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## Partial Melting of Subducted Oceanic Crust and Isolation of Its Residual Eclogitic Lithology

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# Partial melting of subducted oceanic crust and isolation of its residual eclogitic lithology

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Oceanic lithosphere is produced at mid-ocean ridges and reinjected into the mantle at convergent plate boundaries. During subduction, this lithosphere goes through a series of progressive dehydration and melting events. Initial dehydration of the slab occurs during low pressure metamorphism of the oceanic crust and involves significant dewatering and loss of labile elements. At depths of 80–120 km water release by the slab is believed to lead to partial melting of the oceanic crust. These melts, enriched in incompatible elements (excepting Nb, Ta and Ti), fertilize the overlying mantle wedge and produce the enriched peridotitic sources of island arc basalts. Retention of Nb, Ta and Ti by a residual mineral (e.g. in a rutile phase) in a refractory eclogitic lithology within the sinking slab are considered to cause their characteristic depletions in island arc basalts. These refractory eclogitic lithologies, enriched in Nb, Ta and Ti, accumulate at depth in the mantle. The continued isolation of this eclogitic residuum in the deep mantle over Earth's history produces a reservoir which contains a significant proportion of the Earth's Ti, Nb and Ta budget.

Both the continental crust and depleted mantle have subchondritic Nb/La and Ti/Zr ratios and thus they cannot be viewed strictly as complementary geochemical reservoirs. This lack of complementarity between the continental crust and depleted mantle can be balanced by a refractory eclogitic reservoir deep in the mantle, which is enriched in Nb, Ta and Ti. A refractory eclogitic reservoir amounting to *ca.* 2% of the mass of the silicate Earth would also contain significant amounts of Ca and Al and may explain the superchondritic Ca/Al value of the depleted mantle.

## 1. Introduction

The production of oceanic lithosphere at mid-ocean ridges and its subsequent reinjection into the mantle at convergent plate boundaries are the two most important crust–mantle differentiation processes operating in the Earth today. Hofmann & White (1980, 1982), Chase (1981) and Ringwood (1982) suggested that these two processes are also ultimately responsible for the formation of intraplate basalt source regions. The aim of this paper is to examine some of the consequences of slab melting processes. Attention is focused on the fate of the subducting slab at depths below which island arc basalts (IAB) are generated (i.e. over 100 km). There is a need to understand the compositions and subsequent history of refractory eclogitic materials produced during the partial melting of subducted oceanic crust in the island arc environment.

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407

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[ 181 ]

The subduction of oceanic lithosphere into the mantle involves a continuous process of increasing metamorphism and dehydration within the slab. It is likely that components added to the uppermost portions of the oceanic crust during its migration from ridge to subduction trench undergo rapid mineralogical changes and substantial dehydration during the early phases of metamorphism. A significant amount of this hydrous component is transferred into the overlying lithosphere at relatively shallow levels (less than 80 km). When the slab reaches depths of 80–120 km increasing temperature, combined with the release of volatiles may lead to partial melting. At this stage, oceanic crust becomes transformed to quartz eclogite. Any partial melts derived from these lithologies migrate into the mantle wedge, enriching this region in incompatible elements.

It is widely considered that IAB form by the partial melting of refertilized peridotitic lithologies in the wedge overlying a subducting slab (Nicholls & Ringwood 1973). In most instances hydrous, silica-saturated basaltic melts of the island arc magma series are observed to display characteristic depletions<sup>†</sup> in Ti, Nb and Ta<sup>‡</sup>. It is widely believed that the depletions are caused by the retention of these elements in a titanite phase (such as rutile) during partial melting (Saunders *et al.* 1980). Thus, if slab melting occurs, the residual eclogite would be relatively enriched in Ti and Nb. (There are a few examples where such depletions are not found in these magmas and this is attributed to the subduction of young oceanic lithosphere at relatively high temperatures (Leeman *et al.* 1990).)

Refractory eclogitic lithologies thereby produced are transported deep into the mantle by the descending slab. This material is not recognized in mantle samples carried up as xenoliths, nor is its geochemical signature of Nb and Ti-enrichments observed in basalts derived from the mantle. Tarney *et al.* (1980) and Ringwood (1990) suggested that this refractory eclogitic material may become trapped deep in the mantle and accumulate to form a substantial geochemical reservoir. This material, which has been produced over geologic time (more than 2 Ga), would constitute an isolated reservoir in the mantle and contain enhanced levels of Nb and Ti relative to other incompatible (lithophile) elements.

