

Re-visiting barium isotope compositions of mid-ocean ridge basalts and the implications

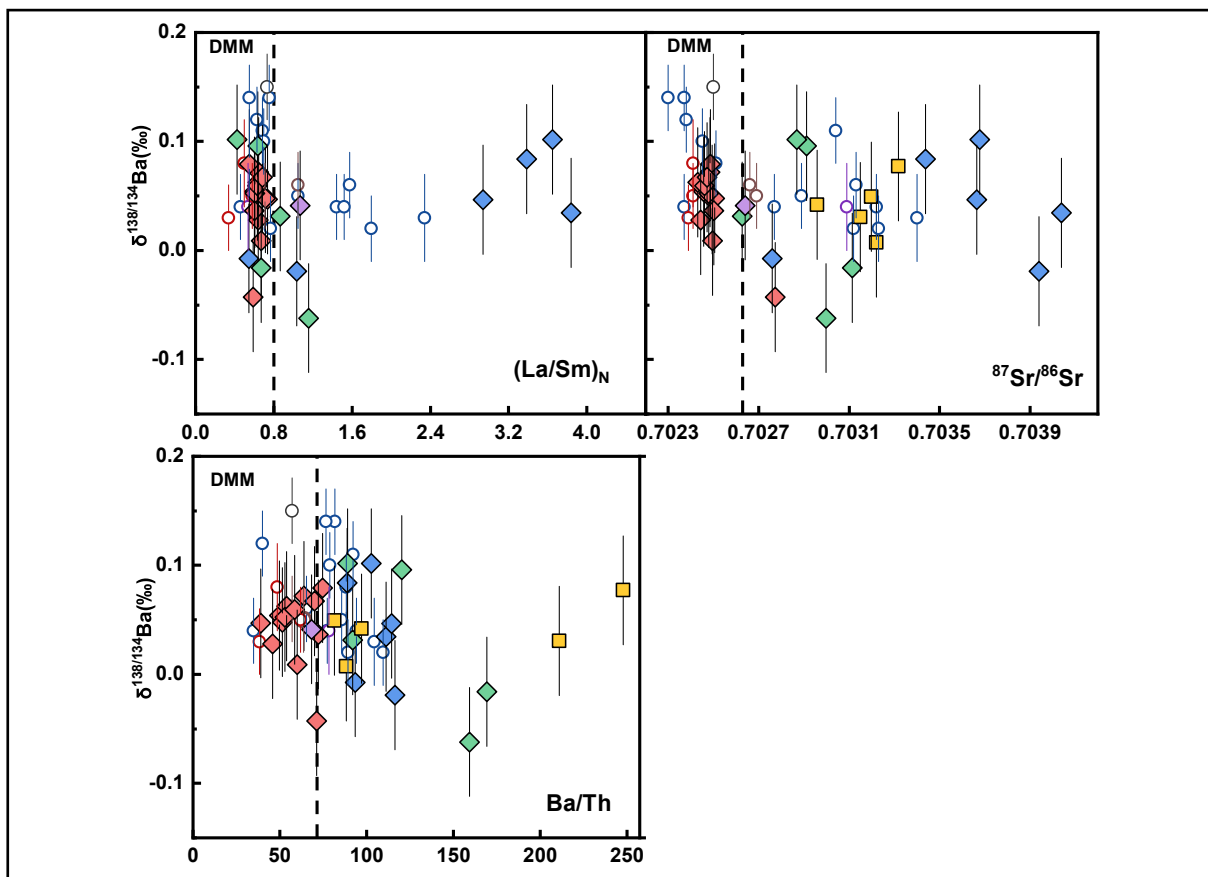
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Graphical abstract




We estimate the average $\delta^{138/134}\text{Ba}$ of the depleted MORB mantle (DMM) as $+0.05\text{‰}\pm 0.05\text{‰}$ (2SD, $n=16$) based on D-MORBs.

Public summary


- The $\delta^{138/134}\text{Ba}$ of the global MORBs range from -0.06‰ to $+0.15\text{‰}$.
- This study obtains the average $\delta^{138/134}\text{Ba}$ of the DMM as $+0.05\text{‰}\pm 0.05\text{‰}$ (2SD, $n=16$), which is much lower than the previous estimation.
- Ba isotope compositions of the E-MORBs could be sourced by the incorporation of subducted AOC and/or sediments.

