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Nb and Pb in oceanic basalts: new constraints on mantle evolution

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Nb/U ratios and Ce/Pb ratios are surprisingly uniform at 47 ± 10 and 25 ± 5 , respectively, in both mid-ocean ridge basalts (MORB) and ocean island basalts (OIB). We show that these ratios also characterize the mantle sources of *both* types of oceanic basalts, and that these mantle sources have been fractionated from the primitive-mantle ratios of Nb/U = 30 and Ce/Pb = 9. The respective ratios in the continental crust are even lower, namely Nb/U = 10 and Ce/Pb = 4. Therefore, OIB cannot be derived from a primitive portion of the mantle, from mixtures of primitive and depleted mantle, or from recycled continental crust. The portion of the primitive mantle from which the continental crust and the residual (MORB plus OIB source) mantle has been differentiated is estimated to be about 50%, but the uncertainties are such that whole-mantle differentiation cannot be ruled out.

We propose the following simple model to satisfy the above new constraint on mantle composition: The differentiated part of the mantle, chemically depleted after separation of the major portion of the continental crust, was subsequently internally rehomogenized. This depleted but chemically homogeneous mantle region was then differentiated into MORB and OIB source regions. The primary (continental crust–mantle) differentiation fractionated the Nb/U and Ce/Pb ratios, but the secondary (MORB source–OIB source) differentiation did not. Following the model of Hofmann and White [1,2], we suggest that the mechanism chiefly responsible for the secondary differentiation is the formation and subduction of oceanic crust. It is volumetrically by far the most important ongoing differentiation process on Earth and, over the course of Earth history, has created at least ten times as much oceanic crust as the present-day volume of continental crust.

Because the residual mantle was homogenized (though depleted in incompatible elements) after the primary differentiation, the isotopic and chemical heterogeneities exemplified by the isotope ratios of Sr, Nd, Hf, and Pb, and by trace element ratios such as K/Rb, were created during the secondary differentiation. During this process, the bulk partition coefficients of Nb and Ce were very similar to those of U and Pb, respectively. This is in contrast with the primary differentiation, during which U was more incompatible than Nb, and Pb more incompatible than Ce.

1. Introduction

In this paper, we describe a new way of using trace element ratios to constrain the present-day composition of the Earth's mantle and its evolution. This method differs from established approaches of using isotope and trace element ratios: unlike isotope ratios which yield time-integrated mother-daughter ratios of the source, and unlike conventional indicator ratios like La/Sm, K/Rb, or Zr/Nb, all of which are known to be easily fractionated by at least some igneous processes (for example at small degrees of melting), a trace element ratio that is uniform in all types of oceanic basalts (MORB and OIB) and is indepen-

dent of the absolute concentrations of the elements involved, is almost certainly unfractionated relative to the same element ratio in the mantle source, regardless of location and general degree of source and/or melt depletion or enrichment. In other words, the measured element ratio in the basalts is the same as the present-day ratio in the mantle.

Several such ratios have been established in the past, e.g. Zr/Hf, Nb/Ta, Ba/Rb, Cs/Rb, K/U and Y/Ho [3–7]. In these cases (with the possible exception of Cs/Rb), there is good reason to believe that the ratios are not only unfractionated in the present-day mantle, but that they also represent the bulk-silicate Earth, which is synonymous with the “primitive”-mantle composition. In other words, the element pairs behaved so much alike during all the processes affecting the con-

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centrations of the elements, that their ratios retained their original, primitive values.

What distinguishes the new "tracer ratios", Nb/U and Ce/Pb, from the previously established ones is that they demonstrably differ from the primitive-mantle values. The fact that such uniform but non-primitive ratios exist in the present-day mantle, places a new, and in our opinion important constraint on the evolution of the mantle.

2. Global geochemistry of Nb and Pb

The elements niobium and lead have unusual geochemical properties, which have been noticed by previous workers. Nearly all recent oceanic basalts have Pb-isotopic compositions that require an increase in the U/Pb and Th/Pb ratios at some time in the past, but substantially later than the accretion of the Earth. A simple loss of Pb from the mantle (combined with some Th/U fractionation) would accomplish this, and several authors have speculated whether the missing lead has gone into the core [8–10], or into the continental crust [11]. Newsom et al. [12] have investigated the possibility of late Pb migration to the core by studying the abundance of another, more highly chalcophile element, Mo, and concluded that such a late migration of chalcophile elements into the core did not occur. They favor the other alternative, migration to and storage in the continental crust. Niobium, on the other hand, has for some time been known to be deficient in the continental crust and in subduction-related volcanics. Wood et al. [13] and Tarney et al. [14] observed that Ta (an element of nearly identical ionic radius and charge as Nb) and Nb are "overabundant" in oceanic island basalts. However, no such anomalies were noticed in MORB. Hofmann et al. [15] have compared average abundances of MORB and continental crust by using generalized Coryell-Masuda diagrams [16], and found that Nb, Ta, Pb, and Sr do not simultaneously conform to a smooth abundance pattern on the diagrams for continental and oceanic crust, respectively. All the other (lithophile) trace and major elements conform to and indeed define such smooth patterns. This implied that Nb (and Ta) may be anomalous not only in OIB, but also in MORB.

3. Analytical methods and results

We have analyzed the MORB and OIB samples for Nb, U, Ce and Pb by spark source (SSMS) and thermal ionization mass spectrometric isotope dilution (ID). Part of the data have been published previously [6,12]. The analytical methods have also previously been described [17–19]. The results are listed in Table 1.

