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Constraints from Thorium/Lanthanum on Sediment Recycling at Subduction Zones and the Evolution of the Continents

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Arc magmas and the continental crust share many chemical features, but a major question remains as to whether these features are created by subduction or are recycled from subducting sediment. This question is explored here using Th/La, which is low in oceanic basalts (<0·2), elevated in the continents (>0·25) and varies in arc basalts and marine sediments (0·09–0·34). Volcanic arcs form linear mixing arrays between mantle and sediment in plots of Th/La vs Sm/La. The mantle end-member for different arcs varies between highly depleted and enriched compositions. The sedimentary end-member is typically the same as local trench sediment. Thus, arc magmas inherit their Th/La from subducting sediment and high Th/La is not newly created during subduction (or by intraplate, adakite or Archaean magmatism). Instead, there is a large fractionation in Th/La within the continental crust, caused by the preferential partitioning of La over Th in mafic and accessory minerals. These observations suggest a mechanism of 'fractionation & foundering', whereby continents differentiate into a granitic upper crust and restite-cumulate lower crust, which periodically founders into the mantle. The bulk continental crust can reach its current elevated Th/La if arc crust differentiates and loses 25–60% of its mafic residues to foundering.

KEY WORDS: *arc magmatism; continental crust; delamination; thorium; sediment subduction*

INTRODUCTION

Continents currently grow at convergent margins through magmatic additions and island arc collisions. Not only is this an observable process, but it leaves a lasting mark in chemical similarities between arcs and the average continental crust (Taylor & McLennan, 1985; Hofmann, 1988; Kelemen, 1995; Rudnick, 1995; Albarède, 1998). The preponderance of andesites at convergent margins originally led to the 'Andesite Model' for continental growth (Taylor, 1967), which creates continents of intermediate composition directly above subduction zones. Although some laboratory experiments have created silicic magmas by low-degree partial melting of peridotites (e.g. Baker *et al.*, 1995) and melt–mantle reaction models can generate high Mg-number andesites in the mantle (Kelemen, 1990), most modern arcs require parental basalt (Kay, 1980; Arculus, 1981; Tatsumi *et al.*, 1983; Pearcy *et al.*, 1990; Holbrook *et al.*, 1999). The net addition to arcs is predominantly basalt, with most andesites being created by fractional crystallization, assimilation and/or mixing. Thus, the andesitic continents cannot be generated by wholesale accretion of modern arcs, and this remains one of the major outstanding problems in geology (Rudnick, 1995; Davidson & Arculus, 2004).

Nonetheless, geochemical characteristics indicate a clear association between arcs and the continents. Certain trace-element ratios, such as Ce/Pb and Th/Nb, have similar values in arc magmas and the continental crust, although distinct from oceanic crust values. For example, with few exceptions, oceanic basalts [including mid-ocean ridge basalts (MORB) and ocean island basalts (OIB)] have Ce/Pb > 20 (Hofmann, 1988), whereas the average value for the bulk continental crust (BCC) is 3·3–4·1 (Rudnick & Fountain, 1995; Wedepohl, 1995; Gao *et al.*, 1998; McLennan, 2000), which is well within the range of arc basalts (1–10; Noll *et al.*, 1996). Low Ce/Pb in arc basalts derives from preferential partitioning of Pb with respect to Ce into slab aqueous fluids (Brenan *et al.*, 1995; Kogiso *et al.*, 1997), or from partial

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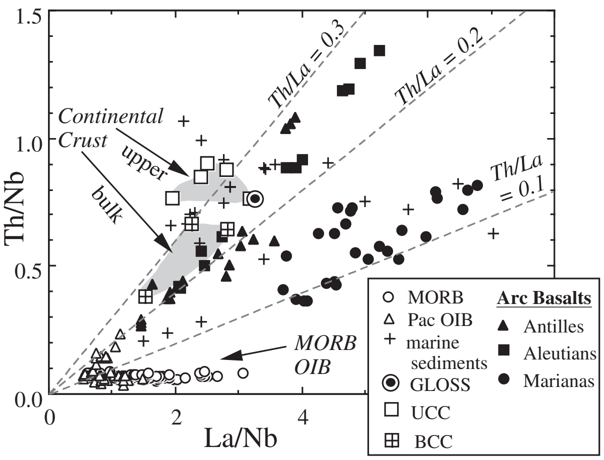

Fig. 1. Th/Nb vs La/Nb in mid-ocean ridge basalts (MORB), oceanic island basalts (OIB), arc basalts, marine sediments and continental averages. Gray fields are average upper continental crust (UCC) and bulk continental crust (BCC) estimates (UCC Th/La = 0.33 ± 0.05, 2σ; BCC Th/La = 0.27 ± 0.05). MORB data from Niu & Batiza (1997); Pacific OIB from database provided by Tim Elliott (samples with Th/Nb > 0·1 are from Society and Pitcairn islands); global subducting sediment (GLOSS) and trench sediment averages from Plank & Langmuir (1998); sediments with La/Nb > 8 are not shown for clarity. Marianas arc: Elliott *et al.* (1997); Aleutians and Antilles arcs: new ICP–MS data in Electronic Appendix B; continental averages: Taylor & McLennan (1985); Condie (1993); Rudnick & Fountain (1995); Gao *et al.* (1998); McLennan (2000); Barth *et al.* (2000); Jahn *et al.* (2001).

melting of subducting basalt and/or sediment (Tatsumi, 2000; Kelemen *et al.*, 2003*b*). These processes through time can account for the low Ce/Pb of the continents and high Ce/Pb of the mantle (Hofmann, 1988; Miller *et al.*, 1994; Chauvel *et al.*, 1995).

Another feature shared by arc basalts and the continents is a depletion in Nb and Ta, usually termed the 'Nb anomaly'. This depletion in Nb is usually identified on a mantle- or chondrite-normalized trace-element diagram by low abundance of Nb with respect to Th or La—elements which have similar partition coefficients to Nb during mantle melting. The Nb-anomaly is also reflected in the La/Nb ratio, which, in oceanic basalts, is commonly <2·5 and, in arc basalts, is typically >2 (Fig. 1). Recent estimates of Nb concentration in the bulk continental crust yield La/Nb of 2–3 (Gao *et al.*, 1998; Plank & Langmuir, 1998; Barth *et al.*, 2000). Albarède (1998) has emphasized the overlap between continents and oceanic mantle in La/Nb, but the separation in Th/Nb is very clear (Fig. 1). Indeed, Th/Nb is a better reflection of the Nb-depletion than La/Nb because the order of relative incompatibility during mantle melting is Th>Nb>La, and so mantle depletion leads to high La/Nb (with no Nb-anomaly), but low Th/Nb. Figure 1 shows the similarity in Th/Nb between the continents and arcs, and the difference from oceanic basalts.

The geochemical similarities between arcs and continents have been used to estimate the mass proportion of continents formed at subduction zones. Based on the average La/Nb of arc basalts and the bulk continents, Rudnick (1995) calculated 85–90% of the continents being formed of arcs; recent revisions to Nb estimates for the bulk continents increase this value to as much as 95% (Plank & Langmuir, 1998; Barth *et al.*, 2000). This mixing model assumes that high La/Nb is created at subduction zones, and then imparted to the continents. This simple calculation does not include, however, the effects of recycling sedimentary material at subduction zones. Figure 1 shows that marine sediments may also have high La/Nb and Th/Nb, like the continents from which sedimentary La, Nb and Th are primarily derived. Arc magmas may contain a significant portion of these continentally derived elements, via recycling of components from subducting sediment. Although studies comparing arc output and trench input find evidence for creation of the Nb-anomaly during sediment melting in the slab (Elliott *et al.*, 1997; Turner *et al.*, 1997; Class *et al.*, 2000), some of the Nb-anomaly will derive from recycling of the sediment's initial Nb-anomaly (Johnson & Plank, 1999). In the end-member scenario, where high La/Nb is created in the Archaean and subduction since then has only recycled inherited La/Nb, there would be no sensitivity in mixing models to arc additions.

Thus, it is important to separate the continental signatures that are created in the subduction zone from those that are inherited. How much of the similarity between arc magmas and the continents is a result of inheritance of the continental signature via recycling of subducted sediment, and how much is newly created in the subduction zone by slab dehydration/melting and then imparted to the continents? The answer to this question is fundamental to the origin of the continents, and, in particular, the proportion of the continents that were created from subduction-zone magmatism.

In order to evaluate this question, this paper compares the sediment input and arc output for several subduction zones, focusing on the element ratio Th/La. Although the Nb-anomaly is an excellent discriminator between MORB–OIB and arc lavas, it is caused by three independent processes: (1) prior mantle depletion in Nb (Ewart & Hawkesworth, 1987; Niu & Batiza, 1997; Lundstrom *et al.*, 1998); (2) enrichment in Th and La relative to Nb in rutile-saturated partial melts from the slab (Ryerson & Watson, 1987; Kelemen *et al.*, 1993; Elliott *et al.*, 1997); (3) inheritance from subducting sediment. Focusing on Th and La alone simplifies this problem because both elements are generally enriched in arc basalts relative to MORB (unlike Nb), and so are less sensitive to assumptions about the prior state of mantle depletion. Another reason to focus on Th and La is that, unlike Pb, the enrichment is not complicated by major additions from the basaltic layer of the downgoing plate (Miller *et al.*, 1994). Several lines of evidence suggest that excess Th and rare earth elements (REE) in most arc basalts derive largely from subducted sediment, with minor contributions from subducted MORB. These arguments include Th/Ce vs $^{143}Nd/^{144}Nd$ systematics (Hawkesworth *et al.*, 1997), Ce-anomalies, U-series and Nd-isotope systematics (Elliott *et al.*, 1997), the lack of Th- and La-enrichment during ocean crust alteration (Staudigel *et al.*, 1996; Kelley *et al.*, 2003), the lack of Th- and La-mobility during blueschist- and eclogite-facies metamorphism (Arculus *et al.*, 1999; Becker *et al.*, 1999, 2000; Spandler *et al.*, 2003), and the MORB-like Th–Na intercept to the global arc array at zero Th-sediment flux (Plank & Langmuir, 1993). Exceptions include high-Mg-number andesites (or adakites) with high Th and light rare earth element (LREE) concentrations and high $^{143}Nd/^{144}Nd$ (Kelemen *et al.*, 2003*b*). Thus, variations in Th/La in most arc basalts will depend largely on variations in the composition of subducting sediment, and less so on the composition of subducting altered basalt or background mantle, both of which are more difficult to constrain.

Although variations in Th/La are not as familiar to geochemists as the classic ratios that illustrate continental signatures (e.g. Ce/Pb, Nb/U and La/Nb), they are also useful in this regard. Figure 1 plots two measures of the Nb-anomaly (Th/Nb and La/Nb), as well as lines of constant Th/La, which clearly distinguish oceanic basalts (MORB and OIB) from the continental crust. The bulk and upper continental crust have Th/La $\sim 0{\cdot}3$, whereas MORB are $<0{\cdot}1$ (Fig. 1). OIB have Th/La $\sim 0{\cdot}1$, with some anomalously low ratios in Koolau basalts (Frey *et al.*, 1994) and some high ratios in Society and Pitcairn basalts, which, based on other chemical arguments, may include recycled continental sources (White & Duncan, 1996; Eisele *et al.*, 2002). Primitive mantle and chondrites have Th/La $\sim 0{\cdot}12$ (Hofmann, 1988; Sun & McDonough, 1989). Thus, even including the full range of mantle heterogeneity, the mantle has Th/La $< 0{\cdot}2$. The continents are enriched with respect to average oceanic basalts by roughly a factor of three. Both arc basalts and marine sediments vary between mantle and continental values, and the next section focuses on how these variations are related. If arc basalts possess similar Th/La to the locally subducted sediment, then this argues for a signature inherited from subducting sediment, and the continental crust from which sedimentary Th and La are derived. If, on the other hand, arc and sediment variations are not related, or arcs have higher Th/La than the locally subducted sediment, then high Th/La would be created in the subduction zone by preferential enrichment of Th in slab fluids and/or melts. The difference between these two outcomes has fundamental implications for the origin of continental crust.