Re-visiting barium isotope compositions of mid-ocean ridge basalts and the implications

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Supporting Information

Abstract: Barium (Ba) isotopes can be used as potential tracers for crustal material recycling in the mantle. Determination of the Ba isotope composition of the depleted mantle is essential for such applications. However, Ba isotope data for mantle-derived basalts are still rare. In this study, we reported high-precision Ba isotope data of 30 oceanic basalts including 25 mid-ocean ridge basalts (MORBs) from geochemically and geologically diverse mid-ocean ridge segments and five back-arc basin basalts. The $\delta^{138/134}\text{Ba}$ values of these samples varied from -0.06% to $+0.11\%$, with no systematic cross-region variation. Together with published data, we constrained the average $\delta^{138/134}\text{Ba}$ of global MORBs to $+0.05\% \pm 0.09\%$ (2 standard deviation, $n = 51$). Based on depleted MORBs that have $(\text{La}/\text{Sm})_N < 0.8$, low $^{87}\text{Sr}/^{86}\text{Sr} (< 0.70263)$, and low $\text{Ba}/\text{Th} < 71.3$, we estimated the average $\delta^{138/134}\text{Ba}$ of the depleted MORB mantle (DMM) as $+0.05\% \pm 0.05\%$ (2SD, $n = 16$) that is significantly lower than the DMM ($\approx 0.14\%$) reported previously. If a new estimation of the DMM is applied, it is unreasonable to infer that the Ba isotope signatures of the “enriched-type” MORBs (E-MORBs) could be attributed to pervasive sediment recycling in the upper mantle. We, therefore, conclude that the Ba isotope compositions of the E-MORBs could be sourced from the incorporation of subducted altered oceanic crust and/or sediments depending on the Ba isotope composition and other geochemical information of the local mantle.

Keywords: barium isotopes; mid-ocean ridge basalt; upper depleted mantle; subducted crustal materials

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1 Introduction

Barium (Ba) is a highly incompatible element during mantle melting, thus, it is much more enriched in the upper continental crust^[1] and marine sediments^[2] than in the mantle^[3]. Ba is also fluid mobile during slab subduction^[4]. Ba has seven stable isotopes: ^{130}Ba (0.11%), ^{132}Ba (0.10%), ^{134}Ba (2.42%), ^{135}Ba (6.59%), ^{136}Ba (7.85%), ^{137}Ba (11.23%), and ^{138}Ba (71.70%)^[5]. Previous studies have found that Ba isotope compositions ($\delta^{138/134}\text{Ba} = [(^{138/134}\text{Ba}_{\text{sample}} / ^{138/134}\text{Ba}_{\text{SRM3104a}}) - 1] \times 1000\%$) of subducted crustal materials such as marine sediment, altered oceanic crust (AOC), and continental rocks^[6–9] are distinct from the mantle ($0.05\% \pm 0.06\%$)^[10]. For example, diamictites have a substantial variation in $\delta^{138/134}\text{Ba}$ from -0.23% to $+0.47\%$ ^[6]. Therefore, Ba isotopes have recently been suggested as sensitive tracers for crustal material recycling in mantle-derived igneous rocks^[7, 8, 11].

Magma produced annually in mid-ocean ridge settings accounts for 75% of global magmatic output^[12]. Mid-ocean ridge basalts (MORBs) represent mafic melts derived from a simple melting history of the depleted upper mantle, providing a critical way to constrain the composition of the upper mantle^[13]. Substantial chemical heterogeneity has been observed in global MORBs^[13–15]. The ratios of highly incompatible trace elements (such as La/Sm) in MORB vary by more than an order of magnitude^[13]. A previous study has proven that Ba isotope variation in MORBs is not caused by mantle melting and/or

fractional crystallization^[7]. Thus, the $\delta^{138/134}\text{Ba}$ values of the MORBs should reflect their mantle source signatures. It is thus reasonable to use Ba isotope data to identify the contribution of recycled materials to the source of the MORB if the enriched composition in the mantle is related to the addition of materials from surface reservoirs.