Nb/U ratios versus Nb concentrations are shown in Fig. 1. Special care was taken to ensure sample freshness, because U concentrations are known to be easily affected by low-temperature alteration. In particular, MORB samples may take up significant amounts of U from seawater. Therefore, all our MORB samples have been hand picked to contain only completely unaltered basalt glass. The OIB samples were also screened to select fresh samples from historic eruptions wherever possible. Despite these efforts, it is possible that some of the scatter in Fig. 1 is caused by alteration. Nevertheless, the least-squares linear fit of the Nb/U ratio versus Nb concentration has a slope that does not significantly differ from zero. The mean of the Nb/U ratios is $Nb/U = 47 \pm 10$ (1 standard deviation of the population). This differs significantly from the chondritic value of $Nb/U = 30$ [20] and from estimates of the continental-crust average of $Nb/U = 9-12$ [21–24].

Ce/Pb ratios versus Ce concentrations are shown in Fig. 2. Many of the samples represented in Fig. 2 are the same as those shown in Fig. 1, but the overall data base is smaller. Nevertheless, it is clear that the least-squares fit also has a zero slope and that the mean $Ce/Pb = 25$ is larger than the bulk-earth value of 9 (inferred from the U/Pb ratio derived from terrestrial lead samples and from the chondritic Ce/U ratio of 76 [12]).

4. Trace element ratios in basalts and their source rocks

Normalized abundance plots of the Coryell-Masuda type (which for unknown but deplorable reasons are frequently called "spidergrams" [25]) suffer not so much from the uncertainty of the normalizing quotient (in this case the primitive-mantle abundances, which are reasonably well known for the lithophile elements), but from the lack of generally applicable criteria as to the order

TABLE 1

Analytical results

Sample	Nb ^a (ppm)	U (ppm)	Ce (ppm)	Pb (ppm)	Nb/U ^f	Ce/Pb ^f
<i>Mid-ocean ridge basalts</i>						
<i>Atlantic Ocean</i>						
205	2.54	0.0561 ^d	15.8 ^a	0.576 ^a	45.3	27.4
192	2.42	0.0598 ^d	13.1 ^a	0.507 ^a	40.5	25.8
198	2.25	0.0585 ^d	15.5 ^a	0.495 ^a	42.3	31.3
		0.0478 ^b		0.496 ^b		
941	4.71	0.0952 ^d	14.6 ^a	0.711 ^a	49.5	20.5
937	3.21	0.0662 ^d	11.4 ^a	0.556 ^a	48.5	20.5
744	4.49	0.0838 ^d	12.2 ^e	0.454 ^a	53.6	26.9
968	1.28	0.0255 ^d	5.74 ^a	0.201 ^a	50.2	28.6
965	2.06	0.0523 ^d	8.96 ^a	0.399 ^a	39.4	22.5
367	2.27	0.0473 ^d	6.76 ^a	0.406 ^a	48.0	16.7
962	1.45	0.0330 ^d	4.57 ^a	0.204 ^a	44.4	23.3
		0.0323 ^b		0.189 ^b		
GS 7309-75	6.97	0.129 ^d	14.7 ^b	0.520 ^b	54.0	28.3
GS 7309-94	3.69	0.0836 ^d	11.0 ^b	0.495 ^b	44.1	22.2
P 6909-28	5.15	0.0993 ^d	14.2 ^b	0.589 ^b	51.9	24.1
200	21.3	0.428 ^d	29.2 ^a	1.13 ^a	52.0	27.0
		0.391 ^b		1.03 ^b		
<i>Pacific Ocean</i>						
798	3.96	0.0741 ^d	10.6 ^a	0.463 ^a	53.4	22.9
973	2.17	0.0435 ^d	7.54 ^a	0.345 ^a	49.9	21.9
D 10-1	5.07	0.112 ^d	13.8 ^a	0.592 ^a	45.3	23.3
D 10-2	6.18	0.125 ^d	17.8 ^a	0.610 ^a	49.4	29.2
D 10-3	5.61	0.116 ^d	14.4 ^a	0.495 ^a	48.4	29.1
R3-3 D-10	5.57	0.104 ^d	17.4 ^b	0.709 ^b	53.6	24.5
R3-3 D-30	4.74	0.115 ^d	15.7 ^b	0.686 ^b	41.2	22.9
768	1.18	0.0215 ^d	5.76 ^a	0.362 ^a	62.9	16.4
		0.016 ^b		0.340 ^b		
K10A D33A	5.93	0.106 ^c	23.1 ^c	0.684 ^c	55.9	33.8
K62A D143G	6.48	0.115 ^c	12.8 ^c	0.426 ^c	56.3	30.0
K71A D130H	6.83	0.144 ^c	20.7 ^c	0.561 ^c	47.4	36.9
K73A D123H	0.690	0.008 ^c	3.75 ^c	0.168 ^c	86.3	22.3
H70	14.4	0.276 ^d	24.4 ^a	1.38 ^a	52.2	17.7
<i>Indian Ocean</i>						
F83	1.89	0.0455 ^d	11.8 ^a	0.645 ^a	41.5	18.3
AII93-11-103		0.034 ^c	9.12 ^c	0.514 ^c		17.7
3095		0.038 ^c	9.13 ^c	0.505 ^c		18.1
<i>Ocean island basalts</i>						
<i>Azores</i>						
F-33	46.2	1.38 ^c	74.9 ^c	3.02 ^c	36.4	24.6
		1.16 ^a	73.7 ^a			
SM-12	62.4	1.55 ^a			40.3	
SM-6	68.5	1.39 ^a			49.3	
P-21	34.7	0.710 ^a			48.9	
<i>Galapagos</i>						
Sant. E-20	13.9	0.279 ^a			49.8	
Isab. ZOB6	23.6	0.475 ^a			49.7	
<i>St. Helena</i>						
2882	38.5	0.857 ^a			44.9	
2926	73.2	1.45 ^c	103 ^c	2.83 ^c	46.6	34.3
		1.69 ^a	91 ^a			
2928	61.6	1.31 ^a			47.0	
102	130	2.51 ^a	160 ^c	4.74 ^c	51.8	33.8