Th/La VARIATIONS IN MARINE SEDIMENTS AND ARC BASALTS

Th/La variations in marine sediments

Th/La in marine sediments varies with the proportions of terrigenous, hydrogenous and volcaniclastic sources. Plotted in Fig. 2 are Th/La vs Al_2O_3/P_2O_5 ratios for representative lithologies and average trench columns. The dominant control on sediment Th/La is mixing between terrigenous sediments, which have high Al_2O_3/P_2O_5 and upper-crustal Th/La of 0·3–0·4, and metalliferous sediments, which have low Th/La and Al_2O_3/P_2O_5 because of high REE concentrations in fish debris phosphate and hydrogenous Fe–Mn oxides [see discussion and references given by Plank & Langmuir 1998]. The other dominant component is volcaniclastic material, which can have low Th/La, reflecting mantle values. These components combine to create subducting sedimentary columns which vary in Th/La by a factor of seven globally, from near average upper-crustal values at the Antilles, Java and northeast Honshu margins, to lower volcaniclastic values at Vanuatu, and even lower metalliferous–phosphatic values at the Marianas and Tonga margins. Thus, sediments with different Th/La subduct at different margins, and provide a signal of variation to look for in the corresponding arc volcanics.

Th/La variations in arc basalts

It is important to recognize, however, that arc basalts are mixtures of mantle and subducted sources. Whereas sediments may exert a strong control on mixed compositions, the final Th/La in the arc magma will depend on the proportion of sediment to mantle. A simple bulk-mixing calculation using normal-mid-ocean-ridge basalt (N-MORB) mantle (e.g. 0·014 ppm Th and 0·23 ppm La; Salters & Stracke, 2004) and the southern Antilles subducting sediment (15 ppm Th, 48 ppm La; Plank & Langmuir, 1998) shows that Th/La of the mixture will approach within 95% of the sediment ratio after only 6% addition of this sediment to an N-MORB mantle source. Based on the Banda sediments, Vroon *et al.* (1995) performed a similar calculation, which was also constrained by Nd-isotopes. Other isotopic mixing arguments, as well as consideration of the total mass of sediment subducted relative to mantle mass, indicate that mixing proportions for individual arcs will be much less than 6%, and so many arcs should have Th/La between mantle and sediment values. Thus, these mixing calculations predict that in places where little sediment subducts, arcs should have approximately mantle Th/La, whereas, in places with a high flux of subducted sediment, the Th/La of the arc should approach the sediment ratio.

This relationship is in fact observed. For high sediment flux margins (>0·32 Mg/yr/cm arc length), there is a

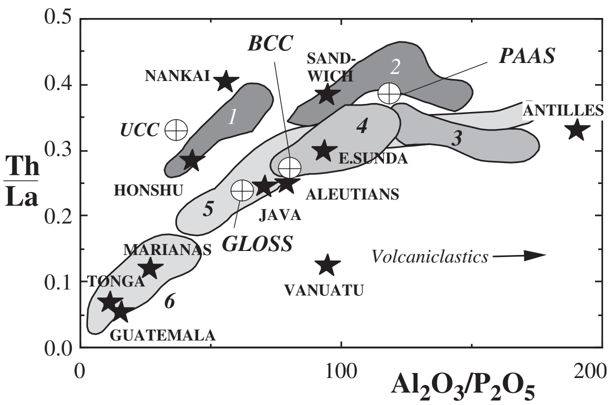

Fig. 2. Th/La vs Al_2O_3/P_2O_5 in marine sediments. Fields are for regional or lithological units (1: S. Pacific terrigenous, 2: S. Atlantic terrigenous, 3: Antilles terrigenous, 4: Aleutian terrigenous, 5: Indonesian Cretaceous sediments, 6: metalliferous and phosphatic clays); stars are trench averages from Plank & Langmuir (1998; for confidence level 1 and 2 margins). Upper continental crust (UCC) and bulk continental crust (BCC) Th/La from Fig. 1; post-Archaean average shale (PAAS) from Taylor & McLennan (1985), and global subducting sediment (GLOSS) from Plank & Langmuir (1998). The dominant variation is between high Th/La and Al_2O_3/P_2O_5 terrigeneous material, and low Th/La and P-rich metalliferous sediments. Al_2O_3/P_2O_5 variations at high Th/La are probably due to variable degrees of weathering of terrigenous sources. Data sources for fields: Plank & Langmuir (1998) and unpublished ICP–MS data for ODP 701 (Sandwich) sediments; Kay & Kay (1988); Ben Othman *et al.* (1989); Plank & Ludden (1992); Zhou & Kyte (1992); Peate *et al.* (1997).

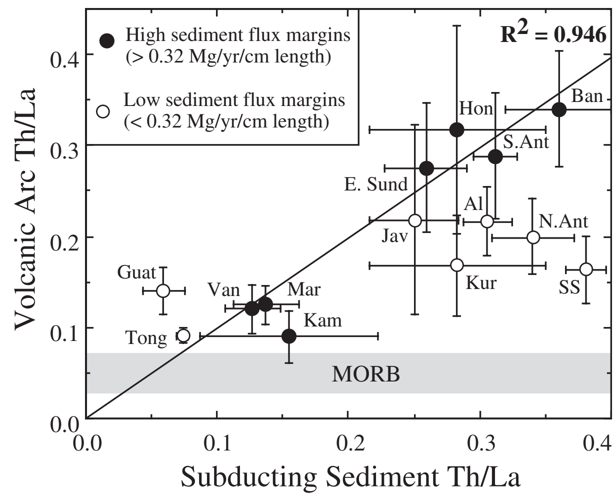

Fig. 3. Average Th/La in subducting sediment columns and volcanic arcs. Margins include all those in Plank & Langmuir (1998), except those for which there are insufficient volcano data or poor control on sediment compositions (e.g. confidence level 4 columns). Sedimentary fluxes and Th/La from Plank & Langmuir (1998), and Vroon *et al.* (1995) for Banda. Arc Th/La is the average for the arc, based on average of basalts from each volcano (see Table 1 and Electronic Appendix A for abbreviations, values and references). Th/La correlates well for margins with the highest sediment flux (filled symbols); the best-fit line intersects the origin and has a slope very close to 1 (slope = 0.99 ± 0.12; Kamchatka is excluded from the linear regression—its sediment composition is based on distant reference sites that do not penetrate basement). As expected for lower sediment flux margins (open symbols), arc Th/La is shifted significantly toward mantle values (< 0·1). Two sigma uncertainties are shown for arc averages. Uncertainties on the bulk sediment ratio derive from variations in: (1) unit thicknesses subducted; (2) analytical errors; (3) real variations in Th, La and Th/La downhole. The first effect is difficult to quantify; the second effect is generally small (< 10%); the third effect can be evaluated from the number of analyses available for each reference site. A Monte Carlo error analysis is used where Th and La are allowed to vary randomly within 2σ of the average value for each lithological unit. The error bars are the range in average Th/La of the column for 90% of the trials.

good correlation between Th/La in arc basalts and Th/La in the local sediment column (filled symbols in Fig. 3; Table 1; see also Electronic Appendix A available at http://www.petrology.oupjournals.org). This sediment flux threshold would correspond to 3–6% mass of sediment relative to mass of mantle melted [mantle melting mass flux is calculated from arc growth rates of 30–60 km^3/Ma/km arc length from Reymer & Schubert (1984) and Dimalanta (2002); 2·8 g/cm^3 arc density, and 15% melting of the arc mantle]. At sediment fluxes below this threshold, the mantle should dominate the arc Th/La. Indeed, arcs corresponding to the lower sediment flux margins (open symbols in Fig. 3) generally fall below the sediment value, trending toward mantle values (Th/La < 0·1). Taking all of the arcs together, however, there is a clear influence on the arc from the composition of sediment subducted. Where the subducting sediment has Th/La > 0·2, the arcs have Th/La >0·15, and where the sediment has a value <0·2, the arcs are <0·15. This break in the sediment ratio corresponds to a predominance of terrigenous material (Th/La > 0·2; Fig. 2) vs slowly deposited metalliferous and phosphate-rich sediments (Th/La < 0·2). Thus, the sedimentological processes that mix different sedimentary components on the seafloor ultimately influence the composition of basalts erupted at nearby volcanic arcs. This provides further evidence, along with ^{10}Be- (Tera *et al.*, 1986), Nd- and Pb-isotopes (White *et al.*, 1985), and trace-element fluxes (Plank & Langmuir, 1993), that local sediments are recycled through the subduction zone. Vroon *et al.* (1995) was perhaps the first to note that sediment trace-element ratios may be preserved in adjacent arc volcanics (in this case, Banda). I have extended this work to show that an element ratio can be used much like an isotope ratio to trace sediment recycling on a global basis.

Not only is there a relationship between Th/La input and output, but the slope of the correlation is near unity for the high sediment flux margins (Fig. 3). This result suggests that there is little change in Th/La during sediment recycling in subduction zones. Arcs with high sediment flux inherit the sediment ratio. This is not simply a matter of arc cannibalism, as local arc ash is a minor component of bulk sediment columns (Plank & Langmuir, 1998). Although there is a good deal of scatter in Fig. 3, few of the data points indicate higher ratios in

Table 1: Th/La and Sm/La in average arc basalts and subducted sediments

	n	SiO_2	Th/La arc average	± 2σ	Th/La bulk sed	± M.C.	Sm/La mantle	± regr.	Th/La sed comp	±	Ref.
Tonga	10	<55·0	0·09	0·008	0·074	0·005	3·0	1·0	0·12	0·01	1, 2, 3
Vanuatu	30	<51·0	0·12	0·02	0·13	0·02	0·8	0·20	0·13	0·01*	4, 5, 6
Java	9	<53·0	0·20	0·10	0·25	0·03	0·6	0·15	0·23	0·03*	8, 9, 10
E. Sunda	15	<54·0	0·27	0·06	0·26	0·03	1·4	0·30	0·30	0·02*	10, 11
Banda	14	<59·0	0·34	0·06	0·36	0·04	1·2	0·20	0·37	0·03*	12
Marianas	13	<53·0	0·12	0·02	0·14	0·02	1·3	0·35	0·14	0·02	7
Honshu	13	<53·0	0·32	0·11	0·28	0·07	0·8	0·10	0·24	0·04*	13
Kuriles	5	<54·0	0·17	0·06	0·28	0·07					14, 15
Kamchatka	7	<52·0	0·09	0·02	0·16	0·07	0·9	0·20	0·14	0·01*	16
Aleutians	7	<53·0	0·22	0·04	0·31	0·02	0·65	0·05	0·32	0·03	1
Guat-ES	11	<55·0	0·14	0·02	0·059	0·02	0·6	0·15	0·19	0·02*	1
N. Antilles	13	<52·5	0·20	0·04	0·34	0·03	0·94	0·15	0·32	0·03	1
S. Antilles	50	<52·5	0·29	0·07	0·31	0·02	0·94	0·15	0·40	0·02	1, 17–20
S. Sandwich	18	<54·0	0·16	0·04	0·38	0·02	1·8	0·20	0·34	0·06	1, 21
Average			0·25	0·07	0·24	0·06					

n, number of samples in arc average, below silica cut-off; M.C., uncertainties calculated using Monte Carlo method described in Fig. 3; regr., uncertainties are from error envelope on the regression, as explained in Fig. 4. Uncertainty in Th/La sedimentary components derives from range in mantle Sm/La, except for those cases denoted by *, where mantle Sm/La is fixed, and error is 2σ of average Th/La for each sample. (See Electronic Appendix A for notes on regressions and data). Bulk sediment Th/La from Plank & Langmuir (1998). Arc average Th/La is based on average Th and La concentrations of each of the 14 arcs, not the average of the 14 ratios. Average sediment Th/La is GLOSS (Plank & Langmuir, 1998), with M.C.-derived uncertainty on ratio from standard deviation of Th and La. Arc Th/La references given in table and keyed to below:
1: Electronic Appendix B; 2: Turner *et al*. (1997); 3: Ewart *et al*. (1998); 4: Peate *et al*. (1997); 5: Dupuy *et al*. (1982); 6: Gorton (1977); 7: Elliott *et al*. (1997); 8: Whitford (1975); 9: Varne & Foden (1986); 10: Stolz *et al*. (1990); 11: Hoogewerff *et al*. (1997); 12: Vroon (1992); 13: Gust *et al*. (1995); 14: Bailey *et al*. (1987); 15: Ryan (1995); 16: Hochstaedter *et al*. (1996); 17: Gravatt (1997); 18: Thirlwall & Graham (1984); 19: White & Dupre (1986); 20: Dupuy *et al*. (1985); 21: Pearce *et al*. (1995).

the arc than in the sediment. Thus, there is little evidence that the high Th/La of the continental crust is created by processes occurring in the subduction zone.

