Cerium/lead and lead isotope ratios in arc magmas and the enrichment of lead in the continents

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Lead is anomalously enriched in the Earth's continental crust, and in the magmas that give rise to new continental crust at convergent margins. A detailed study of volcanic rocks from the Aleutian Island arc shows that this enrichment is a continuing process, and results from the efficient non-magmatic transfer of mantle-derived lead into the source of convergent-margin magmas. This process, acting through time, can also account for the pervasive depletion of lead in the oceanic mantle.

MOST elements with similar solid–melt distribution coefficients have similar concentration ratios in the bulk silicate Earth, the continental crust, and basalts formed by mantle melting at mid-ocean ridges (MORB) and oceanic islands (OIB)[1–3]. The moderately incompatible element pair cerium and lead (Ce and Pb) is an exception. Despite their similar melting behaviours, Pb is preferentially partitioned into the continents, with enrichments similar to those of highly incompatible elements like rubidium and uranium (Rb and U)[3–5]. Thus, compared with the bulk Earth, the Ce/Pb ratio is low in the continents and high in oceanic basalts (Fig. 1).

Suggested explanations of the preferential partitioning of Pb into the continental crust include: (1) Pb behaves magmatically as a highly incompatible element during continent formation, but as a moderately incompatible element during generation of oceanic basalts[5]; (2) extra Pb is added to the continents by non-magmatic (for example, hydrothermal) processes[4]; (3) Pb was enriched in the continents primarily during the Archaean and early Proterozoic by processes different from the present day[5]; and (4) Pb is carried from the subducted oceanic crust to the sources of continent-building magmas by fluids before melting[5–9].

These explanations can be further evaluated through the study of convergent margin volcanoes, which represent recent additions to the continental crust. Most arc lavas have low Ce/Pb, similar to the continents (Fig. 1), but like oceanic basalts they

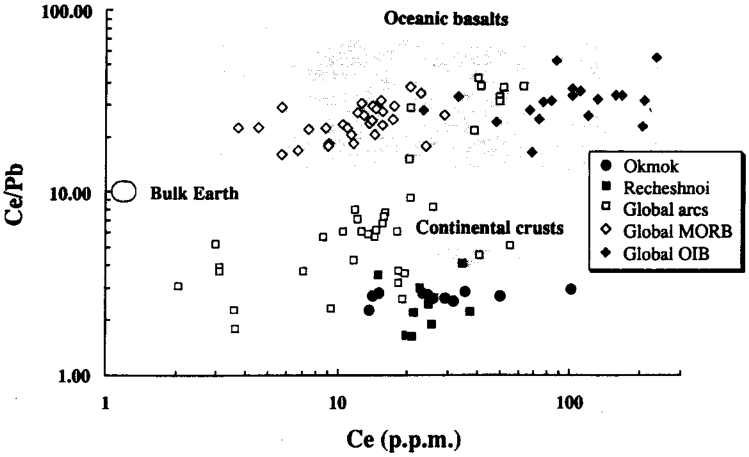

FIG. 1 Global comparison of Ce/Pb ratios in oceanic basalts, convergent margin lavas, the continental crust and the bulk Earth. Logarithmic axes are used in order to balance relative variations. Data for Okmok and Recheshnoi volcanoes (on Umnak island, Aleutian Islands) are from this work. All other data are taken from literature. Only samples with Pb concentration determined by isotope dilution or spark source mass spectrometry are included. Mid-ocean ridge basalt (MORB) and oceanic island basalt (OIB) data from refs 4, 5, 57. Arc data from refs 17, 53, 58–63. The only arc data extending into the field of oceanic basalts are from the high-calcium series lavas from Grenada[63].

are derived principally from melting of the mantle. New trace-element and Pb isotope data for lavas from two neighbouring Aleutian volcanoes (Table 1) place additional constraints on the origin of their low Ce/Pb ratios, and reveal a process that can explain the preferential enrichment of Pb in the continents. The volcanoes' proximity reduces variations in tectonic factors that may affect the composition of arc lavas, for example, the amount and composition of subducted sediment and the age of the subducting lithosphere, thus comparison of these sample suites presents a more controlled experiment than is possible by studying isolated lavas from widely separated volcanoes. We show that Ce and Pb behave similarly during mantle melting to form arc basalts, as they do during the formation of MORB and OIB[3–5], but that mantle Pb is preferentially transferred to the arc magma source before melting. The global fractionation of Pb from Ce reflects non-magmatic enrichment processes associated with the creation and subduction of oceanic crust over the Earth's history.