In this model, the residual materials enriched in Nb and Ti occur not in the overlying lithospheric mantle, but in the subducted slab. It is difficult to completely assess the compositional variation in the continental lithospheric mantle; however, some constraints can be provided by examining the composition of peridotite xenoliths brought up in basalts. Peridotite xenoliths generally do not show any clear evidence for the storage of this residual, Nb, Ti-enriched, component (Jochum *et al.* 1989; McDonough 1990). The continental lithospheric mantle is believed to have an overall enrichment of incompatible elements, with a pattern which is similar to that seen intraplate basalts (McDonough 1990). Although this mantle reservoir has a superchondritic Nb/La ratio, it also possesses a subchondritic Ti/Zr ratio and a chondritic to subchondritic Ti/Eu ratio indicating that it is depleted in Ti and only

<sup>†</sup> The terms *enriched/enrichments* and *depleted/depletions* describe the abundance of an element relative to other elements or the absolute value of a ratio relative to the Primitive Mantle ratio. In this paper enrichments or depletions of elements are relative to elements with similar incompatibility (e.g. Nb/La and Ti/Zr) during melting of oceanic basalt sources (Sun & McDonough 1989).

<sup>‡</sup> Throughout this discussion it is assumed that Nb and Ta are inseparable during most mantle processes, although it is recognized that these elements may be fractionated by certain phases. A Nb/Ta ratio of 17, the chondritic value, is assumed to apply to lavas ranging from mafic to ultramafic in composition and to peridotites (Jochum *et al.* 1989). Therefore, further discussions will be restricted to Nb and it is assumed that the behaviour of Ta is identical to that of Nb.

slightly enriched in Nb. Thus, this evidence does not imply that the continental lithospheric mantle represents an important Nb, Ti-enriched reservoir within the Earth.

It has recently been suggested that peridotite xenoliths commonly have depletions in high field strength elements (Ti, Zr, Nb and Ta) and that this material is representative of a world-wide shallow reservoir that is the source of IABS (Salters & Shimizu 1988). The basis for this model was that the relative abundances of Ti, Zr and the rare earth elements in clinopyroxenes from anhydrous spinel peridotite xenoliths reflected the bulk rock character. This assumption, however, has been shown to be incorrect for a number of spinel peridotite xenoliths (McDonough & Frey 1989). Additionally, it has been demonstrated that substantial quantities of Ti are found in orthopyroxenes coexisting with clinopyroxenes in these xenoliths, while more than 95% of the Eu, which has a similar incompatible melting behaviour to Ti, is hosted in the clinopyroxenes (McDonough *et al.* 1991). This indicates that, although clinopyroxenes from anhydrous spinel peridotite xenoliths contain nearly the total budget of the rare earth elements, this phase does not contain the same relative amount of Ti and therefore the incompatible element pattern of the clinopyroxene will not necessarily reflect that of the bulk rock. Given these observations, this model (Salters & Shimizu 1988) is not considered valid.

## 2. Evidence for a refractory eclogite reservoir

The continued storage and isolation of refractory eclogitic lithologies transported to the deep mantle by the subducting slab would have a significant influence on the distribution of some key elements (including Nb and Ti) in the mantle. The production and recycling of oceanic lithosphere is a process considered to have occurred throughout the Phanerozoic and probably much of the Precambrian. Accordingly, it is useful to examine the evidence for sequestering significant quantities of refractory eclogite, enriched in Nb and Ti in a deep mantle reservoir and to explore some geochemical consequences of such a reservoir.

There are several pieces of evidence which support the existence of a deep mantle reservoir composed of refractory eclogite enriched in Nb and Ti. The light rare earth (LREE) enriched continental crust is often believed to have a complementary composition to that of the depleted upper mantle, the source region of LREE-depleted mid-ocean ridge basalt (MORB). The average continental crust is believed to possess a subchondritic Nb/La ratio (Taylor & McLennan 1985) (table 1). Interestingly, N-type MORBs generally have chondritic to subchondritic Nb/La ratios, mostly in the range of 0.8–1.0 (Sun *et al.* 1979; Hofmann 1988) and their source regions would have at least a subchondritic ratio, given that Nb is widely regarded as being more incompatible than La during MORB genesis. This indicates that the Nb/La values of the depleted mantle and continental crust are not complementary relative to the primitive mantle (table 1). As noted earlier, the low La and Nb abundance and the relatively low, but superchondritic, Nb/La value of the continental lithospheric mantle (table 1) are not sufficient to balance the continental crust and depleted mantle with the primitive mantle. Thus, a fourth reservoir, having a superchondritic Nb/La composition and high Nb abundance, is required to balance the continental crust and depleted mantle (Saunders *et al.* 1988; Sun & McDonough 1989).

