

Role of recycled oceanic basalt and sediment in generating the Hf–Nd mantle array

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Following its subduction, oceanic crust either contributes to the source of island-arc volcanic rocks or it is recycled into the mantle¹. Most^{2,3}, but not all authors⁴ believe that recycled crust is incorporated into the plume source of oceanic basalts. The hafnium (Hf) and neodymium (Nd) isotopic compositions of basalts from oceanic islands and mid-ocean ridges exhibit a linear relationship—the mantle array—which is thought to result from mixing between material from the depleted mantle and an enriched recycled component. Here, we model the Hf–Nd isotopic composition of oceanic basalts as a mixture of recycled oceanic crust and depleted mantle and find that recycling of basalt alone is not sufficient to reproduce the mantle array. We conclude that oceanic sediments, which have a relatively high $^{176}\text{Hf}/^{177}\text{Hf}$ ratio, must also be recycled. Combining oceanic sediments with recycled oceanic basalts and subsequent mixing with depleted mantle peridotite produces Hf and Nd isotopic compositions that coincide with the mantle array. The composition of bulk continental crust requires the existence of a complementary low $^{176}\text{Hf}/^{177}\text{Hf}$ reservoir, which we suggest is zircon-rich sediment.

Figure 1 shows the mantle array and the compositions of worldwide oceanic sediments in an ε_{Hf} versus ε_{Nd} plot. Ocean-island basalts (OIB) and mid-ocean ridge basalts (MORB) have an ε_{Hf} of +1.28 at $\varepsilon_{\text{Nd}} = 0$, a value higher than the accepted bulk silicate Earth (BSE) value⁵, but within error of the new values suggested by Bouvier *et al.*⁶. In contrast, sedimentary material exhibits a large range of Nd and Hf isotopic compositions, but almost all oceanic sediments have elevated ε_{Hf} at a given ε_{Nd} , their position being related to the sedimentary process that produced them. Hydrogenous sediments such as Fe–Mn crust and nodules have the highest ε_{Hf} at a given ε_{Nd} , deep-sea clays and biogenic sediments have intermediate values and terrigenous sediments have the lowest ε_{Hf} (ref. 7).

Using the average composition of MORB given in Table 1, we can calculate the evolution path on which such basalts would lie, had they been formed in a similar manner throughout Earth's history (see Supplementary Information, Fig. S1). This array, shown in Fig. 2a, is clearly different from the 'mantle array', suggesting that recycling of oceanic basaltic crust alone cannot account for the Nd and Hf isotopic compositions of MORB and OIB even if the recycled material is mixed with ambient depleted mantle. The 'mantle array' has a much shallower slope than the

oceanic crust evolution path in Fig. 2a, requiring involvement of another component with low ε_{Nd} associated with high ε_{Hf} . We suggest that this component is oceanic sediments.

The average Nd and Hf isotopic compositions of oceanic sediments are difficult to evaluate because of a paucity of ε_{Nd} and ε_{Hf} data and the large range in these data. Plank and Langmuir⁸ calculated an average chemical composition for global subducted sediments (GLOSS; see Table 1) and provided estimates for most trace elements as well as for Sr, Pb and Nd isotopes. However, owing to the scarcity of Hf isotopic data, they could not provide an average Hf isotopic value. To estimate this value, an average of all measured values could be calculated. However, this could produce a questionable result because (1) the total number of analysed samples is not large (<200) and (2) two groups (the sediments present in front of the Lesser Antilles arc⁹ and the Fe–Mn crusts and nodules^{10,11}) dominate the database (see Fig. 1, inset). Mean values calculated from the entire sample set are $\varepsilon_{\text{Nd}} = -7.5$ and $\varepsilon_{\text{Hf}} = -1.3$. Alternatively, the average composition of the sedimentary pile sampled during Leg 185 in the western Pacific Ocean could be used. Details of the geochemistry of the sedimentary pile are found elsewhere¹²; here, we emphasize that the petrological and geochemical characteristics of these sediments are typical of deep-sea sediments and it is the first complete drill core on which both Hf and Nd isotopes were analysed. The ε_{Nd} of the sedimentary pile is -5.9 and its $\varepsilon_{\text{Hf}} = +4.4$ (ref. 13; see Supplementary Information, Table S1). Finally, to associate an ε_{Hf} value with the Nd isotopic composition recommended for GLOSS, we used the trend defined by island-arc lavas in the Nd–Hf isotopic space (see Fig. 2b) arguing that sediments recycled into the mantle are similar to those that contaminate the mantle wedge source of island-arc volcanics. This technique provides an ε_{Hf} value of about 0 for the GLOSS ε_{Nd} value of -8.9 , leading us to use an ε_{Hf} value of $+2 (\pm 3)$ in our modelling (see Table 1). These values, which are shown by a rectangle in Fig. 2b, lie significantly above the mantle array and overlap the fields of both ferromanganese crust and oceanic clay and mud.