Geological background

Okmok and Recheshnoi, adjacent volcanoes on Umnak island, Aleutian Islands, Alaska, are separated by only 45 km along the volcanic front of the arc. They are, however, chemically distinct, following classic tholeiitic and calc-alkaline differentiation paths, respectively[10]. Okmok is an active shield volcano that experienced a caldera-forming eruption approximately 2,500 years ago[11]. Our samples are lavas and pyroclastics associated with its most recent phases of volcanism[12], including historic eruptions. Recheshnoi is a smaller, glacially-eroded stratovolcano. Our samples represent both pre- and post-glacial phases of volcanism[12]. Miller *et al.*[10] have shown that the major- and trace-element differences between parental lavas from the two volcanoes can be accounted for by different degrees of partial melting of a similar mantle source. The samples from Okmok appear to be related by differentiation of parental magmas, whereas those from Recheshnoi require more complex relationships. The overall difference in extent of melting between Okmok and Recheshnoi provides an exceptional opportunity to investigate the behaviour of Pb in arc magmas.

Analytical results and implications

Umnak lavas exhibit linear correlations between Pb isotope ratios and Ce/Pb (Fig. 2), with most of the variation represented by Recheshnoi lavas. Okmok lavas have nearly constant Pb isotope and Ce/Pb ratios among rock types ranging from basalt to rhyolite. The uniform Pb isotope ratios in Okmok lavas indicate that the lavas are related by differentiation of melts derived from a homogeneous source, as suggested by Miller *et al.*[10]. In Recheshnoi lavas, Ce/Pb correlates with Pb isotope ratios (Fig. 2*c*), but not with concentrations (Fig. 3*d*), suggesting that variations in Ce/Pb result primarily from heterogeneity in the mantle source, and not from magmatic processes. The simple relationships among Okmok lavas and more complicated ones among lavas from Recheshnoi are further supported by excellent correlations of Pb abundances with Ce, U and Rb abundances in the Okmok suite ($R^2 = 0.995$, 0.970 and 0.986, respectively) and poorer correlations for the same element pairs in the Recheshnoi suite ($R^2 = 0.286$, 0.684 and 0.747).

The Okmok data reveal the behaviour of Pb during magmatic differentiation in comparison to that of Ce, U and Rb (Fig. 3*a*–

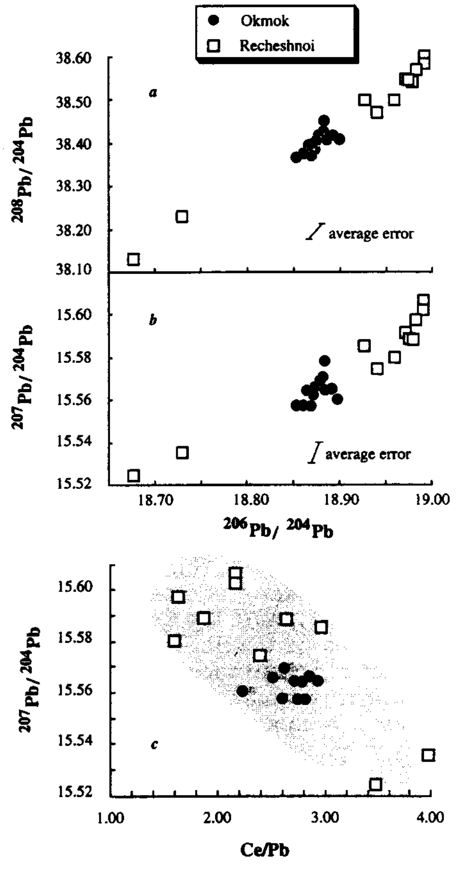

FIG. 2 Lead isotope ratios for lavas from Umnak island. *a*, Correlated variations in the ^{208}Pb/^{204}Pb and ^{206}Pb/^{204}Pb ratios. *b*, Variations in the ^{207}Pb/^{204}Pb ratio with the ^{206}Pb/^{204}Pb ratio. *c*, Correlation between ^{207}Pb/^{204}Pb and Ce/Pb ratios. Average 2σ uncertainty of 0.21‰ per a.m.u. is illustrated by the error bars in *a* and *b*.

