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Estimates of mantle thorium/uranium ratios from Th, U and Pb isotope abundances in basaltic melts

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The relationship between the abundances of Th, U and Pb isotopes in basalt melts and the [Th/U] ratio of their source is assessed. A simple melting model is used to show that whereas the activity ratio ($^{230}\text{Th}/^{232}\text{Th}$) in the initial melt before extraction is equal to the bulk source ratio, that in the extracted melt may be higher. The difference depends upon the rate of melting relative to the half-life of ^{230}Th (73 ka). Only when the rate is fast compared to this half life will ($^{230}\text{Th}/^{232}\text{Th}$) in the extracted melt provide a correct estimate of [$^{232}\text{Th}/^{238}\text{U}$] in the source and therefore of its [Th/U] ratio. This is normally not the case for MORB, and a better estimate of source [Th/U] ratio is derived from [$^{232}\text{Th}/^{238}\text{U}$] ratio in the basalt, which does not depend upon the rate of melting. Available data for MORB glasses give a best estimate for their source [Th/U] = 2.58 ± 0.06 . This value is less than both that of the bulk Earth of 3.9 ± 0.1 , and of the source of plume basalts from Iceland and Hawaii, which are 3.3 and 3.2 respectively.

These estimates contrast with the [$^{232}\text{Th}/^{238}\text{U}$] ratio required to produce the radiogenic $\{^{208}\text{Pb}/^{206}\text{Pb}\}$ atomic ratio of MORB over 4.55 Ga. This averages 3.8 and is little different from the average derived from Pb-isotopes in plume basalts. These observations are most easily reconciled if Th, U and Pb are efficiently stripped from the mantle by melting and have a residence time there of ≤ 1 Ga. The [Th/U] ratio of 2.6 for the upper mantle requires melt fractions of $\leq 1\%$ to be involved in transferring U and Th from this region into the continents. Such melt fractions are present in subduction zones and in the source regions of continental alkali basalts.

1. Introduction

In recent years the physical controls on the generation and extraction of mantle partial melt have become much better understood (see Spiegelman, this symposium). This understanding has resulted in renewed interest in the information that melt compositions provide about the depth and amount of melting in the Earth. Th, U and Pb are all highly incompatible elements, which partition strongly into the melt and are therefore expected to be depleted in the mantle residues even when the melt fractions are small. ^{232}Th , ^{235}U and ^{238}U decay to Pb via a series of intermediate daughter products of which some, notably ^{230}Th ($t_{1/2} = 73$ ka) and ^{226}Ra ($t_{1/2} = 1.6$ ka) are particularly useful in studies of melting and melt separation (Allègre & Condomines 1982; Cortini 1984; McKenzie 1985; Williams & Gill 1989). Also U and Th have decayed to stable isotopes of Pb over some 4.5 Ga and Pb isotope ratios in the Earth therefore record its [Th/U] ratio. It has been commonplace (Galer & O'Nions 1985; Condomines *et al.* 1988; Goldstein *et al.* 1991; Sigmarsson *et al.* 1992)

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to assume that the ($^{230}\text{Th}/^{232}\text{Th}$) activity ratio in a melt is equal to the bulk ($^{238}\text{U}/^{232}\text{Th}$) ratio in the source region, and then to calculate $[\text{Th}/\text{U}]$ directly from ($^{230}\text{Th}/^{232}\text{Th}$). The use of ($^{230}\text{Th}/^{232}\text{Th}$) for this purpose avoids possible Th–U fractionation during crystallization of the melt. Unfortunately the relationship between ($^{230}\text{Th}/^{232}\text{Th}$) in the melt and source $[\text{Th}/\text{U}]$ depends critically upon the details of melting and melt-extraction, and ($^{230}\text{Th}/^{232}\text{Th}$) in the melt need not equal ($^{238}\text{U}/^{232}\text{Th}$) in the source. Therefore this approach may lead to significant errors in the estimate of mantle $[\text{Th}/\text{U}]$.

Galer & O'Nions (1985) used different estimates of the mantle $[\text{Th}/\text{U}]$ ratio derived from Th-, U- and Pb-isotope abundances in mid-ocean ridge basalts to deduce important information about the circulation pattern in the mantle. In particular they argued that the residence time of Th, U and Pb in the upper mantle must be considerably less than the age of the Earth. This geochemical argument is one of the principal reasons for believing that there is only limited exchange of material between the upper and lower mantle. However, their argument depended on the use of ($^{230}\text{Th}/^{232}\text{Th}$) to estimate the present value of $[\text{Th}/\text{U}]$ in the upper mantle, using the assumption that the ($^{230}\text{Th}/^{232}\text{Th}$) activity ratio in a melt is equal to the bulk ($^{238}\text{U}/^{232}\text{Th}$) ratio in the source region. Since this assumption is not correct, and since the constraint that Galer & O'Nions (1985) imposed on mantle circulation is so central to any attempt to understand mantle convection, it is essential to re-examine their whole argument. This we do below, and show that Galer & O'Nions's (1985) results are correct, even though one part of their argument is not.

