.0           | 5.10               | 14.1     |
| Zr                                   | —                 | 255            | 77                 | 75       |
| Y                                    | —                 | 26             | 33                 | 24       |
| La                                   | 31.7              | 41.2           | 5.92               | 8.58     |
| Ce                                   | 64.8              | 84.5           | 14.8               | 19.7     |
| Nd                                   | 32.3              | 40.2           | 11.0               | 11.50    |
| Sm                                   | 6.68              | 8.08           | 3.59               | 3.06     |
| Eu                                   | 2.25              | 2.66           | 1.30               | 1.10     |
| Gd                                   | 6.20              | 7.20           | 4.83               | 3.66     |
| Dy                                   | 4.75              | 5.44           | 5.84               | 4.13     |
| Er                                   | 2.09              | 2.42           | 3.72               | 2.54     |
| Yb                                   | 1.55              | 1.81           | 3.67               | 2.46     |
| Lu                                   | 0.211             | 0.247          | 0.568              | 0.385    |
| Pb                                   | 2.08              | 3.85           | 0.75               | 1.20     |
| Th                                   | 3.01              | 4.52           | 0.51               | 0.85     |
| U                                    | 0.86              | 1.05           | 0.19               | 0.27     |
| <sup>87</sup> Sr/ <sup>86</sup> Sr   | 0.70292           | —              | 0.70317            | 0.70319  |
| <sup>143</sup> Nd/ <sup>144</sup> Nd | 0.512857          | —              | 0.513101           | 0.513086 |
| <sup>206</sup> Pb/ <sup>204</sup> Pb | 20.896            | 18.552         | 19.332             | 19.351   |
| <sup>207</sup> Pb/ <sup>204</sup> Pb | 15.791            | 15.606         | 15.563             | 15.570   |
| <sup>208</sup> Pb/ <sup>204</sup> Pb | 40.131            | 39.045         | 38.826             | 38.878   |

Neodymium and strontium isotope data for Chain 43(104–16 and 104–18) and St Helena samples are from White & Hofmann (1982) (see their CH43 106–16 and 106–18 sample numbers); however, for 104–16 we report the strontium isotope ratio for an acid-leached sample (which was normalized relative to 0.70800 for the E&A standard).

& Hart (1986) emphasized that EM2 is almost exclusively restricted to the southern hemisphere. It could have originated from the delamination of subduction-zone-related metasomatized continental lithosphere of Gondawana or the recycling of the mantle wedge above the subduction zones. However, they do not preclude the earlier suggestion by Hart (1984) that this regional EM-type anomaly in the southern hemisphere existed since the Archaean and might be controlled by global

convection patterns. Hawkesworth *et al.* (1986), on the other hand, favour the idea that the EM-type mantle in the southern Atlantic (Gough, Walvis Ridge, Tristan da Cunha) has a shallow origin due to the thermal remobilization and detachment of the continental lithosphere of southern Africa from South America during the breakup of Gondawana. More recently, Hart *et al.* (1986) pointed out that HIMU and EM1 mantle types are often spatially related and share the characteristic of lying below the mantle

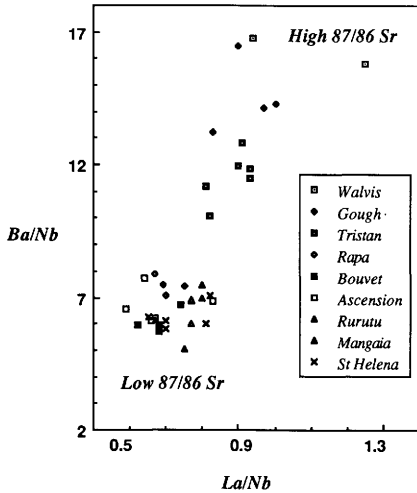


Fig. 4. Positive correlation between Ba/Nb and La/Nb ratios of HIMU-type (low  $^{87}\text{Sr}/^{86}\text{Sr}$ ) and EM-type (high  $^{87}\text{Sr}/^{86}\text{Sr}$ ) OIB. Data sources: Richardson *et al.* (1982); Palacz & Saunders (1986); Weaver *et al.* (1986); this paper.

array on the  $\epsilon_{\text{Nd}}$  (vertical axis) versus  $^{87}\text{Sr}/^{86}\text{Sr}$  plot (Fig. 2). They suggested a subcontinental lithospheric mantle origin for both HIMU and EM1 mantle types through mantle metasomatism by silicate melts.

### The niobium issue

The La/Nb variation in some oceanic basalts can be seen in Fig. 6. N-type MORBs have high La/Nb ( $>1.0$  ( $\text{La}/\text{Ta} > 17$ )), E-type MORBs have lower La/Nb ( $<1.0$ ), and HIMU-type OIBs have much lower La/Nb (0.6–0.7). Given that the oceanic crust once processed through the subduction zone could have a lower La/Nb ( $<1.0$ ), it has been proposed that the low La/Nb ratios (relative to the chondritic ratio of

0.95) observed in some OIBs, especially HIMU-type (Figs. 4 and 6), reflect the mantle source character of the recycled oceanic crust which has experienced dehydration/partial melting in the subduction zone region (Weaver *et al.* 1986). However, this interpretation is not unique, because low La/Nb ratios in the mantle source could also be the result of mantle metasomatism and/or small degrees of partial melting, since niobium is more incompatible than lanthanum (Fig. 2). On the other hand, high La/Nb ratios ( $\geq 0.9$ ) found in many (most?) EM1 and EM2 types of OIB could be due to the introduction of subducted sediment (with high La/Nb ratios, Fig. 6) into the OIB source, or it could be due to the presence of a residual niobium-bearing titanate mineral during magma generation. The effects of partial melting on La/Nb ratios can be assessed by several observations. Two MORB samples from  $45^\circ\text{N}$  in the Mid-Atlantic Ridge (Chain 43, 104–16 and 104–18) have identical lead, strontium and neodymium isotopic compositions (Fig. 7 and Table 4). The sample that is light REE enriched also has a much lower La/Nb ratio, consistent with its representing a lower percentage of partial melt derived from the same source as the light-REE-depleted sample. Figure 8 shows similar partial-melting effects on the La/Nb ratio of basalts from Loihi Seamount. The Loihi Seamount tholeiites and basanites have similar strontium and neodymium isotopic compositions. In contrast, the tholeiites have La/Nb ratios which are close to the chondritic value, whereas the basanites have La/Nb ratios as low as the HIMU samples of Fig. 6. These data argue strongly against the idea that the HIMU source must have a low La/Nb ratio inherited from the subducted oceanic crust. Either the recycled oceanic crust model is incorrect, or the La/Nb ratio of the recycled oceanic crust has been increased before final diapiric rise. The basalts

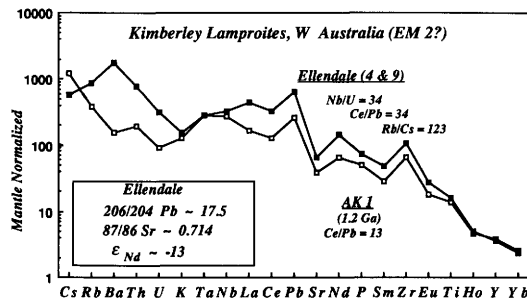


Fig. 5. Mantle-normalized diagram of EM2-type Miocene lamproites from W Kimberley and 1.2 Ga lamproites from E Kimberley, western Australia. Data source: Jaques *et al.* (in press). See Table 1 for normalizing values.

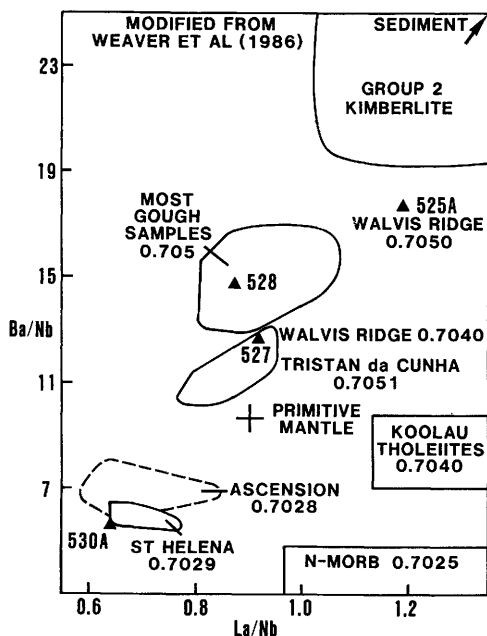


Fig. 6. Positive correlation between Ba/Nb and La/Nb ratios of basalts from St Helena, Ascension, Tristan da Cunha and Walvis Ridge (modified from Weaver *et al.* 1986). Data for Koolau tholeiites, N-type MORB, group II kimberlites and sediments are added for comparison.

from Haleakala, Maui, also show a consistent variation in La/Nb ratios with degree of partial melting: the basanites representing the lower degrees of partial melting have lower La/Nb ratios than the tholeiites which are derived by larger degrees of partial melting. However, in contrast to the Loihi basalts, the tholeiitic and alkalic basalts from Haleakala are derived from isotopically different mantle sources (Chen & Frey 1985).

In addition to reflecting the source character, high La/Nb ratios in OIBs can be produced if a residual titanate mineral is present during open-system processes in the source (*eg* metasomatic enrichment or partial melting) or during magma differentiation. Nephelinites and basanites of the Honolulu series from Oahu are good examples (Fig. 8). They show relative depletions in titanium, niobium, tantalum, zirconium and hafnium and have Ti/Eu ratios ( $\approx 3000$ ) less than half those normally observed in OIBs (about 6000, close to the chondritic ratio approximately 7800). Clague & Frey (1982) suggested that a residual titanate mineral is responsible for the niobium depletion relative to lanthanum. Additionally, it is interesting that

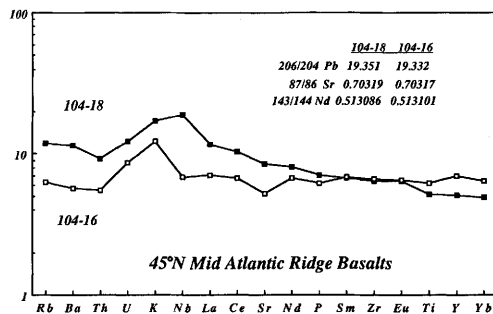


Fig. 7. Comparison of mantle-normalized patterns for two MORB samples from 45°N from the Mid-Atlantic Ridge. These basalts have similar lead, strontium and neodymium isotope compositions but different La/Nb ratios which can only be attributed to melting. See Table 1 for normalizing values.

high La/Nb ratios (1.6), similar to those found in the Honolulu series, are also found in some Koolau tholeiites (Fig. 8), although these two Oahu basalt series are derived from isotopically different sources (Roden *et al.* 1984). In contrast with the Oahu case, EM samples from Walvis Ridge and Gough (Fig. 4) with high La/Nb ratios have Ti/Eu ratios close to the chondritic ratio, suggesting that a titanate mineral does not play a role in the generation of these basalts. We therefore agree with Weaver *et al.* (1986) that the high La/Nb ratios of these EM-type basalts reflect a mantle source characteristic, possibly resulting from the involvement of subducted sediments. This conclusion is further supported by the high Ba/Nb,  $^{87}\text{Sr}/^{86}\text{Sr}$  (Fig. 6) and  $^{208}\text{Pb}/^{206}\text{Pb}$  commonly observed in EM-type OIBs and typical of sedimentary material. However, we would emphasize that sediment subduction, along with the oceanic crust, is not a unique solution for the generation of EM-type mantle. The addition of a fluid or melt derived from an altered subducted oceanic crust, with or without sediment, into the overlying mantle wedge or adjacent continental lithospheric mantle may also generate high Ba/Nb and La/Nb ratios.

#### Mid-ocean ridge basalt source connection of the HIMU-type mantle

HIMU-type OIBs are characterized by very low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (as low as 0.7027) similar to some N-type MORBs, high  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios ( $\approx 21.0$ ) but low inferred Th/U ratio in the source (approximately 3.3, see below). It is now generally accepted that the HIMU-type mantle

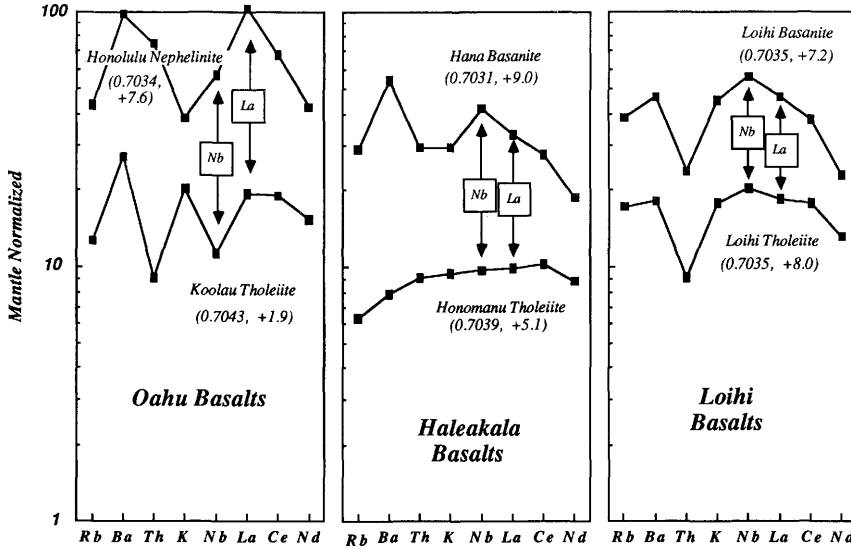


Fig. 8. Comparison of mantle-normalized patterns of Rb, Ba, Th, K, Nb, La, Ce and Nd for selected Hawaiian basalts. The samples used include Koolau tholeiite (WW 9980), Honolulu nephelinite (68 Pb 2), Honomanu tholeiite (C122), Hana basanite (65–11), Loihi tholeiite (24–7) and Loihi basanite (17–7). Data sources: Clague & Frey (1982); Frey & Clague (1983); Roden *et al.* (1984); Staudigel *et al.* (1984); Chen & Frey (1985). See Table 1 for normalizing values.

was originally derived from a MORB-type component more than a billion years ago; however, there is disagreement regarding the processes responsible.

