Barium isotope evidence for pervasive sediment recycling in the upper mantle

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The upper mantle, as sampled by mid-ocean ridge basalts (MORBs), exhibits significant chemical variability unrelated to mechanisms of melt extraction at ridges. We show that barium isotope variations in global MORBs vary systematically with radiogenic isotope and trace element ratios, which reflects mixing between depleted and enriched MORB melts. In addition, modern sediments and enriched MORBs share similar Ba isotope signatures. Using modeling, we show that addition of ~0.1% by weight of sediment components into the depleted mantle in subduction zones must impart a sedimentary Ba signature to the overlying mantle and induce low-degree melting that produces the enriched MORB reservoir. Subsequently, these enriched domains convect toward mid-ocean ridges and produce radiogenic isotope variation typical of enriched MORBs. This mechanism can explain the chemical and isotopic features of enriched MORBs and provide strong evidence for pervasive sediment recycling in the upper mantle.

INTRODUCTION

The chemistry of oceanic island basalts (OIBs) is generally thought to reflect the influence of recycled material that was introduced into the mantle during subduction of crustal lithologies and brought back to the surface via plumes (1, 2). Although the chemistry of mid-ocean ridge basalt (MORB) is relatively homogeneous compared to that of OIBs, the source region of MORB (the depleted MORB mantle or DMM) also displays substantial chemical and isotopic variation (2). For example, enriched MORB (E-MORB) has high concentrations of incompatible elements, fractionated trace element ratios (for example, high La/Sm and Ba/La), and more radiogenic 87Sr/86Sr isotope ratios compared to depleted MORB (D-MORB) (3). Conversely, major element differences between MORB types are subtle and likely relate to higher water and alkali content in E-MORB, rather than mechanisms of melt extraction at the ridge (4–7). Although evidence from He isotopes has suggested that some of this variation is likely related to the introduction of primordial lower mantle material into the upper mantle (8–11), differences between E-MORB and D-MORB cannot be explained by the influence of deep mantle reservoirs (3, 12). Therefore, a substantial portion of the DMM heterogeneity is probably related either to (i) internal redistribution of different components, for example, through delamination of lithospheric mantle (13), fluid metasomatism, and melt-rock reactions (14, 15) or to (ii) direct exchange between DMM and surface reservoirs such as addition of sediments and altered oceanic crust (AOC) to the upper mantle in subduction zones (5, 16). From a global perspective, it is difficult to distinguish between these different hypotheses because most of these models can theoretically account for the trace element and radiogenic isotope differences observed in the spectrum between E-MORB and D-MORB. Many types of geochemical measurements, such as trace element and radiogenic isotope ratios, have struggled to discriminate between these models. A potential means to this end is by using novel stable isotope tools because processes that cause significant stable isotope fractionation are primarily found in low-temperature environments (for example, sediment precipitation and hydrothermal alteration). Therefore, stable isotopes are potentially more direct tracers of recycling processes than trace elements and radiogenic isotopes.

Here, we use Ba (barium) stable isotope measurements to investigate the origin of DMM heterogeneity. Barium is a highly incompatible element that is enriched up to 100 times more in E-MORB compared to normal MORB (N-MORB) (3, 17). Barium is also fluid mobile (18) and is one of the most commonly used elements to track slab-derived fluids in subduction zones (19). In addition, Ba can be highly enriched in sediments (20), up to 10,000 times compared to DMM (Fig. 1). Thus, the strong Ba enrichments found in E-MORB could be explained by low-degree melting occurring within the mantle, by fluid fluxing in subduction zones, and/or via introduction into the mantle of Ba-rich crustal components such as sediments. Here, we use Ba isotopes to investigate the origin of DMM heterogeneity. The new data provide the first strong evidence for pervasive global sediment recycling in the MORB source away from plume influence, and we show that the subducted sediment-rich material plays a key role in the formation of the E-MORB reservoir in subduction zones.