TABLE 1 (continued)

Sample	Nb ^a (ppm)	U (ppm)	Ce (ppm)	Pb (ppm)	Nb/U ^f	Ce/Pb ^f
<i>Samoan Islands</i>						
VP-1	49.7	1.10 ^a			45.2	
VP-2	44.3	0.498 ^a			89.0	
UPO-7	76.1	1.62 ^c	169 ^c	5.02 ^c	45.7	33.7
		1.71 ^a				
82-MT-15	36.4	0.740 ^c	67.7 ^c	2.43 ^c	46.5	27.9
		0.824 ^a				
JKU-1	58.0	1.61 ^a			36.0	
US-1	41.5	1.12 ^a			37.1	
SAV-1	50.9	1.05 ^a			48.5	
<i>Hawaiian Islands</i>						
<i>Loihi Seamount</i>						
Dredge 2	18.1	0.294 ^a			61.6	
Kil DAS 69-1-3	16.3	0.334 ^a			48.8	
Kil DAS71-1213-136	12.5	0.278 ^a			45.0	
KL-2	17.0	0.330 ^a	33.7 ^c	1.02 ^c	51.4	33.0
		0.332 ^a				
ML-3B	10.0	0.177 ^c	23.6 ^c	0.856 ^c	53.5	27.0
		0.197 ^a	22.6 ^a			
<i>Tristan da Cunha</i>						
TR-1	148	3.40 ^c	209 ^c	9.28 ^c	42.2	22.9
		3.62 ^a	216 ^a			
TR-4	74.3	1.79 ^c	122 ^a	4.70 ^c	41.5	26.0
TR-5	87.4	2.23 ^a			39.2	
TR-6	98.7	2.46 ^a			40.1	
<i>Gough Island</i>						
G-8	46.0	1.09 ^a			42.2	
<i>Society Islands</i>						
Hauh 769	75.2	3.73 ^a			20.2	
Tahi 343	45.5	1.10 ^a			41.4	
Tahi 351	47.3	1.01 ^a			46.8	
Tahaa 73-185	61.3	3.06 ^a			20.0	
<i>Comoros</i>						
AJ10-1	39.4	0.708 ^a			55.6	
AJ21-9	42.8	0.864 ^a	69.5 ^b	4.24 ^b	49.5	16.4
<i>Reunion</i>						
RE 24-1	26.5	0.629 ^c	49.0 ^c	2.06 ^c	42.1	23.8
<i>Macquarie Islands</i>						
60825	57.4	1.46 ^a			39.3	
60701	27.5	0.590 ^a			46.6	
47979	7.49	0.170 ^a			44.1	
40428	32.9	0.800 ^a			41.1	
38390	11.9	0.256 ^a			46.5	
38334	6.78	0.145 ^a			46.8	
3845	4.11	0.0899 ^a			45.7	

^a SSMS.^b ID.^c Newsom et al. [12].^d Jochum et al. [6].^e INAA (Spettel and Göpel, unpublished).^f Element ratios calculated from the mean concentrations in case of multiple analyses.