On lead isotope ratio plots (Fig. 9) each HIMU island exhibits a small range of isotopic variation. To estimate time of isolation for the HIMU-type mantle, we use the lead isotopic composition evolution of the depleted upper

mantle, as suggested by Zartman & Doe (1981), to calculate a two-stage lead isotopic evolution. Their version II lead isotopic growth curves for the depleted mantle are consistent with the available lead isotope data for Archaean and Proterozoic komatiites and basalts derived from depleted mantle, as well as Phanerozoic ophiolites. Feasible solutions to our calculations are evaluated by comparing the calculated  $\mu_2$  values

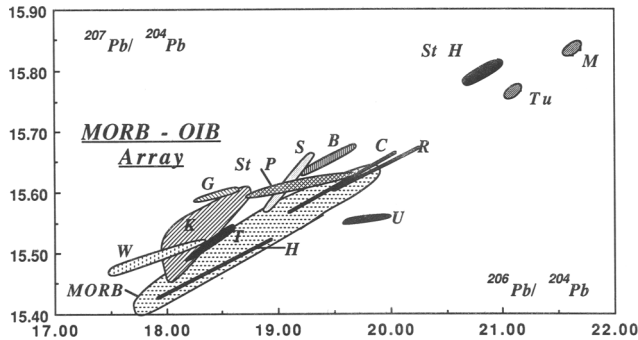


Fig. 9. Simplified  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  plot for oceanic basalts from mid-ocean ridge (MORB), Walvis Ridge (W), Hawaiian Islands (H), Kerguelen (K), Gough (G), Tristan da Cunha (T), Society Islands (S), St Paul's Rocks (St P), Ua Pou (U), Ross Island (R), Canary Islands (C), Bouvet (B), St Helena (St H), Tubuai (Tu) and Mangaia (M). Data sources: Sun (1980); Cohen & O'Nions (1982); Richardson *et al.* (1982); Roden *et al.* (1984); Vidal *et al.* (1984); Palacz & Saunders (1986); Stille *et al.* (1986); Dupuy *et al.* (1987); Wright & White (1987).

( $^{238}\text{U}/^{204}\text{Pb}$ ) needed to generate the observed HIMU  $^{206}\text{Pb}/^{204}\text{Pb}$  and the resulting  $^{207}\text{Pb}/^{204}\text{Pb}$  values with the measured  $\mu$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  values. These results (Fig. 10) indicate that the isolation time must be greater than 1 billion years, for otherwise the  $\mu$  value in the source would have to be higher than that measured in the sample, which is contrary to the inference that uranium is more incompatible than lead (Fig. 1). However, the calculated  $^{207}\text{Pb}/^{204}\text{Pb}$  value with less than 1 billion years of isolation is lower than the measured value; therefore a longer isolation time is required. Using a reasonable  $\mu_2$  value and considering  $^{207}\text{Pb}/^{204}\text{Pb}$  heterogeneity ( $\pm 0.05$ ) in the Precambrian depleted mantle, we obtain an isolation time of  $2.0 \pm 0.2$  Ga (Fig. 10). Since the HIMU source is related

to the MORB source through mantle fractionation processes, it is not surprising that similar age information can be derived from the slope connecting HIMU data with the MORB field on Fig. 9, assuming that the slope represents an isochron. A mantle source isolation age calculated in this way for the other two oceanic islands—Tubuai and Mangaia—gives 1.7 Ga (Palacz & Saunders 1986), similar to the St Helena case. An isolation time of about  $1.0 \pm 0.2$  Ga is required to derive the most radiogenic  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio (19.99) in the Ua Pou (Marquesas Archipelago) tholeiites from a depleted MORB-type mantle, assuming a reasonable  $\mu_2$  value of  $20 \pm 2$  in the mantle source. This is the youngest isolation time calculated for HIMU-type OIBs.

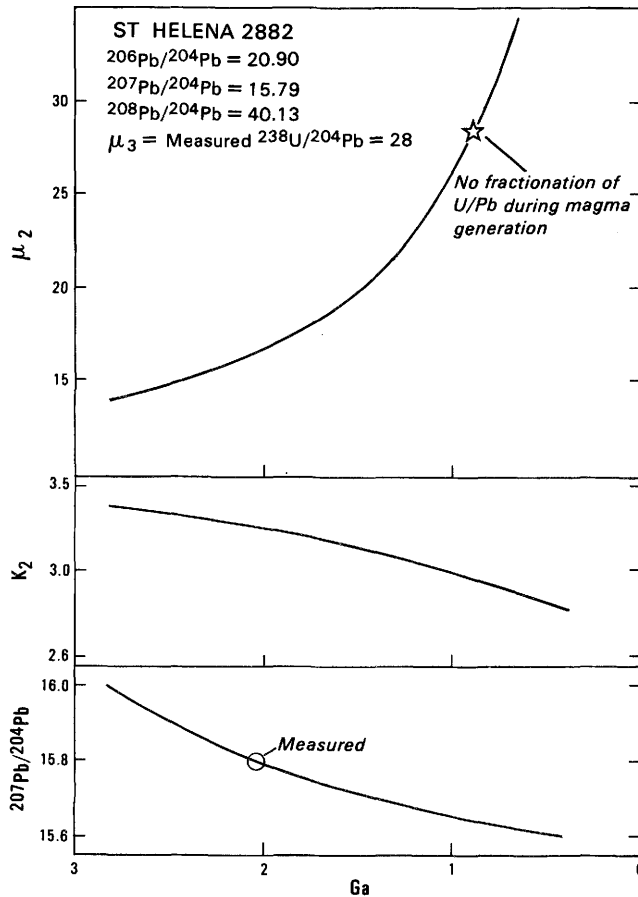


FIG. 10. Model calculations for the lead isotope evolution of a St Helena sample (2882) assuming that it was derived from a depleted upper mantle MORB-type source some time ago. When an isolation time is assigned, specific values of  $\mu_2$  and  $K_2$  are required to match the measured  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios. At 2.0 Ga, model calculations give the best solution to match the measured  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $\mu$  values.



It is important to point out that if St Helena, Tubuai, Mangaia and Ua Pou samples are not derived from pure HIMU end-members but either (i) contain an EM-type component with low  $^{206}\text{Pb}/^{204}\text{Pb}$  but high  $^{207}\text{Pb}/^{204}\text{Pb}$  (eg Duncan *et al.* 1986), or (ii) are derived from a recently enriched high- $\mu$  reservoir (eg St Paul's Rock; Roden *et al.* 1984) followed by mixing with depleted asthenosphere (Fig. 9), then the age of the HIMU isolation could be considerably younger. Such an interpretation may apply to much of the non-HIMU OIB lead isotope data (see later).

Model calculations for the  $^{208}\text{Pb}/^{204}\text{Pb}$  evolution of St Helena samples (Fig. 10) yield a Th/U ratio of  $3.30 \pm 0.05$  in the mantle source starting at 2.0 Ga ago. This value is lower than the measured Th/U ratios in St Helena samples (3.5–3.8) (Weaver *et al.* 1986; this paper), consistent with the fractionation of thorium from uranium during OIB magma generation. Similar conclusions are reached through  $^{230}\text{Th}/^{232}\text{Th}$  studies on young OIB (eg Oversby & Gast 1968; Newman *et al.* 1984).

Recently, Dupuy *et al.* (1987) presented a strong case for a connection between the recycled oceanic crust and HIMU-type OIB sources on the basis of their study of Ua Pou Island, Marquesas Archipelago. They emphasized that Ua Pou tholeiites are highly relatively depleted in most incompatible elements (barium, rubidium, thorium, uranium, potassium, niobium and light REEs) and have mantle-normalized patterns (Fig. 11) showing mirror images of those for island arc basalts, *ie* these

tholeiites have high Nb/La, Ce/Pb, U/Pb and Hf/Lu ratios. Dupuy *et al.* suggested that the mantle source of the Ua Pou tholeiites contains residual oceanic crust formed by dehydration and partial melting during subduction.

These unusual Ua Pou tholeiites with concave-downward REE patterns (Fig. 11) offer a rare opportunity to evaluate the recycled oceanic crust model. They have high nickel (155–550 ppm),  $\text{TiO}_2$  (3.7%–4.1%) and cerium (61–78 ppm), comparable with those of other HIMU OIBs considered in this study. Consequently, based on the arguments presented earlier, it would be reasonable to expect more than 20% fractionation of the La/Nb ratio during magma generation. The measured La/Nb ratio (0.85) of these tholeiites is higher than those of other HIMU OIBs (St Helena, 0.69; Ascension, 0.65; Mangaia, 0.77) but similar to that of the EM-type OIB of Tristan da Cunha (0.86). After a 20% correction for the partial-melting effect (based on studies of Hawaiian nephelinites discussed earlier), the mantle source for Ua Pou tholeiites has La/Nb = 1.06, *ie* it actually shows niobium depletion relative to lanthanum. The lack of a positive niobium anomaly relative to lanthanum in their mantle source weakens the argument of a recycled oceanic crust model for the Ua Pou tholeiites, or at least makes it unnecessary.

The high Hf/Lu ratios (22–28) observed in the Ua Pou tholeiites have been used by Dupuy *et al.* to support the recycled oceanic crust model. However, since hafnium is much more

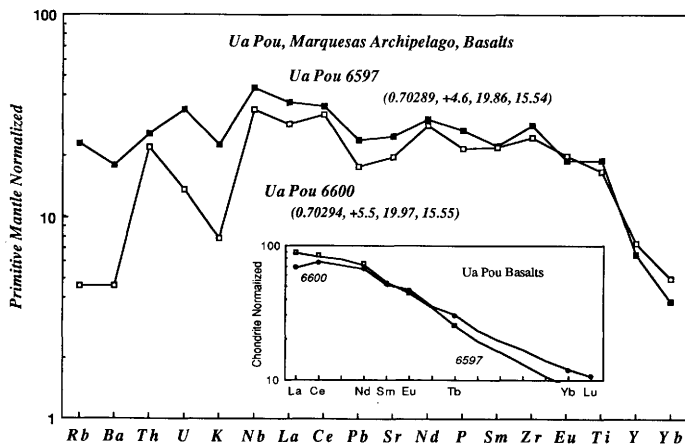


FIG. 11. Mantle-normalized diagram of two HIMU-type OIB samples from Ua Pou. They have concave-downward patterns in the light REE region. Data from Liotard *et al.* (1986) and Dupuy *et al.* (1987). See Table 1 for normalizing values.

incompatible than lutetium during OIB generation, this argument may not be valid. A comparison of Sm/Hf is more appropriate because these elements are similarly incompatible (Fig. 1). In fact, the Sm/Hf ratio of Ua Pou tholeiites (1.43) is equal to that of the primitive mantle (Table 1) suggesting that hafnium has not been fractionated from samarium by processes involved in the generation of HIMU-type mantle. Although we agree with Dupuy *et al.* that the very high Ce/Pb ratios of Ua Pou tholeiites (38–78) are very unusual for OIBs ( $25 \pm 5$ ), these ratios are also much higher than those of other HIMU-type OIBs shown in Table 2. We do not have a good explanation for this anomaly.

The neodymium isotope data presented by Duncan *et al.* (1986) and Dupuy *et al.* (1987) require that the mantle source of Ua Pou tholeiites has an Sm/Nd ratio lower than chondrite, after isolation from the MORB-type source about 1 billion years ago. Combining this information with niobium and REE data, we suggest that this mantle has a concave-downward REE pattern with niobium depletion similar to the pattern of many Hawaiian tholeiites (eg Fig. 8).

In order to make a correct choice between the two processes proposed for generation of the HIMU-type mantle, *ie* through recycling of altered oceanic crust or migration of silicate melt from the depleted mantle into the lithosphere, critical evaluation of the two processes is required. Some MORB and OIB tholeiites (*ie* Iceland) have light-REE-depleted or flat patterns with positive niobium kicks on the mantle-normalized diagram (La/Nb less than the chondritic value). These data support the idea of recycling oceanic crust in the MORB and OIB sources and decreasing La/Nb through the subduction zone dehydration/partial-melting process. However, if the oceanic crust recycling model is correct for the HIMU character, then alteration and subduction of this crust (dehydration and partial melting) must decrease the La/Nb ratio by 20% or more and the U/Pb ratio by a factor of 2 without significantly (>20%) affecting the Rb/Cs, Rb/Sr, Th/U, Ce/Pb and Nb/U ratios. This does not seem likely. Taking Th/U as an example, a model calculation of the lead isotope evolution of the HIMU-type St Helena sample (2882, Fig. 10) requires that the Th/U actually increases slightly relative to the MORB source at about 2.0 Ga ago. Furthermore, dehydration and partial melting is an effective 'depletion' mechanism. In order to generate a St Helena-type OIB source character an enrichment process after subduction, such as megacrith melting (Ringwood 1982), is required.