TABLE 1 Analyses of lava from two Aleutian island volcanoes

Sample	SiO_2	MgO	Ce	Pb	U	Rb	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Okmok volcano									
87-03-01	53.39	4.10	26.04	9.97	1.23	26.63	18.869	15.557	38.370
87-06-01	55.55	3.30	30.48	—	—	35.36	18.884	15.578	38.449
87-08-02	56.99	2.90	33.17	—	1.46	44.05	18.872	15.562	38.392
87-08-09	57.52	2.78	36.09	12.57	1.79	39.90	18.874	15.566	38.401
87-17-02	70.85	0.10	102.85	34.92	3.83	102.69	18.871	15.564	38.397
Qaf70	51.35	5.13	15.32	5.42	0.61	13.81	18.861	15.557	38.372
Qcb1	52.11	4.36	31.93	12.63	1.46	31.16	18.893	15.565	38.415
Qcb7	52.55	4.09	23.55	8.40	1.01	22.92	18.867	15.564	38.393
Qcb12	54.50	3.22	50.98	18.68	2.41	51.17	18.886	15.564	38.406
Qcb16	53.19	4.08	29.43	11.22	1.34	27.89	18.878	15.569	38.418
Qcf3	50.05	5.06	14.26	5.23	0.53	11.00	—	—	—
Qdf1	50.05	6.08	13.85	6.18	0.53	10.57	18.899	15.560	38.409
Qef1	54.67	3.69	24.90	8.99	1.20	26.93	18.854	15.557	38.365
Recheshnoi volcano									
LUM16	61.12	3.16	24.80	10.34	1.75	39.81	18.941	15.574	38.468
LUM17	57.82	3.98	20.29	12.34	1.54	35.87	18.984	15.597	38.568
LUM18	54.84	4.69	21.35	—	—	35.45	18.973	15.591	38.546
LUM19*	59.25	3.82	35.35	8.88	2.27	30.92	18.730	15.535	38.227
LUM20	63.65	1.51	37.41	17.23	2.87	69.74	18.992	15.602	38.585
LUM21	50.07	10.10	15.18	4.35	0.51	12.18	18.678	15.524	38.130
LUM22	63.07	1.85	23.17	7.79	1.20	31.67	18.928	15.585	38.498
LUM33	59.16	3.82	25.46	13.58	2.00	48.46	18.977	15.589	38.540
LUM37	54.93	7.67	21.31	13.32	2.11	39.54	18.961	15.580	38.497
LUM42	60.71	3.20	21.57	9.92	1.78	43.64	18.992	15.607	38.598
ABy9(23)†	57.40	4.00	26.30	9.93	2.04	51.21	18.981	15.588	38.539

Analysis techniques: SiO_2, MgO and Ce were measured by direct current plasma emission spectrometry at Lamont-Doherty and reported in ref. 10 along with other major and trace elements. Rb, U and Pb concentrations were measured by isotope dilution at the Max-Planck-Institut, Mainz on unleached powders, and Pb isotope ratios on leached whole-rock chips for Okmok samples and leached powders for Recheshnoi samples. Leaching was in hot 6N HCl for 2 h. Chemical techniques were similar to those described previously at MPI-Mainz[10,17,53,54]. Pb isotope ratios are corrected for mass fractionation by ~1.5‰ per atomic mass unit (a.m.u.), based on multiple analyses of the NBS 982 standard. 2σ errors (external) on the standard were 0.45‰ ($n=16$) and 0.26‰ ($n=15$) per a.m.u. during two measuring periods. Each sample was measured at least twice in order to ensure reproducibility of the analyses. 2σ errors (external) on samples were 0.21‰ per a.m.u., excluding two outliers (Qdf1 and LUM20), whose inclusion brings the error to 0.27‰ per a.m.u. Further analytical details are presented in ref. 39.

* Major- and trace-element data for sample LUM19 are not given in ref. 10, but are available from D.M.M. on request.

† SiO_2, MgO and Ce for sample ABy9(23) are from ref. 55.

c). The Ce/Pb ratio varies within a narrow range, between 2.5 and 3 in all but one sample, over nearly an eightfold range of Ce concentrations. This constancy holds also for Recheshnoi, albeit with greater scatter (Fig. 3*d*). In contrast, Rb/Pb and U/Pb increase with increasing concentrations in both volcanoes. These results show that Pb and Ce have similar solid–melt partition coefficients during crystallization, whereas Rb and U are more incompatible, as is true for MORB and OIB[4,5]. The Ce/Pb ratio is therefore largely unaffected by shallow-level differentiation processes at convergent margins.

Source enrichment or melting?

The Ce/Pb ratios of all Umnak samples are within the range of island arc and continental rocks globally, and are a factor of 5–10 lower than in oceanic basalts (Fig. 1). Can the low Ce/Pb be produced by fractionation during mantle melting, or must the Umnak magma source have low Ce/Pb before melting?

We can place limits on the fractionation of Ce/Pb during melting from theory and observation. The maximum enrichment of Pb during fractional fusion would occur if Pb were perfectly incompatible, that is, with a solid–melt distribution coefficient, D_{Pb}, of zero. D_{Ce} is probably less than 0.05 (ref. 10). But even with $D_{Pb}=0$ and D_{Ce} as high as 0.1, the extent of melting required to generate melts with $Ce/Pb=2.5$ (typical of Umnak lavas) would be very small ($\leqslant 1\%$) if the magma source had $Ce/Pb=25$ (typical of oceanic basalts). More realistic values of D_{Ce} would imply even smaller melt fractions of $\leqslant 0.5\%$. Such small extents of melting are inconsistent with the observed major-element compositions of primitive arc lavas[13], which require ~5–25% melting to explain the global range[14,15].

The lack of Ce/Pb fractionation during melting is also illustrated by the Umnak data. Miller *et al.*[10] have shown that Okmok and Recheshnoi can be related by different extents of melting of broadly similar source compositions, with ~20% melting for Okmok and ~7% for Recheshnoi. If Pb were more incompatible than Ce, smaller extents of melting would lead to lower Ce/Pb, but instead the Ce/Pb ratios in Recheshnoi lavas bracket those of Okmok. The U/Pb and Rb/Pb ratios in Recheshnoi lavas are higher than in Okmok (Fig. 3), consistent with U and Rb being more incompatible than Pb during melting.