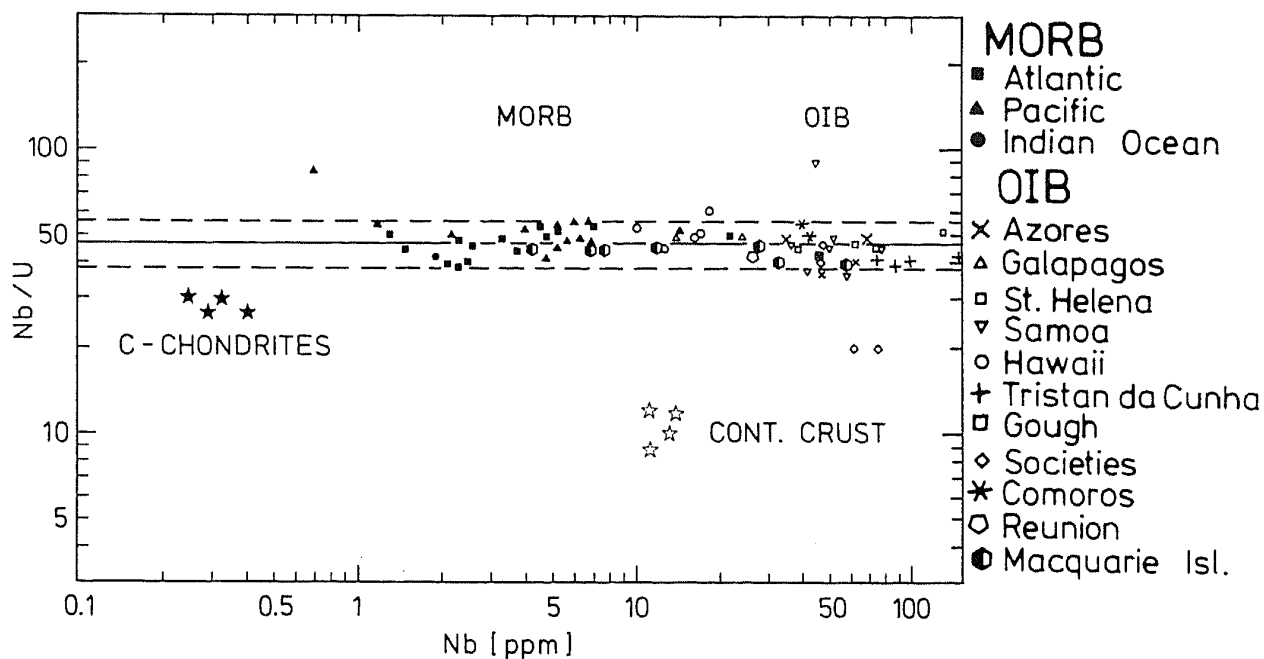


Fig. 1. Nb/U ratios versus Nb concentrations in fresh glasses of mid-ocean ridge basalts (MORB) and oceanic island basalts (OIB). The Nb/U ratio of 47 ± 10 (1σ) is significantly higher than the ratios found in the carbonaceous chondrites (solid stars) Orgueil, Murchison, Murray and Allende (Nb: Jochum et al. [20]; U: Tatsumoto et al. [60]) and estimates for average continental crust (open stars) [21–24].

in which to place the elements on the abscissa. Because of this, it is not always easy to identify abundance anomalies unambiguously when using this diagram. Most commonly, though implicitly, the normalized abundances in ordinary (“N-type”) MORB are used to order the sequence of elements

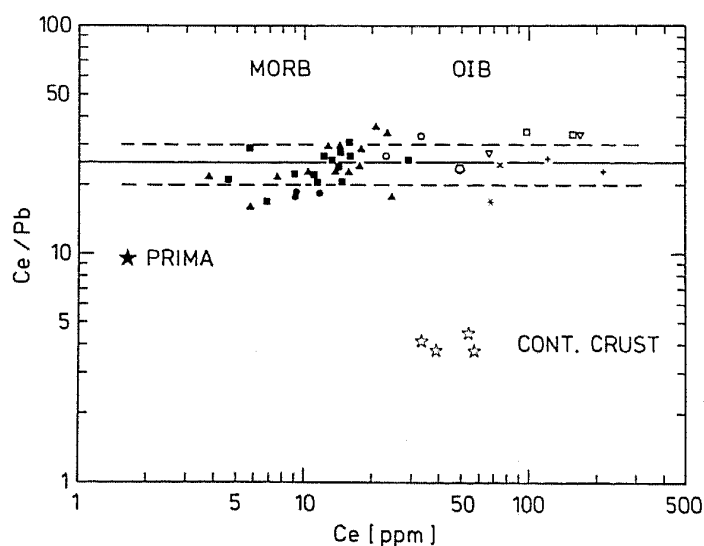


Fig. 2. Ce/Pb ratios versus Ce concentrations in oceanic basalts. Symbols are as in Fig. 1. Instead of chondrite values, we show our best estimate for the bulk silicate earth, the star labeled PRIMA (= primitive mantle). It is derived from the chondritic value of $Ce/U = 76$ and a terrestrial value of $U/Pb = 0.12$ estimated from terrestrial Pb isotopic abundances.

in such a way that a smooth abundance pattern is created (see for example fig. 4 of Sun et al. [26], which is the basis of most subsequent publications on this subject). By this procedure, it is a priori impossible to detect any anomaly in the abundance pattern for that set of samples. Because of this, we believe that the statement of Weaver [27] to the effect that Nb and Ta abundances are normal in MORB but overabundant in OIB is not justified by the data. Application of this same procedure to REE patterns in shales would obliterate the positive Eu anomaly that is almost universally present in these rocks [22].

To avoid the difficulty just discussed, we have chosen to search for other trace elements, which not only correlate well with Nb and Pb in oceanic basalts, but which form approximately constant concentration ratios with Nb and Pb. These elements are U and Ce, respectively. The reason for this procedure is as follows: When an element ratio is fractionated by the partial melting process at all, the degree of fractionation will in general vary with the melt fraction. Only under special conditions may an element ratio in the melt be uniform and independent of the magnitude of the melt fraction. This is best illustrated by using the (“batch”) equilibrium, non-modal melting equa-

tion with constant partition coefficients, as introduced by Shaw [28]:

$$\frac{C}{C^\circ} = \frac{1}{D^\circ + F(1-P)} \quad (1)$$

where C° is the concentration in the source, C the concentration in the melt, D° the bulk partition coefficient of the minerals weighted in the proportions in which they exist in the original source, and P the bulk partition coefficient of the minerals weighted in the proportions in which they enter the melt.

The concentration ratio of two elements (labeled by subscripts 1 and 2) in the melt is therefore:

$$\frac{C_1/C_2}{(C_1/C_2)_0} = \frac{D_2^\circ + F(1-P_2)}{D_1^\circ + F(1-P_1)} \quad (2)$$

Normally, the concentration ratio changes as a function of melt fraction, so that equation (2) starts with a value of D_2°/D_1° when $F \ll D_{1,2}$, and ends up with a value of one when $F \gg D_{1,2}^\circ$ and $P_{1,2}$. Also normally, when $D_1^\circ > D_2^\circ$, we have $P_1 > P_2$, and at low and intermediate melt fractions the concentration ratio in the melt will be $C_1/C_2 < (C_1/C_2)_0$ because element 1 is preferentially retained in the source. We may also write the equation for the concentration ratio in another form by eliminating F , as shown by Minster and Allègre [29], and obtain:

$$\frac{C_1}{C_2} = \left[D_2^\circ - D_1^\circ \left(\frac{1-P_2}{1-P_1} \right) \right] \cdot \frac{C_1}{C_2^\circ} + \frac{C_1^\circ}{C_2^\circ} \left(\frac{1-P_2}{1-P_1} \right) \quad (3)$$

which is a straight line in C_1/C_2 vs C_1 space if P_1 and P_2 are constants. This line has the slope:

$$S = \frac{1}{C_2^\circ} \left[D_2^\circ - D_1^\circ \left(\frac{1-P_2}{1-P_1} \right) \right] \quad (4)$$

The concentration ratio C_1/C_2 is constant and independent of both the melt fraction and of the absolute concentrations when this slope $S = 0$.

