

LETTERS

Thallium isotopic evidence for ferromanganese sediments in the mantle source of Hawaiian basalts

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Ocean island basalts are generally thought to be the surface expression of mantle plumes, but the nature of the components in the source regions of such mantle plumes is a subject of long-standing debate. The lavas erupted at Hawaii have attracted particular attention, as it has been proposed that coupled ^{186}Os and ^{187}Os anomalies reflect interaction with the Earth's metallic core^{1,2}. It has recently been suggested, however, that such variations could also result from addition of oceanic ferromanganese sediments to the mantle source of these lavas^{3–5}. Here we show that Hawaiian picrites with osmium isotope anomalies also exhibit pronounced thallium isotope variations, which are coupled with caesium/thallium ratios that extend to values much lower than commonly observed for mantle-derived rocks. This correlation cannot be created by admixing of core material, and is best explained by the addition of ferromanganese sediments into the Hawaii mantle source region. However, the lack of correlation between thallium and osmium isotopes and the high thallium/osmium ratios of ferromanganese sediments preclude a sedimentary origin for the osmium isotope anomalies, and leaves core–mantle interaction as a viable explanation for the osmium isotope variations of the Hawaiian picrites.

The isotopic compositions of ocean island basalts (OIB) are easily resolvable from those of the mantle-derived basalts erupted at mid-ocean ridges (mid-ocean-ridge basalts, MORB), and therefore it is clear that the sources of these types of magmatism must also be different. One model infers that OIB originate from a deep mantle source, which was previously contaminated with ocean crust that entered the mantle via subduction zones⁶. On the basis of $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ isotopic evidence, it was proposed that the Earth's core may also contribute up to 0.5–1% by weight to some mantle plumes^{1,7–9}. These arguments have been supported by the elevated Fe/Mn ratios of Hawaiian picrites that also exhibit Os isotope anomalies¹⁰. However, the lack of tungsten isotope anomalies in some of the same samples⁴ may exclude a core source, though it has been suggested that W, Os and Fe/Mn ratios could be decoupled during core–mantle reaction processes¹⁰. As an alternative to core–mantle interaction, it was noted by several authors that oceanic ferromanganese (Fe–Mn) sediments display very high Pt/Os, such that they would develop high $^{186}\text{Os}/^{188}\text{Os}$ over time^{3–5}. Addition of ancient Fe–Mn sediments into a mantle source, therefore, could also explain the elevated $^{186}\text{Os}/^{188}\text{Os}$ ratios observed for some mantle plumes.

As pointed out in ref. 3, additions of Fe–Mn sediments to a mantle source should generate ^{186}Os isotope anomalies that are accompanied by significant Tl isotope variations. Such a co-variation is expected because Fe–Mn sediments have high Tl concentrations and fractionated Tl isotope compositions with $\epsilon^{205}\text{Tl}$ values as high as +15 (refs 11, 12). Moreover, recent studies have shown that the

continental crust and upper mantle are characterized by relatively constant Tl isotope ratios of $\epsilon^{205}\text{Tl} = -2.0 \pm 0.5$ (refs 13, 14). This indicates that the Tl isotope system may be an excellent monitor of Fe–Mn sediment additions to OIB source regions. We have therefore measured the Tl abundances and isotope compositions of nine Hawaiian picrites that have previously been investigated for ^{187}Os – ^{186}Os isotope systematics¹ and two additional picrites from Mauna Kea and Kilauea¹⁵.