This observation also holds for the global arc data set. Fractionation-corrected Ce and sodium abundances ($Ce_{6.0}$ and $Na_{6.0}$) correlate with one another, and much of the global range in these values can be explained by different extents of melting[15]. However, smaller extents of melting (higher $Na_{6.0}$) do not correlate with lower Ce/Pb ratios.

Therefore, from theory and observation, within a single arc and globally, it is clear that Pb is not significantly fractionated from Ce by partial melting. Cerium and Pb have similar behaviours during mantle melting in all modern tectonic environments. The low Ce/Pb in arc volcanics must result from a ubiquitous enrichment of Pb in convergent margin magma source regions. Cerium itself is enriched in the Umnak source relative to MORB mantle[10], therefore, the Pb enrichment must be even greater to explain the low Ce/Pb.

Origin of the extra Pb

To understand the enrichment process, it is necessary to identify the origin of the extra Pb in Umnak lavas. From isotope data alone, the sources of Aleutian magmas have been successfully modelled as mixtures of mantle periodotite, with low $^{207}Pb/^{204}Pb$, and small amounts (1–3%) of subducted sediment having high $^{207}Pb/^{204}Pb$ (refs 16, 17). It has also been suggested[18] that the low Ce/Pb in arc lavas may reflect such a subducted sediment component.

Our Pb isotope data provide further evidence that the low $^{207}Pb/^{204}Pb$ source component is mantle-derived. These data form a linear array between north Pacific MORB (taken to represent the Pacific oceanic mantle) and the average of sediments from Deep Sea Drilling Project (DSDP) Hole 183 (ref. 19), just outside the Aleutian trench near Umnak (Fig. 4*a*). On the basis of the Pb isotope ratios of the Pacific mantle and DSDP sediments ($^{206}Pb/^{204}Pb = 18.3$–18.6 and $^{206}Pb/^{204}Pb \approx 19.2$, respectively), between 40 and 60% of the Pb in Okmok lavas is derived from the 'mantle component'.

Whereas the Pb isotope data clarify the relative amounts of mantle and sediment Pb in Umnak lavas, the Ce and Pb concentration data provide new constraints on the source of the mantle Pb. Because the Ce/Pb has not been significantly fractionated by melting or crystallization, it closely reflects the magma source composition. If addition of sediment to the mantle wedge underlying the arc was entirely responsible for the low Ce/Pb, then the Umnak lavas should lie on a mixing array between Pacific mantle and sediment in a plot of $^{207}Pb/^{204}Pb$ versus Ce/Pb. Such a mixing line clearly does not pass through the Umnak data (Fig. 4*b*). Even samples having low $^{207}Pb/^{204}Pb$, with their Pb derived primarily from mantle sources, have Ce/Pb approximately a factor of five lower than oceanic basalts. Thus, the low Ce/Pb in Umnak lavas cannot be explained solely by addition of sediment to the mantle wedge, but requires enrichment of the magma source by a component with mantle-derived Pb and low Ce/Pb before melting.

Additional constraints on the source of this component result from the correlation between Ce/Pb and $^{207}Pb/^{204}Pb$ (Fig. 2*c*). If this correlation is interpreted as a mixing array, one end-member has high $^{207}Pb/^{204}Pb$ and low Ce/Pb, and probably represents subducted sediment. The second end-member, which is the dominant source of mantle Pb in Umnak lavas, must have Ce/Pb <6 even with $^{207}Pb/^{204}Pb$ as low as 15.45, an isotope ratio that clearly reflects a mantle source. This low $^{207}Pb/^{204}Pb$, low Ce/Pb source component could result from fluid-phase extraction of Pb from the subducted MORB crust. Fluid phases may preferentially extract Pb relative to Ce from the oceanic crust as a result of (1) metamorphic dehydration of the subducted basalt[20,21], and (2) hydrothermal circulation through the basaltic crust at the mid-ocean ridge, which pre-concentrates MORB Pb near the surface of the oceanic crust in metalliferous sediments and sulphides before subduction[8,9,22–25], increasing its potential for contribution to the arc magma source. Alternatively, fluid derived from the subducted crust might preferentially extract mantle Pb if it continuously equilibrates with the mantle wedge as it migrates toward the melting region[26,27]. If the mantle-derived component has $^{206}Pb/^{204}Pb \approx 18.47$ and $^{207}Pb/^{204}Pb \approx 15.50$ (typical of north Pacific MORB), then Ce/Pb is ~4 in this component (Fig. 4*b*) and it provides ~40% of the Pb in Okmok lavas. Thus the Umnak lavas provide strong evidence for selective enrichment of mantle-derived Pb, and there are reasonable mechanisms to generate the appropriate component and transfer it into the arc magma source region.