Unmixing the mantle and sediment contributions to arc Th/La

The relationship between arc and sediment Th/La (Fig. 3), although significant, is dependent on a small number of arcs with a large subducted sediment flux. For the other arcs, the mantle contribution obscures the sediment's Th/La. If there were a way to correct for the effect of mantle dilution, then the sedimentary mixing component could be examined for each arc to further test the correlation in Fig. 3. One way to accomplish this is to exploit the mixing relationships observed for individual samples within each arc, in particular, those for which high-quality trace-element data have been obtained (See Electronic Appendix A). Toward this end, new ICP-MS (inductively coupled plasma mass spectrometry) trace-element data are reported here for approximately 70 mafic samples from five arc systems (Electronic Appendix B, available at http://www.petrology.oupjournals.org). Several arc suites form trends consistent with variable amount of mixing between slab sediment and the mantle. For example, Fig. 4 shows Th/La vs Sm/La for basaltic samples from the Lesser Antilles arc. Both Th/La and Sm/La should vary, depending upon the proportion of sediment and mantle in basalt genesis, and, indeed, the Lesser Antilles data trend between a component with high Sm/La that could lie within the MORB array and a component with high Th/La that lies near the actual sediment subducting at the Lesser Antilles margin. Sm/La is a useful parameter because it is a measure of the extent of LREE depletion or enrichment and so is well understood from the REE pattern. Moreover, mixing lines are straight lines on plots of Sm/La vs Th/La, and so end-members are simple to calculate. Straight lines, however, could also result if both ratios were dominated by La variations, in which case Th/La and Sm/La would be highly positively correlated. This is clearly not the case, as MORB, OIB and arc data form inverse trends; in fact, for the Antilles, Th/La increases as both Th and La increase. These relationships are not consistent with La control, but are consistent with sediment–mantle mixing.

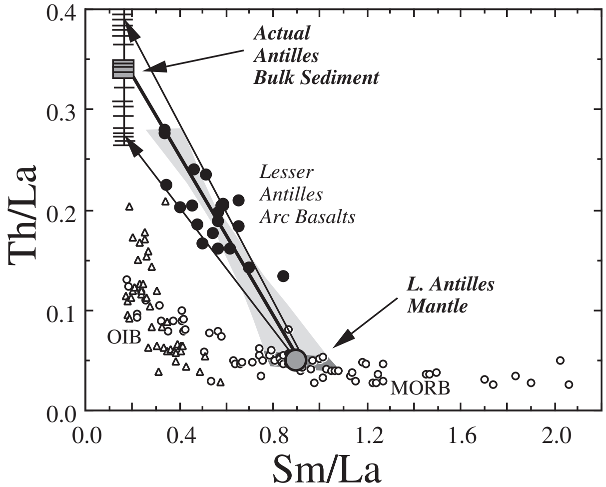

Fig. 4. Variation of Sm/La vs Th/La to illustrate mantle–sediment unmixing calculations. Lesser Antilles arc basalts form a trend consistent with mixing between MORB-type mantle and a sedimentary component. Bold line is linear regression of Antilles basalts (R = –0·76). Shaded field is confidence band on the regression line [from Till (1974)]. The intersection of the regression line and confidence band with the MORB array (open circles) gives the composition of the Lesser Antilles mantle, prior to contributions from the subduction zone. The other end of the arc regression line projects to the sedimentary component from the slab, which in this case is identical to the actual composition of the bulk sedimentary column being subducted beneath the Northern Antilles margin (gray box). In practice, the sedimentary component is calculated for each data point by projecting from the average Antilles mantle to the Sm/La value for the bulk sediment (hatch marks). Thus, the Antilles arc data array provides an independent estimate of the local mantle (Sm/La = 0·94 ± 0·15) and the sedimentary component from the slab (Th/La = 0·32 ± 0·03). The Antilles mantle is very close to average N-MORB [0·96, Hofmann (1988)], although other arcs tap different kinds of mantle (see Figs 5 and 6; Table 1). MORB from Niu & Batiza (1997); OIB (open triangles) from Pacific database provided by Tim Elliott; bulk sediment is for the northern Antilles, from Plank & Langmuir (1998). Arc data are all new ICP–MS data from Electronic Appendix B, and include predominantly the northern islands (Dominica and north, and St Vincent in the south). All samples plotted have <52·5% SiO_2, and are from islands that show limited crustal contamination based on limited variation in $^{87}Sr/^{86}Sr$ with silica [following arguments of Davidson (1987) and isotopic data of White & Dupre (1986)].

All of the arc data can be interpreted in this way, and the trends can be used to obtain independent estimates for the mantle and sedimentary mixing components for each arc. Returning to the case of the Lesser Antilles (Fig. 4), a line regressed through the data intersects the MORB–OIB mantle array at Sm/La of ~0·9 [very near N-MORB at Sm/La = 1·0 (Sun & McDonough, 1989; Hofmann, 1988)]. This end-member approximates the mantle prior to slab additions. Each arc data point can then be projected from the mantle to calculate the high Th/La sediment component potentially involved. In practice, it is assumed that the high Th/La component has the same Sm/La as the bulk subducted sediment, but even projecting to the y-axis would not change the results significantly for the Lesser Antilles (Fig. 4). Experiments conducted at 2 GPa (Johnson & Plank, 1999) show that Sm/La is not fractionated during sediment dehydration at 700°C, but is lowered by a factor of 1·6 in sediment melts at 800°C. If Sm/La in the sedimentary component is reduced by this factor, then the resulting effect on Th/La of the sediment end-member is generally small (for Fig. 4, Th/La of 0·36 vs 0·34).

Figure 5 shows diverse mixing trends for the arcs considered here. For example, Marianas and eastern Aleutian basalts appear to mix toward different mantle compositions and different sedimentary components. The Marianas mantle is more depleted (higher Sm/La) than N-MORB (~1·0), whereas the Aleutian mantle is comparable with a more enriched MORB (i.e. with a flat REE pattern), consistent with other inferences based on high-field-strength elements (Woodhead *et al.*, 1993; Elliott *et al.*, 1997; Pearce *et al.*, 1999; Electronic Appendix B). On the other hand, the eastern Aleutians mixes toward sediment with higher Th/La than that for the Marianas arc, consistent with higher Th/La in the bulk sediment column subducting there (Fig. 5a). Despite complexities introduced by multiple components, crustal contamination and variable data quality (see notes in Electronic Appendix A), this procedure provides independent estimates of the mantle and sediment components for each convergent margin. This has been an elusive goal in studying subduction zone systems, where a minimum of four sources are often involved (mantle, slab sediment, slab basalt and upper plate lithosphere). Upper crust contamination is minimized here by examining only basalts, although contamination is clearly an issue for several arcs built on high Th/La continental material (see Honshu, Fig. 5h). Slab basalt aqueous contributions are also minimized by focusing on 'fluid-immobile elements' Th, La and Sm. Thus, this procedure attempts to isolate sediment and mantle components, and so provides a useful control in the multi-component mixing problem.

The composition of the sub-arc mantle

The sub-arc mantle composition, although not the focus of this paper, is an interesting by-product of the unmixing calculation. Studies of individual arcs have variously argued for N-MORB-type mantle (e.g. Stolper & Newman, 1994), ultra-depleted mantle (e.g. Ewart & Hawkesworth, 1987; Woodhead *et al.*, 1993) and enriched mantle (e.g. Morris & Hart, 1983; Reagan & Gill, 1986). Often, these conclusions are based on isotopic data, which can be ambiguous with respect to enriched mantle vs sediment, or high-field-strength elements, which reflect a combination of mantle depletion and slab enrichment (Elliott *et al.*, 1997). The technique given here is useful in this regard, in that it explicitly accounts for slab enrichment (using Th/La). The primary assumption in this technique is that melting processes

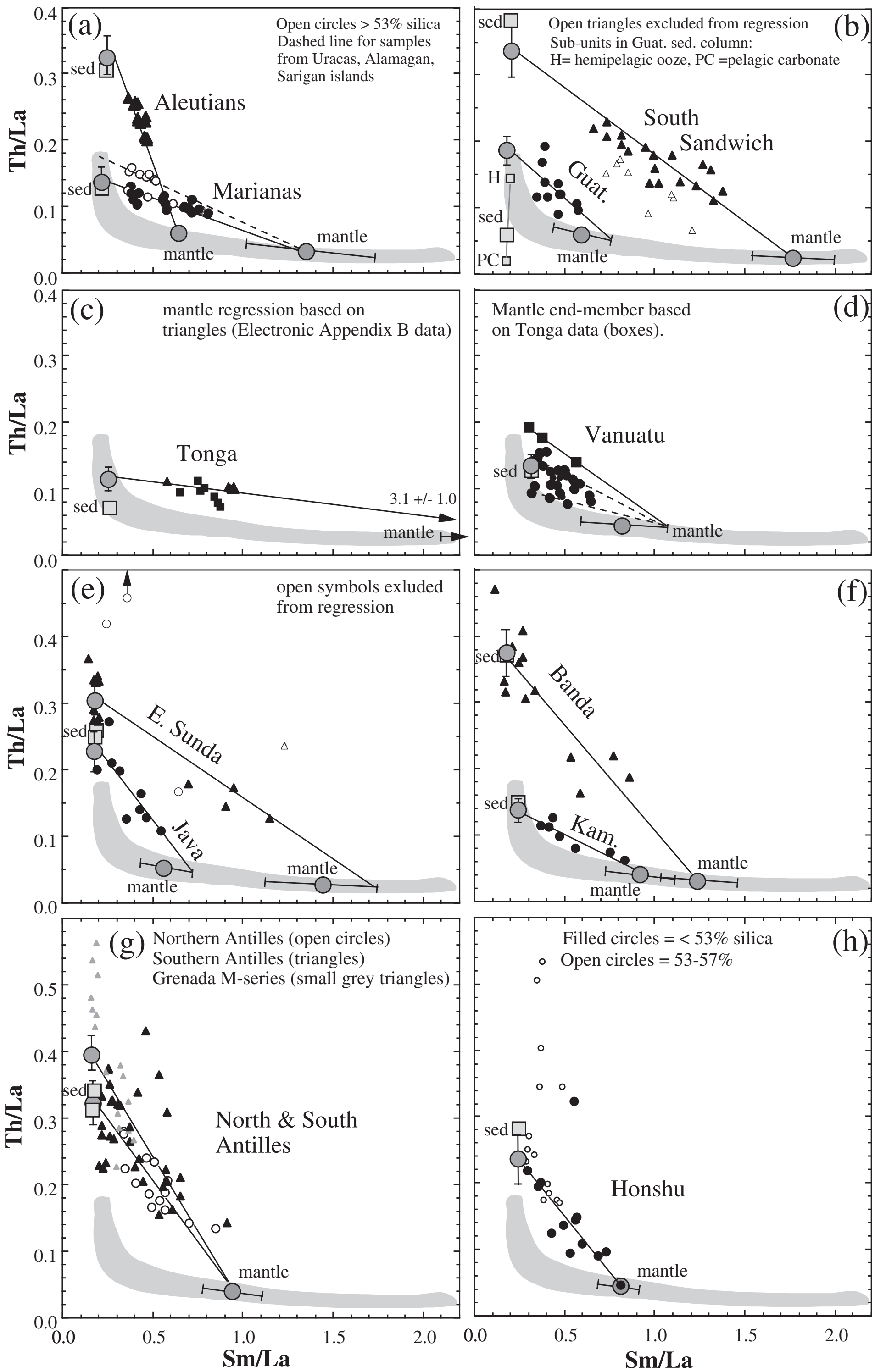

Fig. 5. Sm/La vs Th/La in arc basalts, and inferred mantle and sediment mixing end-members (large gray filled circles) calculated by regression through the arc data (as in Fig. 4). MORB and OIB mantle shown as light gray field; actual sediment compositions [from Plank & Langmuir (1998)] are shown as large boxes. Line is drawn between calculated mantle and sedimentary components. Note that each arc array unmixes to a unique mantle composition, which varies from Sm/La more depleted than N-MORB (1·0) to Sm/La approaching E-MORB (0·4; see Fig. 6), and a unique sedimentary composition, which is very similar to the actual sediment subducted. In some cases, the mantle end-member used to back-project each arc point lies at the upper range of the regression, in order to prevent impossible or widely varying sediment components. Detailed notes on data and regressions for each arc given in Electronic Appendix A.