There are two possible conditions where this is true. The first is when:

$$D_1^\circ = D_2^\circ = 0 \quad (5)$$

which requires that:

$$P_1 = P_2 = 0 \quad (5')$$

and therefore:

$$\frac{C_1}{C_2} = \frac{C_1^\circ}{C_2^\circ} \quad (6)$$

This is the limiting case when both elements are perfectly incompatible and the concentration ratio in the melt is therefore always equal to the ratio in the source. Examples of this situation are the uniform Ba/Rb and Cs/Rb ratios in oceanic basalts (MORB and OIB) [5].

The second possible, and potentially troublesome, condition for a zero slope is derived directly from (4):

$$\frac{D_2^\circ}{D_1^\circ} = \frac{1-P_2}{1-P_1} \quad (7)$$

in which case:

$$\frac{C_1}{C_2} = \frac{D_2^\circ \cdot C_1^\circ}{D_1^\circ \cdot C_2^\circ} \quad (8)$$

Condition (7) is possible only under two rather special circumstances, the first of which is the trivial condition:

$$D_2^\circ = D_1^\circ \text{ and } P_2 = P_1. \quad (9)$$

In this case, equation (6) is still valid, that is the concentration ratio in the melt is the same as that in the source. Examples are elements with (nearly) identical ionic charges and radii, such as Zr-Hf, Nb-Ta, and Y-Ho.

The second circumstance is given by special combinations of D° and P , which are distinguished by the property that:

$$D_2^\circ > D_1^\circ \text{ and } P_2 < P_1 \text{ (or vice versa)} \quad (10)$$

and which satisfy equation (7). Such combinations of D° and P are given in Fig. 3. This shows that at least one of the two P values must in general be quite large (e.g. $P_1 \geq 0.5$) if the ratio of D° values is very different from unity (e.g. $D_2^\circ/D_1^\circ \geq 2$). (Exceptions to this rule exist for peritectic relationships, which permit negative P -values for certain compatible elements, for example Ni if olivine is produced during melting. However, this is not relevant to the incompatible elements treated in this paper and will not be further elaborated.)

The trace elements considered in this paper are all moderately to highly incompatible in the major mineral assemblages of the mantle that are capa-

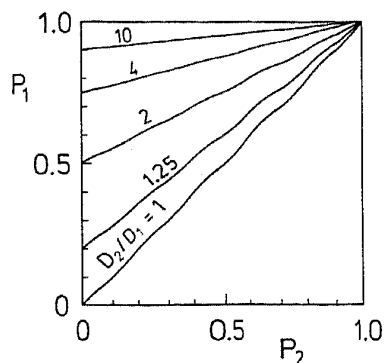


Fig. 3. Relationship of the bulk partition coefficients P_2 and P_1 , derived from equation (7) for different ratios of the bulk partition coefficients D_2^0/D_1^0 of two elements 1 and 2. This shows the conditions where equilibrium partial melts yield constant concentration ratios C_2/C_1 , that are independent of melt fraction.

ble of producing basaltic melts. Minor minerals (such as phosphates or titanium oxides) that may have large partition coefficients for U, Nb, Ce or Pb will in general constitute less than 1 percent of the mantle assemblages. As a consequence, the range of possible melt fractions, for which Fig. 3 and condition (10) holds, is severely limited by the large magnitude of P_2 . The reason for this limitation is that the mineral phase responsible for the large difference between D_2^0 and P_2 must have a large partition coefficient for element 2, and it must be present in very small proportion in the source (thus permitting the small bulk D^0 value) but enter the melt in large proportion (thus causing the large bulk P value). This means that the critical mineral phase that is responsible for the phenomenon is used up at very small melt fractions. The maximum melt fraction to which such a phase survives in the residue is given by:

$$F_{\max} = x/p$$

where x is the weight fraction of the mineral in the initial source and p is the fraction it contributes to the melt (nomenclature of Shaw [28]). Because of this limitation, the conditions described by equations (7) and (10) are of little practical significance when the range of melt fractions encountered is at least on the order of 1–10% as it must be if both OIB and MORB melts are concerned. All of this merely confirms that which is intuitively obvious, namely that any melt-concentration ratio that is constant over a wide range of melt fractions is also identical to the source-

concentration ratio. We shall now apply this conclusion to the results shown in Figs. 1 and 2.

5. Constraints on OIB-source reservoirs and mantle evolution

Figs. 1 and 2 show that Nb/U and Ce/Pb ratios are essentially the same in the mantle sources of both MORB and OIB, but they are significantly different from the respective ratios in carbonaceous chondrites (Fig. 1) and in the primitive Earth's mantle (Fig. 2) and from those in the continental crust. This is contrary to the trace element patterns normally encountered. For example, Rb/K, Th/U, and La/Sm ratios are all significantly lower in MORB than in the primitive mantle and in the continental crust, but all these ratios do not remain uniform but become larger, as more enriched MORB or yet more enriched OIB samples with higher absolute concentrations of incompatible elements are considered.

The fact that the elements depleted in the MORB mantle will normally form concentration dependent ratios (cf. Rb/K, Th/U, La/Sm) is conventionally explained in one of two fundamentally different ways: (1) Variable depletion causes variable element ratios in the depleted residue. This can be readily derived from equation (1). (2) The depleted region in the mantle is well homogenized and has uniform element ratios. The variable ratios actually observed in MORB and OIB result from mixtures of this homogenized, depleted reservoir (having low Rb/K, Th/U, and La/Sm) with one or more undepleted (primitive) or enriched reservoirs with high Rb/K, Th/U, and La/Sm ratios. (A possible third explanation that would ascribe all the observed effects to complex melting mechanisms [30,31] or to crystal fractionation of initially identical primary magmas [32] is excluded because of the isotopic differences between MORB and OIB.)