It has been suggested by Weaver *et al.* (1987) and Saunders *et al.* (1988) that refractory eclogitic lithologies produced by the processing of subducted oceanic crust

Table 1. *A mass balance calculation for elements in the continents and mantle reservoirs*

(Mass is expressed in  $10^{25}$  g. The concentrations of Ti, Zr, Nb and La are expressed in p.p.m., and those of Ca and Al are given in wt %.)

| relative contribution            | mass (%) | Ti (%) | Zr (%) | Nb (%) | La (%) | Ca (%) | Al (%) |  |  |  |
|----------------------------------|----------|--------|--------|--------|--------|--------|--------|--|--|--|
| continental crust                | 0.5      | 2      | 5      | 8      | 14     | 1      | 2      |  |  |  |
| continental l. mantle            | 2.5      | 1      | 2      | 3      | 4      | 1      | 1      |  |  |  |
| depleted mantle                  | 40       | 25     | 29     | 21     | 22     | 37     | 36     |  |  |  |
| refractory eclogite <sup>a</sup> | 2.0      | 17     | 9      | 13     | 5      | 5      | 6      |  |  |  |
| undepleted mantle                | 55       | 55     | 55     | 55     | 55     | 55     | 55     |  |  |  |
| silicate Earth                   | 100      |        |        |        |        |        |        |  |  |  |

|                                  | mass | Ti    | Zr  | Nb    | La   | Ca (%) | Al (%) | Ti/Zr | Nb/La | Ca/Al |
|----------------------------------|------|-------|-----|-------|------|--------|--------|-------|-------|-------|
| silicate Earth                   | 403  | 1275  | 11  | 0.71  | 0.69 | 2.67   | 2.45   | 116   | 1.03  | 1.09  |
| continental crust                | 2.2  | 5400  | 100 | 11    | 16   | 5.3    | 8.4    | 54    | 0.69  | 0.63  |
| continental l. mantle            | 10   | 550   | 8   | 1.0   | 0.90 | 1.4    | 1.1    | 69    | 1.11  | 1.27  |
| depleted mantle                  | 160  | 800   | 8   | 0.375 | 0.38 | 2.5    | 2.2    | 100   | 0.99  | 1.13  |
| refractory eclogite <sup>a</sup> | 8    | 10500 | 50  | 4.5   | 1.7  | 6.4    | 7.4    | 210   | 2.65  | 0.87  |
| undepleted mantle                | 223  | 1275  | 11  | 0.71  | 0.69 | 2.67   | 2.45   | 116   | 1.03  | 1.09  |

<sup>a</sup> The proposed reservoir of refractory eclogite, enriched in Nb and Ti and carried in the down going slab, was produced during island arc magmatism; its composition and mass has been modelled in this calculation (see text for further explanation). The composition and mass of the continental crust are from Taylor & McLennan (1985). The composition and mass of the continental lithospheric mantle are from McDonough (1990). The composition of the depleted mantle is derived from a melting model based on a relatively primitive MORB composition (Sun & McDonough 1989); its mass is assumed to be about 40% of the mass of the primitive mantle. The composition of the undepleted mantle is set equal to that of the primitive mantle (Sun & McDonough 1989) and its mass makes up the remainder of the silicate Earth system.