Secular depletion of Pb in the mantle

We have seen that the Umnak data place new constraints on the present-day fluxes of Ce and Pb at convergent margins. Preferential transport of mantle Pb relative to Ce into arc magmas is required. This produces arc crust with low Ce/Pb, and increases the Ce/Pb ratio in the residual mantle from which the extra Pb is derived. Therefore the Ce/Pb fractionation observed in the Aleutians today operates in the correct sense to account for the difference between the mantle and continental crust. Could subduction processes acting through geological time produce the global fractionation of Pb from Ce between the Earth's mantle and continents?

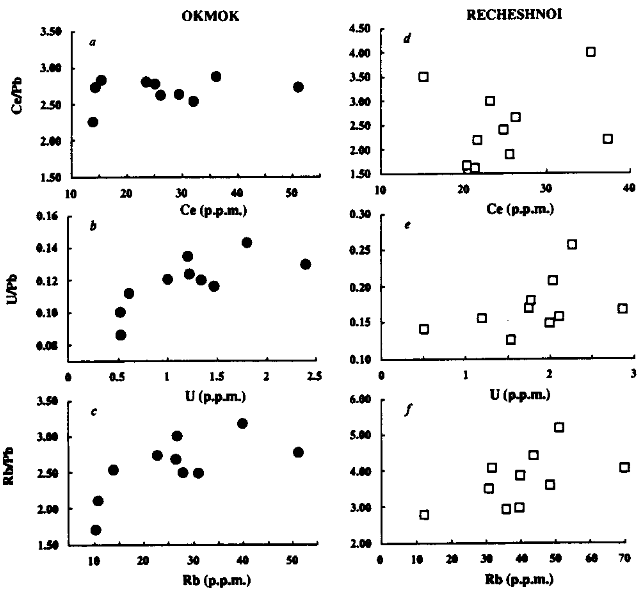

FIG. 3 Variation of the ratios of Ce, U and Rb to Pb during crystallization of the Umnak island lavas. *a* and *d*, Ce versus Ce/Pb for Okmok (excluding rhyolite sample 87-17-02) and Recheshnoi volcanoes, respectively. *b* and *e*, U versus U/Pb. *c* and *f*, Rb versus Rb/Pb. The vertical axes are scaled to show the same relative range of variation within each volcano.

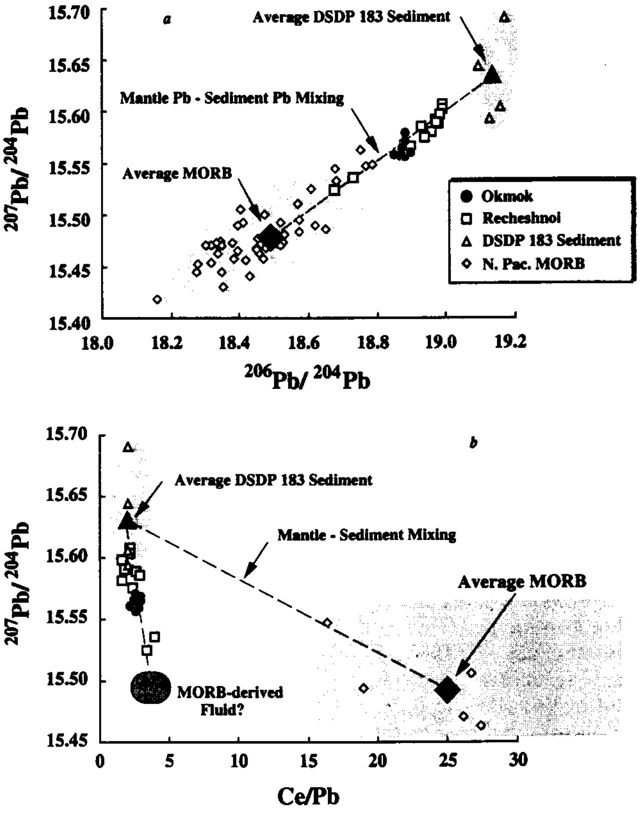

FIG. 4 Constraints on Umnak source components derived from Ce/Pb and Pb isotope ratios. *a*, Comparison of the Pb isotope ratios of Umnak lavas with those of north Pacific MORB and oceanic sediments just outside the Aleutian trench (Deep Sea Drilling Project Hole 183). *b*, Adds Ce/Pb elemental ratios to the comparison and shows that a component with low $^{207}Pb/^{204}Pb$ and low Ce/Pb is required to explain the Umnak data. Pb isotopes are shown for DSDP 183 sediment samples A2 7B4, A2 9A1 and A2 10A4 (from ref. 19) and sample 19-183-38-3, 20-21 (B. Peucker-Ehrenbrink, personal communication). Average Ce/Pb ratio for Pacific pelagic clays is from ref. 18.