2. Th, U and Pb isotopes in melts

The isotopes of interest here are the two long-lived parents, ^{238}U ($t_{1/2} = 4.47$ Ga) and ^{232}Th ($t_{1/2} = 14$ Ga), and their respective stable daughter products, ^{206}Pb and ^{208}Pb , together with ^{230}Th ($t_{1/2} = 73$ ka), the radioactive intermediate daughter in the ^{238}U decay series. At radioactive equilibrium in the mantle (^{238}U) = (^{230}Th) and therefore ($^{230}\text{Th}/^{232}\text{Th}$) = ($^{238}\text{U}/^{232}\text{Th}$), where () are used to denote the activities of the isotopes concerned, [] the concentration by weight, and { } atomic ratios. The presence or absence of this equilibrium in mantle partial melts has been extensively documented and discussed (see, for example, Condomines *et al.* 1988). In principle there are three different measures of the $[\text{Th}/\text{U}]$ ratio in the mantle, which may be derived from ($^{232}\text{Th}/^{230}\text{Th}$), [$^{232}\text{Th}/^{238}\text{U}$], or { $^{208}\text{Pb}/^{206}\text{Pb}$ } ratios.

The effects of partial melting on these radioactive and stable isotopes are now considered using the melting model described by McKenzie (1985), which is similar to dynamic melting model of Langmuir *et al.* (1977) and of Williams & Gill (1989). Melting is assumed to occur at a constant rate as pressure decreases and the melt produced is in chemical and radioactive equilibrium with the matrix. The melt fraction by volume ϕ remains constant throughout the melting region, from which melt is extracted continuously and instantaneously. Melt once extracted is unable to re-equilibrate with the matrix and is mixed completely with melts extracted at other depths. The equations governing the conservation of ^{238}U , ^{232}Th and ^{230}Th are (McKenzie 1985)

$$da_p/dt = -\alpha_p a_p, \quad (1)$$

$$da_r/dt = -\alpha_d a_r, \quad (2)$$

$$\text{and} \quad da_d/dt = -\alpha_d a_d + \lambda_d((F_d/F_p) a_p - a_d), \quad (3)$$

where $\lambda_d = \lambda_{230}$, and a_p and a_d are the true activities of the parent ^{238}U and daughter ^{230}Th , but $a_r = \lambda_{230}[^{232}\text{Th}]$, is not. It is convenient to define a_r in this way so that

$$a_d/a_r = [^{230}\text{Th}/^{232}\text{Th}] \equiv R. \quad (4)$$

F is given by

$$F = (K\rho_s(1-\phi)/\rho_f\phi + 1)^{-1}, \quad (5)$$

where K is a partition coefficient, ρ_s and ρ_f are the densities of the solid and the melt, ϕ is the melt fraction present in the source by volume, and

$$\alpha = F\Gamma/\rho_f\phi, \quad (6)$$

where Γ is the melting rate. Equations (1)–(3) assume that $1 \gg K_p, K_d$, and therefore all expressions obtained below are accurate only to $O(K_d)$ or $O(K_p)$, whichever is larger. Throughout the discussion below we neglect the difference in density between the solid and the melt and therefore take $\rho_s = \rho_f = \rho$. We also assume that $1 \gg \phi$, when

$$\alpha = \Gamma/\rho(K + \phi) \quad (7)$$

and

$$F = \phi/(K + \phi). \quad (8)$$

The solutions to equations (1)–(3) are (McKenzie 1985)

$$a_p(t) = a_p(0) e^{-\alpha_p t}, \quad (9)$$

$$a_r(t) = a_r(0) e^{-\alpha_d t}, \quad (10)$$

$$a_d(t) = a_d(0) e^{-(\lambda_d + \alpha_d)t} + a_p(0) [\lambda_d F_d / (\lambda_d + \alpha_d - \alpha_p)] (e^{-\alpha_p t} - e^{-(\lambda_d + \alpha_d)t}). \quad (11)$$

It is generally assumed that the $[^{230}\text{Th}/^{232}\text{Th}]$ ratio, R , in the melt in equilibrium with the matrix is equal to that in the bulk source. This result is easily proved. The mean concentration \bar{c} of ^{238}U , ^{230}Th and ^{232}Th of the combined matrix and melt are

$$\bar{c}_p = c_f^p \phi \rho / F_p, \quad \bar{c}_d = c_f^d \phi \rho / F_d, \quad \bar{c}_r = c_f^r \phi \rho / F_d, \quad (12)$$

respectively, where c_f is the concentration in the melt. Hence the bulk source ratio $[^{230}\text{Th}/^{232}\text{Th}]$, R_B , is given by

$$R_B \equiv \frac{\bar{c}_d}{\bar{c}_r} = \frac{\phi \rho c_f^d / F_d}{\phi \rho c_f^r / F_d} = \frac{c_f^d}{c_f^r}. \quad (13)$$

Therefore at the onset of melting

$$R_B(0) = \bar{c}_d(0)/\bar{c}_r(0) = a_d(0)/a_r(0) = R(0). \quad (14)$$

Furthermore, since (^{230}Th) and (^{238}U) are equal in radioactive equilibrium, it follows that

$$\lambda_d \bar{c}_d = \lambda_p \bar{c}_p. \quad (15)$$

Dividing by $\lambda_d \bar{c}_r$ gives

$$R_B(0) = (\lambda_p/\lambda_d) \bar{c}_p/\bar{c}_r. \quad (16)$$

If therefore $R_B(0)$ or $R(0)$ can be determined, so can \bar{c}_p/\bar{c}_r , the $[\text{U}/\text{Th}]$ ratio of the source. Substitution for \bar{c} in equation (15) using (12) gives

$$(c_f^d(0)/F_d) \lambda_d = (c_f^p(0)/F_p) \lambda_p. \quad (17)$$

Therefore

$$a_p(0)/a_d(0) = F_p/F_d \quad (18)$$

and hence from equation (14)

$$G_f(0) = (F_p/F_d) R(0) = (F_p/F_d) R_B(0), \quad (19)$$

where

$$G_f = a_p/a_r = (\lambda_p/\lambda_d) [^{238}\text{U}/^{232}\text{Th}]_f. \quad (20)$$