At present, there are no experimental data to show how these trace elements (and the La/Nb ratio discussed earlier) will be fractionated during partial melting in the garnetite stability field. However, upward migration of CO<sub>2</sub>-rich silicate melts such as kimberlite, carbonatite and nephelinite from the LVZ at the top of the depleted asthenosphere could be an effective mechanism to achieve the HIMU characteristics (including Th/U) and real geological observations are available to support this idea (eg Green 1971; Kay 1979; Menzies & Murthy 1980; Sun 1980; Hart *et al.* 1986). These CO<sub>2</sub>-rich silica-undersaturated melts have low Rb/Sr ratios but high U/Pb ratios (see earlier) and match the characteristics of the HIMU type. Thus, the HIMU character can be fully satisfied by this melting process, since thorium is more incompatible than uranium, which is more incompatible than lead, and residual phlogopite can hold back more rubidium from the melt during small degrees of partial melting. The choice between oceanic and continental lithosphere for the HIMU component will be evaluated later.

#### Subduction zone processes and EM-type mantle

EM2-type mantle with high Rb/Sr and <sup>87</sup>Sr/<sup>86</sup>Sr ratios is commonly considered to be a product of the migration of water-rich fluids or melts enriched in potassium, rubidium and barium associated with subduction zones (eg Menzies 1983; White 1985; Zindler & Hart 1986), whereas the chemical and isotopic character of EM1-type mantle, with high Ba/Nb and La/Nb ratios, has been interpreted by Weaver *et al.* (1986) as the product of sediment subduction. In this section we point out some weaknesses of the subduction-zone-related models, emphasize the need for alternative mechanisms and propose more definite tests for sediment involvement in OIB sources.

As discussed earlier, high Ba/Nb and La/Nb ratios observed in many EM-type OIBs are not necessarily diagnostic of sediment involvement in their source. Except for Gough, Walvis Ridge and Aitutaki (Table 3), there is a general lack of strong trace-element indication of sediment recycling. Mixing as little as 1% of pelagic sediment (with Pb=25 ppm, Pb/Ce=0.6) with subducted oceanic crust (or 0.2% for MORB-type peridotite mantle) is expected to change the Nb/U, Ce/Pb and Rb/Cs ratios considerably from the nearly constant values ( $47 \pm 10$ ,  $25 \pm 5$ ,  $80 \pm 20$ ) for MORB and OIB (Hofmann & White 1983; Hofmann *et al.* 1986; Newsom *et al.* 1986). For example, the Ce/Pb ratio could

be reduced to about 14. Furthermore, a mixture of about 0.5% average shale (Taylor & McLennan 1985, Table 2.9) and a model OIB source (based on the OIB data in Table 1) would produce a source capable of generating an EM-type OIB with consistent key element ratios as found in Table 3 (eg Nb/U=42, Ce/Pb=20, Nb/Pb=11, K/U=13 000, K/Nb=275, Nb/Th=11). Additionally, the introduction of such a small sediment component 1.0–2.0 Ga ago would also be consistent with the variation in strontium and neodymium isotopic compositions observed in EM-type OIB (eg Bouvet versus Gough islands).

However, if sediment subduction is invoked to explain the isotope evolution and the development of negative europium anomalies in some EM-type mantle (see below), then some modification of this simple mixing model is required. In this connection, it is interesting to note that the ratios Nb/U  $\approx$  34, Ce/Pb  $\approx$  13, Rb/Cs  $\approx$  123 (Fig. 5) of Miocene lamproites from western Australia (Jaques *et al.* 1988) are not very different from values for MORB and OIB mentioned above. Isotope and trace-element characteristics (including a 20% negative europium anomaly) of these lamproites (extreme EM2 types) strongly suggest the involvement of sediments in their mantle source (Nelson *et al.* 1986; Jaques *et al.* 1988). Since the EM-type OIBs in Table 3 require much less sediment involvement than these lamproites, the lack of a large amount of variation in Nb/U, Ce/Pb and Rb/Cs ratios may not be a strong argument against involvement of a minor amount of sediment (2% or less) in some EM-type mantle. However, mixing of small amounts of pelagic sediment with oceanic crust is not capable of generating the  $^{208}\text{Pb}/^{206}\text{Pb}$  characteristics of the EM1-type mantle in the S Atlantic. Using lead isotope evolution curves for the depleted mantle and upper crust (sediment source) given in Zartman & Doe (1981), a model calculation for sediment–oceanic crust mixing at 1.5–2.0 Ga with 50% of the lead contributed by the 1% subducted sediment (as suggested by Weaver *et al.* 1986) requires a Th/U ratio of 5.0 to generate the observed  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio. This value is much higher than the value (approximately 3.7) estimated for the Tristan da Cunha source. In general, most oceanic basalts (EM, MORB, HIMU) come from source regions with Th/U ratios of 3.8 or less, as has been demonstrated by  $^{230}\text{Th}/^{232}\text{Th}$  studies, or by a reduction of 15%  $\pm$  5% of the measured Th/U of fresh basalts to correct for the Th/U fractionation during melting (eg Oversby & Gast 1968). In our opinion, EM1-type OIB in the S Atlantic does not represent a

mixture of sediment and oceanic crust. It is more likely to be derived from an enriched mantle wedge or lithosphere above the subduction zone, with some input from the subducted sediments.

Secondly, a subduction zone environment is not required for at least some EM1-type mantle. Enrichment can be achieved by silicate melt migration from mantle plumes with less depleted character than a MORB source (eg Bouvet, Hawaii or OIBs lying isotopically closer to the primitive mantle). EM1-type mantle generated in this way will have higher Th/Nb and Th/Ta ratios than the HIMU-type mantle, whereas Ba/Nb, Rb/Nb and La/Nb ratios could be similar to the HIMU type owing to a low alkali character controlled by residual potassium-bearing minerals and the fact that niobium is more incompatible than lanthanum. These characters are shared by some group I kimberlites with  $^{87}\text{Sr}/^{86}\text{Sr} = 0.704\text{--}0.705$  and some EM2 OIBs such as Sao Miguel (White *et al.* 1979; Le Roex 1986). Le Roex (1986) emphasized that the trace-element and isotope data for group I kimberlites cannot be explained by the sediment subduction model. Instead, they are probably evolved from less depleted or close to primitive mantle material.

Although the discussion presented above sounds negative towards the connection between sediment subduction and the formation of EM-type mantle, we do believe that sediment subduction has left an important fingerprint on the geochemistry of at least some EM-type OIBs (eg Walvis Ridge, Gough, Society Island, Samoan Islands). Further detailed geochemical studies of both EM1 and EM2 end-members are required to establish this case firmly. We suggest that accurate estimation of the europium anomaly in OIBs can be of special importance for the evaluation of the effect of the subduction of sediment and altered oceanic crust on the OIB source as well as on  $f\text{O}_2$  during magma generation. Since plagioclase, which has a high  $K_d$  for  $\text{Eu}^{2+}$ , is neither a residual mineral during alkali basalt genesis nor an early liquidus mineral during magma differentiation, europium anomalies measured in primitive alkali basalts reflect the combined effects of source character and  $f\text{O}_2$  during magma generation. Sun & Hanson (1975a) suggested that the 2%–5% positive europium anomaly commonly observed in OIBs is due to the existence of  $\text{Eu}^{2+}$  ( $\geq 10\%$ ) in addition to  $\text{Eu}^{3+}$  under low  $f\text{O}_2$  mantle conditions and the fact that  $\text{Eu}^{2+}$  ( $\approx \text{Sr}$ ) is more incompatible than  $\text{Eu}^{3+}$  and its neighbouring  $\text{Sm}^{3+}$  and  $\text{Gd}^{3+}$ . Sediments derived from various terranes have different

amounts of negative europium anomaly (eg MacLennan & Taylor 1981), with up to 35% europium depletion for modern crustal rocks. The available accurate REE data indicate that HIMU OIBs have a 4%–6% positive europium anomaly whereas EM2 OIBs from Samoan and Society islands show up to a 4%–6% negative europium anomaly (eg Sun & Hanson 1975a; Newsom *et al.* 1986; Palacz & Saunders 1986; McDonough & Sun, unpublished data), consistent with the sediment subduction model. In contrast, EM-type OIBs from Gough and Tristan da Cunha have a 2%–5% positive europium anomaly despite our belief that sediment has been involved in their mantle source. Either the sediment which was subducted and ultimately incorporated into their source has a small negative europium anomaly (*ie* from Archaean terranes) and/or more probably the sediment effect has been compensated by an increase of the  $\text{Eu}^{2+}/\text{Eu}^{3+}$  ratio during source modification (eg dehydration and partial melting of the subducted sediments) and magma generation under more reducing environments than for other OIBs. To test further the significance of the negative europium anomaly in some primitive OIBs, we propose that samples with a strong sediment lead isotope signature are most suitable, because modern sediments have a distinct and strong negative europium anomaly.

#### Continental lithosphere connection of the Dupal anomaly and the low neodymium array

Hart (1984) pointed out that EM-type OIBs are concentrated in the southern hemisphere, are globe encircling in extent, and are centred at latitude 30°S. He named this isotopically anomalous region the Dupal anomaly region and suggested that it may have been in existence in the southern hemisphere since Archaean times. In terms of the model, the occurrences of EM-type OIBs in the northern hemisphere, eg the Azores, Oahu Island (Koolau tholeiites) and the Japan Sea, and numerous occurrences of EM-type continental alkali basalts, tholeiites and kimberlites have to be considered as exceptions to the general rule or due to crustal contamination. Later, Zindler & Hart (1986) suggested that the enhanced rate of Pangean subduction into the Dupal mantle (Anderson 1982) may account for localization of EM2-type OIBs in the southern hemisphere. If this interpretation is correct, then EM2 anomalies in the southern hemisphere are a relatively young subduction-related phenomenon surrounding the Pangean continents, but are not circum-global.

This is consistent with the absence of the Dupal anomaly in the Pacific mid-ocean ridge of the southern hemisphere (Maccougall & Lugmair 1986; White *et al.* 1987). Furthermore, Archaean and Proterozoic Dupal-like anomalies observed in komatiites and galena and feldspar in granites of the southern continents (Africa, Australia, India), where there is abundant early Archaean crust, are likely to be a result of crustal contamination. For example, some late Archaean komatiites (and associated NiS mineralization) of the Yilgarn Block, western Australia, have been contaminated by early Archaean felsic crust which resulted in Dupal-type lead anomalies (Sun *et al.*, in press). In contrast, Hawkesworth *et al.* (1986) suggested that the Dupal anomaly in the southern Atlantic (*ie* Walvis Ridge, Gough, Tristan da Cunha and the Discovery Table Mounts) may be of shallow origin and due to the thermal reactivation and detachment of the metasomatized lithosphere of southern Africa and South America before the breakup of Gondwana. The continental lithospheric delamination model of McKenzie & O'Nions (1983) is attractive because there is the opportunity to generate a variety of mantle types in the continental lithosphere within close proximity through subduction-zone-related and unrelated processes. The superposition of the products of different processes is possible. It also allows long-term isolation of the enriched mantle within the lithosphere before delamination and recycling back into the convecting mantle.

More recently, Hart *et al.* (1986) also seem to favour an ultimate origin for the Dupal anomaly from the continental lithosphere. They pointed out that EM1- and HIMU-type OIBs often show close association in occurrence and share the same character of long-term low Rb/Sr ratio compared with OIBs within the mantle array on an  $^{87}\text{Sr}/^{86}\text{Sr}$  versus  $\epsilon_{\text{Nd}}$  plot (Fig. 2). HIMU- and EM1-type OIBs have lower  $\epsilon_{\text{Nd}}$  values than the mantle array. There appears to be a lower limit on this plot for OIB data defined by connecting the HIMU and EM1 end members. Hart *et al.* (1986) named this limiting line a 'LoNd' (low  $\epsilon_{\text{Nd}}$ ) array. (Since HIMU and EM1 are characterized by having lower  $^{87}\text{Sr}/^{86}\text{Sr}$  values due to lower time-integrated Rb/Sr ratios than samples within the mantle array, it might be more appropriate to call the array a 'LoSr' (low  $^{87}\text{Sr}/^{86}\text{Sr}$ ) array.) They suggested that this LoNd array was developed within the subcontinental lithosphere through the introduction of silicate melts of different chemical and isotopic compositions (p. 1556): '... EM1 end member being slightly modified primitive mantle, and the

HIMU end member being metasomatically produced, possibly during subduction episodes preceding lithosphere accretion.' It is interesting to note that many of the Mesozoic and Cenozoic carbonatites of worldwide occurrence, not limited to the southern hemisphere, also fall on or close to this LoNd array (eg Bell & Blenkinsop 1987; Dudas *et al.* 1987; Nelson *et al.* 1987). This is also true for some group 1 kimberlites (Kramers *et al.* 1981; Smith 1983).

The association of HIMU- and EM-type OIBs in some ocean island or island groups of the southern Pacific (Vidal *et al.* 1984; Palacz & Saunders 1986; Dupuy *et al.* 1987) and Walvis Ridge (Fig. 6) does not offer a firm argument for identifying their parentage (eg continental lithosphere). Alternative mechanisms can be suggested, eg mixing of different types of mantle components within the convective upper mantle. In addition, we would like to emphasize that the regional but isolated occurrences of HIMU (eg St Helena, Ascension, Cape Verde, New England Seamounts, Canary Islands, Ahaggar, Cameroon Line, Guadalupe, SW Pacific islands, eastern Australia, South Island, New Zealand, and Ross Island and Mary Byrd Land, Antarctica) or EM (Gough, Tristan da Cunha, Kerguelen, Samoa) without an accompanying LoNd counterpart are quiet common. The regional distribution tendency of the Dupal anomaly (S Atlantic, Indian and SW Pacific Oceans) and the HIMU anomaly (some of which are probably of shallow asthenospheric origin) also requires serious consideration in any genetic model.