Barium isotope fractionation and cycling in surface environments

Barium has seven stable isotopes (130, 132, 134, 135, 136, 137, and 138). Studies of high-precision stable Ba isotopes were only recently developed (21) with almost all subsequent studies focusing on the Ba isotope systematics of low-temperature processes and environments such as seawater (22–24), experimental barite precipitation (21), isotope fractionation during plant “biolifting” (25), and during diffusive transport (26). Barium isotope compositions have been reported using the conventional δ notation, albeit referenced to different standards and using different sets of isotopes, most commonly as 138Ba/134Ba or 137Ba/134Ba. In principle, all these notations reflect the same intrinsic isotope variation and can easily be recalculated to the same notation. However, as in our previous studies, we report here our values with the 138Ba/134Ba ratio relative to the National Institute of Standards and Technology (NIST) 3104a standard:

$$\delta^{138/134}_{\text{Ba}_{\text{NIST}}} = 1000 \times (\frac{138\text{Ba}_{\text{sample}}}{138\text{Ba}_{\text{sample}}})^{134\text{Ba}_{\text{sample}}} - 1)$$
the observed Ba isotope variation of MORBs could be caused by a number of different processes, including contamination by deep
magma ascent, high-temperature stable isotope fractionation during melting and/or fractional crystallization, and last, crustal recycling processes. In the following, we argue that only the latter process is likely to explain our data set.

The Ba isotope variation of MORB observed here cannot reflect influence from deep mantle reservoirs with or without ancient recycled material. Anomalous He isotope compositions of mantle-derived melts (both higher and lower than MORB) are often interpreted to reflect influence from deep mantle reservoirs that may contain ancient recycled crustal materials. However, almost all samples investigated here record N-MORB He isotope ratios (table S1), suggesting that deep mantle reservoirs did not play a significant role in their source regions. In addition, the two samples with the lowest and highest $^3$He/$^4$He (5.70 and 9.04 Ra, respectively; table S1) do not have anomalous Ba isotope compositions compared to the remainder of the samples, which further supports the absence of anomalous Ba isotope compositions from deep mantle reservoirs in the data set.

We also rule out assimilation as a likely cause for the observed Ba isotope variation. Because of the relatively high MgO concentrations for the studied samples (most samples exhibit MgO > 7.5%; table S3), assimilation of hydrothermal AOC is expected to be limited. Nonetheless, given that Ba is a highly incompatible element, it is possible that MORB melts with low initial Ba concentrations are particularly sensitive to assimilation. This process would be consistent with the observation that all the heaviest Ba isotope compositions are found for samples with Barium concentrations that <25 μg/g. As a consequence, the assimilant (presumably AOC) should be characterized by heavy Ba isotope compositions, which is consistent with the data for AOC presented here (table S4) and elsewhere (34). However, AOC is also characterized by more radiogenic Sr isotope compositions relative to unaltered MORB, and thus, the highest $\delta^{138/134}\text{Ba}_{\text{NIST}}$ values should also be accompanied by more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (fig. S1) because Sr/Ba of AOC and MORB are similar (30, 31). There is no association of heavy Ba isotopes with more radiogenic Sr isotopes, and heavy Ba isotope compositions are almost exclusively found in samples with unradiogenic $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7024$ (Fig. 3D), which is opposite from the trend expected from assimilation processes.

Stable isotope fractionation of Ba during melting of the DMM is also not a viable explanation for the isotopic variability of global MORBs, given that Ba is a highly incompatible trace element with a bulk partition coefficient during mantle melting of $D \approx 0.00012$ (17). Therefore, >99% of Ba will be in the melt after ~1% partial melting. Given that the entire range of MORBs represents degrees of melting between 6 and 20% (40, 41), it follows that the net Ba isotope fractionation between the starting mantle composition and the resulting melt will be negligible. By the same reasoning, metasomatism and melt-rock reactions would similarly be incapable of producing the observed Ba isotope variations (see the Supplementary Materials).