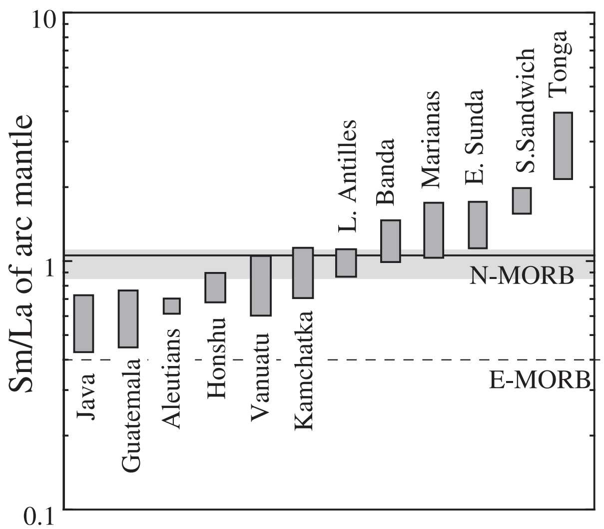

Fig. 6. Sm/La of the arc mantle prior to slab additions. Each bar represents the range of mantle values calculated from Fig. 5 (values given in Table 1). Some arcs tap mantle more LREE-enriched than N-MORB (Java, Guatemala, Aleutians), whereas others tap mantle much more depleted than average MORB (Tonga, S. Sandwich). N-MORB and E-MORB from Sun & McDonough (1989). Shaded horizontal bar is average Pacific MORB (0.98 ± 0.03, 2σ; *n* = 145 from PetDB, 20°N–20°S).

have a small effect on the Th/La and Sm/La of the mantle source. Strictly speaking, the mantle end-member identified here is a mantle melt and will include melting and melt-reaction processes. Partial melting will cause negligible variations in Th/La, because both elements are highly incompatible, but may contribute to variations in Sm/La. For example, 5% batch melting leads to 15% lower Sm/La than in the source (assuming $D_{La} = 0{\cdot}001$ and $D_{Sm} = 0{\cdot}01$), but this is a small effect compared with the range in MORB and arc basalts (>400%; Figs 4 and 6). Thus, Sm/La extrapolated from the arc data may be largely a function of the mantle-source composition.

Figure 6 illustrates differences in Sm/La of such inferred sub-arc mantle sources, from compositions approaching E-MORB (Java and Aleutians) to compositions more depleted than average MORB (Tonga and South Sandwich). Most melting processes will decrease Sm/La relative to the mantle source (as above), so Sm/La mantle end-members presented here are minima. For this reason, the following discussion focuses on high Sm/La (i.e. depleted mantle) regions. The inferred mantle compositions in Fig. 6 can be compared with those from Pearce & Parkinson (1993), who plotted Nb vs Y to identify depleted vs enriched mantle sources. Our results are consistent for depleted arcs (Tonga, Sandwich, Marianas), but not for arcs with higher Nb. For example, the Lesser Antilles arc plots in the enriched mantle field on Pearce & Parkinson's Nb/Y diagram, whereas the results here suggest that the Lesser Antilles mantle source may be depleted mantle typical of N-MORB. Nb may derive from enriched mantle and/or subducted sediment (Turner *et al.*, 1996; Elliott *et al.*, 1997), and so may be a less reliable indicator of mantle-source enrichment than projected Sm/La compositions, from which sediment contributions are explicitly removed.

Nonetheless, both techniques support the existence of highly (LREE) depleted mantle beneath some arcs. Several other studies have suggested that such depleted mantle may originate from melting in back-arc regions, which may deplete mantle that later melts beneath the arc (e.g. Ewart & Hawkesworth, 1987; Woodhead *et al.*, 1993). Among the five arc sources that are more depleted than average MORB (Tonga, South Sandwich, E. Sunda, Marianas and Banda, Fig. 6), three are in regions with nearby, recent back-arc spreading. For these three arcs, there is also a suggestion that the extent of mantle depletion in the arc correlates with spreading rate in the back-arc (i.e. Sm/La decreases from Tonga to South Sandwich to the Marianas arc as spreading rate decreases from Lau to Scotia to the Mariana back-arc). The very depleted mantle beneath Banda and E. Sunda is unexpected, as there is currently no back-arc spreading. It is possible that dynamic effects (stalling?) associated with continental margin subduction lead to progressive melt depletion beneath E. Sunda and Banda. Of the other seven arcs, which have normal MORB or more enriched mantle, there is no active back-arc spreading within 400 km of the arc. Thus, the mantle sources beneath arcs vary in composition, much like the MORB mantle, but more highly depleted sources may be generated by concurrent back-arc spreading.

Finally, this work, combined with others (Woodhead *et al.*, 1993; Elliott *et al.*, 1997; Pearce *et al.*, 1999), argues strongly against OIB-type mantle in places such as the Marianas, where Sr-, Nd- and Pb-radiogenic isotopes overlap with some OIB (e.g. Morris & Hart, 1983; Stern & Ito, 1983). The preponderance of evidence now suggests that the Marianas mantle is more depleted than average MORB mantle, and that non-MORB isotopic ratios (e.g. $^{87}Sr/^{8}6Sr$, $^{143}Nd/^{144}Nd$) and trace-element ratios (Th/La-, Th/Nb-, Ce-anomalies) derive from subducted sources.

Th/La in sedimentary components that recycle to the arc

The main purpose of the unmixing calculation is to provide estimates of Th/La in the sedimentary component that recycles to the arc. Figure 7 compares Th/La in the sedimentary column subducting at the trench with Th/La in the sedimentary component calculated from the arc mixing trends. The relationship is very close to one-to-one. Within uncertainties, most arcs mix toward a component that has the same Th/La as the sediment subducted.

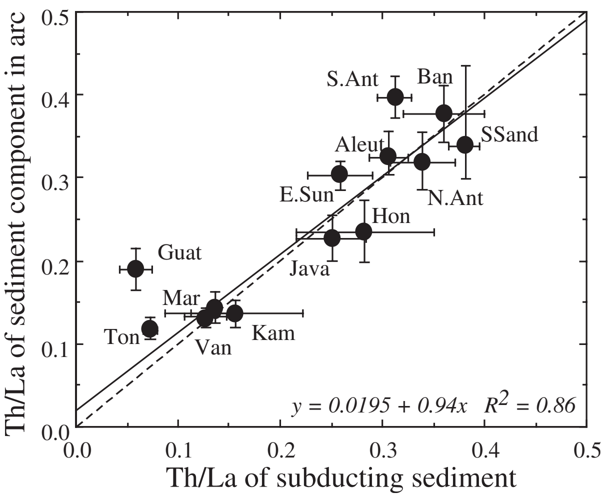

Fig. 7. Th/La in subducting sediment (as in Fig. 3) vs Th/La in the sedimentary component projected from the arc data (as in Fig. 5). This diagram is analogous to Fig. 2, except that arc data have been corrected for dilution with the mantle, to reveal the sedimentary mixing component for each arc (as shown in Fig. 5). Note that Th/La of the sedimentary component in the arc is virtually identical to Th/La in the sediment subducting at the trench. This provides strong evidence that Th and La are not fractionated significantly in the subduction zone, and that arcs inherit sedimentary values. Dashed line has a slope of one; continuous line is linear regression through the data (excluding Guatemala; equation and R^2 given). Horizontal error bars as in Fig. 3; vertical error bars as in Table 1.

Although the correlation is strong ($R^2 = 0{\cdot}86$), a few arcs are significantly displaced from the correlation line (Fig. 7). Most of the Honshu arc taps a component that has lower Th/La than the estimated bulk sediment. The ratio within the sedimentary column varies greatly, however, with values above 0·35 in the upper diatom and pelagic clay units, and values below 0·1 in the lower clay and chert unit (Cousens *et al.*, 1994; Plank & Langmuir, 1998). Thus, the average Th/La is very sensitive to the proportions of the different pelagic units. Although these pelagic units do not vary greatly in thickness on the seafloor, dynamic effects during subduction, such as frontal accretion or underplating (von Huene & Scholl, 1991), may affect the final subducted composition. Independent evidence for loss of the upper sedimentary unit in the Honshu fore-arc comes from a lack of ^{10}Be in the arc (Tera *et al.*, 1986), ^{10}Be profiles in the fore-arc that are consistent with frontal accretion (Morris *et al.*, 2002) and Pb-isotopic compositions that are shifted toward the lower pelagic units (Cousens *et al.*, 1994; Gust *et al.*, 1995). Loss of the upper 165 m of the Honshu sediment section will lower Th/La from 0·28 to 0·24, in better accord with the main arc trend (Fig. 5). Alternatively, Th/La will increase in the Honshu arc average if some of the anomalously high Th/La compositions shown in Fig. 5h are included, but these compositions are generally found in more silicic volcanics (>53 wt % SiO_2), which are interpreted as crustally contaminated.

Arcs that plot significantly above the correlation line in Fig. 7 include Tonga, Guatemala, E. Sunda and the S. Antilles. The high S. Antilles values arise from the unusually high values in the southern end of the arc, in Kick-em-Jenny volcano and the M-series of Grenada (Fig. 5g). Basalts from these islands have higher $^{87}Sr/^{86}Sr$ (>0·7045) than those from the rest of the Lesser Antilles arc, and this feature has been interpreted as a product of crustal assimilation (Davidson, 1987; Thirlwall *et al.*, 1996). If such high $^{87}Sr/^{86}Sr$ samples are excluded from the S. Antilles average (which excludes all samples from Kick-em-Jenny and St Lucia), then the S. Antilles sedimentary component shifts from 0·40 ± 0·02 to 0·36 ± 0·02, closer to the estimate for the subducting sedimentary column (0·31 ± 0·02). However, most of the very thick sediment wedge (>1500 m) subducting beneath the S. Antilles is unsampled, and so the sedimentary column is poorly known (Plank & Langmuir, 1998). Thus, better control on the sediments and volcanics in the southern portion of the Lesser Antilles arc are needed before determining whether this fractionation is real. Like Honshu, the E. Sunda sediment average depends critically on the proportion of the main lithologic units present (Plank & Langmuir, 1998), namely, Cretaceous clays (with Th/La = 0·25) and Cenozoic carbonate turbidites (with Th/La = 0·34). Nearby ODP Site 765 contains more carbonate turbidites than DSDP 261, and so has a bulk Th/La = 0·29 instead of 0·26 (Plank & Ludden, 1992), which is closer to the arc value and may be more typical of the Australian margin crust subducted beneath E. Sunda. Thus, given uncertainties in the layer thickness of the different units (particularly the carbonate turbidites), the E. Sunda arc may reflect the bulk sediment subducted. Indeed, increases in Th/La along the arc, from Java to E. Sunda to Banda, and from the northern to the southern Antilles, are qualitatively consistent with increasing proximity to continental crust (and high Th/La terrigenous material) in each of those cases. Unfortunately, proximity to continental crust leads to greater uncertainties in bulk sediment estimates, as a result of thick (and undrilled) sedimentary sections, as well as the dynamic complexities of incipient arc–continent collision.

Unlike the Antilles and Sunda cases, Guatemala and Tonga are difficult to reconcile with small differences in layer thicknesses or uncertainties in the sediment subducted. In both cases, sedimentary compositions are well known, and all of the arc values exceed the bulk sediment composition (Fig. 5b and c). Moreover, all of the Tonga sedimentary units have Th/La < 0·07, except for the upper brown clay unit (Th/La = 0·25). The thickness of the brown clay unit would have to be increased from 10 to 80 m in order to raise the bulk sediment Th/La to that of the Tonga arc (0·115). This seems unlikely, as it would require doubling the thickness of the sedimentary column and, whereas under-plating is always likely, spontaneous thickening is less so. Like Tonga, all of the Th/La ratios in the Guatemala arc data exceed the value in the bulk sediment. The Guatemala bulk sediment has very low Th/La because of the low ratio in the lower pelagic carbonate unit. This is the only dominantly carbonate section in all of the margins considered here, and so the shift of the Guatemala arc could derive from fundamentally different partitioning between fluids and carbonate vs siliciclastic lithologies. Alternatively, Carr *et al.* (1990) proposed that Sr- and Nd-isotopic compositions for some Guatemala volcanics have been affected by crustal contamination, and this could raise Th/La as well. Several basalts in Guatemala and El Salvador, however, which have high $^{143}Nd/^{144}Nd$ (>0·5129; Fuego, Conchagua) and do not appear crustally contaminated, still have higher Th/La than the bulk sediment subducted. Thus, this fractionation may be real and could arise from the different carbonate lithologies subducted at the Middle America trench. Finally, Tonga and Guatemala sediments are noteworthy in their high relative abundance of biogenic apatite, which may fractionate Th from La in the direction observed (see below).