Better knowledge of the Ba isotope composition of the upper mantle is essential for the application of Ba isotopes in tracing mantle heterogeneity. However, estimates of $\delta^{138/134}\text{Ba}$ in the mantle are rare. Nielsen et al.^[7] reported $\delta^{138/134}\text{Ba}$ values of MORB glasses from the Mid-Atlantic Ridge (MAR), East Pacific Rise (EPR), Juan de Fuca Ridge (JdF), Central Indian Ridge, and Southwest Indian Ridge ranging from $+0.02\%$ to $+0.15\%$. According to the composition of their most depleted MORBs, they defined the average $\delta^{138/134}\text{Ba}$ of the depleted MORB mantle (DMM) as $\sim +0.14\%$. Based on the measurement of mantle-derived carbonatites from Canada, East Africa, Germany and Greenland, Li et al.^[10] found that the $\delta^{138/134}\text{Ba}$ of most carbonatites vary from -0.04% to $+0.12\%$, thus suggesting that the average $\delta^{138/134}\text{Ba}$ of their mantle source is $+0.05\% \pm 0.06\%$ (2SD). The average $\delta^{138/134}\text{Ba}$ of the MORBs ($+0.07\% \pm 0.08\%$, 2SD) reported by Nielsen et al.^[7] is generally indistinguishable from that of the carbonatites reported by Li et al.^[10]. However, the $\delta^{138/134}\text{Ba}$ value of the DMM suggested by Nielsen et al.^[7] was much

higher. This contradiction hinders the application of Ba isotopes in mantle geochemistry.

In this study, we report new high-precision Ba isotope data for several well-known regions of MORB and back-arc basin basalt (BABB) samples and incorporate these data into a critically compiled database that includes data from a previous study^[7]. With these data, we attempted to re-estimate the average Ba isotope composition of the DMM and further constrain the enriched components in the mantle source of the “enriched-type” MORB (E-MORBs) with Ba isotopes.

2 Sample description

We analyzed 25 MORB samples from different mid-ocean ridge segments. They were from the EPR at 9–10°N, the MAR at 35°N, the Gakkel Ridge (GR) at 82–87°N, and the Southeast Indian Ridge at 50°S (SEIR). These samples were collected from ridge segments with spreading rates varying from lower than 1.5 cm/year to approximately 11 cm/year^[12]. In addition, five BABB samples from the Lau Basin at the Australian-Pacific plate boundary were also measured, two of which were andesitic lavas with low MgO content. All samples chosen were fresh lavas^[16–18].

According to the relative depletions and enrichments of highly incompatible elements, Arevalo and McDonough^[19] divided MORBs into two groups: MORBs with $(\text{La}/\text{Sm})_{\text{N}}$ ^[3] (chondrite-normalized La/Sm) < 1 are defined as “normal-type” MORB (N-MORB), and those with $(\text{La}/\text{Sm})_{\text{N}} > 1$ are defined as E-MORB. The samples span a broad range of chemical and radiogenic isotope compositions, including the typical N-MORB and E-MORB based on their variations in $(\text{La}/\text{Sm})_{\text{N}}$ (0.55–3.84). The major and trace element abundances of these samples have been previously characterized^[16, 17, 20–22]. In particular, their MgO contents range from 2.7 wt% to 9.1 wt%, SiO₂ range from 47.6 wt% to 58.5 wt%, and Ba range from 7 to 453 μg/g. More details (such as the location and chemical composition) are documented in Table 1.

3 Analytical methods

Whole rock Ba and Sr isotope analyses were performed in the CAS Key Laboratory of Crust-Mantle and Environments at the University of Science and Technology of China (USTC). Sr was chemically purified following the method reported by Chen et al.^[23]. Approximately 120–150 mg of the sample powder was digested in a mixture of concentrated HF-HNO₃-HCl. Sr was then separated from the matrix using a quartz column with a 2 mL AG50W-X8 cation exchange resin (200–400 mesh). The total procedural blanks were < 0.5 ng. Ba was chemically purified follow the method reported by Nan et al.^[6, 24]. Sample powders containing ~2 μg of Ba were digested in a mixture of concentrated HF-HNO₃-HCl. Ba was then separated from the matrix using a Teflon column with a 2 mL AG50W-X12 cation exchange resin (200–400 mesh). To avoid matrix effects from light REEs (e.g., La, Ce, and Nd), a second column with 0.5 mL AG50W-X12 resin was used for further purification. The yield of the purification process was > 99%. The total procedural blanks were < 0.5 ng. Purified

samples were dried and diluted with 2% (m/m) HNO₃ for instrumental measurements.