If melt is now extracted from the whole column that is melting, and accumulated for a time t , the $[^{230}\text{Th}/^{232}\text{Th}]$ ratio in the accumulated melt is given by

$$R(t) = \int_0^t a_d(t') dt' / \int_0^t a_r(t') dt'. \quad (21)$$

In the limit as $t \rightarrow \infty$ integration of equations (10) and (11) gives

$$R(\infty) = \frac{a_d(0)}{\lambda_d + \alpha_d} \left(1 + \frac{\lambda_d F_d}{\alpha_p F_p} \left(\frac{a_p(0)}{a_d(0)} \right) \right) / \left(\frac{a_r(0)}{\alpha_d} \right). \quad (22)$$

Substitution of equations (14) and (18) into (22) gives

$$R(\infty) = R_B(0) (\alpha_d/(\lambda_d + \alpha_d)) (1 + \lambda_d/\alpha_p). \quad (23)$$

Equation (23) shows that $R(\infty)/R_B(0)$, the ratio of $[^{230}\text{Th}/^{232}\text{Th}]$ is the accumulated melt to that in the source, depends upon λ_d , α_d and α_p , and therefore on both the melting rate Γ and the ^{230}Th decay rate, as well as on the partition coefficients K_p and K_d .

Consider first *slow* melting where $\lambda_d (= 9.5 \times 10^{-6} \text{ a}^{-1}) \gg \Gamma/\rho\phi$, and therefore $\lambda_d \gg \alpha_d, \alpha_p$. Substitution of equation (7) into (23) then gives

$$R(\infty)/R_B(0) \approx \alpha_d/\alpha_p = (K_p + \phi)/(K_d + \phi). \quad (24)$$

Thus whenever $K_p > K_d$, $R(\infty)/R_B(0) > 1$, and $[^{230}\text{Th}/^{232}\text{Th}]$ in the extracted melt will exceed that in both the initial melt and the bulk source. $[^{230}\text{Th}/^{232}\text{Th}]$ in the extracted melt is often used as a direct measure of the $[\text{Th}/\text{U}]$ source ratio, but in fact it will underestimate it by an amount which depends on K_p , K_d and the melt fraction ϕ present during melting. For this reason the estimates of $[\text{Th}/\text{U}]$ in the MORB source made by Galer & O'Nions (1985) that were based on $[^{230}\text{Th}/^{232}\text{Th}]$ are likely to be in error.

If on the other hand *rapid* melting takes place, and $\alpha_p, \alpha_d \gg \lambda_d$, then equation (23) simplifies to $R(\infty) = R_B(0)$ and the $[^{230}\text{Th}/^{232}\text{Th}]$ in the extracted melt equals that in the bulk source. These results were first obtained by Williams & Gill (1989).

Equation (14) shows that $[^{230}\text{Th}/^{232}\text{Th}]$ in the initial melt is equal to that in the bulk source. The same result is not in general true for $[^{238}\text{U}/^{232}\text{Th}]$. Equation (19) shows that the $[^{238}\text{U}/^{232}\text{Th}]$ in the initial melt is not equal to the bulk ratio, R_B , unless $F_p = F_d$, that is $K_p = K_d$, rather than $K_p > K_d$, which is the expected situation.

The $[^{238}\text{U}/^{232}\text{Th}]$ ratio in melt extracted during a time t is proportional to G_f , where

$$G_f(t) = \int_0^t a_p(t') dt' / \int_0^t a_r(t') dt'. \quad (25)$$

In the limit as $t \rightarrow \infty$ integration gives

$$G_f(\infty) = \alpha_d a_p(0)/\alpha_p a_r(0) = (\alpha_d/\alpha_p) G_f(0). \quad (26)$$

Substitution for α_d and α_p from equation (7) gives

$$G_f(\infty) = [(K_p + \phi)/(K_d + \phi)] G_f(0), \quad (27)$$

where the term in square brackets is $R(\infty)/R_B(0)$ (see equation (24)). Even though $1 \gg K_p, K_d, \phi$, this term is the ratio of these small quantities, and may therefore differ

substantially from unity. If $K_p > K_d$ [$^{238}\text{U}/^{232}\text{Th}$] in the accumulated extracted melt will exceed the ratio in the melt at the start of extraction. This result is to be expected, because U will be retained by the matrix more than Th during the initial melting, but will eventually all be extracted as melting proceeds.

Substitution in equation (27) for $G_f(0)$ from equation (19) and for F_d and F_p from (8) gives

$$G_f(\infty) = R_B(0). \quad (28)$$

Substitution for $R_B(0)$ and $G_f(\infty)$ using (16) and (20) then gives

$$[^{238}\text{U}/^{232}\text{Th}]_f = \bar{c}_p/\bar{c}_r. \quad (29)$$

$[^{238}\text{U}/^{232}\text{Th}]$ in the accumulated extract will therefore give the bulk source value. Unless other complicating factors become important, such as alteration or low pressure crystal fractionation, $[^{232}\text{Th}/^{238}\text{U}]$ in the melt should be a reliable measure of $[\text{Th}/\text{U}]$ in the bulk source, and is to be preferred for this purpose to estimates based upon $(^{230}\text{Th}/^{232}\text{Th})$.