in the island arc environment are transported deep into the mantle and reincorporated in the source regions of oceanic basalts (MORB and oceanic intraplate basalts (OIB)). This hypothesis, however, is inconsistent with data for N-type MORBs which show that these basalts are not enriched in Nb (Sun *et al.* 1979; Hofmann 1988; Sun & McDonough 1989). It has been demonstrated above that N-type MORBs are, in fact, depleted in Nb with respect to La. Additionally, it can also be argued that N-type MORBs are not enriched in Ti. These basalts generally have chondritic to subchondritic Ti/Zr (figure 1a), Ti/Eu and Ti/Gd ratios. Significant fractionation of these element ratios is not expected during MORB genesis, because Ti, Zr, Eu and Gd have relatively similar incompatibility at these high degrees of melting (Sun & McDonough 1989). Thus, ratios of these elements in MORBs tend to reflect their source values. By comparison, the fractionation of Th and U, two elements with differing incompatibility and both of which are much more incompatible than Ti and related elements, is generally on the order of 10% or less during MORB genesis (Condomines *et al.* 1988; Ben Othman & Allègre 1990). Ratios of Ti/Zr, Ti/Eu or Ti/Gd, which are *ca.* 10% higher in the N-type MORB source are still in the range of chondritic to subchondritic compositions. These observations indicate that the source region of N-type MORBs is either depleted in Ti relative to Zr, Eu or Gd, or possesses relatively unfractionated Ti/Zr, Ti/Eu or Ti/Gd ratios. The average continental crust has a subchondritic Ti/Zr value (figure 1b) and is thus not complementary to the depleted mantle (table 1).

It is unlikely that refractory eclogitic lithologies produced by the processing of



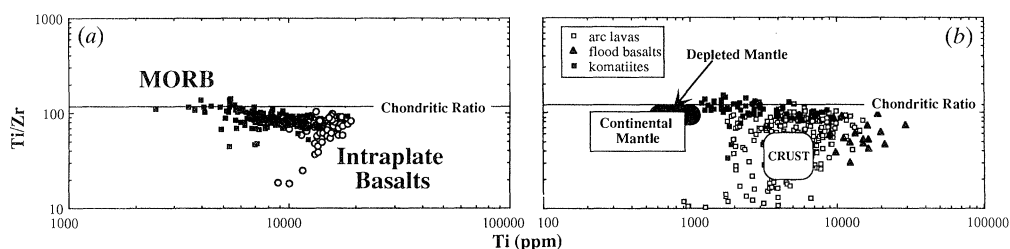


Figure 1. Ti/Zr against Ti (p.p.m.) plot for (a) mid-ocean ridge basalts (MORB) and intraplate basalts; (b) island arc basalts, flood basalts, and komatiites. The estimated fields for the bulk continental crust (crust), the continental lithospheric mantle and depleted mantle (MORB source region) are also shown in (b). Data are from the literature. The bulk silicate Earth has a chondritic Ti/Zr value of 115. Komatiites tend to have relatively chondritic Ti/Zr values, while all other rocks have subchondritic Ti/Zr values. To produce a balanced bulk silicate Earth there must be another reservoir with a significant complement of Ti and having a superchondritic Ti/Zr. A refractory eclogitic reservoir enriched in Nb and Ti and having a superchondritic Ti/Zr would be capable of providing this necessary complement.

subducted oceanic crust in the island arc environment are reincorporated in the source regions of intraplate basalts. There is little disagreement that the sources of intraplate basalts can be related to the recycling of oceanic crust into the mantle; however, models of this type differ greatly in explaining the timing and processes whereby their sources are refertilized (Hofmann & White 1980, 1982; Chase 1981; Ringwood 1982). It is widely held that the strong enrichments of incompatible elements in intraplate basalts coupled with their often depleted Nd and Sr isotopic ratios relative to bulk Earth ratios require that their source regions have been refertilized. Hofmann *et al.* (1986) made the important observation that intraplate basalts and MORBs possess similar Nb/U and similar Ce/Pb ratios, which are distinct from the primitive mantle ratio and those of average continental crust. The constancy of these ratios over a range of melting conditions can be explained by similar incompatibility of Nb and U (and likewise for Ce and Pb) during the genesis of these oceanic basalts (Hofmann *et al.* 1986). Both the MORB source, which is depleted in incompatible elements, and the intraplate basalt source, which is enriched in incompatible elements, share non-primitive mantle ratios of Ce/Pb and Nb/U that are for the most part complementary to the continental crust. These observations led Hofmann *et al.* (1986) to conclude that the source regions of oceanic basalts were rehomogenized after a major differentiation process which lead to extraction of much of the continental crust from the mantle.