Using the estimated compositions of oceanic sediments and oceanic basaltic crust (Table 1), we model the mantle array as a mixture of recycled oceanic crust and associated oceanic sediments, together with depleted mantle. We assume that the oceanic crust and sediments formed by similar processes and were recycled into the mantle for the past 3 Gyr. To calculate their initial isotope ratios

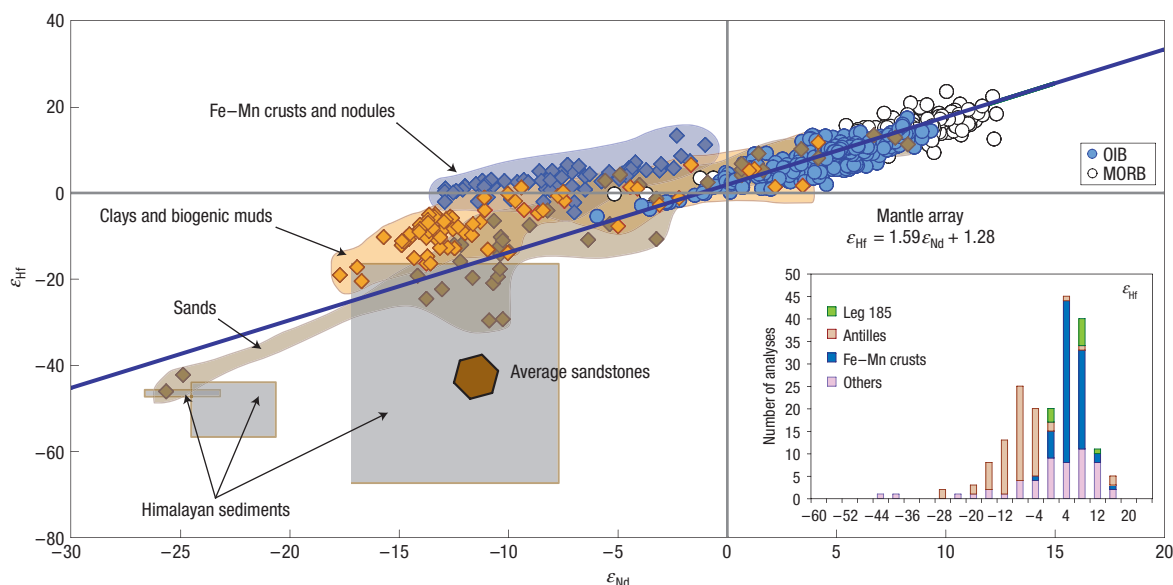


Figure 1 ϵ_{Hf} and ϵ_{Nd} values of oceanic basalts and oceanic sediments. OIB: blue circles, MORB: white circles, oceanic sediments: diamonds. Fields for Himalayan sediments were constructed using Nd whole-rock data and Hf data on zircons²⁰. The large hexagon is the average sandstone value (Table 1). The OIB array follows the relationship $\epsilon_{\text{Hf}} = 1.51\epsilon_{\text{Nd}} + 1.39$. When OIB and MORB are combined, the relationship is essentially unchanged: $\epsilon_{\text{Hf}} = 1.59\epsilon_{\text{Nd}} + 1.28$. Data from the literature^{9–11,13,18,20–27}, GEOROC²⁸ and PETDB²⁹ databases, and unpublished data from C.C. and M.C. Inset: Histogram of ϵ_{Hf} values for sediments shown in the main panel. Sediments are grouped by colour according to their origin.