The uniform, but fractionated Nb/U and Ce/Pb ratios are not consistent with the first of the above explanations, variable depletion. If the separation of the continental crust left a variably depleted residual mantle region, this region must have been subsequently (or concurrently) homogenized so as to produce uniform Nb/U and Ce/Pb. It is then very difficult to escape the conclusion that the other incompatible-element ratios (as well

as the isotopic ratios) were also homogenized at the same time, because mixing in the mantle is almost certainly caused by convective stirring, not any purely chemical (or diffusive) process [33].

The Nb/U and Ce/Pb ratios also constrain the possible source reservoirs of ocean island basalts. They are *not* consistent with the idea that the OIB are derived from a *primitive* or relatively undepleted region of the mantle, because these ratios do not have primitive values and show no tendency toward them. This is a strong negative constraint on the sources of all the oceanic-island basalts sampled for this study. It cannot be offset by evidence such as may be obtained from noble gases, because any such evidence can at best provide necessary, but certainly not sufficient conditions for a primitive source reservoir.

The results are also not consistent with the hypothesis that OIB are derived from a lower mantle that has been modified by exchange with the core (e.g. "core pumping" [10] invoked to remove Pb from the lower mantle), while MORB are derived from a separately convecting upper mantle that has been depleted by crust formation. Such a hypothesis would require that the two separate interactions, namely that with the crust and that with the core, would change the Nb/U and Ce/Pb ratios in such a way that each of these ratios would then be non-primitive but identical in the two mantle reservoirs. We reject this hypothesis simply because it requires too much special pleading.

Finally and for the same reasons, the trace element enrichment characterizing the OIB sources cannot be ascribed to recycled continent-derived sediments (as proposed, for example, by Armstrong [34] or by White and Hofmann [35]), and in this case the discrepancy in the diagnostic trace element ratios is even greater. This latter conclusion has previously and independently been reached on the basis of Lu/Hf ratios in sediments [36] and other geochemical evidence [37].

Not eliminated by this constraint are "intra-mantellic" enrichment processes, such as melt migration proposed, for example, by Green and Liebermann [38] and by Anderson [39], or recycling of subducted *oceanic* crust [1,2,40,41]. Such processes are consistent with our data as long as they do not change Nb/U and Ce/Pb.

6. Mass balance for crust and mantle

It is generally accepted that the depletion of incompatible elements found in MORB and their mantle sources is complementary to and caused by the separation of the (correspondingly enriched) continental crust. This complementary behavior also applies to the elements Nb, U, Ce and Pb. The mass balance between continental crust (subscript CC), residual mantle (subscript RM), and primitive mantle (subscript PM) is:

$$U_{CC} = \frac{(Nb/U)_{RM} \cdot U_{PM} - Nb_{PM} + X_{CC} \cdot Nb_{CC}}{(Nb/U)_{RM} \cdot X_{CC}} \quad (11)$$

and:

$$Pb_{CC} = \frac{(Ce/Pb)_{RM} \cdot Pb_{PM} - Ce_{PM} + X_{CC} \cdot Ce_{CC}}{(Ce/Pb)_{RM} \cdot X_{CC}} \quad (12)$$

where the chemical symbols U, Nb, Ce, and Pb denote the concentrations or concentration ratios of these elements in the reservoirs indicated by the subscripts. X_{CC} is the weight percentage of the continental crust relative to that portion of the primitive mantle which has been fractionated by this crust-mantle differentiation. These equations are evaluated in Figs. 4 and 5. In contrast with all published mass balances based on isotopic data [42-46], which include the MORB source as the only residual mantle reservoir, these balance equations include explicitly both the MORB and OIB source reservoirs. This intrinsic advantage is offset by our comparatively poor knowledge of the crustal abundances of U and Pb. Published estimates of these abundances differ by as much as a factor of two (Figs. 4 and 5).

Fig. 4 shows the mass balance for Nb and U. The primitive mantle values of Nb = 630 ppb and U = 21 ppb are 2.6 times the respective abundances in C1 chondrites [20]. This procedure has been justified for refractory elements by Jagoutz et al. [47] and agrees well with more recent estimates [48]. The crustal abundance of Nb = 11 ppm is taken from Taylor and McLennan [21]. The results of equation (11) are not very sensitive to errors in this value. The shaded area in Fig. 4 is the percentage of continental crust relative to the total silicate portion of the Earth ($X_{CC} = 0.55\%$