For completeness the isotopes of Pb are discussed briefly. ^{232}Th , ^{235}U and ^{238}U undergo radioactive decay to ^{208}Pb , ^{207}Pb and ^{206}Pb respectively. These Pb isotopes, together with ^{204}Pb which does not have a radioactive parent, are all stable. They all have a straightforward behaviour during melting because the rate of change of their concentrations due to radioactive decay is too slow for any measurable change to occur during melt extraction. In relationship to the equations derived above, melting is always rapid in the case of Pb. Therefore, if Pb is in chemical equilibrium in the source rock before melting starts, the relative abundances of ^{208}Pb , ^{207}Pb , ^{206}Pb and ^{204}Pb are identical in the accumulated melt, the initial melt and the source, regardless of what assumptions are made about K_{Pb} and about whether or not the melt itself is in chemical equilibrium with the matrix. Reconstruction of the time averaged value of $[\text{Th}/\text{U}]$ for a source from Pb-isotope ratios is therefore straightforward. Because Pb is highly incompatible during MORB melt production, and $K_{\text{Pb}} \approx K_{\text{U}} \approx K_{\text{Th}} \ll 1$, Pb, like U and Th, will be almost completely removed by melts, even when the melt fractions are small.

3. Estimation of mantle $[\text{Th}/\text{U}]$

The $[\text{Th}/\text{U}]$ ratio for mantle source regions may be estimated in principle from the Th-, U-, and Pb-isotope abundances in basalts extracted from them. Such estimates are now made from the Th, U and Pb data available for basalts in the light of the above considerations of their behaviour during melting. To avoid the effects of alteration on Th- and U-isotope abundances, only those analyses made on basalt glasses are used to estimate $[\text{Th}/\text{U}]$. Published data of this sort are strongly biased to samples obtained from the East Pacific ridges. Of the analyses from ocean ridge basalts summarized in table 1, only the set published by Jochum *et al.* (1983) contain a large number of Atlantic samples.

From the above arguments it is clear that $(^{230}\text{Th}/^{232}\text{Th})$ of basalts should not be used to estimate mantle $[\text{Th}/\text{U}]$. Rather $[\text{Th}/\text{U}]$ ratios of the basalts themselves are likely to provide a more reliable estimate. This is evident in table 1, where four sets of ocean ridge basalt analyses, for which Th- and U-isotope data exist, each have $[^{232}\text{Th}/^{238}\text{U}]$ ratios calculated from $(^{230}\text{Th}/^{232}\text{Th})$ that are less than the measured $[^{232}\text{Th}/^{238}\text{U}]$ ratios of the basalts themselves. This result is to be expected, because $(^{230}\text{Th}/^{238}\text{U})$ is greater than 1.0 in each of the four data-sets. Measured $[^{232}\text{Th}/^{238}\text{U}]$

Table 1. Th–U isotopes in MORB and ocean islands
(All uncertainties are 1σ .)

measured [$^{232}\text{Th}/^{238}\text{U}$]	measured ($^{230}\text{Th}/^{232}\text{Th}$)	measured ($^{230}\text{Th}/^{238}\text{U}$)	[$^{232}\text{Th}/^{238}\text{U}$] calculated from col. 2
ocean ridge basalts			
East Pacific Rise, 13°N ($n = 9$) ^a	1.31 ± 0.05	1.10 ± 0.13	2.33 ± 0.08
2.56 ± 0.29			
Juan da Fuca Ridge ($n = 16$) ^b	1.30 ± 0.11	1.17 ± 0.10	2.37 ± 0.24
2.76 ± 0.28			
Gorda Ridge ($n = 11$) ^b	1.19 ± 0.10	1.15 ± 0.07	2.58 ± 0.22
2.91 ± 0.23			
East Pacific Rise, 12°N – 27°S ($n = 11$) ^c	1.62 ± 0.42	1.07 ± 0.11	2.01 ± 0.49
2.26 ± 0.65			
Atlantic and East Pacific ($n = 18$) ^d	—	—	—
2.42 ± 0.39			
average of all oceanic ridges	—	—	—
2.58 ± 0.06			
ocean island basalts			
Iceland ($n = 24$) ^e	1.11 ± 0.05	1.20 ± 0.07	2.80 ± 0.13
3.27 ± 0.12			
Hawaii ($n = 13$) ^f	1.05 ± 0.06	1.06 ± 0.08	2.96 ± 0.17
3.19 ± 0.33			

^a Othman & Allègre (1990). [$^{232}\text{Th}/^{238}\text{U}$] ratios by TIMS, ($^{230}\text{Th}/^{232}\text{Th}$) by alpha-counting.

^b Goldstein *et al.* (1991). All ratios by TIMS.

^c Rubin & Macdougall (1988). All ratios by alpha-counting.

^d Jochum *et al.* (1983). Ratios by spark source MS. The three samples with the largest errors were omitted from the average.

^e Sigmarsson *et al.* (1992). [$^{232}\text{Th}/^{238}\text{U}$] by TIMS and ($^{230}\text{Th}/^{232}\text{Th}$) by alpha-counting.

^f Newman *et al.* (1984). All ratios by alpha-counting.

ratios in ocean ridge basalts show variations that are larger than analytical errors. Though samples from the Juan da Fuca and Gorda Ridges have the highest average values (table 1), they are indistinguishable from the others at the 2σ level. A best estimate for the mantle [Th/U] ratio of 2.58 ± 0.06 ($1\sigma_m$) is obtained from all 65 samples in table 1.