A residual Nb–Ti-bearing phase, believed to be stable during the production of the refractory eclogitic lithology, is suggested to be responsible for causing the depletions of Nb and Ti in IAB (Saunders *et al.* 1980). This phase would be responsible for fractionating the Nb/U ratio between the melt and residue. A relatively constant Nb/U ratio in the source of MORB and intraplate basalts (Hofmann *et al.* 1986) is unlikely to be maintained if the sources of intraplate basalts were generated from these refractory eclogite lithologies.

Zindler & Hart (1986) defined a diversity of intraplate basalt compositional types including: HIMU (high  $\mu$  (or high  $^{206}\text{U}/^{204}\text{Pb}$ )), EM (enriched mantle) and PREMA (prevalent mantle). These basalt types display systematic variations in their chemical and isotopic compositions (figures 2 and 3). Although differences are small, HIMU basalts have higher Nb/U, Nb/Th, U/Pb and Ce/Pb and lower Nb/La, Rb/Sr

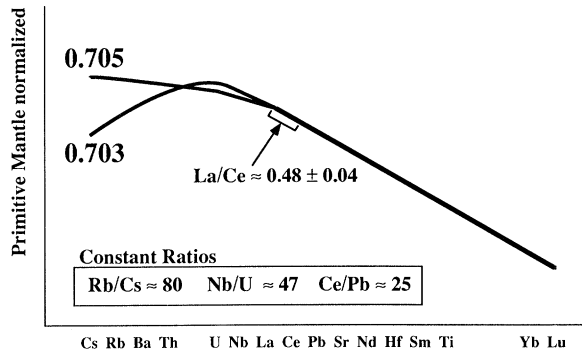


Figure 2. Schematic mantle normalized diagram illustrating the abundance pattern of incompatible elements in HIMU and EM-type intraplate basalts. The elements are ordered according to their relative incompatibility, with Cs, Rb and Ba being the most incompatible during melting (Sun & McDonough 1989). The idealized HIMU basalt has an incompatible element enriched pattern with elements more incompatible than Nb having a more depleted trend. This pattern is characteristically associated with high  $^{206}\text{Pb}/^{204}\text{Pb}$  and low  $^{87}\text{Sr}/^{86}\text{Sr}$  values. The idealized EM basalt is shown as also having an incompatible element enriched pattern, with elements more incompatible than Nb showing greater enrichments and higher  $^{87}\text{Sr}/^{86}\text{Sr}$  values than the HIMU basalts. Constant ratios of Rb/Cs, Nb/U and Ce/Pb are found in most unaltered intraplate basalts and MORB. Additionally, most alkalic intraplate basalts have a relatively constant La/Ce value (Sun & McDonough 1989).

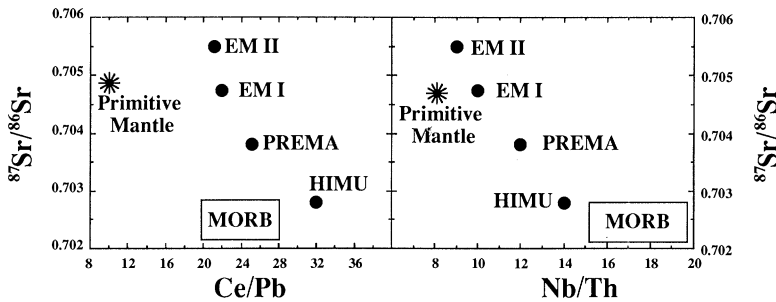


Figure 3. A schematic Ce/Pb and Nb/Th versus  $^{87}\text{Sr}/^{86}\text{Sr}$  diagram showing the range of values found in intraplate basalts, MORB and the primitive mantle. The terms HIMU, PREMA, EM I and EM II are from Zindler & Hart (1986) and represent the range of intraplate mantle reservoirs yet identified. These reservoirs are generally distinguished by their Sr, Nd and Pb isotopic compositions. These diagrams, however, illustrate that these intraplate basalt types can also be distinguished by certain element ratios. The values of Ce/Pb, Nb/Th and  $^{87}\text{Sr}/^{86}\text{Sr}$  for these mantle reservoirs and the primitive mantle are taken from table 3 in Sun & McDonough (1989). The continental crust has much lower Ce/Pb and Nb/Th values and a considerably higher  $^{87}\text{Sr}/^{86}\text{Sr}$  value.

and K/Nb values than EM basalts (figure 2) which are coupled with lower  $^{87}\text{Sr}/^{86}\text{Sr}$  (figure 3) and higher  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios in HIMU than in EM basalts (see also table 3 of Sun & McDonough 1989). This systematic co-variation in chemical and isotopic compositions is consistent with models which suggest that the peridotitic source of intraplate basalts has been refertilized early in its evolution by intramantle melting and fractionation processes (Ringwood 1982, 1990; Sun & McDonough 1989). The coherent regularities in chemical and isotopic composition within and between intraplate basalt types is unlikely to be produced by enrichment processes such as hydrothermal alteration of oceanic crust or contamination by continental-derived sediments.