The long isolation time (up to 2 Ga) required by the isotope data of OIBs has been a major consideration of many people in favouring the model of continental lithosphere delamination. In this respect, it is surprising to see that the OIB members of the LoNd array have well-defined isotopic correlations on strontium versus neodymium and lead versus strontium plots (Hart *et al.* 1986). Since the extent of low  $\epsilon_{Nd}$  values below the main array is a function of Rb/Sr fractionation and isolation time, in addition to other variables such as Sm/Nd ratio, a well-regulated mantle LoNd array is not expected. Hart *et al.* (1986) pointed out that there are many EM1-type continental peralkaline rocks (eg Leucite Hills, Smoky Butte) which fall well below the LoNd array. The lack of an obvious influence of the low neodymium array by these extremely low  $\epsilon_{Nd}$  components from the continental lithosphere formed in the Archaean (eg Dudas *et al.* 1987) may imply that (i) delamination of continental lithosphere with Archaean isotopic signatures is not feasible or

very minor in modern times, (ii) metasomatized continental lithosphere formed at 2 Ga or less is abundant on the worldwide scale and dominates the scene, or (iii) delamination of continental lithosphere is sufficient but not necessary for OIB generation, and survival times of 2 Ga or less in the convecting mantle are possible (Gurnis & Davies 1986). The last option will be further discussed in later sections.

A major drawback to the continental lithosphere delamination model is that there is a general lack of OIB samples showing strong subduction-zone-related chemical and isotopic characteristics, which are commonly found in many continental mafic and ultramafic volcanic rocks. As shown in Figs 5 and 12, relative depletion of titanium, phosphorus, niobium, tantalum and strontium, but extreme enrichment of lead and the presence of up to 20% negative europium anomalies, reflecting sediment subduction effects (McLennan & Taylor 1981), have been observed in many post-orogenic and intraplate mafic to ultramafic peralkaline volcanics (group II kimberlites of southern Africa and lamproites from western Australia) which are considered to be derived from the continental lithosphere modified by subduction zone processes (eg Duncan *et al.* 1984; Thompson *et al.* 1984; Nelson *et al.* 1986; Jaques *et al.* 1988). Among these samples there is often a positive correlation between the size of the negative europium anomaly and the  $^{87}Sr/^{86}Sr$  ratio (and Sr/Nd ratio) which is thought to reflect the effect of subducted sediment, with high  $^{87}Sr/^{86}Sr$ , large negative europium anomalies (about 30% but variable depending on the source rocks) and low Sr/Nd ratios (eg Alibert *et al.* 1986). In this connection, negative europium anomalies observed in Samoan and Society alkalic basalts can be considered as a good indication of sediment involvement in their mantle sources.

Detailed chemical and isotopic studies of Mesozoic Karoo basalts of southern Africa, Parana basalts of South America, African kimberlites and modern Dupal OIBs in the S Atlantic (eg Smith 1983; Smith *et al.* 1986; Duncan *et al.* 1984; Hawkesworth *et al.* 1984, 1986; Le Roex 1986) have offered an opportunity to evaluate different models suggesting their source relationships and mechanisms of magma generation. Based on hot-spot trace reconstructions and geochemical data, Le Roex (1986) concluded that group I kimberlites are not Dupal type (represented by Walvis Ridge and Gough Island) but are related to Bouvet and Marion type hot-spots, whereas group II kimberlites are related to the Dupal islands.

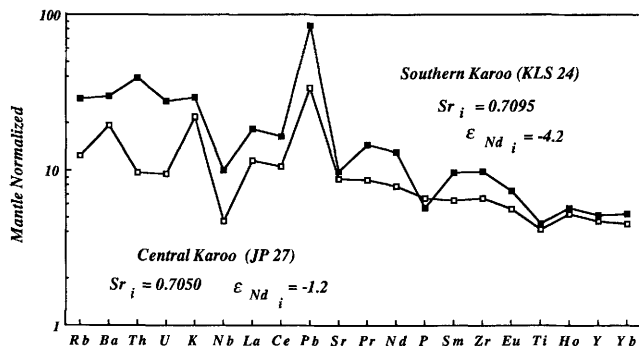


FIG. 12. Mantle-normalized diagram of two selected least-fractionated basalts from southern Karoo and central Karoo. They show strong signatures of sediment and subduction-zone-related processes. Data from Duncan *et al.* (1984). See Table 1 for normalizing values.

Some clinopyroxene megacrysts from the group I kimberlites (eg the Kimberley pool) actually have HIMU-type isotopic compositions (eg Kramers 1977). The group II kimberlites have higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.707–0.710), lower  $\epsilon_{\text{Nd}}$  values (–5 to –12), and less radiogenic lead isotopic compositions ( $^{206}\text{Pb}/^{204}\text{Pb} \approx 17.2$ –17.9) compared with the high P–Ti (HPT) basalts of Parana and northern Karoo as well as the Dupal islands of the southern Atlantic (Hawkesworth *et al.* 1986). As shown in Fig. 13, northern Karoo basalts have mantle-normalized diagrams (especially for Ce/Pb and La/Nb) similar to but still not quite the same as Dupal OIBs. If we accept the asthenospheric origin of Dupal OIBs and at least a partial asthenospheric origin for the group II kimberlites, it seems reasonable to suggest that the geochemical difference between them and the northern Karoo basalts is due to the involvement of the continental lithosphere (including crustal contamination) of southern Africa, which has a strong

signature of sediment subduction combined with subduction zone processes (*ie* depletion in niobium, strontium, phosphorus and titanium, a negative europium anomaly and an enrichment in lead). Alternatively, this crustal signature may be derived from sediment subduction beneath Gondwana.

A magnification of this subduction-zone-related character is shown in the least fractionated Mesozoic southern Karoo basalts (Fig. 12) with about a 15% negative europium anomaly. These basalts have more radiogenic lead and strontium isotopic compositions but lower  $\epsilon_{\text{Nd}}$  values than group II kimberlites and the high phosphorus, titanium northern Karoo and Parana basalts (Smith 1983; Mantovani *et al.* 1985; Hawkesworth *et al.* 1986). Additionally, the isotopic and chemical characteristics of southern Karoo basalts are shared by the relatively contemporaneous Ferrar dolerites of the Trans-Antarctic mountains and the Tasmanian dolerites (Hergt 1987). Hergt (1987) has shown

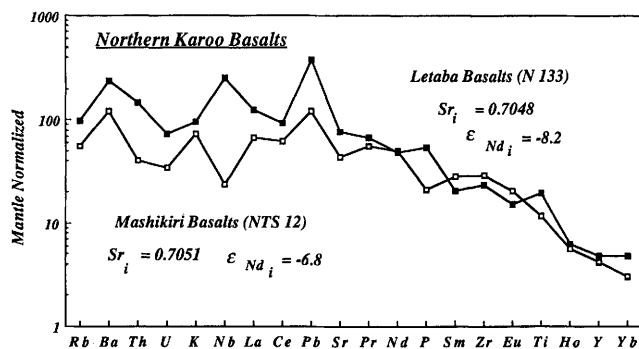


FIG. 13. Mantle-normalized diagram of two selected least-fractionated basalts from northern Karoo. They have similar  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios but lower  $\epsilon_{\text{Nd}}$  values than Dupal-type OIB from the S Atlantic Ocean. Data from Duncan *et al.* (1984). See Table 1 for normalizing values.

that these dolerites have mantle-normalized patterns which mimic terrigenous sediments and have strontium, neodymium and lead isotopic compositions (0.710, 0.5123, 18.9, 15.64, 38.8 respectively) which strongly suggest a sediment component influence. Cox (1978) suggested that the Mesozoic Gondwana flood basalts are a product of back-arc volcanism related to subduction along the Pacific margin (*ie* close to the southern Karoo occurrence, Trans-Antarctic Mountain range, and Tasmania versus northern Karoo). If his model is favoured and correct, involvement of subduction zone processes as well as melting of the Gondwana lithosphere could be responsible for the crustal characteristics (*ie* low strontium, phosphorus, titanium, niobium and high lead) of these types of basalts.

Mantle plume activity induced by either thermal blanketing of the Gondwana supercontinent (Anderson 1982) surrounded by subduction of cold lithosphere or by lithosphere subduction in the back-arc environment could be the long-lasting hot-spot source for the Dupal anomaly in the southern Atlantic and Indian Oceans. Chemical and isotopic characteristics of the plume material can be modified by contributions from the subduction-zone-related processes (*eg* sediment subduction for low phosphorus, titanium Tasmanian and Ferrar dolerites and basalts of southern Karoo and Parana) or interactions with the continental lithosphere which could have been modified by this same subduction zone process (*eg* group II kimberlites). In this connection, we agree with Zindler & Hart (1986) that Pangean sediment subduction may also have left its influence on the EM2-type OIBs in the S Pacific region (*eg* Samoan and Society islands OIBs with negative europium anomalies and low Ce/Pb). Some residual effects from the recycled mantle wedge on the source character of the mid-ocean ridges, back-arc basins and volcanic arcs is also likely.

The alternative interpretation is that the Dupal anomaly in the S Atlantic is a result of thermal reactivation, remobilization and detachment of the southern African and South American lithosphere (*eg* Hawkesworth *et al.* 1986). This is inferred from the occurrences of HPT basalts in the northern Karoo and Parana which are chemically and isotopically similar to the Dupal OIBs. However, on this model there is difficulty in explaining the lack of a strong signature of subduction zone processes (observed in southern Karoo and some Parana basalts) in the Dupal OIBs. Furthermore, the long-lasting (more than 100 Ma) distinctive chemical and isotopic character of hot-spot traces of the Cameroon line – St Helena, Ninety

East Ridge – Kerguelen and Walvis Ridge – Tristan da Cunha also favours a deep stable mantle origin. In this connection, it is worthwhile to point out that the HPT volcanism at about 130 Ma in Parana and Etendaka and the Jacupiringa carbonatite, on the E coast of Parana (Roden *et al.* 1985), could be related to the Walvis Ridge – Tristan da Cunha hot-spot trace.

On a worldwide scale, the lack of a strong subduction zone signature in OIBs and MORBs suggests that the effects of sediment subduction have been short-circuited in the volcanic arc, mantle wedge and continental lithosphere above it. The sediment does not subduct to as great a mantle depth (*eg* 500 km or more) as the oceanic crust (*eg* Sun 1980; Nakamura *et al.* 1985). Although earlier subduction zone effects have been detected in some young oceanic basins (*eg* Woodlark Basin, SW Pacific; Johnson *et al.*, in press) and back-arc basins (*eg* Saunders & Tarney 1979; Cohen & O'Nions 1982), the recycled wedge material in most cases is probably very refractory and depleted in incompatible elements. Thus it will have only a limited effect or no effect on MORB and OIB chemistry. Delamination and/or thermal erosion of continental lithosphere once situated above subduction zones should introduce a strong subduction zone signature into the convecting mantle. To make this model successful it is required that the continental lithosphere is generally formed by non-subduction-zone-related processes such as plume underplating (*eg* Ringwood 1982; McDonough & McCulloch 1987) or alternatively, after subduction ceased, it has been strongly modified on a worldwide scale by upward migration of CO<sub>2</sub>-rich silicate melts from the asthenosphere and/or intraplate magmatism (as observed in many mantle xenoliths).

### Mixing of oceanic island basalt mantle components and interpretations of lead isotope data

On a combined lead, strontium and neodymium isotope ratio plot, the fields for five OIB groups defined by White (1985) all extend towards, and overlap with, the MORB group, suggesting mixing with a MORB-type component. Little mixing appears to have occurred between the four other groups. Detailed geochemical studies of seamount basalts from the N Pacific by Zindler *et al.* (1984) document small-scale heterogeneities in the mantle sources for the basalts.

However, systematic studies of the circum-global MORB system have shown large-scale regional heterogeneities and large-scale mixing of different mantle types (eg Schilling *et al.* 1985).

Since the isotopic characteristics of distinct mantle types is an integrated product of fractionation of parent–daughter elements and isolation time, no fixed end-member should be expected. Consequently, mantle mixing with four to five component fields in strontium, neodymium and lead isotope space will generate a volume of mixing products. The mantle plane suggested by Zindler *et al.* (1982) contains most of the OIB data, but it is only an approximation.

Often, more than one mantle type can be sampled in a single island or island group. For example, Li & Hart (in press) suggest that four mantle components (PREMA, recycled metasomatized continental lithosphere, ancient recycled oceanic crust and MORB source) are required to explain the lead, strontium and neodymium isotopic variations observed in Hawaiian basalts. Combined isotope and trace-element studies can offer important constraints on the geometrical relationships of different types of magma sources and magma generation processes. It is now well established that Hawaiian post-erosional alkali basalts have lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios but higher  $\epsilon_{\text{Nd}}$  than the underlying shield-building tholeiites and associated pre-erosional alkali basalts (eg Chen & Frey 1985; Li & Hart, in press). In terms of the relative isotopic characteristics of alkali basalts versus tholeiites, the Hawaiian situation is the opposite of that observed for seamount basalts

by Zindler *et al.* (1984), who suggested that the isotopic differences between the alkali basalts and tholeiites are due to different degrees of melting of a veined mantle. The isotope data suggest that interaction of the mantle plume (source for tholeiites) with the oceanic lithosphere and/or its immediately underlying asthenosphere is important, especially for the post-erosional alkali basalts (eg Tatsumoto 1978; Sun 1980; Chen & Frey 1985; McDonough *et al.* 1985). The inverse correlations between La/Ce, Nb/La and Ba/La with  $^{87}\text{Sr}/^{86}\text{Sr}$  observed in many Hawaiian basalts have been interpreted as the result of a combination of mixing of different mantle sources and the effects of variable degrees of partial melting. In Figs 14a and b,  $^{87}\text{Sr}/^{86}\text{Sr}$  versus La/Nb and Ba/La respectively are shown for the Hawaiian basalts. Post-erosional alkali basalts with low  $^{87}\text{Sr}/^{86}\text{Sr}$  are mainly derived from a MORB-type source at the base of the Hawaiian oceanic lithosphere and/or in the asthenosphere immediately below it. Strong fractionation of Ba/La and La/Nb ratios from those of the MORB source is consistent with the idea that they have quite different degrees of incompatibility on the mantle-normalized diagram.