Given the above arguments, the Ba isotope data presented here for MORBs can only be explained by addition of an isotopically distinct Ba component to the upper mantle that generated an EMM reservoir. The range of Ba isotope values observed for MORB represents mixtures between melts extracted from the enriched MORB mantle (EMM), characterized by $\delta^{138/134}\text{Ba} \approx 0.03\%$ and generally high Ba concentrations, and DMM, characterized by $\delta^{138/134}\text{Ba} \approx 0.14\%$ and generally low Ba concentrations. Mixing calculations between average D-MORB and E-MORB melt compositions show that the data are consistent with these mixing relationships (Fig. 3), supporting our contention that Ba isotope variation in MORBs derives from exchange between DMM and surface reservoirs.

Mixing between DMM and a light Ba source can reconcile the overall patterns between several trace elements (for example, Rb/Sr and La/Sm), radiogenic (for example, Sr and Nd), and Ba stable isotope data, albeit with some scatter outside the narrowly defined mixing lines that are calculated, assuming complete homogeneity of the EMM and DMM reservoirs. In detail, this assumption is not justified as melt depletion, and mantle enrichment processes would without doubt generate some heterogeneity in both trace element concentrations and radiogenic isotope ratios. Hence, it is not surprising to find some outliers
from the idealized mixing lines presented in Figs. 3 and 4. The scatter outside the E-MORB to D-MORB mixing lines is particularly strong for trace element ratios that show relatively little overall variation in global MORB such as Ba/Th and Ce/Pb (Fig. 4), but this is expected given the small differences between EMM and DMM for these trace element ratios. However, considering that different regions of DMM and EMM were generated by a distinct set of processes (for example, melt diple- tion and mantle refertilization events), it is remarkable that MORB samples from all regions around the globe broadly fit a single mixing relationship between Ba isotopes and other indicators of mantle enrichment. This observation strongly implies that the material with relatively uniform Ba isotope compositions was responsible for producing the EMM reservoirs.

To identify the source of isotopically light Ba contaminating the mantle, we surveyed modern sediments and AOC for their Ba isotope compositions. We examined 31 modern core top sediments from different locations around the globe, with a total of 11: altered basalts from ODP Hole 504B and DSDP Hole 442B, as well as the supercomposite (42) from DSDP Hole 417/418 (table S4). We find that the average sediment Ba isotope composition is $\delta^{138/134}\text{Ba} = 0.01\%$ (±0.04 SD), within error of the E-MORB value of $\delta^{138/134}\text{Ba} \approx 0.03\%$. This value is identical to that recently found for an extensive survey of South Atlantic bulk sediments (28). The altered basalt samples display a large range of values from $\delta^{138/134}\text{Ba} \approx -0.09$ to $+0.33\%$. Because of the narrow range and strong similarity between sedimentary and E-MORB Ba isotopes, it is reasonable to conclude that the Ba isotope variations observed in global MORB are most likely due to addition of sediment material to the upper mantle. In contrast, the large Ba isotope variation observed for AOC relative to EMM (Fig. 1) implies that AOC did not contribute significantly to the Ba budget of EMM. This conclusion is also supported by quantitative mixing calculations between DMM and AOC (fig. S1) that predict a much wider range in Ba isotopes for MORB than observed. However, even if average AOC uniformly yielded a value of $\delta^{138/134}\text{Ba} \approx 0.05$, similar to the DSDP 417/418 supercomposite (table S4), then unradiogenic $\delta^{87/86}\text{Sr}/\delta^{138/134}\text{Ba}$ and light Ba isotopic compositions would not be produced with DMM-AOC mixing (fig. S1) because of the radiogenic $\delta^{87/86}\text{Sr}/\delta^{138/134}\text{Ba}$ found in AOC due to hydrothermal alteration (30, 31). Thus, AOC addition would not be able to simultaneously account for all the Sr and Ba isotope compositions. In addition, Nd isotopes would likely be unaffected by AOC mixing because hydrothermal alteration does not modify Nd isotopes. Hence, sufficient AOC mixing could produce Sr and Ba isotope values broadly similar to the EMM end-member, whereas Nd isotopes could not be. The Sr-Ba mixing lines (fig. S1) would remain almost identical if, instead of bulk AOC addition, hydrous AOC melts were considered because Ba/Sr is not significantly fractionated during partial melting of AOC at high pressures and temperatures (18). It should be noted that the lack of influence on Ba isotopes from AOC does not preclude the presence of recycled oceanic crust in the source of MORB (7). However, since sediments contain one to two orders of magnitude more Ba than oceanic crust (20), our Ba isotope composition for MORB is overwhelmingly controlled by sediment addition rather than AOC.