Intraplate basalts show a range of Nb/La ratios from about 0.9 to 1.7, with many having a value of between 1.1 and 1.4 (as compared to MORB with ratios of 0.8–1.0). Weaver *et al.* (1987) and Saunders *et al.* (1988) suggest that the sources of typical oceanic intraplate basalts, particularly the HIMU basalts having high Nb/La values (more than 1.4), are derived by the addition of a component of recycled oceanic crust enriched in Nb and Ti. This interpretation is not unique; the high Nb/La ratios in these lavas do not necessarily reflect the source ratios (Sun & McDonough 1989). The relative abundance of Nb and La in intraplate basalts is very sensitive to the degree of partial melting involved in their genesis as well as the processes which have contributed to the refertilization of their source. Unlike MORBs, which are believed to be generated by large degrees of partial melting, many intraplate basalts are generated by lower degrees of melting and thus the source and lava Nb/La ratios will differ. Sun & McDonough (1989) have addressed this issue also. They observed that several Hawaiian basalt suites revealed markedly different Nb/La ratios and that a range of Nb/La ratios was produced by variable degrees of partial melting and, in some cases, by the (postulated) presence of a residual titanate mineral. Additionally, Sun & McDonough (1989) highlighted the fact that a Ua Pou (French Polynesia) tholeiite having HIMU chemical and isotopic characteristics possesses a subchondritic Nb/La value: i.e. it shows a Nb depletion relative to La. Moreover, intraplate basalts, including HIMU, EM and PREMA, do not show any evidence for excess Ti in their sources. They typically display subchondritic ratios of Ti/Zr (figure 1), Ti/Eu and Ti/Gd. Thus, these observations, in addition to the fact that the chemical and isotopic covariation found in intraplate basalts cannot be explained easily by such models, seem to imply that refractory eclogitic lithologies produced by the processing of subducted oceanic crust in the island arc environment are not reincorporated into the source regions of intraplate basalts.

It has recently been suggested that flood basalt volcanism may be the earliest phase of intraplate magmatism associated with the initiation of an ascending mantle plume (White & McKenzie 1989; Campbell & Griffiths 1990). If this is so these lavas may yield significant geochemical and isotopic information about the nature of the plume (intraplate) source region. Campbell & Griffiths (1990) suggested that the early phase picrites of the flood basalt provinces faithfully represent the geochemical composition of the plume source. In figure 4, examples are shown from the North Atlantic, Reunion-Deccan and Siberian provinces that have slight LREE-enrichments and do not display anomalous enrichments or depletions of Nb (i.e. they lack any observable 'Nb-kick'). These lavas have geochemical characteristics similar to EM-type intraplate basalts and their sources. Campbell & Griffiths (1990) cite other plume head picrites as possessing strong incompatible element-enrichments. However, they are not considered to be representative of these source regions and may have been contaminated by continental crust (Sun & McDonough 1989).

Archaean komatiites that are not contaminated by continental crust and N-type MORB are believed to be derived by large degrees of partial melting. Large volumes of mantle may have been sampled during the generation of these lavas. Interestingly, the mantle-normalized patterns of incompatible elements of both the komatiite and MORB samples shown in figure 4 are rather uniform and show a smoothly increasing depletion of elements with increasing incompatibility and no 'Nb-kick'. Such patterns are not expected for a mantle source region which has been modified by the addition of recycled oceanic crust enriched in Nb and Ti. A peridotite sample has a similar pattern to those shown by these lavas (figure 4), but at lower absolute