In view of the high frequency of inferred mantle mixing phenomena, it is desirable to reconsider the age significance of the lead isotopic data for OIBs. Earlier we suggested that lead isotope data for HIMU-type OIB indicated source isolation ages ranging from 1.0 Ga (Ua Pou) to 2.0 Ga (St Helena). Except for those OIB samples from individual islands having negative slopes on  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$

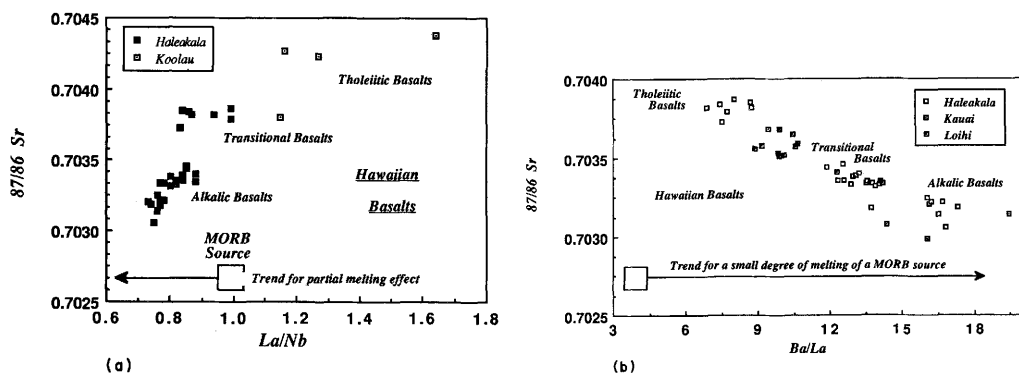


FIG. 14. Plots of (a)  $^{87}\text{Sr}/^{86}\text{Sr}$  versus La/Nb and (b)  $^{87}\text{Sr}/^{86}\text{Sr}$  versus Ba/La for selected Hawaiian basalts illustrating the combined effects of mixing of two types of mantle sources and different degrees of partial melting. The trend of changing La/Nb and Ba/La ratios caused by different degrees of partial melting is indicated by the arrow direction.



diagrams, indicating mixing of different types of mantle, the interpretation of other OIB data is not so straightforward. Some EM2-type OIBs from the Society Islands and Sao Miguel have high  $^{207}\text{Pb}/^{204}\text{Pb}$  values and each island group exhibits a steep slope on a plot of  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$ . At the high  $^{206}\text{Pb}/^{204}\text{Pb}$  end this trend is constrained by continental sediments. It is likely that this high  $^{207}\text{Pb}/^{204}\text{Pb}$  character is related to sediment subduction (see earlier), as suggested by White (1985). Even though White (pers. comm., 1987) no longer favours this interpretation, we consider that it may also apply to Kerguelen samples.

Good regression lines are also found for basalts from the Hawaiian Islands (0.94 Ga), Canary Island (1.7 Ga), Iceland (1.5 Ga), Ross Island (1.3 Ga) and the northeastern Pacific seamounts (1.8 Ga). Gough Island and the Discovery Tablemount basalts have a small range of  $^{206}\text{Pb}/^{204}\text{Pb}$  and a shallow slope on the  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  diagram and yield an age close to zero, whereas Walvis Ridge data give an age of about 0.8 Ga. Whether these regression lines have any age significance is not clear. For example, Stille *et al.* (1986) emphasized the mixing character of the Hawaiian basalts and suggested that approximately 0.9 Ga regression slope has no real age significance, although they felt that the general OIB–MORB trend reflects a 1.5–2.0 Ga isolation age from the MORB source for Iceland, Galapagos and Easter Island.

A good example to illustrate the non-unique solution of the 1.8 Ga Pb–Pb isochron of OIB data is given by the study of the St Paul's Rocks in the equatorial Atlantic (Roden *et al.* 1984). These peridotites have young Sm–Nd and Pb–Pb isochron ages ( $\approx 200$  Ma) corresponding to the time of metasomatism in the mantle. The high  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios (up to 19.8, see Fig. 9) and  $^{238}\text{U}/^{204}\text{Pb}$  ratios in the rocks allow  $^{206}\text{Pb}/^{204}\text{Pb}$  to evolve to high values quickly with time. Mixing of this type of mantle with a depleted MORB source can generate Pb–Pb slopes similar to those of the Canary and Ross Islands. However, it is important to point out that the St Paul's sample SE-6 with the least radiogenic lead ( $^{206}\text{Pb}/^{204}\text{Pb} = 18.63$ ) and with  $^{87}\text{Sr}/^{86}\text{Sr} = 0.70347$  has an unusually high  $^{207}\text{Pb}/^{204}\text{Pb}$  ratio (15.61) for OIBs of this type with low  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ .

On the basis of this analysis, we conclude that the available lead isotopic data for OIBs allow for mantle isolation ages ranging from a few hundred million years up to 2.0 Ga. Further research is required to assess the significance of the apparent ages better.

## Mass exchange between the crust and mantle

The idea of continuous recycling of crustal material into the mantle has received attention ever since plate tectonic theory became well accepted. Armstrong (1968, 1981) suggested that the continental crust is mainly formed during the Archaean and has reached a steady state growth since then. He suggested that recycling of continental crustal material is required to keep lead and strontium isotope growth in the depleted mantle. In contrast, Hofmann *et al.* (1986) emphasized that the observation of constant Ce/Pb ratios ( $25 \pm 5$ ) and Nb/U ratios ( $47 \pm 10$ ) in MORBs and OIBs argues against significant amounts of sediment recycling into the convecting mantle since about 2 Ga ago, as sediment involvement will greatly affect these ratios (Fig. 6). We have also shown in this paper that, except for some EM-type OIBs, there is a general lack of sediment signature in the mantle-normalized diagram of OIBs and MORBs. We suggest that subduction of sediment at the convergent margins has been short-circuited within the mantle wedge above the subduction zone. This idea is consistent with a detailed geochemical study of alkali basalts in the Japan Sea region by Nakamura *et al.* (1985). Consequently, in order to keep the depleted MORB source isotopic growth as observed, input from OIB source and subcrustal lithosphere in the upper mantle and/or from the lower mantle is required.

## Mass exchange between upper and lower mantle

Gast (1968) first suggested that the geochemical characteristics of MORB sources are mainly a product of extraction of small amounts of alkali basalts. In contrast, some lithosphere recycling models require resorption of the subducted oceanic crust into neighbouring fertile upper-mantle peridotite in order to regenerate the MORB source (Allègre & Turcotte 1986). It is obvious that a combination of these two processes is likely to be operative in the mantle. In terms of the model of lithosphere recycling within the upper mantle, the MORB source in the upper mantle is most likely to be the complement to the continental crust. This hypothesis can be tested by a mass balance calculation.

There are various model estimates of elemental abundances in the bulk crust, although these estimates vary by a factor of 2 (eg see the summary by Taylor & McLennan 1985). On a mantle-normalized diagram the continental

crust has an enriched pattern which is in part a mirror image of the depleted MORB pattern. This complementary relationship between the crust and upper-mantle MORB source is commonly accepted as evidence for a mass balanced system. In Table 5 we use the primitive mantle composition presented in Table 1 and estimates of crustal abundances by Taylor & McLennan (1985) to perform some simple calculations. To satisfy crustal abundances of highly incompatible elements (eg, barium, rubidium, caesium, thorium and uranium), 25%–30% of the volume of the upper mantle must be primitive mantle. Using higher estimates of element abundances in the crust, up to 50% primitive mantle is required. Furthermore, if the continental lithosphere (150–200 km thick) is globally or locally enriched in incompatible elements, then depletion of an even higher portion of the convecting mantle is required. Evidence for enriched continental lithosphere comes from studies of continental basalts and ultrapotassic rocks (eg Carlson 1984; Fraser *et al.* 1986; Nelson *et al.* 1986). These rocks always show strong crustal geochemical characteristics (relative depletions of titanium, niobium, phosphorus and strontium on a mantle-normalized diagram, high La/Nb ( $\gg 1$ ) and large negative europium anomalies) and isotopic systematics suggestive of crustal recycling in the early Precambrian.

According to the calculations in Table 5, the residual MORB source in the upper mantle should have a fertile major- and trace-element composition, similar to those of the fertile ultramafic xenoliths studied by Jagoutz *et al.* (1979).

Despite all uncertainties involved in this calculation, it is clear that a major discrepancy between the calculated and observed La/Nb ratios requires special attention. We have argued that the lack of an obvious positive niobium anomaly in the average MORB and OIB sources and continental lithosphere requires a mechanism to fractionate niobium from lanthanum or preferentially withdraw former oceanic crust with low La/Nb ratios from the upper mantle. This can be achieved by subduction of oceanic lithosphere (Creager & Jordan 1984) or subtraction of refractory eclogitic material from the megathrust into the lower mantle and/or at the base of the upper mantle (Ringwood & Irifune 1988). Preferential withdrawal of niobium from the upper mantle can also reduce the discrepancy between the calculated and measured Nb/U ratio of the depleted mantle shown in Table 4. A plot of La/Ta versus La/Sm ratios for MORBs from the literature, along with our estimates of the primitive mantle, is shown in Fig. 15. It is quite clear that transitional-type MORBs and some N-type MORBs with light-REE-depleted to slightly enriched patterns (La/Sm  $\approx 0.8$ –1.8) have tantalum (and niobium) anomalies (La/Ta  $< 17$ ). These results are consistent with the idea of recycling and resorption of the subducted former oceanic crust into the asthenospheric mantle source for these MORBs.

#### Formation of heterogeneous mid-ocean ridge basalt sources

It appears that recycled former oceanic crust is not simply resorbed and mixed into neighbour-

TABLE 5. Mass balance calculation assuming complementary relationship between the bulk continental crust and MORB source (upper mantle)

|   | Rb    | U      | Nb             | La   | Ce    | Pb    | Nd         | Sr   | Sm          | Al%  | Ca%  |
|---|-------|--------|----------------|------|-------|-------|------------|------|-------------|------|------|
| Bulk crust <sup>a</sup> (0.6%)                  | 32    | 0.91   | 8 <sup>b</sup> | 16   | 33    | 8     | 16         | 260  | 3.5         | 8.4  | 5.3  |
| Primitive mantle                                | 0.635 | 0.021  | 0.71           | 0.69 | 1.78  | 0.185 | 1.35       | 21.1 | 0.44        | 2.45 | 2.68 |
| % Bulk mantle                                   | 30    | 25     | 6.5            | 13.5 | 10.8  | 24    | 6.9        | 7.2  | 4.6         | 2.2  | 1.3  |
| % Upper mantle <sup>c</sup>                     | 100   | 83     | 21.6           | 45.1 | 36.9  | 80    | 22.9       | 23.9 | 15.2        | 7.6  | 4.2  |
| Depleted upper mantle<br>after crust extraction | 0.0   | 0.0039 | 0.59           | 0.40 | 1.20  | 0.041 | 1.10       | 16.9 | 0.40        | 2.16 | 2.44 |
|   | La/Nb |        | La/Sm          |      | Sm/Nd |       | Ce/Pb      |      | Nb/U        |      |      |
| Calculated for UM<br>after crust extraction     | 0.68  |        | 1.0            |      | 0.36  |       | 30         |      | 152         |      |      |
| Observed in MORB                                | 0.97  |        | 0.96           |      | 0.36  |       | 25 $\pm$ 5 |      | 47 $\pm$ 10 |      |      |

<sup>a</sup> Bulk crust = 0.4% bulk Earth = 0.6% bulk silicate Earth.

<sup>b</sup> A value of La/Nb = 2.0 is used for crustal abundance ratio.

<sup>c</sup> Upper mantle (UM) = 30% of the total mantle.

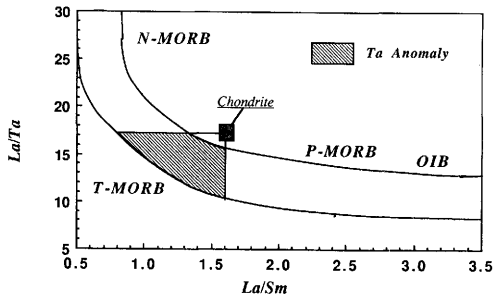


FIG. 15. Schematic diagram showing La/Sm versus La/Ta (Nb) ratios for N-type MORB, T-type MORB and plume-enriched MORB and OIB. The estimate for the earth's primitive mantle is from Table 1. The region which encompasses N-type MORB and T-type MORB with Ta (Nb) 'anomalies' ( $La/Ta < 17.5$ ) is shaded.

ing fertile peridotite and refractory former oceanic lithosphere to regenerate a homogeneous MORB source. The heterogeneities in the trace-element and major-element abundances observed in MORB and inferred mantle sources call for a more sophisticated model. It is important to note that light-REE-enriched MORB from plume-ridge segments (eg the Azores platform) commonly show refractory residual characters in major elements (very low in FeO, Na<sub>2</sub>O) compared with samples from normal ridge segments (eg Langmuir & Hanson 1980). The chemical and isotopic data for this type of MORB implies that the plume source is refractory in major elements (former lithospheric harzburgite?) and was fertilized before plume diapirism. Such enrichment could be achieved through upward migration of silica-undersaturated melts from the LVZ into oceanic lithosphere before subduction (Kay 1979). It could also be achieved through melting of the subducted oceanic crust (eg Ringwood 1982). In contrast with the case of the Azores platform, low-potassium tholeiites from Iceland often show high abundances of FeO and they have positive niobium kicks on the mantle-normalized plot (eg Wood *et al.* 1979). It is likely that the Iceland plume has received a larger amount of recycled former oceanic crust.