at different times in Earth's history, we assumed a linear relationship between the present-day isotopic ratios of average sediment and basalt and the Hf and Nd isotopic ratios of the Earth 4.55 Gyr ago. Both sediments and basalts are then modelled to evolve through time using the average Sm/Nd and Lu/Hf ratios of GLOSS and average MORB (see Table 1 and Supplementary Information, Fig. S1). The loci of the present-day isotopic compositions of sediments and oceanic crust that had formed at different times in the past are shown in Fig. 2a. The main observations are as follows. (1) The present-day average Hf isotopic composition of the sediments is indeed high ($\epsilon_{\text{Hf}} = +2 \pm 3$) relative to its Nd isotopic composition ($\epsilon_{\text{Nd}} = -8.9$), whereas the average basaltic crust has ϵ_{Hf} and ϵ_{Nd} identical to present-day MORB (+13.9 and +8.8). (2) The average $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the sediments are low (0.0142 and 0.1296; see Table 1), which leads to a present-day position of old sediment that is displaced to the left of the mantle array (Fig. 2a). (3) The low $^{176}\text{Lu}/^{177}\text{Hf}$ ratio (0.0270) of basalt, associated with its high $^{147}\text{Sm}/^{144}\text{Nd}$ (0.1986), leads to low ϵ_{Hf} and high ϵ_{Nd} for oceanic crust formed during the Archaean era, which is plotted in the bottom right quadrant of Fig. 2a. Mixing arrays between sediment and basaltic crust with the same age, calculated using the concentrations and isotopic compositions in Table 1, are also shown in Fig. 2a.

Finally, we assume that the recycled oceanic crust and sediment remain together as they are stirred in the convection cells and are not totally mixed into the surrounding mantle.

We carried out a Monte Carlo simulation to generate 50,000 mixtures of oceanic basalt and associated sediments created at different times. The proportion of sediment in the sediment–basalt mixture is constrained to be between 0 and 20%, in accord with the relative thicknesses of sediment and basaltic crust. These calculated mixtures, shown by density fields in Fig. 3a, define a band with a positive slope similar to that of the 'OIB array'. However, petrological constraints such as high Ni contents indicate that oceanic basalts are not created by melting of basalt and

Table 1 Nd, Sm, Lu and Hf concentrations and ϵ_{Hf} and ϵ_{Nd} values for oceanic sediments and basalts as well as for other reference materials or reservoirs.

Sample	Subducted oceanic sediments*	Bulk silicate Earth	Average MORB†	Upper continental crust‡	Average sandstone**
Nd (p.p.m.)	27.00		10.43	26	
Sm (p.p.m.)	5.78		3.42	4.5	
$^{147}\text{Sm}/^{144}\text{Nd}$	0.1296	0.1967†	0.1986	0.1047	0.1047
$^{143}\text{Nd}/^{144}\text{Nd}$	0.51218	0.512638†	0.513088		
ϵ_{Nd}	-8.9	0	8.8		-12
Hf (p.p.m.)	4.06		2.480	5.8	10
Lu (p.p.m.)	0.413		0.480	0.32	0.1
$^{176}\text{Lu}/^{177}\text{Hf}$	0.0142	0.0332‡	0.0270	0.0077	0.0014
$^{176}\text{Hf}/^{177}\text{Hf}$	0.282829	0.282772‡	0.283164		
ϵ_{Hf}	+2 (± 3)	0	13.9		-43
Nd/Hf	6.65	4.44§	4.21	4.48	

*Values published by Plank and Langmuir⁶ for GLOSS except for the Hf isotopes from this study.