To summarize this analysis, arc basalts clearly inherit the Th/La of the local sedimentary column subducted. Within the uncertainties of the calculation, the arc data trend toward a sedimentary mixing component that has the same Th/La as the bulk sediment at the trench. Apart from a few exceptions (Tonga and Guatemala), there is very little evidence that Th and La are fractionated in the subduction zone during sediment recycling to the arc. The predominance of sedimentary columns with bulk Th/La < 0·35 (Fig. 7) and the significant mantle component in most arcs (Fig. 3) means that arc addition has little effect on Th/La in the continental crust. The Th/La in average arc material is 0·25 ± 0·07 (Table 1), compared with 0·27 ± 0·05 for the bulk continental crust (Fig. 1). Although it may appear that the bulk continental crust inherits its Th/La from arcs, the reverse is the case. The prior analysis demonstrates that arcs inherit their Th/La from subducted sediment, and so they do not add 'new' high Th/La material to the continents. The net effect of subduction on Th/La in the continental crust is null: crust is removed as subducted sediment with Th/La of 0·24 ± 0·06 (Table 1), and replaced as arcs with Th/La of 0·25 ± 0·07. Subduction does not appear to create the high Th/La of the continents.

CREATING HIGH Th/La IN THE CONTINENTAL CRUST

If the high Th/La of the continents is not created in subduction zones, then where is it created? Possibilities include other kinds of crustal additions (intraplate magmatism and Archaean magmatism) and other kinds of crustal losses (lower-crustal foundering/delamination), in combination with intracrustal processing. The first issue to consider, however, is the uncertainty in the estimate of the composition of the bulk continental crust.

Uncertainties in the composition of the bulk continental crust

The composition of the bulk continental crust is difficult to estimate with certainty because so little of it is exposed. Whereas the upper continental crust composition is fairly well constrained from average shale and loess compositions (Th/La = 0·33 ± 0·05, average UCC estimates in Fig. 1), the bulk composition of the lower crust is not well known. Current estimates are based on granulite xenoliths and exposed granulite terranes, for which geobarometry indicates equilibration at lower-crustal pressures (Rudnick & Presper; 1990; Gao *et al.*, 1998). The database of Rudnick & Presper (1990), with over 2000 analyses of such granulites, provides a good sampling of the total range in granulite compositions, but there are large uncertainties in knowing how to weight the different compositions to obtain a lower-crustal average. The approach is typically to calculate medians or means from available analyses, and this has yielded estimates that are generally consistent with average P-wave velocities and heat-flow constraints (Rudnick & Fountain, 1995; Gao *et al.*, 1998; Rudnick *et al.*, 1998).

Given the range of lower-crustal compositions, however, is it possible to create a bulk continental crust with Th/La ~ 0·1, similar to the primitive mantle? Figure 8a shows the trend in Th vs Th/La for granulite xenoliths (La vs Th/La is scattered). A minimum value for Th/La in the bulk crust can be calculated by taking the lowest Th/La regions (Chudleigh and McBride; Rudnick *et al.*, 1986; Rudnick & Taylor, 1987; see Fig. 8a) and assuming they make up the entire lower and middle crust (~70% of the crust). Even by using these extreme compositions, the bulk continental crust will still have Th/La > 0·2. There is poor leverage on this calculation, because the lowest Th/La granulites have the lowest Th concentrations, and so the least effect on the bulk crust. These calculations illustrate that the upper crust, which is the best-constrained crustal reservoir, is the dominant control on the composition of the continents because it has such high Th and La concentrations (10 s of ppm). Given the range of possible compositions for the lower crust (Fig. 8a), the bulk continental crust still has significantly higher Th/La than the mantle (0·27 ± 0·05; average BCC estimates in Fig. 1).

Another way to lower Th/La in the bulk continental crust is to add eclogite-facies material below the seismic Moho. Current estimates of the bulk continental crust are based to some degree on seismic velocity models, which

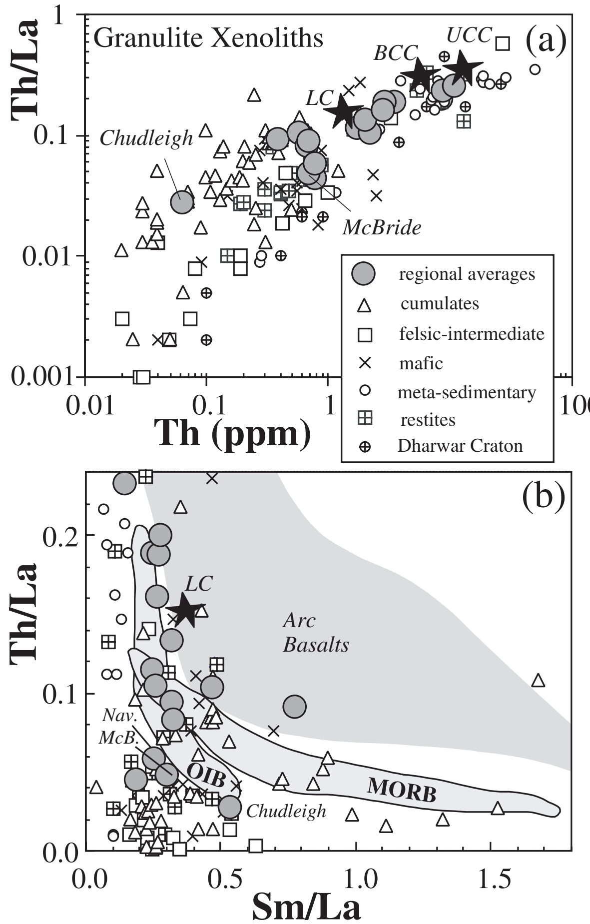

Fig. 8. (a) Th concentration vs Th/La, and (b) Sm/La vs Th/La in granulite xenoliths (Rudnick & Presper, 1990) and samples from the Dharwar Craton, India (Hansen *et al.*, 1995). Regional averages are calculated from the average Th and La concentrations in xenoliths from geographic regions (Rudnick & Presper, 1990). Shown for reference are lower crust (LC), upper continental crust (UCC) and bulk continental crust (BCC) compositions from Rudnick & Fountain (1995). In (b), fields are shown for MORB, OIB and arc basalts (as in Figs 4 and 5). Same symbols used in (a) and (b).

may not include seismically fast pyroxenites within the petrologic crust. For example, xenolith suites in Miocene lavas from the central Sierras contain abundant garnet clinopyroxenites, which, based on geobarometry, are derived from below the seismic Moho (Ducea & Saleeby, 1996). Sparse chemical data from these samples indicate that they are highly depleted in Th and La (~0·1 ppm Th and 3 ppm La; Ducea, 2002) and so have little leverage on bulk continent compositions. Other sub-Moho garnet clinopyroxenites have Th/La ≥ 0·1 (Griffin *et al.*, 1988; Wendlandt *et al.*, 1993), and so cannot drive the continents to mantle values <0·1. Even using the most extreme mafic granulite compositions (McBride xenoliths; Rudnick & Taylor, 1987), adding a 20 km eclogite-facies root to the entire average continental crust (as for the central Sierras) will still not create a bulk continental crust with Th/La < 0·2. Moreover, garnet pyroxenites are not abundant in most lower-crustal or mantle xenolith suites (Schulze, 1989; Rudnick & Presper, 1990) and so may not constitute a major reservoir beneath the continents. Thus, given that the major budget of Th and La resides in the upper crust, and given that the upper crust has a well-constrained Th/La ~ 0·3, it is difficult to create a bulk continent with Th/La < 0·2, even by adding a 'lowermost' crust with extreme compositions.

Intraplate magmatism

Modern oceanic mantle melts (e.g. MORB and OIB) possess low Th/La, generally <0·1 (Fig. 4). Other kinds of intraplate magmas, however, contribute directly to the continents, and thus it is important to asses their Th/La. Indeed, O'Nions & McKenzie (1988) argued that the continents are formed from low-degree mantle melts, typical of those found in small, intraplate seamounts in the Pacific. These seamounts, however, have Th/La < 0·15 (Batiza & Vanko, 1984) and so this model fails to explain the high Th/La (>0·2) of the bulk continental crust. In fact, intraplate basaltic magmas with Th/La > 0·2 are rare. Most flood basalts overlap with OIB compositions, at Th/La < 0·15. Exceptions include some compositions between 0·15 and 0·25 that occur in the Siberian, Columbia River and Keweenawan provinces, where crustal or subduction contamination has been invoked (Carlson, 1984; Klewin & Berg, 1991; Wooden *et al.*, 1993). Th/La ratios > 0·2 are uncommon in potassic rift volcanics, lamproites and nephelinites (Fraser *et al.*, 1985; Anthony *et al.*, 1989; Wilson, 1989). Although some of the Goudini carbonatites have high Th/La (>0·3), this is not a general feature of carbonatites (Nelson *et al.*, 1988). Most carbonatites have Th/La < 0·10, and the few high ratios could represent recycled continental material (Nelson *et al.*, 1988). Although many potassic volcanics do not have high Th/La (East African; Wilson, 1989), those from the Roman province can have Th/La > 0·5 (Rogers *et al.*, 1985). These leucitites, however, may also reflect subducted sediment in their source (Rogers *et al.*, 1987). Thus, in general, mantle-derived magmas do not have high Th/La, except when sediment subduction is independently implicated. The high Th/La of the continents does not appear to be produced by any mantle-melting process.

Archaean magmatism

Another possibility for explaining the high Th/La of the continental crust is to create this feature in the Archaean, with modern tectonic processes having little net effect. This mechanism is analogous to models that create the silicic crust in the Archaean by processes different from those today, such as tonalite genesis during slab melting in the hotter Archaean mantle (e.g. Martin, 1986; Rudnick, 1995). Th/La of the bulk Archaean crust is estimated at 0·17–0·19 [by Rudnick & Fountain (1995) and Taylor & McLennan (1985), respectively]. A more recent revision based on heat-flow constraints (McLennan & Taylor, 1996) yields Th/La of ~0·19 (for a 1:1 mixture of felsic and mafic components). These low values for the Archaean continental crust are consistent with low Th/La in average Archaean mafic and felsic end-members (<0·22; Taylor & McLennan, 1985), in average Archaean felsic, andesitic and basaltic volcanics (<0·2; Condie, 1993), and in average lower crust from platform and shield areas (<0·15; Rudnick & Fountain, 1995). These observations are also consistent with the low Th/La of modern adakites (primitive andesites from the western Aleutians have Th/La < 0·15; Kelemen *et al.*, 2003*b*), which are thought to be derived from melts of the basaltic portion of subducting slabs that interacted with the overlying mantle wedge during ascent. Finally, Condie (1993) showed that Archaean tonalites, granites and felsic volcanics have lower Th/La than their Phanerozoic counterparts. Thus, there is little evidence that the Archaean continents had as high Th/La as the modern bulk crust (0·17–0·19 vs 0·27 ± 0·05). The fractionation between the Archaean continental crust (Th/La ~ 0·18) and the primitive mantle (Th/La ~ 0·12) may be enough to explain the depletion of the MORB reservoir (Th/La ~ 0·05), but it is not enough to explain Th/La in the modern continents.

Further evidence that the Archaean continents had low Th/La comes from the secular increase in this ratio recorded in independent estimates of upper-crust age provinces (Fig. 9). Both sedimentary rock averages (Taylor & McLennan, 1985) and areally averaged juvenile crustal provinces (Condie, 1993) show an increase in Th/La with time (Fig. 9). This observation provides further evidence that high Th/La was not an intrinsic feature of the Archaean continents, but rather that processes operating in the Proterozoic and Phanerozoic have resulted in an evolution toward higher continental Th/La.