A uniformly depleted MORB reservoir which is homogenized through convective mixing may also have added to it a component from the recycled mantle wedge above the subduction zone, convective thermal erosion of the continental lithosphere and plumes or blob components derived from the lower mantle or base of the upper mantle where subducted former lithosphere may accumulate. This could result

in the variation of chemical and isotopic characteristics in different ocean basins (eg the existence of the Dupal anomaly in the Indian Ocean). A veined and plum-pudding type of upper mantle with various scales of old and young heterogeneity can be generated this way.

## Towards an integrated mantle-evolution model

The aim of an integrated trace-element and isotope approach is to improve our understanding of the chemical and dynamic processes operating in the Earth's mantle at present and throughout the geological record. Such an approach is very useful for evaluating the various mantle processes involved in the generation of OIB sources. In order to appreciate the chemical and isotope data fully, it is important to integrate this approach with geophysical and petrological studies of the Earth's mantle. In this regard, we are concerned with (i) the style and time-scale of mantle convection, (ii) the physical and chemical consequences of crust formation, recycling of altered oceanic crust ( $\pm$  sediment) and its resorption into the convective mantle and (iii) the connection between present-day regional chemical and isotopic heterogeneities (eg Dupal, HIMU) and ancient and more recent global tectonic history and mantle convective regimes.

Some controlling factors which can generate distinct features on the OIB mantle-normalized diagram are shown in Fig. 16. The effect of sediment subduction can superimpose a crustal signature (eg positive lead and negative europium, niobium and tantalum anomalies) onto the general pattern. Residual phlogopite may hold back not only potassium and rubidium but also barium and caesium. Partial melting under very high-pressure conditions (eg kimberlite generation) with changing mineral assemblage, mineral/melt  $K_d$  and melting process might greatly modify the mantle-normalized diagram rules.

Ringwood (1982) suggested that enrichment of refractory harzburgite in a subducted megacryst by partial melting of the former oceanic crust near the 650 km phase transition can be a potential source for OIBs. It is expected that, during high-pressure melting, fractionation of some elements between minerals with either a garnetite or a perovskite structure and the co-existing melt can be quite different from melting under low pressure (Kato *et al.* 1987). Consequently, it is worthwhile pursuing detailed

## Factors Controlling the Ocean Island Basalt Pattern

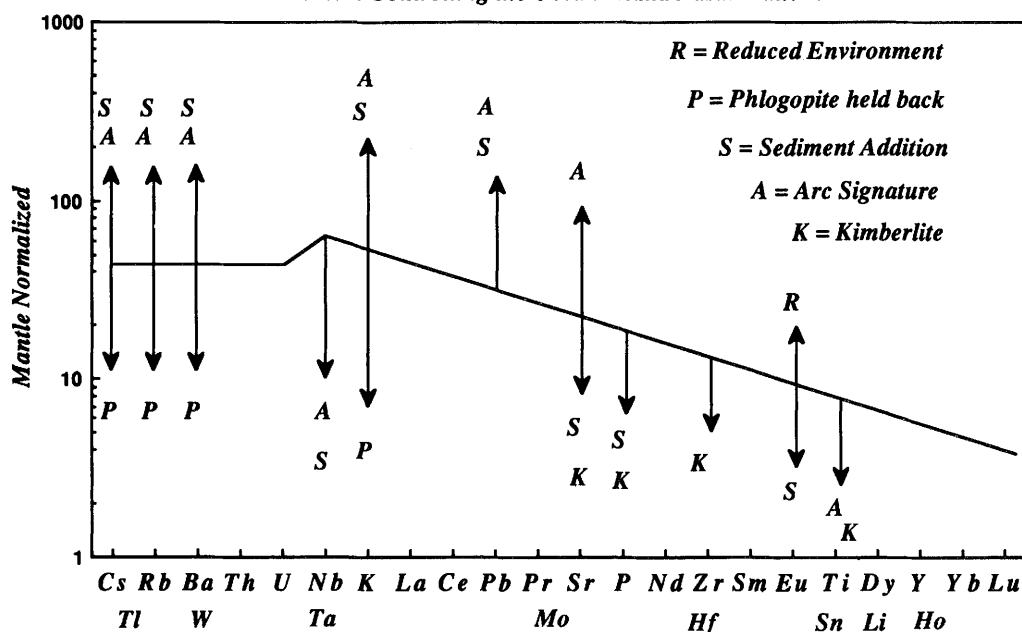


Fig. 16. Schematic description of the effects of various factors which can modify the mantle-normalized pattern of OIBs. For some elements enrichments or depletions may be due to a combination of factors; however, by using several different elements it may be possible to distinguish the relative roles of multiple effects. For example sediment addition (S) and arc signature (A) will both cause increases in caesium, rubidium, barium, potassium and lead; however, strontium is generally enriched in the arc signature, whereas it is generally depleted in the sediment addition.

studies of element ratio systematics (eg Ba–Rb–Cs, Nd–Sr, Nb–La, P–Nd, Ti–Eu, Sm–Zr) and the effect of changing mineralogy on  $K_d$  under different pressure and temperature conditions. Such differences in mineral assemblage and melting conditions may also be responsible for two types of light REE patterns observed in OIBs: (i) the predominant pattern showing a continuous increase from heavy REEs to light REEs with  $La/Ce = 0.46 (\pm 10\%)$  and (ii) a less common type showing concave-downward light REE patterns as in Ua Pou tholeiites (Fig. 11) and most Hawaiian tholeiites.

If whole-mantle convection was important in the early Earth's history, then we suggest that the lower mantle composition would also have been involved in crust formation and mantle differentiation (MORB–OIB). The total absence of OIBs with certain primitive mantle ratios (eg  $Rb/Cs \approx 20$ ,  $Nb/U \approx 30$ ,  $Ce/Pb \approx 9$ ) suggests that the different OIB-type sources have been previously well mixed with the depleted MORB reservoir (Hofmann *et al.* 1986). If some OIB sources are indeed derived from

the core–mantle boundary, as a number of geophysicists seem to prefer, then there are three possible ways in which to explain these constant ratios: (i) the recycled oceanic lithosphere which sank to the core–mantle boundary about 2 Ga ago becomes the plume source, (ii) the upper and lower mantle are well mixed and (iii) mantle material that arises from the core–mantle boundary only initiates the plume activity, whereas the main chemical and isotopic characteristics of OIBs are derived from shallower mantle (1000 km or less).

It has been shown by some geophysicists (eg see a review by Hager & Gurnis 1987) that the global gravity pattern is consistent with whole-mantle convection, with viscosity increasing with depth across the phase transformation (10–100 times), and that oceanic lithosphere subduction can continue into the lower mantle (Creager & Jordan 1984). It has also been shown that the geoid pattern reflects plate tectonic patterns of the last 100–200 Ma (eg Hager & Gurnis 1987). This whole-mantle convection model has the property of faster convective mixing in the upper mantle than the lower

mantle with a corresponding isolation time for chemical heterogeneities ranging from a few hundred million years (the upper mantle) to billions of years (the lower mantle). Although this situation could be crudely similar to the two-layer stratified mantle convection model, the exchange mechanism involving subduction of recycled oceanic crust is different from simple mass exchange between the upper and lower mantle.

The chemical and isotopic consequences of processing altered oceanic crust (with high U/Pb) through the subduction zone, of subjecting it to dehydration and partial melting (La/Nb decreased) and of its later resorption into the convecting mantle requires further evaluation. Could this mechanism fully explain the lead isotopic composition (with  $^{206}\text{Pb}/^{204}\text{Pb}$  on the right-hand side of the geochron) and low Th/U (about 2.0) of the MORB source? Additionally, could it also generate the HIMU-type OIB source? It is true that niobium and tantalum kicks do exist in some MORB and OIB sources (see earlier discussion). This observation is at least partly consistent with the model of oceanic crust recycling. However, most light-REE-depleted MORBs also have niobium- (and tantalum-) depleted patterns (Fig. 14). If HIMU-type mantle sources have distinctly lower La/Nb (eg 0.7) than average N-type MORB (approximately 0.95) as a result of oceanic crust recycling, then one would also expect to find very different Ce/Pb, Nb/U and Rb/Cs ratios, which is not consistent with the available data (Table 3). Furthermore, an increase in the Th/U ratio in the HIMU source region, relative to MORB, has not been and could not be explained by this model.

Since the bulk continental crust has an La/Nb ratio higher by a factor of 2 than the OIB and MORB sources, and these sources have La/Nb ratios approximately equal to the primitive mantle value, then a niobium-rich component is missing from the upper mantle-crust system unless the data in Table 5 are biased or the continental lithosphere is a major reservoir for niobium and has a low La/Nb. We suggest that this niobium-rich component does not reside in the continental lithosphere but has been introduced into the lower mantle through lithosphere subduction and/or has been accumulated at the base of the upper mantle (Ringwood & Irifune 1988). The sequestering of this niobium-rich component is an irreversible process which continuously modifies the geochemical and possibly the geophysical character of the lower mantle. The subduction of oceanic lithosphere, possibly with a metasomatized enriched base, may in-

roduce an enriched reservoir into the lower mantle.

The possibility that the continental lithosphere is a major reservoir for incompatible elements has been proposed previously (eg Brooks *et al.* 1976; Davies 1981; Carlson 1984). Although we also favour the idea that some parts of the lithosphere can be metasomatized, enriched by subduction zone processes and by the upward migration of silica-undersaturated melts from the asthenosphere, we have difficulty in quantitatively evaluating the volumetric importance of this mantle reservoir, especially when the effects of thermal erosion of the lithosphere are taken into account. However, if the continental lithosphere is indeed a major mantle reservoir for incompatible elements, then larger volumes of depleted mantle reservoirs (the whole mantle?) similar to the MORB source are required.

Relatively constant Ce/Pb ( $25 \pm 5$ ) and Nb/U ( $47 \pm 10$ ) ratios in OIBs and MORBs indicate either that they are produced through subduction zone processes (but how?) or that the subduction zone processes only introduce minor noise to the ratios (preferred). The effect of sediment subduction seems to have been short-circuited at the island arc and back-arc volcanic environments. Even in OIBs with a clear sediment signature, the trace-element and isotope data would limit the added sediment component to less than 1%.

Opinion in favour of a subduction zone connection of the Dupal anomaly, whether generated in the metasomatized mantle wedge above the subduction zone or the continental lithosphere, is gaining support. The Dupal anomaly in the S Atlantic and Indian Oceans seems to be related to the breakup of Gondwana. This type of isotopic and chemical anomaly can be expected in other regions with similar tectonic histories but not limited to the southern hemisphere as originally suggested by Hart (1984).

Lead and neodymium isotope data for HIMU-type OIBs require a source isolation age of 1.0–2.0 Ga with a long-term slightly light-REE-enriched character. The 2.0 Ga age may correspond to a major thermal event in the Earth's crust. Large amounts of HIMU- and possibly EM1-type OIB reservoirs might have been formed from the depleted asthenosphere through migration of silica-undersaturated melts from the LVZ into the oceanic and continental lithosphere. Pure HIMU character with low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.7026–0.7028) is observed in several ocean islands, suggesting that these HIMU sources originated from depleted MORB-type mantle. In view of the limited

amount of continental lithosphere available for recycling and a general lack of crustal and subduction zone signatures in OIBs, we favour the idea that the HIMU source character (especially those with  $^{87}\text{Sr}/^{86}\text{Sr}=0.7026-0.7028$ ) is generated by recycling of oceanic lithosphere.

Due to the problem of mantle mixing, no unique isotope isolation age can be established for EM1-type mantle with confidence, whereas trace-element and isotope data of the EM2-type mantle with  $^{206}\text{Pb}/^{204}\text{Pb} \geq 19.0$  seems to suggest the involvement of recently subducted sediments. A range of source isolation ages from a few hundred million years to 2 billion years therefore seems likely for the EM-type reservoirs.

The three-dimensional geometrical relationship between the different OIB-type sources and the depleted upper mantle asthenosphere (MORB source) cannot be clearly established as yet. However, it is evident that post-erosional alkali basalts of the Hawaiian islands and Samoan islands were derived from shallower depths, whereas many OIB sources are derived from greater depths in the form of mantle plumes or isolated blobs.

In conclusion, in order to improve our interpretation of the chemical and isotope data, it is important to integrate a geochemical approach with other approaches based on information derived from high-pressure experimental petrology, the tectonic history of the Earth's crust, geophysical observations and numerical modelling. With a better understanding of the petrological and geophysical processes involved in the dynamic, chemical and isotopic properties of the continental lithosphere we shall have a more realistic flux input for the 'multi-box' models currently used in numerical calculations for the chemical and isotopic evolution of the Earth.

ACKNOWLEDGEMENTS: Constructive suggestions and comments from F. A. Frey, C. J. Hawkesworth, J. Hergt, B. M. Jahn, A. L. Jaques, M. T. McCulloch, Z. A. Palacz, R. Price, R. L. Rudnick, A. D. Saunders and W. M. White are gratefully acknowledged. S.-S. Sun publishes with the permission of the Director, Bureau of Mineral Resources, Geology and Geophysics, Australia.