†Values from Jacobsen and Wasserburg³⁰.

‡Values from Blichert-Toft and Albarède³.

§Calculated using the primitive mantle Nd and Hf concentrations of Hofmann³¹.

¶Values from Su¹⁷ except for Hf isotopes from this work (average of all published values for MORB).

‡Values from McLennan³².

**Values calculated using the following parameters: composition given by Taylor and McLennan³³, ϵ_{Hf} is the average value suggested by Gallet *et al.*²⁰ for continental crust and ϵ_{Nd} is calculated using a 2 Gyr model age for the continental crust and the Hf and Lu contents listed in the table.

sediments alone: peridotite must also be present in the source. We therefore generated mixtures of subducted material and depleted mantle, as shown by density fields in Fig. 3b,c. For a proportion of recycled material between 20 and 30%, the field of calculated values (Fig. 3c) overlaps remarkably well with the compositions of OIB (Fig. 3d). In particular, the position of the OIB array above the BSE position is quite well reproduced. If the proportion of recycled material is maintained between 0 and 15%, a field of

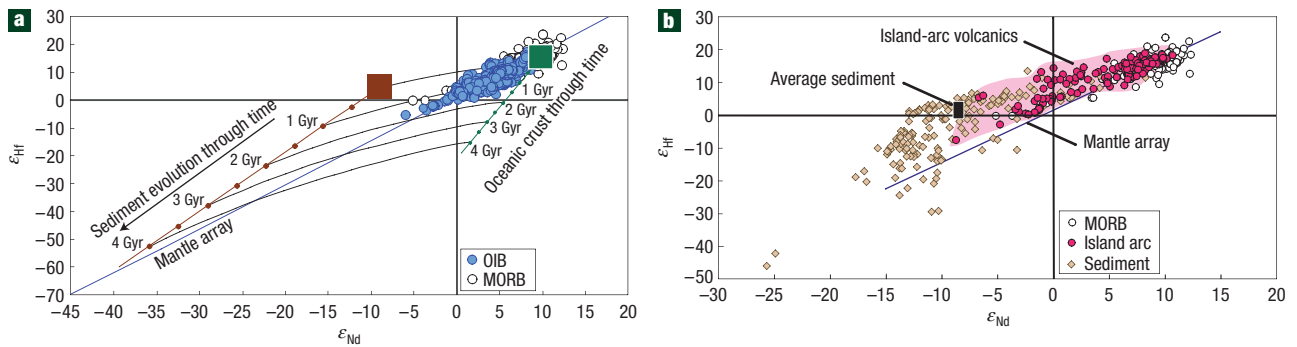


Figure 2 ϵ_{Hf} versus ϵ_{Nd} diagrams comparing modelled and measured data. **a**, MORB and OIB data. The present-day average compositions of oceanic basalt and sediments are shown with green and brown squares. The compositions of similar material formed at various times during Earth's history are shown as evolution paths (green and brown lines); mixing arrays between sediments and basalt are shown as curves. Data sources as in Fig. 1. **b**, Island-arc volcanics (from the GEOROC²⁸ database—pink circles) versus MORB and oceanic sediments. The black rectangle shows our preferred average recycled sediment value: $\epsilon_{\text{Nd}} = -8.9$ from GLOSS, $\epsilon_{\text{Hf}} = +2 \pm 3$ chosen to be consistent with (1) the extension of the island-arc field, (2) the Leg 185 average sediment composition and (3) the average composition of all analysed sediments.