With some straightforward assumptions a further estimate of mantle [Th/U] may be derived from its Pb-isotope composition. Because Pb isotopes should be identical in the mantle source, the initial and the extracted melts, the large number of high-quality Pb-isotope analyses for ridge basalts may be used with confidence. The $\{^{206,207,208}\text{Pb}/^{204}\text{Pb}\}$ ratios for the Pb incorporated in the Earth at the time of its formation can be estimated from meteorite analyses (Tatsumoto *et al.* 1973). The amounts of radiogenic $^{206}\text{Pb}^*$ and $^{208}\text{Pb}^*$ subsequently produced from parent ^{238}U and ^{232}Th in the Earth are derived from differences between the measured $\{^{206,208}\text{Pb}/^{204}\text{Pb}\}$ ratios in basalts and these initial Pb values. It is usual to make the simplifying assumption of closed system mantle evolution from 4.55 Ga to present day, and to term the [$^{232}\text{Th}/^{238}\text{U}$] ratio calculated in this way the single-stage ratio (Galer & O'Nions 1985). This ratio is usually written as an atomic, rather than a weight, ratio and is denoted as $\bar{\kappa}_{\text{Pb}}$, given by (Galer & O'Nions 1985)

$$\bar{\kappa}_{\text{Pb}} = \left\{ \frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*} \right\} \left(\frac{\exp(\lambda_{238}T) - 1}{\exp(\lambda_{232}T) - 1} \right), \quad (30)$$

Table 2. Summary of [Th/U] ratios estimated from Pb isotopes (from Galer & O'Nions 1985)
[²³²Th/²³⁸U] ($\bar{\kappa}_{\text{Pb}}$)

ocean ridge basalts	
Atlantic	3.78 ± 0.07
East Pacific Rise	3.73 ± 0.06
Mid-Indian	3.89 ± 0.11
average = 3.80	
ocean islands	
Hawaii	3.84 ± 0.04
Iceland	3.81 ± 0.03
St Helena	3.75 ± 0.02
Australas	3.75
Ascension	3.81 ± 0.02
Azores	3.84
Bouvet	3.84
Canaries	3.92
Marquesas	3.98 ± 0.04
Guadeloupe	3.99
Tristan da Cunha	4.17
Gough	4.20
Kerguelen	4.24 ± 0.12
average = 3.93	

where $T = 4.55$ Ga, λ_{232} and λ_{238} are the decay constants of ²³²Th and ²³⁸U, and

$$\left\{ \frac{{}^{208}\text{Pb}^*}{{}^{206}\text{Pb}^*} \right\} = \left(\left\{ \frac{{}^{208}\text{Pb}}{{}^{204}\text{Pb}} \right\}_m - \left\{ \frac{{}^{208}\text{Pb}}{{}^{204}\text{Pb}} \right\}_I \right) / \left(\left\{ \frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} \right\}_m - \left\{ \frac{{}^{206}\text{Pb}}{{}^{204}\text{Pb}} \right\}_I \right), \quad (31)$$

where m is the measured ratio in the basalt, and I is the initial ratio of 4.55 Ga from Tatsumoto *et al.* 1973. $\bar{\kappa}_{\text{Pb}}$ values obtained in this way are summarized in table 2. The range obtained from the Pb measurements is from 3.73 to 3.89, and is very different from the average value of 2.58 ± 0.09 derived from the [²³²Th/²³⁸U] ratios in table 1.

In comparison to MORB, Th and U isotopes have been measured in basalts from comparatively few ocean islands. Though useful amounts of data are available for only Iceland and Hawaii, these are sufficient to highlight the important differences that exist between islands and the normal spreading ridges. A large amount of data for Icelandic basalts has been obtained by Sigmarsson *et al.* (1992). The average (²³⁰Th/²³⁸U) ratio is 1.20 ± 0.07 (table 1), a value similar to normal ridge basalts. Again this result means that (²³⁰Th/²³²Th) should not be used to estimate the source [Th/U] directly. Rather [²³²Th/²³⁸U] values provide a better estimate, with [Th/U] = 3.27 ± 0.12 .

A more limited set of data is available for Hawaiian basalts (table 1). The [²³²Th/²³⁸U] data for these (Newman *et al.* 1984) provide an estimate of source [Th/U] = 3.19 ± 0.33 . Thus both the Iceland and Hawaii data have significantly higher source [Th/U] than do the normal ridges. Other ocean islands such as Reunion (Condomines *et al.* 1988) and Samoa (Newman *et al.* 1984) give even higher values for the source [Th/U], up to and even exceeding 4.0. Until more data are available it is not possible to obtain a reliable estimate of the average [Th/U] for the source of plume basalts.

There are more good quality Pb-isotope data for ocean island basalts than there are Th–U isotope data. It is possible to make estimates of mantle [Th/U] from Pb-isotopes ($\bar{\kappa}_{\text{Pb}}$) for Iceland, Hawaii and a number of other islands (table 2). $\bar{\kappa}_{\text{Pb}}$ values

in table 2 range from 4.2 for Kerguelen and Tristan da Cunha to more typical values of 3.81 ± 0.03 for Iceland and 3.84 ± 0.04 for Hawaii to the lowest values so far of 3.75 ± 0.02 for the Australes.

4. Unsupported mantle Pb

Normal spreading ridges have a source $[\text{Th}/\text{U}]$ which averages 2.58 ± 0.06 . This ratio is significantly lower than the average time integrated $[\text{Th}/\text{U}]$ ratio, $\bar{\kappa}_{\text{Pb}} = 3.8$, calculated from the radiogenic $^{208}\text{Pb}^*$ and $^{206}\text{Pb}^*$ abundances. The present-day mantle $[\text{Th}/\text{U}]$ is too low to have produced this radiogenic Pb over 4.55 Ga and therefore the Pb is in effect 'unsupported' by the parent ^{232}Th and ^{238}U (Galer & O'Nions 1985).