## References

- ALIBERT, C., MICHARD, A. & ALBARÈDE, F. 1986. Isotope and trace element geochemistry of Colorado plateau volcanics. *Geochimica et Cosmochimica Acta* **50**, 2735–2750.
- ALLÈGRE, C. J. & TURCOTTE, D. L. 1986. Implications of a two-component marble-cake mantle. *Nature* **323**, 123–127.
- , HAMELIN, B., PROVOST, A. & DUPRÈ, B. 1987. Topology in isotopic multispace and origin of mantle chemical heterogeneities. *Earth and Planetary Science Letters* **81**, 319–337.
- ANDERSON, D. L. 1982. Hotspots, polar wander, Mesozoic convection and the Geoid. *Nature* **297**, 391–393.
- ARMSTRONG, R. L. 1968. A model for the evolution of strontium and lead isotopes in a dynamic Earth. *Reviews of Geophysics* **6**, 175–199.
- 1981. Radiogenic isotopes: the case for crustal recycling on a near-steady-state no-continental growth earth. *Philosophical Transactions of the Royal Society of London* **301**, 443–472.
- BELL, K. & BLENKINSOP, J. 1987. Nd and Sr isotopic compositions of East African carbonatites: implications for mantle heterogeneity. *Geology* **15**, 99–102.
- BROOKS, C., JAMES, D. E. & HART, S. R. 1976. Ancient lithosphere: its role in young continental volcanism. *Science* **193**, 1086–1094.
- CARLSON, R. W. 1984. Isotopic constraints on Columbia River flood basalt genesis and the nature of the subcontinental mantle. *Geochimica et Cosmochimica Acta* **48**, 2357–2372.
- CHEN, C.-Y. & FREY, F. A. 1985. Trace element and isotopic geochemistry of lavas from Haleakala Volcano, East Maui, Hawaii: implications for the origin of Hawaiian basalts. *Journal of Geophysical Research* **90**, 8743–8768.
- CLAGUE, D. A. & FREY, F. A. 1982. Petrology and trace element geochemistry of the Honolulu Volcanics, Oahu: implications for the oceanic mantle below Hawaii. *Journal of Petrology* **23**, 447–504.
- COHEN, R. S. O'NIONS, R. K. 1982. Identification of recycled continental material in the mantle from Sr, Nd and Pb isotope investigations. *Earth and Planetary Science Letters* **61**, 73–84.
- COX, K. G. 1978. Flood basalts, subduction and the break-up of Gondwanaland. *Nature* **274**, 47–49.
- CREAGER, K. C. & JORDAN, T. H. 1984. Slab penetration in the lower mantle. *Journal of Geophysical Research* **89**, 3031–3049.
- DAVIES, G. F. 1981. Earth's neodymium budget and structure and evolution of the mantle. *Nature* **290**, 208–213.
- DUDÁS, F. Ö. CARLSON, R. W. & EGGLE, D. H. 1987. Regional middle Proterozoic enrichment of the subcontinental mantle source of igneous rocks from central Montana. *Geology* **15**, 22–25.
- DUNCAN, A. R., ERLANK, A. J. & MARCH, J. S. 1984. Regional geochemistry of the Karoo igneous

- province. *Special Publication of the Geological Society of South Africa* **13**, 355–388.
- DUNCAN, R. A., MCCULLOCH, M. T., BARCZUS, H. G. & NELSON, D. R. 1986. Plume versus lithospheric sources for the melts at Ua Pou, Marquesas Island. *Nature* **303**, 142–146.
- DUPUY, C., VIDAL, P., BARCZUS, H. G. & CHAUVEL, C. 1987. Origin of basalts from the Marquesas Archipelago (south central Pacific Ocean): isotope and trace element constraints. *Earth and Planetary Science Letters* **82**, 145–152.
- FODOR, R. V., BAUER, G. R., JACOBS, R. S. & BORNHORST, T. J. 1987. Kahoolawe Island, Hawaii: tholeiitic, alkalic and unusual hydrothermal(?) "enrichment" characteristics. *Journal of Volcanology and Geothermal Research* **31**, 171–176.
- FRASER, K. J., HAWKESWORTH, C. J., ERLANK, A. J., MITCHELL, R. H. & SCOTT-SMITH, B. H. 1986. Sr, Nd and Pb isotope and minor element geochemistry of lamproites and kimberlites. *Earth and Planetary Science Letters* **76**, 57–70.
- FREY, F. A. & CLAGUE, D. A. 1983. Geochemistry of diverse basalts types from Loihi Seamount, Hawaii: petrogenetic implications. *Earth and Planetary Science Letters* **66**, 337–355.
- & GREEN D. H. 1974. The mineralogy, geochemistry and origin of lherzolite inclusions in Victorian basanites. *Geochimica et Cosmochimica Acta* **38**, 1023–1059.
- , — & ROY, S. D. 1978. Integrated models of basalt petrogenesis: a study of quartz tholeiites to olivine melilitites from South Eastern Australia utilizing geochemical and experimental petrological data. *Journal of Petrology* **19**, 463–513.
- FUJIMAKI, H., TATSUMOTO, M. & AOKI, K.-I. 1984. Partition coefficients of Hf, Zr, and REE between phenocrysts and groundmasses. *Journal of Geophysical Research* **89**, B662–B672.
- GAST, P. W. 1968. Trace element fractionation and the origin of tholeiitic and alkaline magma types. *Geochimica et Cosmochimica Acta* **32**, 1057–1086.
- GREEN, D. H. 1971. Composition of basaltic magmas as indicators of conditions of origin: application to oceanic volcanism. *Philosophical Transactions of the Royal Society of London* **268**, 707–725.
- GREEN, T. H. 1978. Rare earth geochemistry of basalts from Norfolk Island, and implications for mantle inhomogeneity in the rare earth elements. *Geochemical Journal* **12**, 165–172.
- GURNIS, M. & DAVIES, G. F. 1986. The effect of depth-dependent viscosity on convective mixing in the mantle and the possible survival of primitive mantle. *Geophysical Research Letters* **13**, 541–544.
- HAGER, B. H. & GURNIS, M. 1987. Mantle convection and the state of the earth's interior. *Reviews of Geophysics* **25**, 1277–1285.
- HANSON, G. N. 1977. Geochemical evolution of the suboceanic mantle. *Journal of the Geological Society of London* **134**, 235–253.
- HART, S. R. 1984. A large-scale isotope anomaly in the Southern Hemisphere mantle. *Nature* **309**, 753–757.
- , GERLACH, D. C. & WHITE, W. M. 1986. A possible new Sr–Nd–Pb mantle array and consequences for mantle mixing. *Geochimica et Cosmochimica Acta* **50**, 1551–1557.
- HAWKESWORTH, C. J., MANTOVANI, M. S. M., TAYLOR, P. N. & PALACZ, A. 1986. Evidence from the Parana of south Brazil for a continental contribution to Dupal basalts. *Nature* **322**, 356–359.
- , NORRY, M. J., RODDICK, J. C. & VOLLMER, R. 1979.  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from the Azores and their significance in LIL-element enriched mantle. *Nature* **280**, 28–31.
- , ROGERS, N. W., VAN CALSTEREN, P. & MENZIES, M. A. 1984. Mantle enrichment processes. *Nature* **311**, 331–335.
- HERGT, J. M. 1987. *The Origin and Evolution of the Tasmania Dolerites*. Unpublished PhD thesis, Australian National University.
- HOFMANN, A. W. & WHITE, W. M. 1982. Mantle plumes from ancient oceanic crust. *Earth and Planetary Science Letters* **57**, 421–436.
- , & —, 1983. Ba, Rb and Cs in the Earth's mantle. *Zeitschrift für Naturforschung* **38a**, 256–266.
- , JOCHUM, K. P., SEUFERT, M. & WHITE, W. M. 1986. Nb and Pb in oceanic basalts: new constraints on mantle evolution. *Earth and Planetary Science Letters* **79**, 33–45.
- JAGOUTZ, E., PALME, H., BADDENHAUSEN, H., BLUM, K., CENDALES, M., DREIBUS, G., SPETTEL, B., LORENZ, V. & WÄNKE, H. 1979. The abundances of major, minor and trace elements in the Earth's mantle as derived from primitive ultramafic nodules. *Proceedings of the 10th Lunar and Planetary Science Conference, (Geochimica et Cosmochimica Acta, Suppl. 11) Vol. 2*, 2031–2050.
- JAQUES, A. L., SUN, S.-s. & CHAPPELL, B. W. 1988. Geochemistry of the Argyle (AK1) lamproite pipe, Western Australia. *Proceedings of the 4th International Kimberlite Conference*. Geological Society of Australia Special Publication, in press.
- JOCHUM, K. P., SEUFERT, H. M., SPETTEL, B. & PALME, H. 1986. The solar-system abundances of Nb, Ta, and Y, and the relative abundances of refractory lithophile elements in differentiated planetary bodies. *Geochimica et Cosmochimica Acta* **50**, 1173–1183.
- JOHNSON, R. W., JAQUES, A. L., LANGMUIR, C. H., PERFIT, M. R., STAUDIGEL, H., DUNKLEY, P. N., CHAPPELL, B. W., TAYLOR, S. R. & BAEKISAPA, M. 1987. Ridge subduction and forearc volcanism: petrology and geochemistry of rocks dredged from the western Solomon arc and Woodlark basin. In: TAYLOR, B. & EXON, N. F. (eds) *Marine Geology, Geophysics, and Geochemistry of the Woodlark Basin — Solomon Islands Region*, Circum-Pacific Council of Energy and Mineral Resources, Earth Science Series, in press.
- KATO, T., IRIFUNE, T. & RINGWOOD, A. E. 1987. Majorite partitioning behavior and petrogenesis of the earth's upper mantle. *Geophysical Research Letters* **14**, 546–549.

- KAY, R. W. 1979. Zone refining at the base of lithospheric plates: a model for steady-state asthenosphere. *Tectonophysics* **55**, 1–9.
- KRAMERS, J. D. 1977. Lead and strontium isotopes in Cretaceous kimberlites and mantle-derived xenoliths from southern Africa. *Earth and Planetary Science Letters* **34**, 419–431.
- , SMITH, C. B., LOCK, N. P., HARMON, R. S. & BOYD, F. R. 1981. Can kimberlites be generated from an ordinary mantle? *Nature* **291**, 53–56.
- KUEHNER, S. M., EDGAR, A. D. & ARIMA, M. 1981. Petrogenesis of the ultrapotassic rocks from the Leucite Hills, Wyoming. *American Mineralogist* **66**, 663–667.
- LANGMUIR, C. H. & HANSON, G. N. 1980. An evaluation of major element heterogeneity in the mantle sources of basalts. *Philosophical Transactions of the Royal Society of London, Series A* **297**, 383–407.
- , BENDER, J. F., BENICE, A. E., HANSON, G. N. & TAYLOR, S. R. 1977. Petrogenesis of basalts from the FAMOUS area: Mid-Atlantic Ridge. *Earth and Planetary Science Letters* **36**, 133–156.
- LE ROEX, A. P. 1986. Geochemical correlation between southern African kimberlites and South Atlantic hotspots. *Nature* **324**, 243–245.
- LI, S. & HART, S. R. 1986. Sources of evolution of Hawaiian volcanism: isotopic constraints. *Earth and Planetary Science Letters*, in press.
- LIOTARD, J. M., BARSCZUS, H. G., DUPUY, C. & DOSTAL, J. 1986. Geochemistry and origin of basaltic lavas from Marquesas Archipelago, French Polynesia. *Contributions to Mineralogy and Petrology* **92**, 260–268.
- MACDOUGALL, J. D. & LUGMAIR, G. W. 1986. Sr and Nd isotopes in basalts from the East Pacific Rise: significance for mantle heterogeneity. *Earth and Planetary Science Letters* **77**, 273–284.
- MANTOVANI, M. S. M., MARQUES, L. S., DE SOUSA, M. A., CIVETTI, L., ATALLA, L. & INNOCENTI, F. 1985. Trace element and strontium isotope constraints on the origin and evolution of Paraná continental flood basalts of Santa Catarina State (Southern Brazil). *Journal of Petrology* **26**, 187–209.
- MCDONOUGH, W. F. & McCULLOCH, M. T. 1987. The southeast Australian lithospheric mantle: implications for its growth and evolution. *Earth and Planetary Science Letters* **86**, 327–340.
- , — & SUN, S.-S. 1985. Isotopic and geochemical systematics in Tertiary–Recent basalts from south eastern Australia and implications for the evolution of the sub-continental lithosphere. *Geochimica et Cosmochimica Acta* **49**, 2051–2067.
- , SUN, S.-S., RINGWOOD, A. E. & JAGOUTZ, E. 1987. Rb and Cs in the Earth and Moon. *Lunar and Planetary Science Conference Abstracts*, Vol. 18, 610–611. Lunar and Planetary Institute, Houston.
- MCKENZIE, D. 1984. The generation and compaction of partially molten rock. *Journal of Petrology* **25**, 713–765.
- & O'NIONS, R. K. 1983. Mantle reservoirs and ocean island basalts. *Nature* **301**, 229–231.
- McLENNAN, S. M. & TAYLOR, S. R. 1981. Role of subducted sediments in island-arc magmatism: constraints from REE patterns. *Earth and Planetary Science Letters* **54**, 423–430.
- MENZIES, M. 1983. Mantle ultramafic xenoliths in alkaline magmas: evidence for mantle heterogeneity modified by magmatic activity. In: (eds), HAWKESWORTH C. J. & NORRIS, M. J. *Continental Basalts and Mantle Xenoliths*, 92–110, Shiva, Cheshire.
- & MURTHY, V. R. 1980. Nd and Sr isotope geochemistry of hydrous mantle nodules and their host alkali basalts: implications for local heterogeneities in metasomatically veined mantle. *Earth and Planetary Science Letters* **46**, 323–334.
- MURMATSU, Y. 1983. Geochemical investigation of kimberlites from the Kimberley area, South Africa. *Geochemical Journal* **17**, 71–86.
- & WEDEPOHL, K. H. 1985. REE and selected trace elements in kimberlites from the Kimberley area (South Africa). *Chemical Geology* **51**, 289–301.
- NAGASHIMA, K., MIYAWAKI, R., TAKASE, J., NAKAI, I., SAKURAI, K.-I., MATSUBARA, S., KATO, A. & IWANO, S. 1986. Kimuraitite,  $\text{CaY}_2(\text{CO}_3)_4 \cdot 6\text{H}_2\text{O}$ , a new mineral from fissures in an alkali olivine basalt from Saga Prefecture, Japan, and new data on lokkaite. *American Mineralogist* **71**, 1028–1033.
- NAKAMURA, E., CAMPBELL, I. H. — SUN, S.-S. 1985. The influence of subduction processes on the geochemistry of Japanese alkaline basalts. *Nature* **316**, 55–58.
- NAVON, O. & STOLPER, E. 1987. Geochemical consequences of melt percolation: the upper mantle as a chromatographic column. *Journal of Geology* **95**, 285–307.
- NELSON, D. R., CHAPPELL, B. W., CHIVAS, A. R. & McCULLOCH, M. T. 1987. Geochemical and isotopic evidence for a subducted oceanic lithosphere origin for carbonatites. *Geochimica et Cosmochimica Acta* **52**, 1–18.
- , McCULLOCH, M. T. & SUN, S.-S. 1986. The origins of ultrapotassic rocks as inferred from Sr, Nd and Pb isotopes. *Geochimica et Cosmochimica Acta* **50**, 231–245.
- NEWMAN, S., FINKEL, R. C. & MACDOUGALL, J. D. 1984. Comparison of  $^{230}\text{Th}$ – $^{238}\text{U}$  disequilibrium systematics in basalts from three hot spot regions: Hawaii, Prince Edward and Samoa. *Geochimica et Cosmochimica Acta* **48**, 315–324.
- NEWSOM, H. E., WHITE, W. M., JOCHUM, K. P. & HOFMANN, A. W. 1986. Siderophile and chalcophile element abundances in oceanic basalts, Pb isotope evolution and growth of the Earth's core. *Earth and Planetary Science Letters* **80**, 299–313.
- NICOLAS, A. 1986. A melt extraction model based on structural studies in mantle peridotites. *Journal of Petrology* **27**, 999–1022.
- O'HARA, M. J. & MATHEWS, R. E. 1981. Geochemical evolution in an advancing, periodically replenished, periodically tapped, continuously fractionated magma chamber. *Journal of the Geological Society, London* **138**, 237–277.