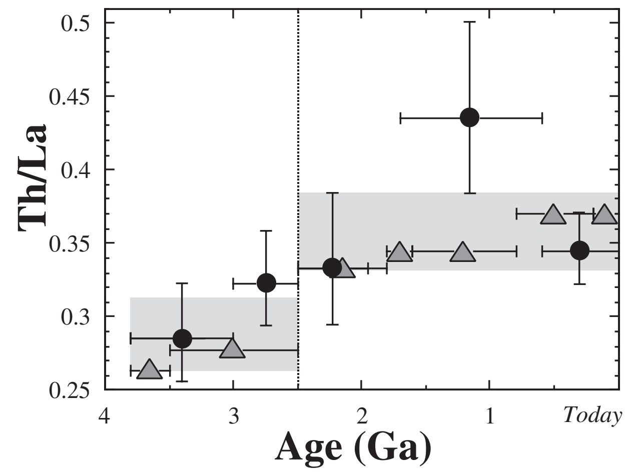

Fig. 9. Secular change in Th/La in the upper continental crust. Filled circles: estimates from Taylor & McLennan (1985) based on fine-grained sedimentary rocks. Triangles: estimates from Condie (1993) based on areal distributions of juvenile surface samples (restored for effects of erosion). Shaded bars are Archaean and post-Archaean average sediments from Taylor & McLennan (1985).

Crustal fractionation and foundering

There is little evidence from the preceding discussion that magmatic additions from the mantle (at subduction zones, in intraplate settings, or during the Archaean) create the high Th/La of the modern continents. This leaves open the possibility of crustal subtractions—in the form of subducted sediment or of foundered/delaminated lower crust. The similarity in Th/La of subducting sediments (0·24 ± 0·06; Table 1), arc basalts (0·25 ± 0·07; Table 1) and the bulk continental crust (0·27 ± 0·05; Fig. 1) means that subduction recycling has no net effect on the continents. On the other hand, there is a large fractionation of Th/La within the continents (Fig. 8a), with the average lower crust (0·15) being more than a factor of two lower than the average upper crust [0·36; using self-consistent estimates of Rudnick & Fountain (1995)]. Periodic loss of the lower crust during delamination or foundering episodes (see below) could remove low Th/La material, thus enriching the continents with time. This will not work if under-plated mafic material simply founders back into the mantle. Mafic material that enters the crust must differentiate into a low-Th/La lower crust and a high-Th/La upper crust for this process to have a net effect on the bulk continent. Several fractionation processes may occur to create a low-Th/La lower crust.

There is abundant evidence that the lower crust contains materials with very low Th/La (<0·1; Fig. 8a) and that some of this depletion is created in the crust. Lower-crustal xenoliths and regional averages are plotted in Fig. 8b to demonstrate that many of these compositions are unlike MORB, OIB or arc basalt. In particular, most mafic granulites and cumulates, as well as regional averages from Chudleigh, McBride and Navajo xenolith fields, are more depleted in Th/La for their Sm/La than common basaltic compositions, despite the fact that their protoliths are basaltic magmas. Some mafic granulites have Th/La within the MORB–OIB array (Fig. 8b) and, although these could reflect primary ratios, many of these granulites have been interpreted as arc basalts (Wendlandt *et al.*, 1993; Mattie *et al.*, 1997), and therefore have probably been shifted to lower Th/La compositions in the crust. These common low-Th/La compositions in the mafic granulite xenolith database could be a result of Th loss during granulite–facies metamorphism, as has been argued by Rudnick & Presper (1990) and Condie & Myers (1999), or could also be an intrinsic feature of plagioclase- and clinopyroxene-rich cumulates (Kelemen *et al.*, 2003*a*). In fact, as many as three separate processes could create low Th/La in lower-crustal mafic granulites: (1) Th loss relative to La in melts during crustal anatexis; (2) Th loss relative to La in fluids during granulite-facies metamorphism; (3) cumulate processes, individually or in combination.

Fractionation of Th/La within the continental crust

Igneous processes are clearly major drivers in the differentiation of the continental crust, as evidenced by the abundance of granites and granodiorites in the upper crust. The prominent negative Eu-anomaly in the upper crust also points to its formation by intra-crustal melting or crystal fractionation, with plagioclase in the residue (Taylor & McLennan, 1985). The high Th/La of the upper crust also has its source in granitic material. Granite and granodiorite plutons and batholiths commonly have Th/La > 0·5, whether they be I-type, S-type or A-type (Winter, 2001). Some batholiths may be internally zoned, with high-Th/La material at the highest elevations (Sawka & Chappell, 1988), resulting from magmatic differentiation. The complement to the granitic upper crust must exist as restites and/or cumulates in the middle and lower crust. Restites have been identified in lower-crustal granulite xenolith suites (Hanchar *et al.*, 1994) and most of them have low Th/La (Fig. 8a).

Accessory minerals appear to control the budget and fractionation of Th and the LREE during igneous fractionation (Sawka & Chappell, 1988). Although apatite, titanite, allanite, monazite, thorite and zircon may all be formed during igneous differentiation (Bingen *et al.*, 1996; Bea & Montero, 1999), only apatite and zircon are common accessory minerals in granulite xenoliths from the lower crust (Leyreloup *et al.*, 1982; Rudnick & Taylor, 1987; Roberts & Ruiz, 1989; Rudnick & Presper, 1990; Wendlandt *et al.*, 1993). Based on sparse partitioning data (from phenocryst-matrix data; no experimental Th-partitioning data exist for either apatite or zircon), apatite appears to favour La > 10× over Th, whereas zircon favours Th > 10× over La, with respect to silicic melts (Mahood & Hildreth, 1983; Mahood & Stimac, 1990; Bea *et al.*, 1994). These inferences are also consistent with measured Th and La in apatite and zircon from metapelite and granodiorite whole rocks (Sawka & Chappell, 1988; Bea & Montero, 1999). Thus, the effect on the bulk partition coefficients will depend on the relative abundance of the two minerals. For most lower-crustal compositions, apatite will be >10× more abundant than zircon (based on the P and Zr contents of these rocks; Rudnick & Presper, 1990) and so apatite will control the relative partitioning of Th and La, producing high-Th/La melts and low-Th/La residues. Adding other potentially dominant residual silicate phases (clinopyroxene, orthopyroxene, plagioclase, garnet and amphibole), most of which partition La over Th (Green, 1994), accentuates this effect. If 0·4% apatite and 0·01% zircon exist in the residue (conservative averages based on the range of P and Zr in lower-crustal granulite xenoliths), Th/La will increase in the melt by a factor of 1·8–4·1 upon 25% melting (or 75% crystallization), using *D* values reported in Table 2. Thus, the observed high Th/La of felsic igneous rocks (granites and granodiorites), the low Th/La of lower-crustal rocks and the theoretical igneous fractionation of these elements support igneous differentiation as one likely cause of the large Th/La fractionation between the upper and lower crust.

Table 2: Th and La partition coefficients

	D_{Th}	D_{La}	Mode (%)	Refs
Plagioclase	0·077	0·15	50	1
Clinopyroxene	0·06	0·2	40	1
Olivine	0	0	10	
Bulk (mafic)	0·06	0·16	100	calc.
Apatite	7·5–41	75–456	0·4	2, 3
Zircon	22–91	1·3–7·2	0·01	2, 3
Mafic assemb.	0·06	0·16	99·6	calc.
Bulk (felsic)	0·16	1·2	100	calc.

Bulk *D* values calculated from modes and mineral *D* values. References for mineral *D* values as follows: 1: GERM, average of basalt and andesite *D* values; 2: early Bishop tuff of Mahood & Hildreth (1983); 3: migmatite leucosome of Bea *et al*. (1994).

Although igneous processes clearly occur and can create the correct sense of Th/La fractionation, some lower-crustal granulites possess extreme Th-depletion, which is difficult to explain by igneous differentiation. Examples include mafic granulites from the Fraser complex, which show >3-fold depletion in Th with no change in the REE pattern (Condie & Myers, 1999). Felsic gneisses from the Dharwar craton in India also show a 100-fold decrease in Th from amphibolite- to granulite-facies metamorphism, with little change in major-element content (Hansen *et al.*, 1995; Fig. 8a). The latter study, in particular, argues for a low-aH_2O fluid (CO_2- and alkali-rich 'salt melt') as the agent of Th-depletion. This process is more difficult to model, because the mechanism of Th-depletion has yet to be quantitatively constrained. Nonetheless, the extreme Th-depletion observed in some granulites argues for a distinct fluid-mediated process that accompanies granulite-facies metamorphism in many lower-crustal regions (e.g. Dharwar, Lewisian and Lofoten granulites; Hansen *et al.*, 1995).

Given that many lower-crustal granulite xenoliths are interpreted as mafic cumulates (Wilkinson & Taylor, 1980; Rudnick *et al.*, 1986; Halliday *et al.*, 1993; Lee *et al.*, 1993; Kelemen *et al.*, 2003*a*), crystal fractionation is another mechanism that may cause internal differentiation of the continents. In general, however, crystal fractionation of mafic to intermediate compositions creates mafic cumulates with low Th/La, but has little effect on Th/La in the liquid. For example, 70% fractional crystallization of plagioclase, clinopyroxene and olivine will cause Th/La in the liquid to increase by only 11%, whereas Th/La in the solid residue will be less than half that of the starting composition (using *D* values in Table 2). This calculation is in accord with observations from comagmatic volcanic suites, which show little change in Th/La in liquids produced by crystal fractionation (of olivine, clinopyroxene, plagioclase, orthopyroxene, oxide), up to the point of apatite saturation (Fig. 10). For example, the Th-enrichment in Anatahan andesites relative to basalts suggests >70% crystal fractionation, during which Th/La varies by <10% (Fig. 10). Not until apatite saturates in silicic compositions (63–64 wt % SiO_2 for Anatahan) does Th/La begin to increase at a higher rate. Thus, the first 50–70% of crystal fractionation will drive compositions from basalt to andesite and create a large mass of low Th/La cumulates, but the low overall *D* values (Table 2) produce little effect on Th/La in the fractionated liquids. The high Th/La of the upper crust is generated predominantly in silicic liquids with high *D* values (Table 2), reflecting saturation in LREE-enriched phases such as apatite.

In summary, basaltic magmas will enter the crust and crystallize, leaving low-Th/La cumulates in the lower crust, and slightly higher Th/La in the melt. Further crystal fractionation, partial melting and/or granulite-facies metamorphism (involving REE-rich accessory phases) is then required to create a high-Th/La upper crust. The final step in enriching the bulk continents in Th/La is then to lose the low-Th/La material from the bottom.

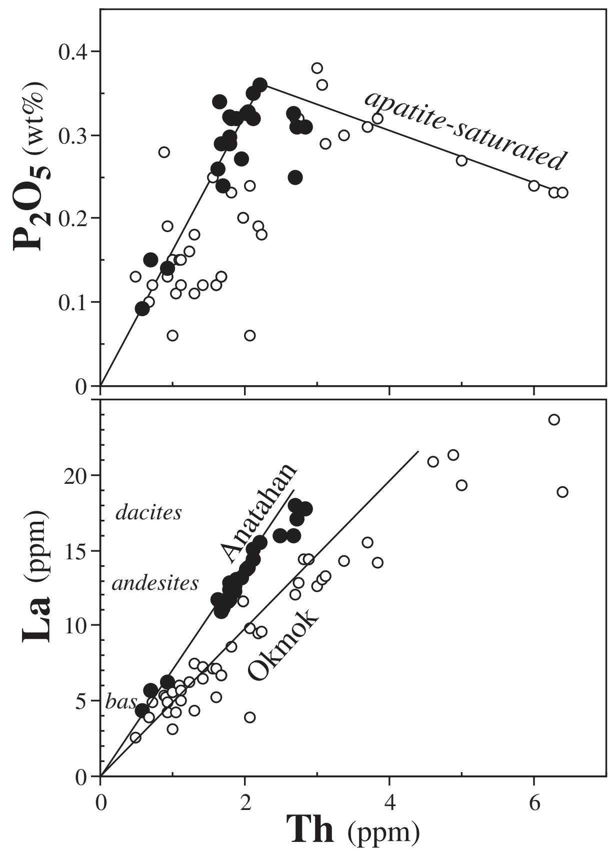

Fig. 10. Variation in Th, La and P_2O_5 in volcanic suites from Anatahan volcano in the Marianas Islands, and Okmok volcano in the Aleutians Islands. Th/La is constant over the first ~70% of crystal fractionation (basalts to andesites/dacites), until apatite saturation, inferred to be the point at which P_2O_5 and Th no longer covary. Apatite partitions La preferentially to Th, and so causes an increase in Th/La of the equilibrium liquid. Basalt, andesite and dacite labels indicate the approximate silica content of the volcanic rocks (<52 wt %, 52–63 wt % and >63 wt %, respectively). Note the fundamentally different Th/La in Anatahan and Okmok, consistent with higher Th/La sediments subducting beneath the Aleutians (Fig. 7). Anatahan data from Wade *et al.* (2005); Okmok data from compilation in Kelemen *et al.* (2003*b*). bas, basalt.