In addition to Pb, radiogenic $^{87}\text{Sr}^*$ is also unsupported by parent ^{87}Rb in the ridge basalt source (Tatsumoto *et al.* 1965). In the case of Rb–Sr this is because Rb is highly depleted in the upper mantle, having been removed to the continental crust, whereas Sr, being a more compatible element, is depleted to a relatively minor extent. However, it is less obvious that this situation should exist for Pb, because, like Th, U and Rb, it is a highly incompatible element and is also strongly concentrated into the continents. Galer & O'Nions (1985) suggested that Th, U and Pb are efficiently stripped from the upper mantle by melting, and have residence time there of less than 1 Ga and probably as short as 0.6 Ga. Their abundance must then be maintained by introduction of material from a less depleted region with $[\text{Th}/\text{U}] \approx 3.8$ into the convecting mantle sampled by the ridges. The basis of their argument for a short residence time of Pb is reproduced in figure 1, and rests simply on the demonstration that there is a restriction on the length of time that mantle Pb could have been resident in region with $[\text{Th}/\text{U}] = 2.6$ and still have a value of $\bar{\kappa}_{\text{Pb}}$ of 3.80. In this simple model τ is the time at which $[\text{Th}/\text{U}]$ is reduced to 2.6, the present upper mantle value, from a value of 3.9. This is a two-stage evolution model, the first stage being 4.55 Ga to τ , with $[\text{Th}/\text{U}] = 3.9$, and the second stage $\tau > t \geq 0$ with $[\text{Th}/\text{U}] = 2.6$. From figure 1 it is evident that $\{^{208}\text{Pb}^*/^{206}\text{Pb}^*\}$ is less than the values observed in the ridge basalts when τ increases beyond 0.6 to 1.0 Ga. The restriction imposed by $\{^{208}\text{Pb}^*/^{206}\text{Pb}^*\}$ is only removed if the first stage, 4.5 Ga to τ , takes place in a region with $[\text{Th}/\text{U}]$ closer to 4.5 than 3.9. With one exception (Allègre *et al.* 1986) this value is higher than recent estimates for bulk Earth $[\text{Th}/\text{U}]$ of 3.9 ± 0.1 , 3.8 ± 0.2 and 3.9 ± 0.1 by Manhès *et al.* (1979), Goldstein & Galer (1991) and Rocholl & Jochum (1991) respectively, and is also higher than all measurements from plume basalts (table 2).

The short residence times for Pb, Th and U implied by these considerations require that these elements are stripped efficiently from the mantle by melting. This is certainly to be expected from recent work by McKenzie & O'Nions (1991) on partial melt distributions derived from the inversion of rare-earth element abundances. The melting processes involved are those that transport Pb, Th and U from the convecting region into the continental crust and mechanical boundary layer. Such transport can involve large melt fractions in plumes and extensional environments, but also small melt fractions in the source regions of island arc and alkali basalts.

The principal question now becomes the source from which Th, U and Pb are introduced into the ridge source. Two possibilities were considered by Galer & O'Nions (1985): the continental lithosphere, and mantle beneath the lower thermal boundary layer of upper mantle convection. The continental crust was considered to

Estimate of mantle thorium/uranium ratios

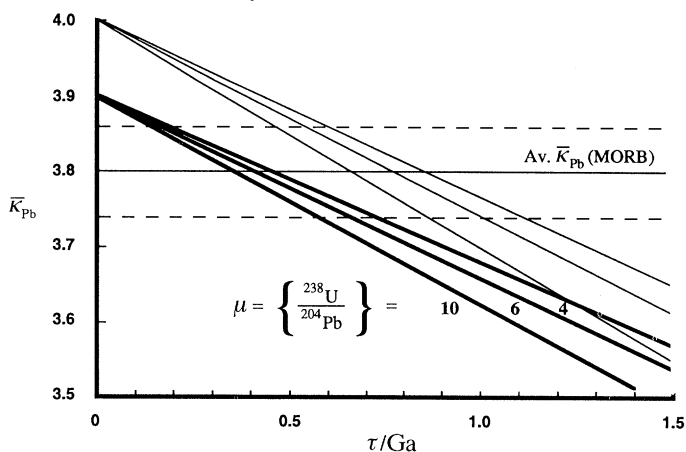


Figure 1. The evolution of Pb-isotopes in a reservoir in which $[^{232}\text{Th}/^{238}\text{U}] = 3.9 \equiv \kappa_1$ at 4.55 Ga, but is reduced to $2.6 \equiv \kappa_2$ at time τ in the past. Results are expressed in terms of $\bar{\kappa}_{Pb}$ (mantle), the time-integrated $[^{232}\text{Th}/^{238}\text{U}]$ ratio for the whole interval 4.55 Ga to 0 required to produce the resultant radiogenic $^{208}\text{Pb}^*/^{206}\text{Pb}^*$. The dependence of $\bar{\kappa}_{Pb}$ (mantle) on the time of $[\text{Th}/\text{U}]$ fractionation, τ , is shown for values of $\mu (= \{^{238}\text{U}/^{204}\text{Pb}\})$ of 4, 6 and 10, which encompass estimates for the MORB source. The heavy solid lines are constructed for $\kappa_1 = 3.9$, the plume basalt average (table 2), and the thin solid lines for $\kappa_1 = 4.0$, the estimated upper limit to the bulk Earth ratio of 3.9 ± 0.1 (Manhes *et al.* 1979). The horizontal line shows the ratio $\bar{\kappa}_{Pb}$ (MORB), the average value for mid-ocean ridge basalts (table 2), and the dotted lines the $\pm \sigma$ range. The model $\bar{\kappa}_{Pb}$ (mantle) values are less than $\bar{\kappa}_{Pb}$ (MORB) for times of fractionation greater than *ca.* 600 Ma. Figure adapted from Galer & O'Nions (1985). Pb isotope evolution is modelled using