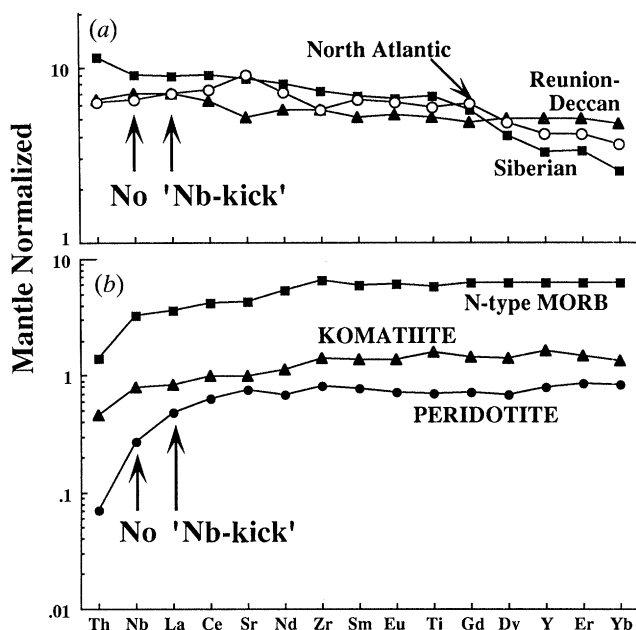


Figure 4. Mantle normalized diagram for mafic to ultramafic lavas and for a peridotite xenolith. The three plume head picrites (a), the komatiite and the N-type MORB represent magmas generated by large degrees of partial melting. The plume head picrites have relatively uniform incompatible element-enriched patterns, while the N-type MORB and komatiite have depleted patterns. Both the enriched and depleted patterns show no obvious 'Nb-kick' (i.e. no obvious depletion or enrichment of Nb relative to adjoining incompatible elements).

concentrations. Jochum *et al.* (1989) suggested that this peridotite pattern is chemically analogous to MORB sources. These data provide additional evidence that the depleted mantle does not possess obvious enrichments in Ti or Nb.

The overall variation of Ti/Zr ratios in a wide variety of lavas, as well as the average ratios for the continental crust, continental lithospheric mantle and depleted mantle (figure 1) further reveals that the continental crust and depleted mantle do not have complementary compositions. The lack of complementarity in both Nb/La and Ti/Zr ratios between the continental crust and depleted mantle can be balanced by invoking a refractory eclogitic reservoir enriched in Nb and Ti which is stored deep in the mantle. A refractory eclogitic reservoir, enriched in Nb relative to La and enriched in Ti relative to Zr, would be capable of providing the necessary complement to balance the continental crust and depleted mantle relative to the bulk silicate Earth (table 1). Table 1 presents the parameters for a simple mass balance calculation. The composition and masses of the continental crust and continental lithospheric mantle are taken from the literature (Taylor & McLennan 1985; McDonough 1990). The mass of the depleted mantle is assumed to be about 40% of the primitive mantle; however, estimates of the size of this reservoir vary greatly (between 20 and 80%). The composition of the depleted mantle is derived from a simple melting model, assuming that MORBs are generated by about 10% partial melting. The mass of the undepleted mantle is set at 55% and its composition is assumed to be equal to the primitive mantle.

From this model the composition and mass of the refractory eclogite reservoir can be estimated. The composition of this reservoir is derived by partially melting an N-

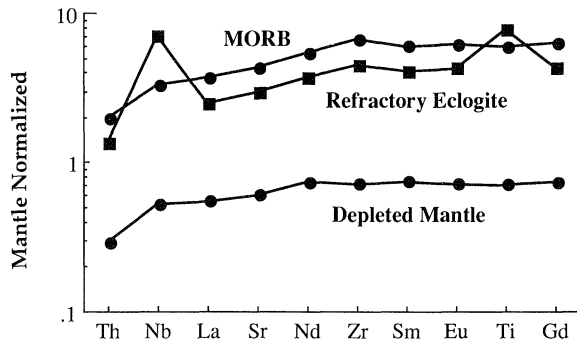


Figure 5. A mantle normalized diagram showing the relative incompatible element patterns of MORB, the depleted mantle (MORB source region) and an estimate of the refractory eclogite reservoir. Mantle normalizing values are from Sun & McDonough (1989).