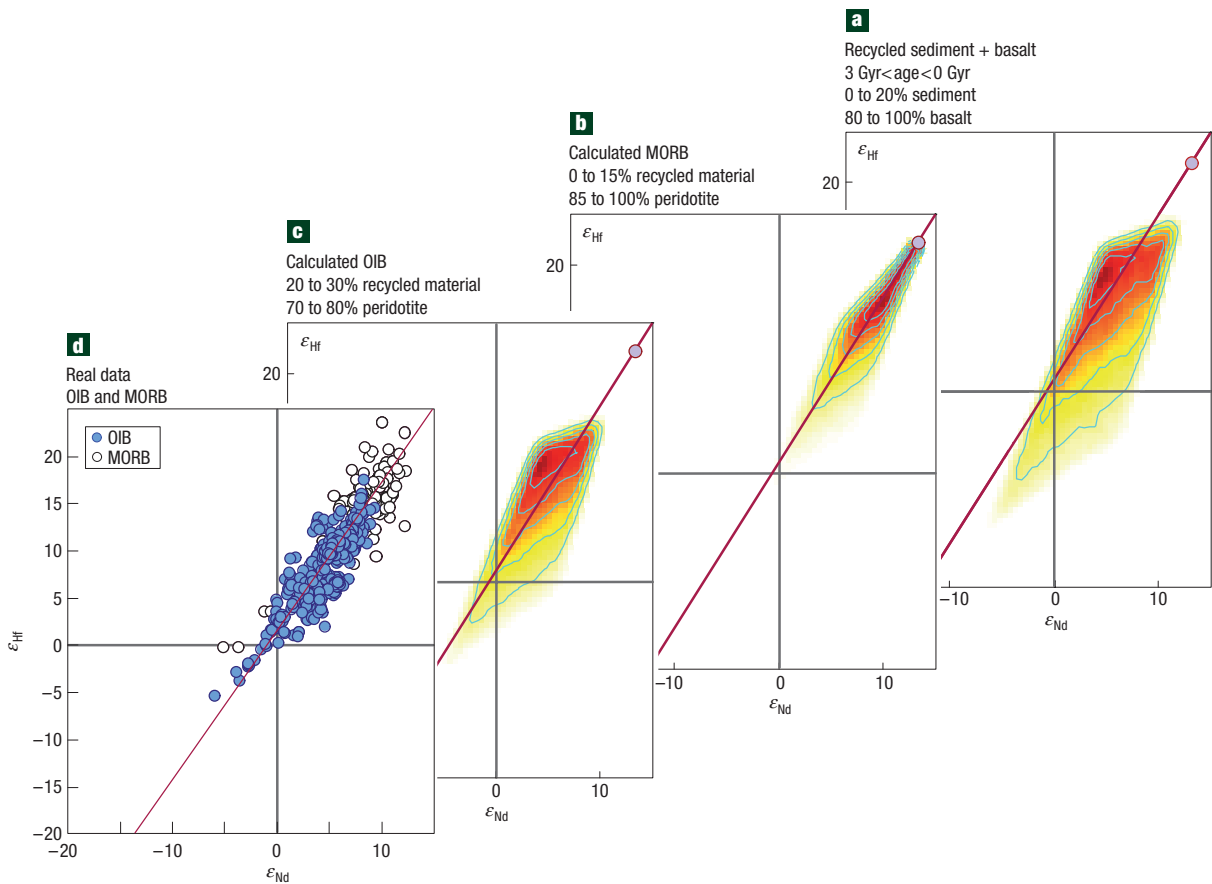


Figure 3 Comparison between our Monte Carlo simulations and measured values for OIB and MORB. **a**, A density plot of 50,000 runs simulating the composition of the recycled material (old oceanic crust and old sediment). Details of the calculation are given in the Supplementary Information. **b,c**, Density plots for simulated MORB and OIB using the procedure described in the Supplementary Information. The grey circles in **a,b** and **c** represent the composition of the depleted mantle. **d**, The same OIB and MORB data set as in Fig. 1.

calculated mixtures corresponding to MORB can also be generated (compare Fig. 3b and d). The amount of recycled sediment in the mixtures is always very low: 0–6% for the oceanic-island basalts and 0–2.2% for MORB. We recognize that 6% sediment

in the source of OIB might be inconsistent with the Sr and Pb isotopic data and trace-element ratios such as Ce/Pb or Nb/U. However, our modelling ignores processes active in the subduction zones where elements such as Rb, Sr, U and Pb are preferentially

removed from the subducted material³, in contrast with Hf and the rare-earth elements which preferentially remain in the slab. The effect of a high sediment contribution to the OIB source is therefore minimized for all elements removed in subduction zones from the subducting material. Similar modelling using other isotopic systems (for example, Pb and Sr) would help constrain the impact of a high sediment contribution, but such modelling is beyond the scope of this manuscript.