Lower-crustal foundering

Many studies have outlined the geochemical evidence and physical mechanisms for lithospheric delamination or foundering. Bird (1979) and Houseman *et al.* (1981) made the case for foundering of mantle lithosphere, but lower-crustal foundering may also occur because of the negative buoyancy of ultramafic cumulates and garnet-bearing mafic lithologies (e.g. Herzberg *et al.*, 1983; Arndt & Goldstein, 1989; Turcotte, 1989; Kay & Kay, 1991; Glazner, 1994; Jull & Kelemen, 2001). Such dense lower crust may develop convective instabilities that sink into the mantle, especially for high temperatures at the Moho (>700°C), high background strain rates, wet olivine mantle rheology and/or thickened crust (Jull & Kelemen, 2001). Cumulate pyroxenites and gabbronorites are particularly susceptible to such a process, and may founder shortly after they form (<10 Myr; Jull & Kelemen, 2001). Cold cratonic foundering episodes are unlikely to occur, due to the high viscosity of the underlying mantle at low temperature, whereas arc, rift or plume settings may all promote lower-crustal loss (Jull & Kelemen, 2001). Partial melting may then occur within the foundered crust (e.g. Ducea & Saleeby, 1998; Kelemen *et al.*, 2003*a*), or subsequently within the crust as hot mantle asthenosphere replaces foundered lithosphere (e.g. Kay & Kay,

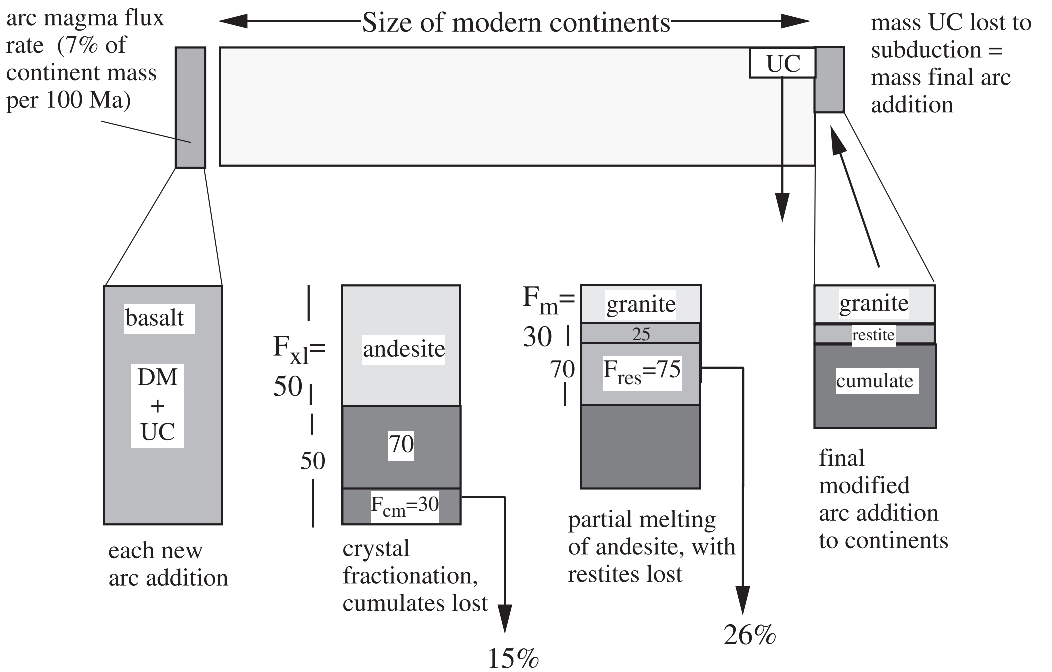

Fig. 11. Illustration of fractionation & foundering model. Model begins at 3 Ga with modern continental mass, and composition equal to Th/La of Archaean bulk crust (Rudnick & Fountain, 1995). Arc magma is added at a constant rate, and its composition is equal to a 15% batch melt of depleted mantle plus all the Th and La in the recycled upper crust increment (UC, see below). The arc crust is then fractionated and melted, where the fraction of liquid remaining after fractional crystallization of cumulates to create arc 'andesite' is F_{xl} (using 'mafic' *D* values in Table 2), and the fraction of partial melting of arc andesite to create 'granite' is F_m (using 'felsic' *D* values in Table 2). A portion of the cumulates (F_{cm}) and restite (F_{res}) is lost to the mantle. The final modified arc addition is then mixed into the evolving bulk continental crust. Upper crust (UC) is subducted into the mantle, and its Th and La are quantitively recycled with each arc magma flux. The mass of UC subducted equals the mass of final modified arc addition, such that continental mass is at steady state. The model takes into account the observed secular increase in UC Th/La (as shown in Fig. 9), by having UC Th/La increase linearly from 0·28 to 0·31 (the modern UC average from Fig. 1, which is a more conservative value that the values in Fig. 9). Examples shown are F_m, F_{xl} and F_{cm} for model curve c in Fig. 12, which generates average BCC Th/La in 3 Ga, after 41% total mafic residues foundered.

1993; Samson *et al.*, 1995). Thus, lower-crustal foundering provides an ideal mechanism to both generate high-Th/La melts and remove low-Th/La cumulates and restites from the continental crust.

Given the kinds of processes outlined above, it is possible to model quantitatively the observed increase in continental Th/La since the Archaean. The purpose here is not to argue for a given crustal growth model, but to demonstrate that within reasonable parameters, the continents can evolve in Th/La to reach the present composition of the BCC. Models begin at 3 Ga, with a BCC Th/La of 0·17 [i.e. Archaean bulk crust from Rudnick & Fountain (1995)]. Arc magma is added at a constant rate, undergoes crystal fractionation which creates arc andesites and mafic cumulates (using 'mafic' *D* values in Table 2) and then partially melts to create granites and restite (using 'felsic' *D* values in Table 2). The distinction between cumulates and restites is somewhat artificial, but is introduced to accommodate the changing *D* values in a simple conceptual way. After igneous differentiation, a portion of the cumulates and restite is lost to the mantle (see Fig. 11 for schematic model). The leftover arc crust is mixed into the existing BCC, thus raising its Th/La. In accord with results from above, arc magma additions attain their Th and La primarily from recycled material from the upper continental crust. In practice, Th and La are extracted from an upper-crustal mass equal to the mass of new arc growth (after foundering), such that there is no net continental growth in this model. Upper-crustal Th and La is mixed with a mass of mantle Th and La [based on depleted mantle values of Salters & Stracke (2004)] required to supply the arc magma mass from 15% mantle melting. Lower mantle-melt fractions lead to a dominance of mantle Th and La (with low Th/La), whereas higher melt fractions may not be typical of average arcs.

Figure 12 shows model output, for a wide range of cumulate and restite fractions created and lost. At zero loss of mafic residues (cumulates or restite), the continents actually evolve to lower Th/La than the Archaean starting point, because of the net input of mantle material with low Th/La. The BCC only evolves to higher Th/La by processing the mantle and recycled crustal material through igneous differentiation, and loss of low-Th/La

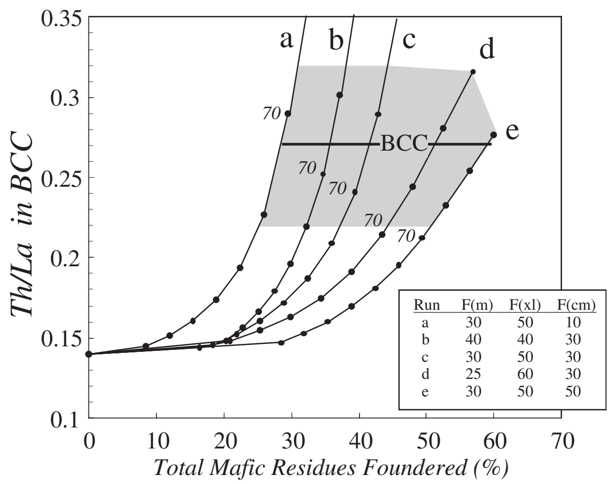

Fig. 12. Th/La in bulk continental crust (BCC) as a function of total mafic residues (restite plus cumulates) foundered to the mantle. Parameters for each curve as defined in Fig. 11. Each tick mark along curve is percent of restite lost from continents (F_{res}), in 10% increments (70% increment is labelled for each curve). BCC line and shaded field are where modern BCC average and uncertainty (from Fig. 1) intersect model curves. For a wide range in parameters, successful models achieve Th/La in modern BCC with 25–60% residue foundering.

residues. As discussed above, the largest effect on Th/La occurs during felsic differentiation, as a result of the effect of an LREE-enriched accessory mineral phase such as apatite. The model is thus particularly sensitive to the proportion of restite lost, because the restites have low Th/La (<0·1) yet higher concentrations than the cumulates (because of the difference in *D* values for the two steps; Table 2). For this reason, loss of cumulates is less efficient than loss of restite, and so drives up total crustal losses without a comparable effect on BCC Th/La (Fig. 12). Models that successfully create today's BCC generally require 60–100% loss of restite and, depending on the additional loss of cumulates, 25–60% total loss of mafic residues (e.g. cumulates plus restite). The lower limit (25%) derives from a minimum of 10% cumulate loss [model (a) in Fig. 12]; it seems unreasonable to founder 60–75% restite but only 10% cumulates, although this could be consistent with the lower-crustal melting and foundering mechanism envisioned by Ducea (2001). The upper limit (60%) derives from a maximum of 100% restite loss [model (e) in Fig. 12].

The model results in Fig. 12 are also dependent on the initial arc magma flux rate, which is 7% of the continental mass, each 100 Myr. Lowering the rates will drive results to 100% restite loss. The 7% rate is >3× higher than the current frequency of juvenile ages over the past 100 Myr, which is closer to 2% (Condie, 1998), or than Reymer & Schubert's (1984) magma-addition rates to the continents, which is also close to 2% of the modern continent mass over the past 100 Myr. The net arc addition rate (after 50% foundering), however, is closer to these estimates. Models with net crustal growth also require larger residue losses. Increasing the mass of the continental crust ultimately requires larger inputs from the mantle, which bring more low-Th/La material to the continents. Such mantle-derived material will have to be highly processed to increase Th/La to that of the BCC. For example, an OIB magma would require 20% partial melting (using felsic *D* values), and then 90% loss of restite to raise Th/La from 0·1 (mantle value) to 0·27 (average BCC value). Thus, net-growth models require more processing and foundering than no-growth models that strongly recycle upper continental crust.

This modelling exercise demonstrates that the bulk continental crust can evolve to high Th/La (0·27 ± 0·05) for a wide range of parameters, which ultimately require 25–60% loss of the arc crust through foundering of mafic cumulates and restite. This range is somewhat of a minimum, given that lower mantle-melting fractions, lower magmatic-flux rates and net crustal growth all require larger restite and total residue losses. Is this magnitude of foundering reasonable or observed? Ducea (2002) has made several arguments that the Sierra Nevada batholith has experienced massive foundering on a grand scale. The current 35 km of granitoid crust appears to have survived nearly 100% foundering of 35–50 km of lower-crustal pyroxenite residues, for total crustal losses of 50–60%. Jull & Kelemen (2001) demonstrated how arc gabbronorites at >25 km depth have a positive density contrast with respect to the mantle, and that effect may limit the thickness of arc and continental crust. Thus, 25–60% foundering of arc crust may be reasonable for continental arcs originally >33–62 km thick, such as the Andes, where delamination has been proposed (e.g. Kay & Kay, 1993), or for mountain belts in general (Nelson, 1992). A study of the Irish Caledonides (Draut *et al.*, 2002) also makes geochemical and rheological arguments for large-scale crystal fractionation and loss of up to 50% of mass to foundering.