- OVERSBY, V. M. & GAST, P. W. 1968. Lead isotope compositions and uranium decay series disequilibrium in recent volcanic rocks. *Earth and Planetary Science Letters* **5**, 199–206.
- OXBURGH, E. R. & TURCOTTE, D. L. 1968. Mid-ocean ridges and geotherm distribution during mantle convection. *Journal of Geophysical Research* **73**, 2643–2661.
- PALACZ, Z. A. & SAUNDERS, A. D. 1986. Coupled trace element and isotope enrichment in the Cook–Austral–Samoa islands, southwest Pacific. *Earth and Planetary Science Letters* **79**, 270–280.
- PATCHETT, P. J. 1983. Importance of Lu–Hf isotopic system in studies of planetary chronology and chemical evolution. *Geochimica et Cosmochimica Acta* **47**, 81–91.
- PHILPOTTS, J. A. & SCHNETZLER, C. C. 1970. Phenocryst-matrix partition coefficients for K, Rb, Sr and Ba, with application to anorthosite and basalt genesis. *Geochimica et Cosmochimica Acta* **34**, 307–322.
- RICHARDSON, S. H., ERLANK, A. J., DUNCAN, A. R. & REID, D. L. 1982. Correlated Nd, Sr and Pb isotope variation in Walvis Ridge basalts and implications for the evolution of their mantle source. *Earth and Planetary Science Letters* **59**, 327–342.
- , GURNEY, J. J., ERLANK, A. J. & HARRIS, J. W. 1984. Origin of diamonds in old enriched mantle. *Nature* **310**, 198–202.
- RICHTER, F. M. 1985. Models of the Archaean thermal regime. *Earth and Planetary Science Letters* **73**, 350–360.
- RINGWOOD, A. E. 1982. Phase transformations and differentiation in subducted lithosphere: implications for mantle dynamics, basalt petrogenesis, and crustal evolution. *Journal of Geology* **90**, 611–643.
- & IRIFUNE, T. 1988. Nature of the 650-km seismic discontinuity: implications for mantle dynamics and differentiation. *Nature* **331**, 131–136.
- RODEN, M. F., FREY, F. A. & CLAGUE, D. A. 1984. Geochemistry of tholeiitic and alkalic lavas from the Koolau Range, Oahu, Hawaii: implications for Hawaiian volcanism. *Earth and Planetary Science Letters* **69**, 141–158.
- , HART, S. R., FREY, F. A. & MELSON, W. G. 1984. Sr, Nd and Pb isotopic and REE geochemistry of St. Paul's Rocks: the metamorphic and metasomatic development of an alkali basalt mantle source. *Contributions to Mineralogy and Petrology* **85**, 376–390.
- , RAMA MURTHY, V. & GASPAR, J. C. 1985. Sr and Nd isotopic composition of the Jacupiranga carbonatite. *Journal of Geology*, **93**, 212–220.
- RYAN, J. G. & LANGMUIR, C. H. 1987. The systematics of lithium abundances in young volcanic rocks. *Geochimica et Cosmochimica Acta* **51**, 1727–1741.
- SAUNDERS, A. D. & TARNEY, J. 1979. The geochemistry of basalts from a back-arc spreading centre in the East Scotia Sea. *Geochimica et Cosmochimica Acta* **43**, 555–572.
- , — & WEAVER, S. D. 1980. Transverse chemical variations across the Antarctic Peninsula: implications for the genesis of calc-alkaline magmas. *Earth and Planetary Science Letters* **46**, 344–360.
- SAWAMOTO, H. 1987. Phase diagram of MgSiO<sub>3</sub> at pressures up to 24 GPa and temperatures up to 2,200 °C — phase stability and properties of tetragonal garnet. In press.
- SCHILLING, J. G., THOMPSON, G., KINGSLEY, R. & HUMPHRIS, S. 1985. Hotspot–migrating ridge interaction in the south Atlantic. *Nature* **313**, 187–191.
- SMITH, C. B. 1983. Pb, Sr and Nd isotopic evidence for sources of southern African Cretaceous kimberlites. *Nature* **304**, 51–54.
- , GURNEY, J. J., SKINNER, E. M. W., CLEMENT, C. R. & EBRAHIM, N. 1985. Geochemical character of southern African kimberlites: a new approach based on isotopic constraints. *Transactions of Geological Society of South Africa* **88**, 267–280.
- STAUDIGEL, H., ZINDLER, A., HART, S. R., LESLIE, T. M., CHEN, C.-Y. & CLAGUE, D. 1984. The isotope systematics of a juvenile intraplate volcano: Pb, Nd, and Sr isotope ratios of basalts from Loihi Seamount, Hawaii. *Earth and Planetary Science Letters* **69**, 13–29.
- STILLE, P., UUNUH, D. M. & TATSUMOTO, M. 1986. Pb, Sr, Nd and Hf isotopic constraints on the origin of Hawaiian basalts and evidence for a unique mantle source. *Geochimica et Cosmochimica Acta* **50**, 2303–2319.
- SUN, S.-s. 1980. Lead isotopic study of young volcanic rocks from mid-ocean ridges, ocean islands and island arcs. *Philosophical Transactions of the Royal Society of London* **297**, 409–445.
- & HANSON, G. N. 1975a. Origin of Ross Island basanitoids and limitations upon the heterogeneity of mantle sources for alkali basalts and nephelinites. *Contributions to Mineralogy and Petrology* **52**, 77–106.
- & — 1975b. Evolution of the mantle: geochemical evidence from alkali basalt. *Geology* **3**, 297–302.
- & — 1976a. Evolution of the mantle: geochemical evidence from alkali basalt: Reply. *Geology* **4**, 626–631.
- & — 1976b. Rare earth element evidence for differentiation of McMurdo volcanics, Ross Island, Antarctica. *Contributions to Mineralogy and Petrology* **54**, 139–155.
- & NESBITT, R. W. 1977. Chemical heterogeneity of the Archaean mantle, composition of the Earth and mantle evolution. *Earth and Planetary Science Letters* **35**, 429–448.
- , — & McCULLOCH, M. T. 1988. Geochemistry and petrogenesis of siliceous high magnesian basalts of the Archaean and early Proterozoic. In: CRAWFORD, A. J. (ed.) *Boninites and Related Rocks*. George Allen and Unwin, London, in press.
- , — & SHARASKIN, A. Y. 1979. Geochemical characteristics of mid-ocean ridge basalts. *Earth and Planetary Science Letters* **44**, 119–138.
- TATSUMOTO, M. 1978. Isotopic composition of lead in

- oceanic basalts and its implication to mantle evolution. *Earth and Planetary Science Letters* **38**, 119–138.
- TAYLOR, S. R. & MCLENNAN, S. M. 1985. *The Continental Crust: Its Composition and Evolution*. Blackwells Scientific, Oxford, 312 pp.
- THOMPSON, R. N., MORRISON, M. A., DICKIN, A. P. & HENDRY, G. L. 1983. Continental flood basalts... Arachnids rule OK? In: Eds. HAWKESWORTH, C. J. & NORRY, M. J. (eds) *Continental Basalts and Mantle Xenoliths*, 158–185. Shiva, Cheshire.
- , —, HENDRY, G. L. & PARRY, S. J. 1984. An assessment of the relative roles of crust and mantle in magma genesis: and elemental approach. *Philosophical Transactions of the Royal Society of London* **310**, 549–590.
- VIDAL, P. & DOSSO, L. 1978. Core formation: catastrophic or continuous? Sr and Pb isotope geochemistry constraints. *Geophysical Research Letters* **5**, 169–172.
- , CHAUVEL, C. & BROUSSE, R. 1984. Large mantle heterogeneity beneath French Polynesia. *Nature* **307**, 536–538.
- WATSON, E. B., BEN OTHMAN, D., LUCK, J. M. & HOFMANN, A. W. 1987. Partitioning of U, Pb, Hf, Yb, Cs, Re, Os between chromian diopsidic pyroxene and haplobasaltic liquid. *Chemical Geology* **62**, 191–208.
- WEAVER, B. L., WOOD, D. A., TARNEY, J. & JORON, J. L. 1986. Role of subducted sediment in the genesis of ocean-island basalts: geochemical evidence from South Atlantic Ocean islands. *Geology* **14**, 275–278.
- WHITE, W. M. 1985. Sources of oceanic basalts: radiogenic isotopic evidence. *Geology* **13**, 115–118.
- & HOFMANN, A. W. 1982. Sr and Nd isotope geochemistry of oceanic basalts and mantle evolution. *Nature* **296**, 821–825.
- , — & PUCHELT, H. 1987. Isotope geochemistry of Pacific mid-ocean ridge basalts. *Journal of Geophysical Research* **92**, 4881–4893.
- , TAPIA, M. D. M. & SCHILLING, J.-G. 1979. The petrology and geochemistry of the Azores Islands. *Contributions to Mineralogy and Petrology* **69**, 201–213.
- WOOD, D. A., JORON, J.-L., TREUIL, M., NORRY, M. & TARNEY, J. 1979. Elemental and Sr isotope variations in basic lavas from Iceland and the surrounding ocean floor. *Contributions to Mineralogy and Petrology* **70**, 319–339.
- WRIGHT, E. & WHITE, W. M. 1987. The origin of Samoa: new evidence from Sr, Nd, and Pb isotopes. *Earth and Planetary Science Letters* **81**, 151–162.
- WYLLIE, P. J. & SEKINE, T. 1982. The formation of mantle phlogopite in subduction zone hybridization. *Contributions to Mineralogy and Petrology* **79**, 375–380.
- ZARTMAN, R. E. & DOE, B. R. 1981. Plumbotectonics — the model. *Tectonophysics* **75**, 135–162.
- ZINDLER, A. & HART, S. 1986. Chemical geodynamics. *Annual Reviews of Earth and Planetary Science* **14**, 493–571.
- , JAGOUTZ, E. & GOLDSTEIN, S. 1982. Nd, Sr and Pb isotopic systematics in a three-component mantle: a new perspective. *Nature* **298**, 519–523.
- , STAUDIGEL, H. & BATIZA, R. 1984. Isotope and trace element geochemistry of young Pacific seamounts: implications for the scale of upper mantle heterogeneity. *Earth and Planetary Science Letters* **70**, 175–195.

SHEN-SU SUN, Division of Petrology and Geochemistry, Bureau of Mineral Resources, Geology and Geophysics, G.P.O. Box 378, Canberra, ACT 2601, and Research School of Earth Sciences, The Australian National University, G.P.O. Box 4, Canberra, ACT 2601, Australia.

WILLIAM F. McDONOUGH, Research School of Earth Sciences, The Australian National University, G.P.O. Box 4, Canberra, ACT 2601, Australia. *Present address*: Max-Planck-Institut für Chemie, Saarstraße 23, D-6500 Mainz, FRG.