Mechanisms of sediment addition to the upper mantle
The fact that addition of sediment-rich material appears to be global in nature indicates that subduction zones are the most likely setting where transfer of sedimentary Ba occurs. By combining Ba isotope signatures with radiogenic isotopes and trace element systematics of the MORBs (see the Supplementary Materials for details), we can further constrain the sequence of events leading to EMM formation.

To do this, we calculate the concentrations of the trace elements Ba, Rb, Sr, La, Ce, Nd, Sm, Pb, and Th for different sediment components that might be released from a subducted slab into the mantle wedge (Fig. 4). We construct mixing relationships for terrigenous sediments, pelagic clays, and global subducted sediment (GLOSS) (20). Fluid compositions were only calculated for Ba and Th, as these two elements...
display highly disparate affinities for aqueous subduction zone fluids (18). Sediment melts were calculated from 10% batch melting of GLOSS using the average partition coefficients of two experiments at 900°C and 3.5 GPa, where a complete data set of all elements considered here was presented (43). Other studies have found similar partition coefficients for sediment melting (44, 45), with the notable exception of Pb, which likely produced somewhat erroneous results due to loss to the capsule during the experiments (43). Given that Pb is expected to behave similarly to Sr (43), which has a melt-solid $K_d \sim 7.5$, we here infer a melt-solid $K_d \sim 5$ for Pb during sediment melting (table S5). Residues of sediment melting used the same partition coefficients as the sediment melting calculations, but it was assumed that 50% of the mass of the original sediment had been removed during arc magma generation before adding sediment residue to the depleted mantle.

There is currently significant debate regarding the nature of the subducted slab at depth in subduction zones. Field evidence, modeling, and geochemical data point toward mélange material playing a key role in arc lava genesis (46–48), which suggests that pure sediment melting as modeled here possibly does not take place in subduction zones. Recent experiments of mélange melting (49) have shown that trace element fractionation similar to that of pure sediment melting is possible under a range of conditions. However, further work is needed before quantitative models of mélange melting can be applied to the formation mechanisms of the E-MORB reservoir.

Our modeling shows, in agreement with previous studies (5), that the mechanism of sediment Ba addition to the upper mantle was not via fluids because high Ba/Th ratios in the E-MORB samples are not observed (Fig. 4D, blue line), which would be expected since aqueous
subduction zone fluids should be characterized by extremely high Ba/Th (18). Furthermore, addition of 0.08% by weight of partial sediment melts to the DMM would change the Ba isotope composition to the EMM value (Fig. 4, purple lines). However, this process would lead to more radiogenic Sr isotopes than EMM, whereas it would have no significant impact on the Nd isotope and La/Sm ratios (Fig. 4). Likewise, addition of 0.1 to 0.3% by weight of bulk terrigenous and GLOSS (20) would produce Ba and Sr isotope values similar to EMM but would again not significantly change trace element ratios or Nd isotopes (Fig. 4, green lines). Mixing 0.4% bulk pelagic clay (20) or 0.8% slab residues left after extraction of arc magmas with DMM produces Ba and Sr isotope values similar to EMM but would again not significantly change trace element ratios or Nd isotopes (Fig. 4). In particular, neither Rb/Sr ratios (Fig. 4) nor Sm/Nd ratios (not shown) would change sufficiently for Nd and Sr isotope ratios of the DMM to evolve with time to the values observed in E-MORB. As suggested by a previous work (5), trace element ratios involving Pb (for example, Ce/Pb) are affected to some degree by sediment mixing processes. However, the amounts of sediment needed to shift Ba isotopes will not change these trace element ratios beyond the range of values observed for D-MORB and E-MORB in general (Fig. 4).