The mantle array is generated by a model incorporating mixtures of recycled ocean crust and oceanic sediments: recycling of sediments alone does not work. Patchett *et al.*¹⁴ and Salters and White¹⁵ already noted that a mixture of deep-sea sediments and mantle peridotite cannot generate the OIB array because the elevated Nd/Hf ratio of the sediment produces an inappropriate mixing array in ε_{Hf} versus ε_{Nd} space. Incorporation of basaltic crust alone, which has trace element and isotopic characteristics similar to MORB^{16,17} produces an array passing well below the BSE¹⁵. The low ε_{Hf} and high ε_{Nd} of old oceanic crust in Fig. 2a results from its low Lu/Hf and high Sm/Nd ratios, which generate such isotopic compositions as time passes. The Nd–Hf isotopic compositions of sediments in Fig. 1 reflect the dominant influence of authigenic processes and a minimal contribution from coarse-grained terrigenous material. This might be explained by deposition of most sediments far from continents.

The average composition of oceanic sediments has an elevated ε_{Hf} compared with its ε_{Nd} , a feature not seen in granitoid rocks from the continental crust¹⁸. It follows that processes acting during the formation of oceanic sediments have influenced their Hf isotopic composition⁷. This leads to the possibility that a reservoir with low ε_{Hf} at a given ε_{Nd} value is produced by sedimentary processes and isolated at the Earth's surface.

Given that the Nd/Hf ratios of deep-sea sediments and upper continental crust differ significantly (Table 1), a complementary reservoir with low Nd/Hf must have been generated by sedimentary processes. Patchett *et al.*¹⁴ noted that zircon-rich sands, which are sequestered on the edges of continents, have high Hf contents and low Lu/Hf ratios. Here, we propose that placers and beach sands rich in heavy minerals, parts of which are mined for Zr and related elements, could represent the sedimentary endmember with low Nd/Hf. We are currently analysing Nd and Hf isotopes in selected samples that might provide the key to unravelling terrestrial Nd–Hf isotopic systematics. Sandstones are common on continental platforms and represent 1% of the continental crust¹⁹. Table 1 shows a preliminary evaluation of their elemental and average present-day isotopic composition. The calculated ε_{Nd} and ε_{Hf} values lie significantly below the mantle array (Fig. 1) and clearly complement the high values found in the oceanic sediments. Sedimentary processes fractionate Lu/Hf and Sm/Nd ratios and Hf and Nd isotopic ratios more efficiently than magmatic processes, leading to large isotopic diversity with time. Vervoort *et al.*¹⁸ already noticed that associated sandstones and shales share similar ε_{Nd} but ε_{Hf} is systematically lower in the sandstones. Given that the 'crustal array' of Vervoort *et al.*¹⁸ is mainly based on fine-grained sediments with few coarse-grained sediments and few granitoids, it might not be representative of the continental crust as a whole. The continental crust might contain a higher proportion of low- ε_{Hf} coarse sediments than previously thought and the 'crustal array' could lie on or just below the 'mantle array' in $\varepsilon_{\text{Hf}} - \varepsilon_{\text{Nd}}$ space. If the currently accepted BSE value⁵ is correct, zircon-rich detrital material could represent the low- ε_{Hf} 'hidden' reservoir; if the estimate of Bouvier *et al.*⁶ is correct, this material merely represents the low- ε_{Hf} component of the continental crust.

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Author contributions

C.C. conceived the model and wrote the paper. E.L. made the numerical simulation. M.C. and J.-C.M. contributed to the data compilation and N.T.A. suggested several important ideas. All authors discussed the results and commented on the manuscript.

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