$$\{^{208}\text{Pb}/^{204}\text{Pb}\}_o = \{^{208}\text{Pb}/^{204}\text{Pb}\}_i + \kappa_1 \mu_1 (\exp(\lambda_{232} T) - \exp(\lambda_{232} \tau)) + \kappa_2 \mu_2 (\exp(\lambda_{232} \tau) - 1)$$

and

$$\{^{206}\text{Pb}/^{204}\text{Pb}\}_o = \{^{206}\text{Pb}/^{204}\text{Pb}\}_i + \mu_1 (\exp(\lambda_{238} T) - \exp(\lambda_{238} \tau)) + \mu_2 (\exp(\lambda_{238} \tau) - 1),$$

where $T = 4.55$ Ga, τ = time of Th/U fractionation, and λ_{232} , λ_{238} are decay constants for ^{232}Th and ^{238}U . 'i' and 'o' are Pb ratios at 4.55 and 0 Ga, κ and μ are the $\{^{232}\text{Th}/^{238}\text{U}\}$ and $\{^{238}\text{U}/^{204}\text{Pb}\}$ ratios respectively, with subscripts 1 and 2 denoting the values for the intervals $4.55 \text{ Ga} < t < \tau$ and $\tau < t < 0$. $\kappa_1 = 3.9$ and $\mu_1 = 8.0$. $\{^{208}\text{Pb}^*/^{206}\text{Pb}^*\}$ and $\bar{\kappa}_{Pb}$ are calculated using equations (30) and (31) in the text.

be an unlikely source because its Pb-isotope composition does not coincide with that of the ridge source, and entrainment from a deeper mantle region was therefore considered most probable. Certainly plume basalts, which are the potential carriers of Pb from this region, have Pb-isotope compositions that fully overlap those of ridge basalts.

5. Melt residues and mantle depletion

There are two ways in which the $[\text{Th}/\text{U}]$ ratio in the upper mantle can be reduced. Either Th can be extracted in preference to U by magma generation (Galer & O'Nions 1985), or U from the crust can be returned to the upper mantle by subduction of altered oceanic crust. Since there is no doubt that both U and Th have been efficiently transferred to the continental crust and mechanical boundary layer by melt movement, we use the same melting model discussed above to show that Galer & O'Nions's proposal can account for the $[\text{Th}/\text{U}]$ ratio of MORB. It is, however, difficult to show that U is not preferentially transported into the upper mantle by subduction, because so little is yet understood about transport in subduction zones.

To be consistent, we continue to use activities, and in addition to a_p and a_r in the melt, define A_p and A_r to be those in the solid residue. Like a_r , A_r is not a true activity. The evolution equations then are

$$dA_p/dt = -\alpha_p A_p \quad (32)$$

and

$$dA_r/dt = -\alpha_d A_r. \quad (33)$$

We first consider the relationship between K_p and K_d that is required to leave a residue with $[Th/U] = 2.6$. The integrated $[^{238}U/^{232}Th]$ in the solid residue after extraction for infinite time is related to $G_s(\infty)$

$$G_s(\infty) = \left(\frac{\lambda_p}{\lambda_d}\right) \left[\frac{^{238}U}{^{232}Th} \right]_s = \int_0^\infty A_p(t') dt' / \int_0^\infty A_r(t') dt'. \quad (34)$$

Since $A_p(0) = K_p a_p(0)$, $A_r(0) = K_d a_r(0)$, and $A_r(\infty) = A_p(\infty) = 0$, equation (34) gives

$$G_s(\infty) = (K_p \alpha_d / K_d \alpha_p) a_p(0) / a_r(0). \quad (35)$$

The ratio in the solid when melting starts $G_s(0)$ is obtained using equation (12) for the total ^{238}U and ^{232}Th per unit volume

$$G_s(0) = \lambda_p \bar{c}_p / \lambda_d \bar{c}_d = (F_p / F_d) a_p(0) / a_r(0). \quad (36)$$

Combining equations (35) and (36) and substituting for α_d and α_p using equation (7) gives

$$G_s(\infty) = (K_p / K_d) G_s(0). \quad (37)$$

If $G_s(0)/G_s(\infty) = 3.9/2.6$, then $K_d = 0.67K_p$. This result is consistent with the general observation that $K_d < K_p$.