The Tl isotope compositions of the Hawaiian picrites vary in $\epsilon^{205}\text{Tl}$ from -3.1 to $+3.8$ (Table 1). The most positive values are about 6 ϵ -units 'heavier' than two Icelandic basalts (Table 1) and the depleted mantle as represented by MORB (Table 1), high-temperature hydrothermal fluids and sheeted dykes from Ocean Drilling Program Hole 504B¹³. Additionally, the Tl isotope data display a negative correlation with Cs/Tl ratios (Fig. 1) and Rb/Tl (not plotted). Thallium and Cs (and Rb) exhibit very similar incompatibilities in igneous processes¹⁶ and are therefore not expected to fractionate significantly during partial melting or magmatic differentiation. As a consequence, it appears likely that a component with positive $\epsilon^{205}\text{Tl}$ and low Cs/Tl contributed to the Hawaiian lavas. In addition to high Tl contents and positive $\epsilon^{205}\text{Tl}$ -values, Fe–Mn sediments are known to display low Cs/Tl ratios¹⁷. The correlation of Fig. 1 is therefore most readily explained by the addition of Fe–Mn sediments into the mantle source region of Hawaiian magmatism.

There are other processes that could generate lavas with positive $\epsilon^{205}\text{Tl}$ -values. Thallium is a highly volatile element, and magma degassing, which is probably a significant factor controlling the abundances of the elements Cd, Bi and Re in Hawaiian basalts¹⁸, could conceivably cause kinetic Tl isotope fractionation. This process would be expected to produce residual degassed lavas with low Tl contents and positive $\epsilon^{205}\text{Tl}$ -values. However, as volcanic exhalations display low Cs/Tl ratios of less than 0.5 (ref. 19), increases in $\epsilon^{205}\text{Tl}$ would be associated with increasing Cs/Tl ratios, which is the opposite of the observed trend (Fig. 1). Degassing can therefore be excluded as the cause of the observed Tl isotope variations.

A recent study has shown that the short-lived radionuclide ^{205}Pb , which decays to ^{205}Tl , was present in the early Solar System²⁰ and therefore probably also at the time of terrestrial core formation. A planetary core with a high Pb/Tl ratio could thus develop a significant Tl isotope anomaly. Moreover, Cs is a highly lithophile element whereas Tl is mildly chalcophile, such that the core is expected to have a low Cs/Tl ratio. If the correlation of Fig. 1 is to be explained by binary core–mantle mixing, this necessitates a core with Cs/Tl ≈ 0 to 2 coupled with $\epsilon^{205}\text{Tl} \approx +4$ to $+6$. The Tl content of the core for a given Tl isotope ratio can be estimated, by calculating the Tl and Pb isotope evolution for terrestrial accretion models very similar to those used of ref. 21. Owing to the low initial Solar System abundance

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Table 1 | Tl isotope compositions and concentrations for Hawaii picrites

Sample	Location	$\epsilon^{205}\text{Tl}$	Tl (ng g^{-1})	Cs (ng g^{-1}) [†]	Rb ($\mu\text{g g}^{-1}$) [†]	Cs/Tl
Kil 1-18	Kilauea	-3.1	16.9	78	6.3	4.6
LO 02-02	Loihi	-2.0	12.2	77	6.5	6.3
ML 1868-9*	Mauna Loa	-1.4	8.5	43	4.3	5.0
Kil 93-1489*	Kilauea	-1.2	14.7	74	7.2	5.0
Kil 1840*	Kilauea	-1.2	10.9	65	7.0	5.9
MK 1-6	Mauna Kea	-0.6	19.8	75	6.9	3.8
Kil 1-7	Kilauea	-0.6	18 \ddagger	71	5.8	3.9
KOO-CF*	Ko'olau	-0.5	22.9	88	7.6	3.8
H-11	Hualalai	0.9	13.5	44	4.5	3.3
KOO-17a*	Ko'olau	1.3	1.7	5	0.3	2.9
ML-2-50	Mauna Loa	3.8	15.1	35	3.4	2.3
RSG 19*	Iceland	-2.0	ND	ND	ND	ND
SNS 14*	Iceland	-1.9	ND	ND	ND	ND
SO157 54DS1	Pacific-Antarctic rise	-1.6	7.4	ND	ND	ND
POS 221 626 DS	Kolbeinsey ridge	-2.5	7.1	ND	ND	ND
TT 152-21	Juan de Fuca ridge	-2.5	9.7	ND	ND	ND
ALV 731-4	Galapagos ridge	-1.8	5.5	ND	ND	ND
CH 98 DR11	Mid-Atlantic Ridge	-0.9	4.7	ND	ND	ND