We begin to address this question with a quantitative evaluation of current element fluxes from the mantle to arc magmas. The calculations assume that the mantle-derived Pb in the Okmok magma source comes entirely from the subducted oceanic crust. Although this component may be derived from both the subducted oceanic crust and overlying mantle wedge, this is unimportant to the elemental budgets over time as long as the subducted oceanic crust and wedge are mixed back into the mantle. Assuming that (1) parental arc magmas have 11.1 p.p.m. Ce (the average of parental magmas for Okmok and Recheshnoi[10]) and 4.42 p.p.m. Pb (thus Ce/Pb = 2.5, like the average in Umnak lavas); (2) the mass of arc magma generated is 1/20 the mass of subducted oceanic crust[28,29]; and (3) the portion of mantle-derived Pb in the magma is 40% (as in Okmok), then the concentration of Pb in the oceanic crust would be reduced by 0.088 p.p.m. (4.42 p.p.m. × 0.05 × 0.40). If Ce/Pb is ~4 in the mantle-derived component of arc magmas (as in Umnak, Fig. 4*b*), the concentration of Ce in the residual MORB would be reduced by 0.354 p.p.m. (4 × 0.088 p.p.m.).

Whereas the average Ce/Pb ratio of the bulk oceanic crust is well-constrained to be ~25 (refs 4, 5), estimates of the abundance of these elements range widely from 7.5–12 p.p.m. Ce and 0.30–0.49 p.p.m. Pb (refs 3, 30). The higher estimate[3] represents an average of 26 MORB glasses, including differentiated lavas. The lower estimate assumes a primary MORB with 10% MgO (W. McDonough, personal communication), which we accept as more appropriate for the bulk oceanic crust. If oceanic crust has 7.5 p.p.m. Ce and 0.30 p.p.m. Pb when formed, the fluxes of Ce and Pb observed in the Umnak source would reduce the Ce concentration by 4.7% (0.354 ÷ 7.5 = 0.047) and the Pb by 29% (0.088 ÷ 0.30 = 0.29). The Ce/Pb ratio in the subducted oceanic crust would therefore increase from 25 to 34 as a consequence of preferential Pb extraction during the present subduction cycle. Over time, this process would lead to a secular increase in the Ce/Pb of the mantle.

To assess the quantitative effect on the mantle through geological time, our calculations assume that the subduction process has always produced the fractional reductions in Ce and Pb concentrations in subducted oceanic crust that are indicated today, that the 'interactive mantle' (the portion depleted to form continents) is the source of MORB and has approximately constant mass, and that the remainder of the mantle is undepleted. Using the refractory element ratio of Ce to U in the primitive mantle from ref. 3 and calculating the U/Pb ratio of the bulk Earth assuming μ (^{238}U/^{204}Pb) = 8.5 ± 0.5 and κ (^{232}Th/^{238}U) = 4.0 ± 0.2, the Ce/Pb ratio of the primitive mantle is 10.7 ± 0.5 (in general agreement with corrections to estimates in refs 3 and 30; A. Hofmann and W. McDonough, personal communication). A simple mass-balance model (Box 1) can then be used to examine the effects of processing the interactive mantle through convergent margins as oceanic crust to produce the increase of Ce/Pb from ~10.7 to ~25 in the present 'depleted mantle' source of MORB and most OIB[3,4].

The continental crust resulting from such convergent margin processing has a Ce/Pb ratio of ~2.5 when Ce/Pb in the depleted mantle reaches 25. If we select a mass for the continental crust, equation (6) (Box 1) defines the requisite mass of the depleted mantle for any concentration of Ce in the continental crust, $C_{\mathrm{cc}}^{\mathrm{Ce}}$. Estimates of the Ce abundance in the bulk continental crust range from 33 to 55 p.p.m. (ref. 31). Using mantle and crustal masses from refs 32–34, generation of this range of Ce concentrations would require the depleted mantle to include 73–121% of the total mantle. For the mass of the depleted mantle, M_{dm}, to be $\leqslant$100% of the total mantle, Ce in the continental crust would have to be $\leqslant$45 p.p.m. Given an average age of ~60 Myr for present-day oceanic crust[35], subduction of the mass of oceanic crust needed to process the interactive mantle over the age of the Earth would require average crustal production rates 2–3 times those of the present day. This requirement may be a natural consequence of the secular cooling of the Earth[36–39].

Although this simple model can account for the global fractionation of Pb from Ce in the silicate Earth, the results are not in complete agreement with some generally held views of the present-day Earth. The flux of Ce from the mantle into the crust is too low relative to the flux of Pb, generating continents with Ce/Pb = 2.5, lower than most estimates, which range from 3.8 to 5.0 (refs 31, 32). This in turn causes the Ce/Pb of the mantle