If the $[Th/U]$ ratio in the upper mantle is less than that of the bulk Earth, there must be a corresponding reservoir in which $[Th/U]$ exceeds that of the bulk Earth. Though there is no evidence for such an effect in the measured continental values of $[Th/U]$ or of $\bar{\kappa}_{pb}$, it is likely to be small and difficult to detect. Highly incompatible elements such as Th, U, Pb, Rb and Cs have abundances in the continental crust that correspond to complete stripping of 30–40% of the mantle by mass. As the argument above shows, these mantle concentrations are not likely to be residual, but are maintained by entrainment (Galer & O'Nions 1985). Though the upper mantle concentrations of these elements are not known precisely, because of their short residence times (Galer & O'Nions 1985) they are unlikely to exceed 10% of the primitive mantle abundances. For continental crust with $[Th/U] = 3.9$ and $[Th] = 4.5$ p.p.m., and an upper mantle with $[Th/U] = 2.6$ and $[Th] = 0.007$ p.p.b., the combined $[Th/U]$ for the crust and mantle is 3.8. This calculation shows that melt extraction can produce a large change in $[Th/U]$ in the upper mantle, where Th and U are strongly depleted relative to the bulk Earth, whereas the corresponding change to $[Th/U]$ in the continents can be small, because most of the U and Th from the upper mantle is now concentrated in the continental crust and mechanical boundary layer.

The same melting model can be used to estimate the efficiency of U and Th extraction required to leave a depleted residue with $[Th/U] = 2.6$. We assume that the melting occurs within a layer of thickness h as the solid material upwells at velocity v . As before we assume that $K_p \ll 1$, and also for simplicity that $\phi \ll K_p$, or fractional melting. If the melting rate Γ is constant, and the total melt fraction by

volume that has been extracted when the matrix reaches the top of the layer is ϕ_t , then

$$\Gamma = v\rho\phi_t/h. \quad (38)$$

The retention efficiency, E_p , is the ratio of ^{238}U in the residual layer of thickness h to its initial value before melt extraction

$$E_p = \int_0^h A_p(z) dz / K_p a_p(0) h, \quad (39)$$

where z is the height above the base of the layer. Since $z = vt$, the integral in equation (39) can be converted to an integral over time. Assuming $A_p(h) = 0$ gives

$$\int_0^h A_p(z) dz = v \int_0^\infty A_p(t) dt = \frac{vK_p a_p(0)}{\alpha_p}. \quad (40)$$

Substitution of equation (40) into (39) gives the retention efficiency

$$E_p = v/\alpha_p = \rho\phi v/F_p \Gamma. \quad (41)$$

Since we assume $K_p \gg \phi$, substitution for F_p from equation (8) reduces (41) to

$$E_p = K_p/\phi_t. \quad (42)$$

If the material entrained into the upper mantle has bulk Earth Th and U contents of 70 and 18 ppb respectively, and is then depleted to 10% of these amounts, the required value of E_p is 0.1, or $\phi_t = 10K_p$. For values of K_p between 10^{-3} and 10^{-4} , the total melt extracted ϕ_t must be in the range of 10^{-2} to 10^{-3} . This calculation is only concerned with the melt fraction that is involved in the transport of Th and U into the continental crust and mechanical boundary layer, where it remains geochemically isolated from the convecting upper mantle. Though the inversion of rare earth element concentrations (McKenzie & O'Nions 1991) shows that the total melt fractions beneath Iceland and Hawaii are much larger than 10^{-2} , and will therefore strip both Th and U from their source regions, the resulting aseismic ridges are subducted with the oceanic lithosphere. Therefore such melting has no long term effect on the [Th/U] ratio, or on the upper mantle concentrations of Th and U. The two processes that are likely to be important are island arc volcanism and the movement of alkali basalts and other small melt fractions into the continental crust and mechanical boundary layer. The inversion calculations (McKenzie & O'Nions 1991) show that the melt fractions in both environments are 10^{-2} or less, and can therefore produce the observed [Th/U] ratio. Except beneath Archaean shields, where the mechanical boundary layer is sufficiently thick to prevent extensive melting, plumes beneath continents will strip Th and U from their source regions. They will therefore have little effect on the [Th/U] ratio of the upper mantle, though they will reduce the concentrations of both elements.

6. Concluding remarks

Modelling of melting and melt extraction suggests that the ($^{230}\text{Th}/^{232}\text{Th}$) activity ratios in basalt melts from normal spreading ridges will not in general yield correct estimates for mantle [Th/U], because melt extraction occurs slowly relative to the decay rate of ^{230}Th . Only where melts are extracted rapidly relative to the ^{230}Th decay can the ($^{230}\text{Th}/^{232}\text{Th}$) ratio be used for this purpose. [$^{232}\text{Th}/^{238}\text{U}$] data for ridge

basalts provides a better estimate, provided that the effects of alteration and low pressure crystallization are unimportant. These effects are minimized by selecting only primitive basalt glasses, and these provide a best estimate of $[\text{Th}/\text{U}] = 2.58 \pm 0.09$ for their source. This ratio is much lower than the bulk Earth value and the time-integrated $^{232}\text{Th}/^{238}\text{U}$ ratios derived from the radiogenic daughter Pb in ridge basalts, as noted previously (Galer & O'Nions 1985). The view that the residence times of Th, U and Pb in the upper mantle must be relatively short, and probably less than 1 Ga, is confirmed.

The Th, U and Pb in the upper mantle are present at about 0.1 of their bulk Earth abundances, and must be sustained by entrainment from material outside of the convecting upper mantle region sampled by melting at ridges, probably by plumes. The observed $^{232}\text{Th}/^{238}\text{U}$ shows that Th is extracted from the upper mantle in preference to U. Since aseismic ridges are subducted by trenches, plume melting in oceanic regions has no effect on the upper mantle concentration of U and Th. The extraction processes concerned are those that transfer these elements to the continental lithosphere, by generating melt beneath island arcs and continental interiors. Inversion calculations show that both often involve melt fractions of 1% or less, and can therefore account for the observed $[\text{Th}/\text{U}]$ of about 2.6.

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