$\epsilon^{205}\text{Tl} = \{[(^{205}\text{Tl}/^{203}\text{Tl})_{\text{meas}} - (^{205}\text{Tl}/^{203}\text{Tl})_{\text{std}}]/(^{205}\text{Tl}/^{203}\text{Tl})_{\text{std}}\} \times 10^4$, where $(^{205}\text{Tl}/^{203}\text{Tl})_{\text{std}}$ is the Tl isotope composition of the NIST 997 Tl isotope standard. ND, not determined.

*Subaerial samples.

[†]Cs and Rb concentrations from ref. 15, except Kil 93-1489 from ref. 30.

[‡]For this sample, the Tl concentration has an uncertainty of $\pm 50\%$, owing to loss of sample during dissolution.

of ^{205}Pb ($^{205}\text{Pb}/^{204}\text{Pb} \approx 1.5 \times 10^{-4}$, ref. 20) and the prolonged accretion of the Earth (99% accreted at ~ 45 Myr after Solar System formation²¹), Tl isotope anomalies in the core only reach sufficient levels (that is, $\epsilon^{205}\text{Tl} > +4$) at very high Pb/Tl ratios of >240 . The following calculation illustrates the maximum attainable Tl concentration for a core with $\epsilon^{205}\text{Tl} \approx +4$, which is the minimum value required to explain the most anomalous Hawaiian sample. The Pb content of the bulk Earth is unknown, but a reasonable upper limit is set by the solar Pb abundance (as defined by CI chondrites), which is about $2,400 \text{ ng g}^{-1}$ (ref. 22). As the silicate portion of the Earth contains about 150 ng g^{-1} Pb (ref. 23), mass balance dictates an upper limit to the Pb concentration in the core of $\sim 7,300 \text{ ng g}^{-1}$. Combining this Pb abundance with a Pb/Tl ratio of 240 yields a Tl content of approximately 30 ng g^{-1} . Assuming that the lower mantle contains 0.5 ng g^{-1} Tl (a low estimate compared to 3 ng g^{-1} estimated in ref. 23), entrainment of more than 10% core material is required to obtain a mantle source with $\epsilon^{205}\text{Tl} > +3.2$, comparable to the largest isotope anomaly found in Hawaii (Table 1). We note that faster accretion rates would lower the needed Pb/Tl (for example, 99% accretion at 30 Myr necessitates $\text{Pb/Tl} > 200$, resulting in a core Tl concentration of $\sim 40 \text{ ng g}^{-1}$). However, this will only reduce the amount of entrained core material to $\sim 8\%$. The quantities of core material required are more than an order of magnitude larger than the most recent estimates based on ^{186}Os anomalies⁷, and inconsistent with the highly siderophile element abundances and Pb isotope compositions of these lavas^{15,24}. Thus, we conclude that the core is not a viable source for the Tl isotope anomalies of mantle plumes.

The above arguments demonstrate that the observed correlation between $\epsilon^{205}\text{Tl}$ and Cs/Tl (Fig. 1) is most readily explained by additions of marine Fe-Mn precipitates. We note that the precipitation of Fe-Mn oxyhydroxides onto submarine basalts does not provide a feasible explanation for the Hawaiian Tl data, as subaerial samples also display Tl isotope effects (Table 1). Moreover, the negative correlation of Tl and Pb isotopes towards unradiogenic values (excluding samples from Ko'olau) (Fig. 2) attests to the ancient nature of the Fe-Mn component and renders assimilation of recent ferromanganese sediments during magma ascent as a cause for the Tl isotope anomalies unlikely. We conclude that the most reasonable process for generating the observed Tl isotopic compositions of Hawaiian basalts is contamination of their mantle source by Fe-Mn sediments. Quantitative modelling of the mixing process is made difficult, however, by possible temporal variations in the Tl isotope composition of sea water and hence of Fe-Mn precipitates¹².