Other predictions of lower-crustal foundering

Thus far, minor elements (Th and La) have been used to identify a major process operating on the continents. Others have argued for the same mechanism to explain systematics for the most important major element—silicon (see reviews of Taylor & McLennan, 1985; Rudnick, 1995; Kelemen *et al.*, 2003*a*; Davidson & Arculus, 2004). The fractionation & foundering model described here provides one way to create high silica in the bulk continental crust (e.g. ~60 wt % SiO_2; Rudnick & Fountain, 1995) from low-silica magmatic additions from the mantle (e.g. basalts with ~50 wt % SiO_2). For example, if arc magmas are added to the continents with 51% SiO_2, then 50% foundering of restites and cumulates with 43% SiO_2 will create a bulk continent with 59% SiO_2. This calculation is compatible with the model results above (25–60% foundering calculated from Th/La systematics), but it demonstrates that the residue must have very low silica. Although such low silica is well below the average of the lower-crustal xenolith population (49–51 wt % SiO_2), approximately 6% of the xenolith database consists of rocks with $\leq$43 wt % SiO_2, in a variety of assemblages (including olivine-rich cumulates and garnet-rich restites). It is possible that such low-silica samples are underrepresented in the current lower crust because they are gravitationally unstable and have foundered, although this is admittedly an unsatisfying conclusion. On the other hand, the Sierras again offer an example consistent with silica, Th/La and mass-flux constraints. The average of Sierran lower-crustal pyroxenite xenoliths, which are viable residues for the Sierran batholith, is 44·8 wt % SiO_2 (Ducea, 2002); 55% foundering of such lower crust (Ducea estimated 50–60%) could create a continent with 59% SiO_2 from a mafic mantle melt (51% SiO_2). Thus, to the extent to which such Sierran-type episodes are significant in the history of continental evolution, the same model that satisfies Th/La may also satisfy silica.

The other question is whether foundered lower crust ever reappears in mantle-derived materials, such as ocean island or ocean flood basalts. Arndt & Goldstein (1989) proposed this to explain some aspects of mantle heterogeneity. They noted how old, depleted lower crust could evolve to isotopic compositions (e.g. moderate $^{87}Sr/^{86}Sr$, low $^{143}Nd/^{144}Nd$ and low $^{206}Pb/^{204}Pb$; Rudnick & Goldstein, 1990), typical of EM-1-type mantle (Zindler & Hart, 1986). Although most recent studies favour subducted sedimentary components in the source of EM-1 and EM-2 mantle (e.g. Weaver, 1991; White & Duncan, 1996; Eisele *et al.*, 2002), it is difficult to discount lower crust as also contributing to mantle enrichment. Notably, lower crust has radiogenic Os (Saal *et al.*, 1998), low Ce/Pb (Rudnick & Fountain, 1995) and lies predominantly within the terrestrial Hf–Nd array (Vervoort *et al.*, 2000). These characteristics are consistent with EM-type mantle. Th/La in lower crust is also compatible with EM-type mantle. Using the results of the fractionation & foundering model above, the lower-crustal flux to the mantle would have Th/La of 0·08–0·12—significantly lower than bulk continental crust, but higher than depleted mantle (0·05), and similar to many OIB. Thus, at least on chemical grounds, some mantle enrichment could derive from foundered lower crust. Consideration of mass fluxes, however, suggests that lower crust is a minor component in the mantle. Assuming 25–60% total crustal losses (Fig. 12) at the rates given in Fig. 11, the total amount of foundered residues in the mantle would constitute a mass of roughly 50–100% of the mass of the modern continents. Thus, foundered lower crust would constitute only 0·3–0·65% of the total mantle mass, compared with 3·5% for subducted slabs over the same 3 Gyr period [using slab fluxes of von Huene & Scholl (1991)]. From the mantle's perspective, subduction is probably one order of magnitude more important in enriching the mantle than lower-crustal foundering.

Lack of Th/La fractionation in subduction zones

The final consideration is why Th and La are fractionated from one another during intracontinental differentiation, but not during slab metamorphism or melting. Arc volcanic data show clearly that Th and La are not substantially fractionated from one another during the process that transports material from sediments on the subduction plate to the source region of arc magmas. The simplest explanation for this would be that sedimentary material is transported in bulk, and so the arc simply inherits the bulk sediment compositions. There are several problems with bulk mixing, however. First, it is difficult to imagine how the subducting sediment would not evolve fluids or melts during prograde slab *P–T* paths. Secondly, bulk mixing of sediment also fails to produce the correct isotopic and trace-element ratios in arc magmas, particularly those ratios involving Nb or Ta (Turner *et al.*, 1996; Elliott *et al.*, 1997; Class *et al.*, 2000). Instead, it is much more likely that sedimentary material is lost from the slab as fluids or melts. Recent studies of high *P–T*, blueschist- and eclogite-facies metapelites find a general lack of mobility of Th and REE up to 650°C, and a lack of Th/La fractionation in prograde paths (Arculus *et al.*, 1999; Spandler *et al.*, 2003). This supports the lack of fractionation of these elements during subduction metamorphism, but many lines of evidence point toward slab sediment melting to explain the large amount of Th recycled to arcs (Johnson & Plank, 1999, and references therein). So, if sediments melt on the downgoing plate, why are Th and La not fractionated as they are during melting in the continental crust?

As argued above, accessory phases can dominant Th/La fractionation during crustal differentiation. As mantle-derived mafic melts evolve into silicic continental crust, apatite may, in large part, control Th/La fractionation. There are reasons to expect that apatite will also be found in equilibrium with silicic melts generated in the subducting plate. In addition to models that predict apatite saturation (Watson, 1980), the high-pressure sediment-melting experiments of Johnson & Plank (1999) show that apatite is stable on both sides of the solidus, from 600 to 900°C at 2 GPa. As expected, these melts show a factor of 1·5 increase in Th/La. However, this starting composition is unusual in that it contains >3 wt % fish teeth apatite (1·6 wt % P_2O_5), which has forced apatite saturation. A recent study (Hermann, 2002) has argued instead for the importance of allanite in controlling Th and LREE budgets in subducting materials. Allanite is equally problematic, as it would also strongly increase Th/La in coexisting melts (Hermann, 2002). It is not clear, however, that allanite is a relevant accessory mineral during sediment melting. The allanite-bearing eclogites studied by Hermann (2002) had alkaline mafic protoliths unlike marine sediments, and the experiments conducted were all P-free, and so unable to saturate phosphate minerals such as apatite or monazite.

In the absence of relevant experiments, other crustal analogues can be used to predict the accessory phase assemblage in equilibrium with slab-sediment melts. Subducting sediments are predominantly pelitic in composition and, in this way, they diverge dramatically from most igneous rocks in the continental crust. Pelites (shales) are notably poor in calcium; to first order, GLOSS consists of 7% biogenic calcite and 93% of a terrigenous component with 2·1 wt % CaO. Thirteen of the 28 trench sections considered by Plank & Langmuir (1998) are virtually calcite free and have <2·5 CaO. Melts of calcium-poor pelites are peraluminous, and generally contain the accessory minerals monazite + zircon, in contrast to calcium-rich melts, which contain apatite + allanite + zircon ± sphene (Lee & Silver, 1964; Rapp & Watson, 1986; Broska *et al.*, 2000). If monazite, and not apatite or allanite, is the major REE phase in equilibrium with metapelite melts in the subducting slab, then it may have a dramatically different effect on Th and La partitioning. Monazite contains weight percent quantities of both Th and La, and evidence from natural monazites indicates that $(Th/La)_{mon}/(Th/La)_{melt}$ is near unity [based on monazite–granite pairs of Wark & Miller (1993) and Bea & Montero (1999); and the granite-hosted monazite average of Rosenblum & Fleischer (1995), which has Th/La of 0·5, which is very near granites themselves]. If subducting sediments have the REE abundances of GLOSS, and generate peraluminous melts (Nichols *et al.*, 1996; Johnson & Plank, 1999), then monazite solubility models (Rapp & Watson, 1986; Montel, 1993) predict monazite saturation at temperatures up to 775°C. Monazite has large but similar *D* values for Th and La, and so melts in equilibrium with monazite would have Th/La similar to their starting composition.

In summary, the pelitic composition of subducting sediments may stabilize different accessory minerals (e.g. monazite) from those (e.g. apatite and allanite) stable in higher-Ca igneous protoliths in the continental crust. These differences would explain the large fractionation of Th and La during continental differentiation, and the lack thereof during subduction. Exceptions may help to test these ideas. For example, all 13 trench sections considered here have low-Ca bulk compositions (<3·5 wt % CaO, or <10% calcium carbonate), except for Guatemala and E. Sunda (60 and 16% calcium carbonate, respectively). The dominance of monazite in low-Ca sediments and apatite–allanite in high-Ca sediments could explain the anomalously higher Th/La in the Guatemala and E. Sunda arcs (e.g. significantly above the line in Fig. 7). The high fish teeth apatite content of the Tonga sediments (with a factor of five higher P_2O_5 than the other trench sections) could also explain the anomalously higher Th/La in the Tonga arc, which is a factor of 1·6 higher than the bulk sediments—almost exactly the same factor predicted in the apatite-rich experiments of Johnson & Plank (1999) based on a Tonga sediment starting material. Thus, the few arcs that show a shift in Th/La are those where unusually apatite-rich or carbonate-rich sediments subduct. Nonetheless, the dominantly pelitic (low-Ca) composition of marine sediments leads in most cases to no significant fraction of Th and La in the subduction zone. Clearly, further experimental work on accessory mineral phase stability and partitioning is needed to clarify the effect of melting on Th/La in continental vs subducting slab conditions.

CONCLUSION

This paper develops the elemental ratio of Th/La as a useful tracer of sediment recycling at subduction zones. Th/La can be traced from the subducting sedimentary package on the downgoing plate to arc magmas, and the combined dehydration and melting processes that deliver slab material to the arc source do not typically fractionate Th from La. Th/La is thus one of the best tracers of slab sediments in arc magmas, and should help to both mass balance modern fluxes as well as identify recycled sediment in ancient arc systems.

Although useful in studying arc systems, the lack of fractionation of Th from La during subduction presents problems for creating the modern continental crust by arc accretion alone. Most other proposed modes of continent formation (intraplate magmatism, small-degree melts, Archaean adakites) also fail to create a continent with higher Th/La than the mantle. Instead, several differentiation processes naturally occur within the continental crust (partial melting, crystal fractionation and granulite-facies metamorphism) to create a high-Th/La upper crust and low-Th/La lower crust. Foundering of 25–60% of lower-crustal cumulates and restite into the mantle can create a bulk continental crust that evolves to high Th/La (>0·2) in 3 Ga. Thus, Th/La provides evidence for continental fractionation & foundering, as well as a means to quantify this process. The weight of evidence from geochemical, geological and geodynamic arguments favours a major process of lower continental foundering throughout most of Earth history. This process is not that different from subduction itself (sinking of high-density, mafic crust into the mantle), but it has one order of magnitude less impact by mass on the mantle than subduction.

Although providing evidence for lower-crustal foundering, this work does not discount arc and intraplate magmatism as the main builders of continental crust. In fact, much of the intracrustal processing could happen within the lifetime of the magmatic arc, as magmas differentiate and residues founder. This work does demonstrate, however, that calculating the relative contribution of arc and intraplate magmas to the continents is not as simple as bulk mixing of average magma types (e.g. Rudnick, 1995; Barth *et al.*, 2000) but, instead, requires consideration of the effects of both sediment recycling and fractionation & foundering on trace-element ratios. For example, even though average arc and intraplate magmas have distinct Th/La, a mixing calculation based on Th/La would be meaningless, as the ratio in arc magmas and continental crust is dominated by recycled sediment and intracrustal fractionation. Previous calculations based on the continent's Nb-anomaly will also need to be reconsidered, taking into account fractionations in the subduction zone as well as in the continental crust.

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SUPPLEMENTARY DATA

Supplementary data for this paper are available on *Journal of Petrology* online.

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