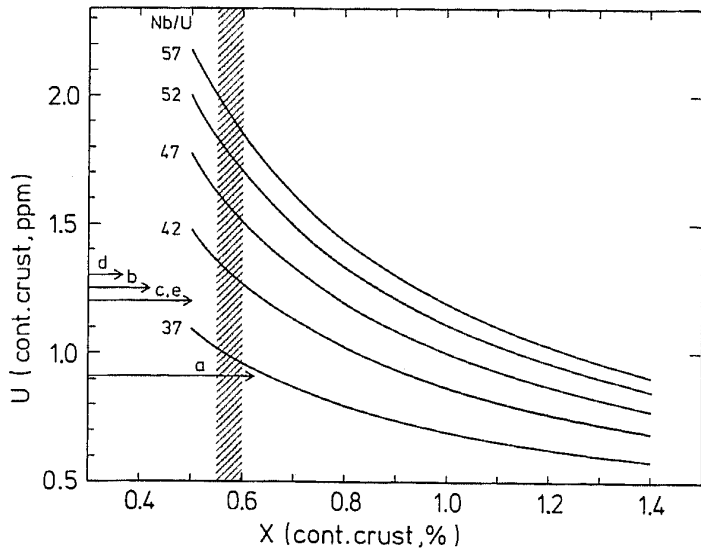


Fig. 4. U concentration in the continental crust as function of mass fraction X of crust relative to the amount of primitive mantle which has been differentiated into crust and residual mantle calculated from equation (11). The shaded region is the mass fraction of crust relative to the *total* primitive mantle. The arrows give estimates of the U abundance in the continental crust according to (a) Taylor and McLennan [22]; (b) Taylor and McLennan [21]; (c) Wedepohl [24]; (d) Weaver and Tarney [23]; (e) Zindler and Hart [61]. The labels correspond to different Nb/U ratios of the primitive mantle. The assumed Nb concentration in the continental crust is 11 ppm. Assumed primitive-mantle abundances are Nb = 630 ppb, U = 21 ppb.

[43]; $X_{CC} = 0.60\%$ [45]). The three curves give the calculated crustal uranium abundances for the present-day mantle ratio of Nb/U = 47 (best

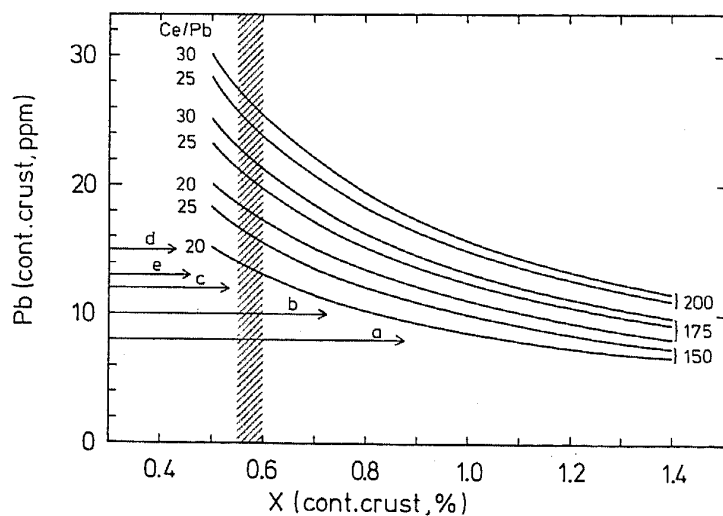


Fig. 5. Pb concentration in the continental crust calculated from equation (12), for three values of Pb in the primitive mantle, 150, 175 and 200 ppb and for the ratios of Ce/Pb = 20, 25, 30. Overlapping curves have been omitted. For further details see Fig. 4.

estimate), 37 and 57 (estimated lower and upper bounds).

The results show that for the shaded region and Nb/U = 47, the crustal abundance of uranium would have to be 1.5–1.6 ppm, which is higher than all four published estimates indicated (0.9–1.3 ppm). If the lowest estimate of crustal uranium (0.9 ppm) is correct, then the Nb/U ratio of the mantle requires that the continental crust amounts to 1.15% of the differentiated crust–mantle system. Unless there are hidden reserves of Nb and U in the subcontinental lithosphere, this would mean that only half the mass of the mantle has been differentiated and that the remainder is still primitive but is *not sampled* by either MORB or OIB. However, in view of the uncertainties in the crustal and mantle abundances involved, we caution against accepting this conclusion uncritically. In this respect, the mass balance based on Nb and U is no better, but probably also no worse, than the balance based on Nd isotopes [45].

Fig. 5 shows the evaluation of equation (12). The three families of curves are for primitive-mantle abundances of Pb = 175 ppb (preferred value), 150 and 200 ppb (estimated lower and upper bounds), and for Ce/Pb ratios of the residual MORB-OIB mantle of 25 (preferred value), 20 and 30 estimated lower and upper bounds; overlapping curves have been omitted for clarity. The “preferred” value of $Pb_{PM} = 175$ ppb is based on a present-day $^{238}U/^{204}Pb = 8.88$, and a present-day Pb-isotopic composition of $206/204 = 18.21$, $207/204 = 15.51$ and $208/204 = 38.86$, all calculated by global inversion [49] and the same U value as above. The shaded region corresponding to $X_{CC} = 0.55–0.60\%$ shows that the preferred parameters would require a crustal Pb concentration of 20 ppm, which is again higher than any of the four published estimates. To be consistent with the lowest estimates of crustal Pb = 8–10 ppm, the crustal mass fraction would have to be at least two to three times greater than the 0.55–0.6% indicated by the shaded region. Again, this would mean that only half of the primitive mantle (or less) has been differentiated to form continental crust and residual (MORB and OIB) mantle. Although this independently confirms the conclusions derived from Fig. 4, we emphasize again the cumulative uncertainties involved. Because of this, we regard the qualitative constraints developed

above as more important and stringent than the quantitative estimates illustrated in Figs. 4 and 5. In the remainder of this paper, it should be understood that the mantle evolution model developed refers only to that portion of the mantle which has been differentiated into continental crust and residual MORB-source and OIB-source reservoirs. Although the magnitude of this portion is still uncertain, it now seems likely that this portion constitutes only about half of the mantle.

7. Mantle evolution model

The simplest model that is consistent with the constraint of a chemically fractionated but re-homogenized (MORB and OIB source) mantle incorporates the following formal stages:

(1) Depletion: The mantle is chemically depleted by the removal of incompatible elements. The relative depletion is greater for U than for Nb, and greater for Pb than for Ce.