If it is assumed that the Fe-Mn sediments are characterized by $\epsilon^{205}\text{Tl} = +10$ (ref. 11), akin to the average value of modern Fe-Mn crusts and nodules, then less than $20 \mu\text{g g}^{-1}$ (of Fe-Mn sediments by weight) need to be admixed to a pristine mantle source to account for the Tl isotope variations of the Hawaiian picrites. The slope of the mixing line that is obtained for this scenario is slightly shallower than the actual data array, however (Fig. 1). A best-fit line through the

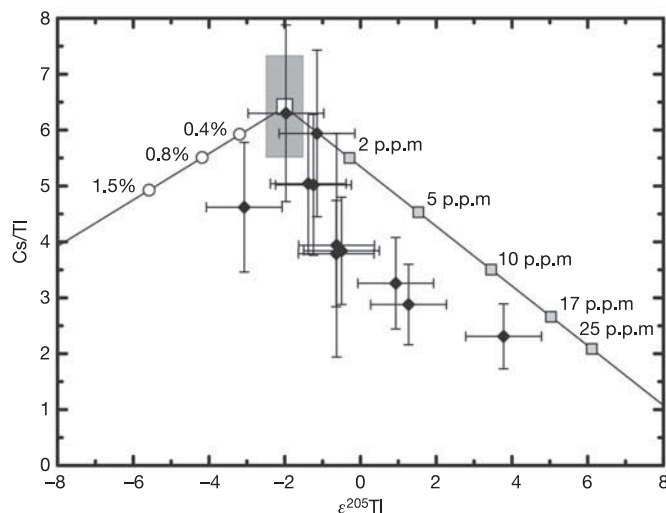


Figure 1 | Thallium isotope compositions of the Hawaiian picrites plotted versus Cs/Tl ratios. Mixing lines between pristine mantle (large open square), Fe-Mn oxyhydroxides (small grey squares) and altered MORB (open circles) are also plotted. The amounts (by weight) mixed into the mantle source are labelled on the mixing lines. For the mantle, the Tl isotope composition is $\epsilon^{205}\text{Tl} = -2.0$ (ref. 13), and a Cs concentration of 7.7 ng g^{-1} , is used³¹. The mantle Tl concentration is estimated to be about 1.2 ng g^{-1} , from $\text{Cs/Tl} = 6.5$ for the Hawaiian sample with the most mantle-like Tl isotope composition (LO 02-02). This Cs/Tl ratio is also consistent with a previous estimate of the mantle's average Cs/Tl ratio³². For the Fe-Mn oxyhydroxides, the Tl concentration and isotope composition are assumed to be $100 \mu\text{g g}^{-1}$ and $\epsilon^{205}\text{Tl} = +10$, akin to values of modern Fe-Mn crusts and nodules^{11,17}. The Cs content of Fe-Mn oxyhydroxides is about 500 ng g^{-1} (ref. 33). Altered MORB is assumed to be characterized by $\epsilon^{205}\text{Tl} = -15$ (ref. 13) and Tl and Cs concentrations of 30 ng g^{-1} (ref. 13). Error bars denote 2 s.d. uncertainties. The large grey shaded rectangle denotes the range of the mantle Cs/Tl and $\epsilon^{205}\text{Tl}$ values.

data would imply that the Fe-Mn component is characterized by $\epsilon^{205}\text{Tl} \approx +5$, which is not unrealistic¹². Alternatively, the deviations of the picrite data from the calculated binary mixing line of Fig. 1 may reflect the additional presence of small amounts (less than about 1%) of recycled low-temperature altered MORB, as was previously suggested on the basis of $^{187}\text{Os}/^{188}\text{Os}$ and oxygen isotopic evidence²⁵. The scatter of the picrite data in a plot of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $\epsilon^{205}\text{Tl}$ can also be readily accommodated, by assuming that the Pb isotope compositions of the samples are dominated by variable additions of Fe-Mn sediments and an additional lithogenic marine sedimentary component, which has a composition that is similar to the upper continental crust (Fig. 2a).