BOX 1 Ce/Pb mass-balance model

THE flux of an element, *i*, from the mantle into the oceanic crust can be described in terms of the cumulative mass of oceanic crust subducted over time, M_{oc}, and the concentration of *i* in the interactive mantle, C_{m}^{i}, by

$$dM_{\mathrm{oc}}^{i} = EC_{\mathrm{m}}^{i}dM_{\mathrm{oc}} \qquad (1)$$

where *E* is a melting function that relates C_{m}^{i} to the concentration of *i* in the oceanic crust ($C_{\mathrm{oc}}^{i} = EC_{\mathrm{m}}^{i}$). A fraction of this flux, f^{i}, is removed from the oceanic crust at convergent margins and added to the continental crust. The remaining fraction is returned to the mantle by subduction of the oceanic crust. The irreversible flux of element *i* out of the mantle is thus equal to the flux of *i* into the continental crust,

$$-M_{\mathrm{m}}dC_{\mathrm{m}}^{i} = f^{i}EC_{\mathrm{m}}^{i}dM_{\mathrm{oc}} \qquad (2)$$

where M_{m} is the mass of the interactive mantle. Formally, the mass of the interactive mantle is the sum of the masses of the continental crust, M_{cc}, and the residual depleted mantle, M_{dm}. Because the mass of the continental crust is only 0.5% of the silicate Earth, to simplify the model we use the approximation $M_{\mathrm{m}} \approx M_{\mathrm{dm}}$. Thus, $M_{\mathrm{dm}} \approx M_{\mathrm{m0}}$, the initial mass of the interactive mantle. Accordingly, the depleted mantle is hereafter assumed to represent the interactive mantle. Rearranging equation (2) and integrating yields:

$$C_{\mathrm{dm}}^{i} \approx C_{\mathrm{m0}}^{i} \exp\left(-\frac{M_{\mathrm{oc}}}{M_{\mathrm{dm}}} f^{i}E\right) \qquad (3)$$

where C_{m0}^{i} is the concentration of *i* in the primitive mantle. The ratio, *R*, of two elements *i* and *j* in the depleted mantle is then given by

$$R_{\mathrm{dm}}^{i/j} \approx R_{\mathrm{m0}}^{i/j} \exp\left(\frac{M_{\mathrm{oc}}}{M_{\mathrm{dn}}} E(f^{j} - f^{i})\right) \qquad (4)$$

where $R_{\mathrm{m0}}^{i/j}$ and $R_{\mathrm{dm}}^{i/j}$ are the ratios in the primitive and depleted mantle, respectively. We assume that *E* represents equilibrium melting with partition coefficients for Ce and Pb of 0.01, and that mid-ocean ridge basalts (MORBs) are produced by an average of 10% melting ($F = 0.1$) (ref. 56). If $f^{\mathrm{Ce}} = 0.047$ and $f^{\mathrm{Pb}} = 0.29$ as is presently observed for the volcanoes on Umnak island, then to increase the Ce/Pb ratio of the interactive mantle from its primitive value, $R_{\mathrm{m0}}^{\mathrm{Ce/Pb}} \approx 10.7$, to its present value, $R_{\mathrm{dm}}^{\mathrm{Ce/Pb}} \approx 25$, requires $M_{\mathrm{oc}}/M_{\mathrm{dm}}$ to be ~0.38. The total mass of mantle melted over geological time to form MORB is M_{oc}/F. Thus to satisfy the model, the interactive mantle would have to be processed ~4 times (0.38 ÷ 0.1), through creation and subduction of oceanic crust.

Substituting $M_{\mathrm{oc}}/M_{\mathrm{dm}} = 0.38$ into equation (3), with $C_{\mathrm{m0}}^{\mathrm{Ce}} = 1.60$ (ref. 3) and $C_{\mathrm{m0}}^{\mathrm{Pb}} = 0.150$, the concentrations of Ce and Pb in the present-day depleted mantle would be 1.36 p.p.m. and 0.055 p.p.m., respectively. Because these calculations assume that the depleted mantle is the complement of the continental crust, the mass of element *i* in the continents, M_{cc}^{i}, is given by

$$M_{\mathrm{cc}}^{i} = M_{\mathrm{m0}}^{i} - M_{\mathrm{dm}}^{i} \qquad (5)$$

where M_{m0}^{i} is the initial mass of *i* in the interactive mantle and M_{dm}^{i} is the mass of *i* in the deleted mantle. Because one of our approximations is that $M_{\mathrm{dm}} \approx M_{\mathrm{m0}}$, equation (5) can be written as

$$\frac{M_{\mathrm{cc}}}{M_{\mathrm{dm}}} \approx \frac{(C_{\mathrm{m0}}^{i} - C_{\mathrm{dm}}^{i})}{C_{\mathrm{cc}}^{i}} \qquad (6)$$

where M_{cc} is the mass of the continental crust and C_{cc}^{i} is the concentration of element *i* in the continental crust. Substituting the equivalent mass-balance approximation for *j* into equation (6), we obtain

$$\frac{C_{\mathrm{cc}}^{i}}{C_{\mathrm{cc}}^{j}} \approx \frac{C_{\mathrm{m0}}^{i} - C_{\mathrm{dm}}^{i}}{C_{\mathrm{m0}}^{j} - C_{\mathrm{dm}}^{j}} \qquad (7)$$

to increase to 25 before a sufficient mass of Ce and Pb has been extracted, yielding concentrations of Ce (1.36 p.p.m.) and Pb (0.055 p.p.m.) in the depleted mantle that are too high relative to present-day MORB sources. With the high mantle abundances generated by the model, mass balance between the crust and mantle (equation (7), Box 1) also requires a depleted mantle that is larger than most previous estimates[5,31,36,37]. Thus, the simple model generates continents with Ce/Pb that is too low, and a depleted mantle that is too large and has Ce and Pb abundances that are too high.