type MORB which is representative of the upper 1–2 km of oceanic crust. Before this crust is melted it is estimated to have about 1.4 wt %  $\text{TiO}_2$ , 85 p.p.m. Zr, 2.9 p.p.m. La and 2.8 p.p.m. Nb (Hofmann 1988; Staudigel *et al.* 1989; Sun & McDonough 1989). This lithology is subjected to about 10% partial melting, leading to a depletion of 40% or more of its inventory of incompatible elements (except for Ti and Nb which are enriched in the residue by 25 and 50%, respectively). Figure 5 compares the incompatible element patterns of N-type MORB, its depleted mantle source and the above refractory eclogite. The total mass of oceanic crust produced and recycled back into the mantle throughout time is estimated to be between 5 and 10% of the mass of the silicate Earth, and is equivalent to about  $2\text{--}4 \times 10^{26}$  g of basalt. This value was derived by assuming that the present thickness of oceanic crust, plate production and consumption rate and area of seafloor (Parson 1981) has remained constant over the past 3.5 Ga. The proportion of subducted oceanic crust involved in island arc magmatism is estimated to be about 25% of the total amount of subducted oceanic crust, which is equivalent to the top *ca.* 1.7 km of a 7 km thick crust. The total mass of refractory eclogitic material is therefore estimated to be *ca.* 2% of the mass of the silicate Earth (table 1 shows that this is equivalent to about four times the mass of the continental crust).

These parameters provide a plausible numerical solution to balance the different silicate reservoirs in the Earth. This solution is non-unique; however, there is only a limited family of solutions which can satisfy the empirical constraints. The composition of the primitive mantle, continental crust, continental lithospheric mantle and undepleted mantle are reasonably well constrained in both their absolute and relative values. Likewise, the relative concentrations of elements in the depleted mantle and refractory eclogite are reasonably well constrained. The only parameter which can be changed is the inventory of elements in the depleted mantle and refractory eclogitic reservoir and these vary as a function of the assumed ratio of mass of depleted mantle to mass of undepleted mantle. The above calculation illustrates that a reservoir composed of refractory eclogitic material, enriched in Nb and Ti and comparable in size to the continental lithospheric mantle, satisfactorily accounts for the inventory of these elements in the entire silicate Earth.

### 3. Discussion

One of the consequences of the model proposed here is that continued storage of refractory eclogitic lithologies, characterized by enrichments in Ti and Nb, would produce a secular change in the composition of the depleted mantle. This process may also affect the abundance of other elements. Using primitive mantle xenoliths and komatiitic lavas, Palme & Nickel (1985) argue that the present day depleted mantle has a non-chondritic Ca/Al ratio. It is generally assumed, however, that the whole mantle started out with a chondritic Ca/Al ratio. Basalts and eclogites both have relatively high Ca and Al contents compared with the mantle and thus progressive accumulation of eclogitic material into an isolation reservoir could change the Ca/Al ratio of the depleted mantle with time. The refractory eclogitic reservoir was assumed to have average CaO and Al<sub>2</sub>O<sub>3</sub> contents of about 9 and 14 wt %, respectively (table 1) comparable with the compositions of MORB and eclogitic xenoliths. If the refractory eclogitic reservoir comprises *ca.* 2% of the mass of the silicate Earth, then it would contain a significant amount of Ca and Al relative to the bulk silicate Earth. This reservoir together with the continental crust would complement the depleted mantle and could produce a balance for the Ca/Al ratio of the bulk silicate Earth.

There may also be additional evidence for a secular change in the composition of the depleted mantle from Ti/Zr systematics. The sources of komatiites and MORBs are considered to have different Ti/Zr compositions. Moreover, it can be shown that Archaean komatiites are derived from depleted mantle sources. A comparison between MORB and komatiites (figure 1) suggests that there has been a secular decrease in the Ti/Zr ratio of the depleted mantle. This change can be attributed to the progressive removal of Ti relative to Zr from the depleted mantle and its storage in a refractory eclogite reservoir.

It is not possible to confidently establish evidence for a secular change of La/Nb ratios in the depleted mantle. More abundant and generally more precise data for Nb in komatiites, MORB and peridotites are needed before this idea can be properly tested. This remains an important goal in mantle geochemistry today.

The geochemical evidence for a refractory eclogitic reservoir isolated in the deep mantle is believed to be strong; however, the processes by which this reservoir have been isolated from the down going slab and kept at depth are poorly understood. Ringwood (1982) and Ringwood & Irifune (1988) suggest that the transportation and trapping of this material in a deep mantle reservoir was facilitated by density segregation. Studies of the viscosities and density contrasts of eclogitic and peridotitic materials and segregation mechanisms involved are likely to provide important insights into this regard.

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