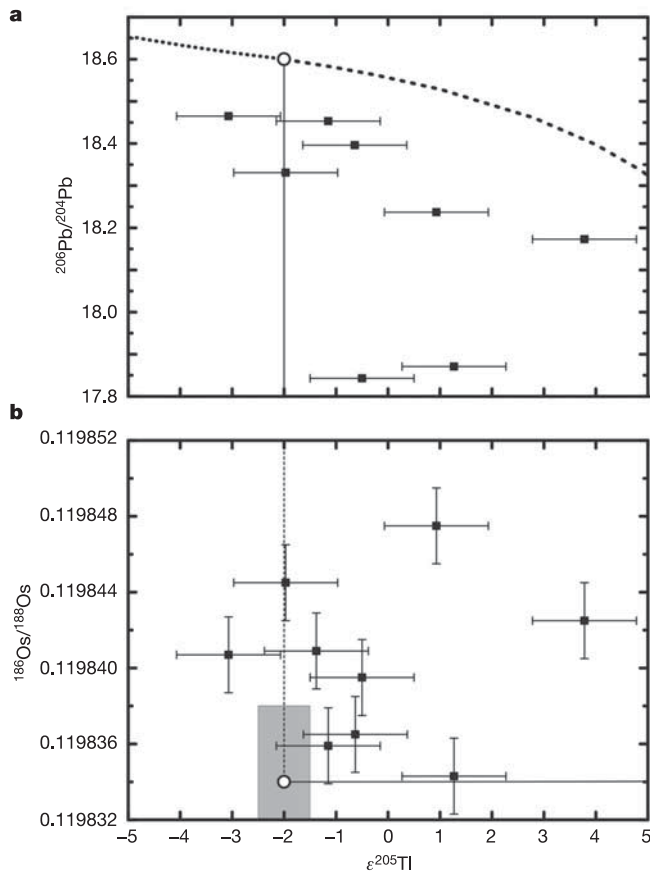


Figure 2 | Thallium isotope compositions of the Hawaiian picrites plotted versus $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{186}\text{Os}/^{188}\text{Os}$ isotope ratios. Error bars denote 2 s.d. uncertainties. **a**, Lead isotope data are from refs 15, 24. Also shown are mixing lines between pristine mantle (open circle) and Fe-Mn sediments (dashed line), a lithogenic sediment component (solid line) and altered MORB (dotted line). The endmember compositions used to construct the mixing lines are as follows. Fe-Mn sediments: Pb = $500 \mu\text{g g}^{-1}$, $^{206}\text{Pb}/^{204}\text{Pb} = 16$, Tl = $100 \mu\text{g g}^{-1}$, $\epsilon^{205}\text{Tl} = 10$; lithogenic sediment component: Pb = $30 \mu\text{g g}^{-1}$, $^{206}\text{Pb}/^{204}\text{Pb} = 17.5$, Tl = $0.6 \mu\text{g g}^{-1}$, $\epsilon^{205}\text{Tl} = -2$; altered MORB: Pb = $0.23 \mu\text{g g}^{-1}$, $^{206}\text{Pb}/^{204}\text{Pb} = 21$, Tl = $0.05 \mu\text{g g}^{-1}$, $\epsilon^{205}\text{Tl} = -15$; pristine mantle, Pb = $0.071 \mu\text{g g}^{-1}$, $^{206}\text{Pb}/^{204}\text{Pb} = 18.6$, Tl = $0.0012 \mu\text{g g}^{-1}$, $\epsilon^{205}\text{Tl} = -2$. It is notable that addition of the lithogenic component has no effect on either Tl isotopes or the Cs/Tl ratio as this component is identical to the mantle values ($\epsilon^{205}\text{Tl} \approx -2$ and Cs/Tl ≈ 6) of these two parameters. **b**, The $^{186}\text{Os}/^{188}\text{Os}$ isotope data are from refs 1, 2. Also shown are mixing lines between mantle (open circle) and Fe-Mn sediments (solid line) and core (dashed line). The grey box indicates the range of normal mantle values. The endmember compositions used to construct the mixing lines are as follows. Fe-Mn sediments: Os = $0.003 \mu\text{g g}^{-1}$, $^{186}\text{Os}/^{188}\text{Os} = 0.1206$, Tl = $100 \mu\text{g g}^{-1}$, $\epsilon^{205}\text{Tl} = 10$; core, Os = $0.3 \mu\text{g g}^{-1}$, $^{186}\text{Os}/^{188}\text{Os} = 0.11987$, Tl = $0.005 \mu\text{g g}^{-1}$, $\epsilon^{205}\text{Tl} = -2$; mantle, Os = $0.003 \mu\text{g g}^{-1}$, $^{186}\text{Os}/^{188}\text{Os} = 0.119834$, Tl = $0.0012 \mu\text{g g}^{-1}$, $\epsilon^{205}\text{Tl} = -2$.