More realistic models of mantle and crustal evolution would have more free parameters, accounting for recycling of continental crust, alternative mechanisms of crustal growth and mantle depletion, and exchange between the MORB mantle and a less-depleted mantle reservoir. Intramantle exchange[31,38], for example, would relax the mass-balance constraints on the size and composition of MORB mantle by distributing the depletion throughout the entire mantle. However, the general success of our simple model illustrates the importance of convergent margin processes for global Ce/Pb fractionation. Although rigorous evaluation of the effects of all simplifying assumptions is beyond the scope of this Article, we will briefly consider some of their implications.

Recycling of continental sediments into the mantle would reduce the rate of depletion caused by continent formation, increasing the total mass of oceanic crust that would have to be processed to satisfy the model. But Nd and Pb concentration and isotope data for Umnak lavas[39,40] and DSDP Hole 183 sediments[19,41,42] show that Pb is transferred preferentially relative to Nd from subducted sediments into the arc magma source. Okmok lavas have Nd/Pb$\approx$1.7, with ~60% of the Pb and ~10% of the Nd derived from subducted sediment. Thus the sediment-derived component returned to the continents through arc magmatism has Nd/Pb$\approx$0.3 ($1.7\times0.1\div0.6$), a factor of ~5 lower than in DSDP-183 sediments. Residual sediment that is recycled to the deep mantle would therefore have higher Nd/Pb (and by inference, higher Ce/Pb) than bulk subducted sediment. Such sediment recycling would inhibit mantle depletion (defined as the decrease in Ce or Pb abundance), but for a given degree of depletion it would lead to higher mantle Ce/Pb and lower crustal Ce/Pb. Depending on the mass of sediment subducted relative to the mass of crust produced, a proportion that could vary greatly over Earth history, sediment recycling could enhance, retard or even reverse the Ce/Pb fractionation described in the simple model.

The flux of Ce to the continents may be increased relative to the flux of Pb by other continent-building mechanisms, such as intraplate magmatism and basaltic underplating[29,43-46]. Because these mechanisms reflect mantle melting without involving the processes that fractionate Pb from Ce, the continental crust that they generate would have high Ce/Pb, similar to the mantle source. The effect of such mechanisms can be modelled by increasing the extraction efficiencies f^{Ce} and f^{Pb} (See Box 1) by equal amounts. Increasing each f by 14.5% yields a reasonable Ce concentration of 0.82 p.p.m. in the depleted mantle, but implies a rather high Ce/Pb of ~6.7 for the continental crust. Thus, intraplate magmatism or underplating might increase the flux of Ce from the mantle sufficiently to yield a reasonable MORB source, but would generate continents with Ce/Pb higher than published estimates.

It is also possible that higher mantle temperatures in the past may have resulted in more widespread melting of the subducted oceanic crust. Because melts would transfer Ce and Pb from the oceanic crust into the arc source with equal efficiency, f^{Ce} and f^{Pb} would be increased by equal amounts. Therefore, the effect on mantle depletion would be similar to that of intraplate magmatism.

An additional process that would deplete Ce and Pb in the MORB mantle, without significantly affecting the Ce/Pb of the continental crust, is the accumulation of subducted oceanic lithosphere in a boundary layer within the mantle, where it is temporarily excluded from convective mixing with the depleted mantle[47 52]. The concentrations of Ce and Pb and the Ce/Pb ratio are likely to be high in the boundary layer because it would contain a higher percentage of relatively young oceanic crust than the convecting mantle. Isolation of this material would retard the increase of Ce/Pb and reduce the abundances of Ce and Pb in the MORB mantle, without increasing the Ce/Pb ratio of the continents. Thus a combination of convergent margin magmatism, boundary layer isolation of subducted crust and the additional continent-building mechanisms discussed above could produce appropriate Ce/Pb ratios in the continental crust and appropriate depletions of Ce and Pb in the MORB mantle.

Implications for mantle differentiation

Data from Umnak island show that fractionation of Pb from Ce by convergent margin processes is continuing. This apparently contradicts the formal three-stage mantle evolution model of Hofmann *et al.*[5], which ignores the role of present-day mantle differentiation in fractionating the Ce/Pb ratio of the mantle. However, a broader interpretation of their model is consistent with our data. To explain the global Ce/Pb fractionation by current processes at convergent plate margins, oceanic crust must have been processed through subduction zones at a higher rate in the past, with a correspondingly higher rate of continental crust production. Subsequent reductions in the rate of crustal growth due to convergent margin magmatism would have also reduced the rate of Ce/Pb fractionation. Thus our data indicate that fractionation of Ce/Pb ratios in the mantle continues, but at a rate lower than the average over Earth history. □

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