(2) Homogenization: During or after the depletion event(s) of stage one, the mantle is internally (re)homogenized.

(3) Internal differentiation: After initial depletion and rehomogenization, the mantle is differentiated into more highly depleted (= MORB source) and relatively enriched (= OIB source) reservoirs. During this renewed differentiation, Nb/U and Pb/Ce are no longer fractionated but remain constant and independent of absolute enrichment or depletion.

The differences between stages (1) and (3) imply a fundamental difference in the fractionation mechanism. Stage (1) must in some way be connected with the formation of continental crust, because its result was the present-day difference in Nb/U and Ce/Pb ratios between crust and mantle. Therefore it seems reasonable to infer that stage (3) differentiation was *not* connected with the formation of continental crust. To the best of our knowledge, the most important ongoing differentiation process in the Earth is the formation of *oceanic* crust. It produces about 20 km³ of enriched rock per year and leaves a depleted residue of about 10 times that volume.

Subduction therefore transfers large quantities of both enriched and depleted material back into the mantle. Numerical mixing experiments [50,51] have suggested that these differentiated reservoirs

should be rehomogenized in the mantle after a comparatively short time. Nevertheless, the combined chemical and isotopic record from MORB and OIB proves beyond reasonable doubt that the mantle is not now in a well-homogenized state. To reconcile the geochemical evidence with the numerical evidence, several authors have suggested a mantle consisting of two layers, a well-mixed depleted layer (= MORB source) underlain by an undepleted, relatively primitive layer (= OIB source) (e.g. [52–54]). As explained above, this type of model can no longer account for the chemistry of the OIB required.

The Nb/U and Ce/Pb ratios confirm what has been known from a wealth of published Pb-isotopic data, namely that ocean island basalts are not derived from primitive-mantle sources. These data also show that these sources can be neither recycled, predominantly continental crust, nor some “quasi”-primitive mantle reservoir that has been modified by late removal of siderophile or chalcophile elements to the Earth's core. The data are, however, consistent with the model of Hofmann and White [1,2], in which the major source component of OIB volcanism is subducted and stored oceanic crust. This model is not inconsistent with the He-isotopic data from OIB, because He may be no more autochthonous in OIB sources than it is in MORB sources. The high ³He/⁴He ratios found in some OIB may be inherited from the time of last mantle homogenization, or primitive He might have migrated into the OIB sources from the Earth's lower mantle or even the core. The only chemical or isotopic data known to us that are difficult to reconcile with this model are ¹²⁹Xe data of Allègre et al. [55]. If this anomaly is indeed confined to the highly depleted MORB sources, then it is not immediately obvious how these sources could have been differentiated from the OIB sources *after* separation and isolation of much of the continental mass. One possible solution to this dilemma has been suggested by Ozima et al. [56], namely that the positive ¹²⁹Xe anomaly is present in the more primitive portions of the mantle (or core). Another possibility might be the reintroduction of atmospheric Xe into the mantle, and specifically the OIB sources, during the subduction of oceanic crust.

One geological evolution model for the Earth

consistent with the above formal, three-stage model is the following:

During Archean (perhaps also Proterozoic) time, the major portion (perhaps as much as 75%) of the continental crust was formed and stabilized, as suggested by the sedimentary chemical record [22,57]. The mantle was depleted in incompatible elements but remained internally well homogenized (or was subsequently rehomogenized) as a result of efficient convective mixing.

Subsequently, both the rate of new continent formation and of internal mantle mixing slowed down significantly, and the mantle became increasingly heterogeneous. The major fractionation process was now partial melting to form oceanic crust enriched in incompatible elements and mantle residues depleted in incompatible elements. These heterogeneities were no longer rehomogenized by efficient convection after subduction. Continued but diminished continent formation and mantle recycling of continent-derived sediments introduced "noise" in the geochemistry of the mantle but were otherwise of minor importance compared with this "intra-oceanic" mantle differentiation. The present-day rate of continent formation has been estimated at $< 1 \text{ km}^3$ per year [58], which is negligible compared with the rate of oceanic crust formation of about 20 km^3 per year.

Present-day oceanic volcanism contains the chemical record of the overall depletion of stage one, as well as the heterogeneities introduced during stage three. Thus, the OIB sources are dominated by former oceanic crust, which is chemically enriched, yet bears the isotopic record of long-term depletion inherited from stage one. Because of this, most (though not all) OIB do have an excess of radiogenic Nd as witnesses of the long history of lower-than primitive Sm/Nd ratios.

Why did Pb behave like a highly incompatible element (similar to Rb) during Archean continent formation but change to only moderately incompatible behavior (similar to Ce) during subsequent mantle fractionation? One possible answer is that Pb was transported to the continental crust by hydrothermal processes (during subduction) in addition to igneous processes. Another possibility is that the net extraction of continental material from the mantle occurred in the feldspar-absent region (i.e. at sufficient depth), whereas partial melting in the MORB environment may occur in

the presence of feldspar, i.e. at relatively shallow depth [59].

In contrast, Nb behaves like a highly incompatible element in all oceanic basalts, but is only moderately incompatible during the extraction of continental material from the mantle. Perhaps Nb is in part retained by Ti oxides in the latter environment, especially if that environment is relatively oxidizing due to the presence of water.

If our general model is valid, then the interpretation of linear arrays formed by Pb-isotopic data for many oceanic islands may well be straightforward: the slopes of these arrays yield the ages of formation and/or subduction of the pieces of ancient oceanic crust and lithosphere that are now the sources of OIB [1,40]. However, it is not obvious, for this model or any other, how these ages should be reconciled with the very young apparent ages inferred from ^{208}Pb and the Th/U ratios in present-day MORB [31].

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