Both of these components must be characterized by unradiogenic $^{206}\text{Pb}/^{204}\text{Pb}$, which is indicative of an old (>2.5 Gyr) age and low time-integrated U/Pb ratios. These conclusions are in accord with the results of a previous study, which suggested that the mantle source of Hawaiian volcanoes was contaminated by ancient (~ 3 Gyr) pelagic sediments²⁶.

It is notable that the very small amounts of Fe-Mn sediments that are required to account for the Tl isotope variations of the Hawaiian picrites will not significantly perturb the Nd and Hf isotope systematics of the samples, and even the Pb isotope compositions are altered only marginally (Fig. 2a). Also, we note that the Fe/Mn ratio is unaffected by such small ferromanganese sediment additions. For example, admixing of $30 \mu\text{g g}^{-1}$ of Fe-Mn sediment will only change the Fe/Mn of a mantle source from 59.6 (ref. 23) to 59.4. Hence the high Fe/Mn ratios recorded by these samples¹⁰ cannot be related to addition of Fe-Mn sediments. In contrast, it was previously suggested that the $^{186}\text{Os}/^{188}\text{Os}$ isotope systematics of the Hawaiian mantle source may be dominated by admixed Fe-Mn sediments³. It is evident, however, that our data exhibit no correlation between Tl and Os isotope compositions (Fig. 2b). This observation is readily explained by the extremely high Tl/Os ratios of about 40,000 (refs 3, 11) for Fe-Mn deposits. Minor additions of such material into a normal mantle source will generate large Tl isotope anomalies, whereas $^{186}\text{Os}/^{188}\text{Os}$ ratios remain constant (Fig 2b). If mixing processes were to be responsible for the isotope systematics of sample LO 02-02 (which displays a significant ^{186}Os isotope anomaly), this would require a contaminant characterized by Tl/Os ≈ 2 . In principle, such a contaminant could be produced from recycled Fe-Mn sediments, by preferential loss of Tl from subducting slabs. Reducing the Tl/Os ratio from 40,000 to 2 requires that more than 99.9% of the original Tl budget is lost during subduction, however. This is unrealistic, given that Tl is less fluid mobile than Pb (ref. 27), and the latter element is typically depleted by 10–90% through fluid mobilization in subduction zones²⁸. The Tl and $^{186}\text{Os}/^{188}\text{Os}$ isotope variations of the Hawaiian picrites are therefore unlikely to have the same origin, and this precludes Fe-Mn sediments as the source of the ^{186}Os isotope anomalies. This interpretation implies that core-mantle interaction is still a viable explanation for the elevated $^{186}\text{Os}/^{188}\text{Os}$ isotope ratios observed for the Hawaiian mantle plume.