To explain the Ba, Sr, and Nd isotopic and trace element systematics of MORBs, a process is required where trace element ratios are strongly fractionated at the same time that sedimentary Ba is added into the mantle. We argue that the introduction of sediment-rich material, likely in the form of melts from subducted slab residues (Fig. 5), induces low-degree (<1%) melting of DMM in subduction zones. Most likely, the incipient melting would be initiated because the sedimentary component contains more water than the depleted mantle. However, the small volume of the enriched low-degree melts would prohibit them from percolating large distances in the upper mantle, and they would freeze back into the mantle above the slab. This process would generate a new enriched reservoir, equivalent to an EMM, characterized by highly fractionated La/Sm, Rb/Sr, and Sm/Nd, as well as the Ba isotope composition of sediments. Subsequently, these domains of fractionated trace elements and light Ba isotopes would require ~100 to 500 million years (Ma) to evolve to Sr and Nd isotope compositions similar to those found in E-MORB (5).

**Pervasive presence of sediment Ba in the upper mantle**

The chemical budget of the upper mantle that can be traced to sediment-derived material differs for each element because the relative concentrations of mantle and sediment vary by many orders of magnitude. Since the budget of Ba is so strongly controlled by sedimentary inputs, however, it is a unique tool to trace recycling. The most comprehensive study of global MORBs (3) has shown that the average composition of MORBs is

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**Fig. 5. Simplified geodynamic schematic of EMM generation.** (A) During subduction, a hydrous sediment-rich component is added at depth to the DMM. Addition of this component triggers incipient partial melting of the DMM (arrow from green to red square). These low-degree partial melts that are contaminated by sedimentary Ba freeze back into the mantle and create the EMM reservoir. (B) Convection of the upper mantle for 100 to 500 Ma causes radiogenic ingrowth (downward arrow) in the EMM reservoir that diverges from the DMM. (C) Melting at ridges generates melts from EMM and DMM that mix in variable proportions to produce hyperbolic mixing relationships between Ba, Nd isotopes, and La/Sm element ratios.
enriched compared to D-MORB, with $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.70282$ and $^{143}\text{Nd}/^{144}\text{Nd} \sim 0.51307$. Given the correlations between Ba, Nd, and Sr isotopes (Fig. 3), we can infer that the average Ba isotopic composition of global MORB is likely $^{138}\text{Ba}/^{136}\text{Ba} \sim 0.04$ to 0.069, which, given D-MORB and sedimentary Ba isotopic compositions of $^{138}\text{Ba}/^{136}\text{Ba} \sim 0.14$ and 0.01, respectively, implies that ~60 to 80% of all Ba in the upper mantle originates from sediments. On the other hand, the fraction of the pure E-MORB component in average MORB would only be 3 to 20% because of the much higher Ba concentrations in E-MORB. In the upper mantle, the proportion of elements that originate from sedimentary material will vary for different elements, but because Ba is so strongly controlled by sedimentary material, that makes it a unique tool to trace pervasive sediment recycling. Thus, using Ba isotope signatures of MORBs away from plume influence, we demonstrate that subducted sediments play a key role in the formation of E-MORB reservoir and that most melts from the upper mantle contain minor amounts (<0.1%) of recycled sediment.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/7/eaa8675/DC1

Table S1. Isotope data for MORB glass samples.
Table S2. Trace element data for MORB glasses in microgram per gram.
Table S3. Major element compositions of MORB glasses.
Table S4. Barium isotopes plotted against Sr isotopes for MORB samples.
Table S5. Partition coefficients used to calculate sediment melting.
Table S6. Barium isotopes plotted against Sr isotopes for MORB samples.

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