METHODS

The Hawaiian picrites and Icelandic basalts were obtained as powders and analysed as received. The MORB glasses were crushed in an agate mortar to chips $<300 \mu\text{m}$ in size, which were handpicked to obtain pieces devoid of any alteration products. Following dissolution of the samples (~ 1 g), Tl was separated from the sample matrix by a two-stage column chemistry procedure previously described in refs 14 and 29. The Tl isotope analyses were performed by multiple collector inductively coupled plasma mass spectrometry at the ETH Zurich, using both external normalization to SRM 981 Pb and standard sample bracketing for mass bias correction²⁹. The external reproducibility (2 s.d.) of the Tl isotope analyses is about $\pm 1 \epsilon^{205}\text{Tl}$ -unit^{14,29}. Procedural blanks for silicate dissolutions and column chemistry are less than 20 pg of Tl (ref. 14), which is $<1\%$ of the Tl analysed in any sample in this study and therefore insignificant. The Tl concentrations were determined by monitoring the ^{205}Tl signal intensities during the isotopic measurements and normalizing these to the ^{208}Pb ion beam from the known quantity of SRM 981 Pb added to the sample solutions. It was also taken into account that Tl is ionized approximately 5% more efficiently than Pb. These data are estimated to be accurate to better than $\pm 25\%$ (ref. 12).

The picrite samples analysed in this study were all selected carefully for their petrographic freshness, with the exception of KOO-17a, which probably has been subaerially altered¹⁵. However, subaerial weathering is not expected to cause significant Tl isotope fractionation¹⁴, though the effect on the Cs/Tl ratio is unknown. The unaltered nature of the samples is also attested by their mantle-like Rb/Cs ratios^{15,30}, which are known to change significantly during both submarine and subaerial alteration³¹.

The number of MORB analyses was limited to five (Table 1) because large samples (~ 1 g) of handpicked and extremely pure glass are necessary for the acquisition of accurate and precise Tl isotope data. The sample size is constrained by the low Tl concentrations of MORB. Only the purest MORB glass

that is completely devoid of Fe-Mn oxyhydroxide coatings or any signs of weathering (for example, devitrification) can be used for analysis, as such alteration products are known to be highly enriched in Tl (refs 12, 32) that is isotopically fractionated^{11,13} (by up to about $10 \epsilon^{205}\text{Tl}$) relative to MORB.

The accretion model used to calculate the Tl isotope composition of the Earth's core is from ref. 21. This model features concomitant collision-driven planetary growth and core formation, where the Earth reaches 99% of its current mass at the putative giant impact that formed the Moon. The mean life of accretion, τ , was set at 15 Myr, which results in a giant impact at 43.5 Myr. The bulk Earth Pb and Tl concentrations were 2,400 and 20 ng g^{-1} , respectively. The model parameters used results in a silicate Earth with slightly too high Tl concentration and isotope composition. However, fitting the parameters (that is, the bulk Earth Pb and Tl concentrations) to accommodate the silicate Earth invariably leads to a core with $\epsilon^{205}\text{Tl} < 4$, even at $\tau = 5$ Myr. Thus, the calculation is made solely for illustrative purposes.

Received 4 August; accepted 18 November 2005.

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Acknowledgements We thank T. Elliott, M. Humayun and R.J. Walker for reviews; A. Brandon for comments; C. Devey, D. Graham, K. Haase, C. Hémond, P. Stoffers and the POS 221 and SO157 scientific parties for providing samples; M. Meier, U. Menet, D. Niederer, B. Rüttsche, C. Stirling, A. Süsli, S. Woodland, H. Williams and the rest of the IGMR group at the ETH for keeping the mass spectrometers and clean laboratories functioning at all times. This study was funded by the ETH Zurich, the Schweizerische Nationalfonds and the Danish Research Agency. This is a publication of the ARC National Key Centre for Geochemical Evolution and Metallogeny of Continents (GEMOC).

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