Ba and Sr isotope measurements were conducted using a Neptune Plus multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Sr isotope ratios were measured in low-resolution mode under “wet” plasma conditions. The measured Sr isotope ratios were corrected for instrumental mass bias by normalizing them to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. The results for the samples and reference materials are listed in Table 1. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of NBS-987 and BCR-2 are 0.710247 ± 0.000011 (2SD, $n = 25$) and 0.705025 ± 0.000009 (2SD, $n = 4$), respectively, which are consistent with the previous study^[25]. Ba isotope ratios were measured using the double-spike (^{135}Ba - ^{136}Ba) method in low-resolution mode under “dry” plasma conditions (Aridus II desolvating nebulizer). The background signal for ^{137}Ba (< 5 mV) is negligible relative to the sample signal (~7 V). The results are reported in δ -notation relative to NIST SRM3104a: $\delta^{137/134}\text{Ba}$ (‰) = $[(^{137/134}\text{Ba}_{\text{sample}})/(^{137/134}\text{Ba}_{\text{SRM3104a}}) - 1] \times 1000$. For comparison, the $\delta^{137/134}\text{Ba}$ values of all the samples were calculated to be $\delta^{138/134}\text{Ba}$ following the mass-dependent fractionation laws ($\delta^{138/134}\text{Ba} \approx 1.33 \times \delta^{137/134}\text{Ba}$). The external precision of $\delta^{137/134}\text{Ba}$ based on the measurement of two in-house standards (USTC-Ba and ICPUS-Ba) is $\leq 0.04\%$ (2SD). We estimate the long-term external precision of $\delta^{138/134}\text{Ba}$ is $\leq 0.05\%$ (2SD), as verified by Deng et al.^[26]. The results for the samples and standard materials are listed in Table 1. The $\delta^{137/134}\text{Ba}$ values of BCR-2 and GSP-2 are in good agreement with previously published values^[6, 24].

4 Results

The Ba-Sr isotope data are presented in Table 1 and Fig. 1. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the MORB and BABB samples range from 0.70243 to 0.70404. The $\delta^{138/134}\text{Ba}$ of the MORB samples range from -0.06 ‰ to +0.11 ‰. E-MORBs (-0.06 ‰ to +0.11 ‰, $n = 7$) show more scattered $\delta^{138/134}\text{Ba}$ than N-MORBs (-0.04 ‰ to +0.08 ‰, $n = 18$), although the difference is within the analytical uncertainty. There are no systematic cross-regional variations. Therefore, $\delta^{138/134}\text{Ba}$ varies from -0.03 ‰ to +0.08 ‰ in EPR MORBs ($n = 13$), from -0.02 ‰ to +0.11 ‰ in MAR MORBs ($n = 6$), and from -0.06 ‰ to +0.10 ‰ in GR MORBs ($n = 6$). One MORB sample in SEIR has a value of $+0.04 \pm 0.03 \%$ (2SD). The $\delta^{138/134}\text{Ba}$ of the five BABB samples range from +0.01 ‰ to +0.08 ‰, which is within the range of MORBs. These values are slightly lower than those of previously reported MORB samples, despite substantial overlapping (+0.02 ‰ to +0.15 ‰^[7]) (Fig. 2). To our knowledge, the five Lau Basin basalts are the first published Ba isotope data for BABBs. On average, $\delta^{138/134}\text{Ba}$ of our samples ($+0.04 \pm 0.08 \%$, 2SD, $n = 30$) is indistinguishable from their average value ($+0.07 \pm 0.08 \%$, 2SD, $n = 21$).

5 Discussion

5.1 Ba isotope systematics of MORBs

The basaltic oceanic ridge samples reported herein span a broad range of geographical distributions and chemical com-

Table 1. Elemental and isotope compositions for the samples and standard materials in this study.

Sample name	Latitude (N)	Longitude (W)	Type	(La/Sm) _N ^a	⁸⁷ Sr/ ⁸⁶ Sr	Ba/Th	$\delta^{137m}\text{Ba}$ (%)	2SD ^b	n^c	$\delta^{136}\text{Ba}^d$ (%)	MgO (wt%)	SiO ₂ (wt%)	Na ₂ (wt%)	Ba (μg/g)	References
<i>9°N OSC lavas on East Pacific Rise</i>															
264-04	9.16	104.19	D	0.67	0.70250	60.0	0.01	0.03	5	0.01	7.0	50.5	2.6	13.2	[17]
265-113	9.09	104.20	D	0.74	0.70249	39.0	0.04	0.04	4	0.05	5.9	51.9	2.5	15.6	[17]
Replicate ^e							0.02	0.04	3	0.03					
266-01			D	0.60	0.70246	49.7	0.04	0.00	2	0.05	6.8	51.0	2.6	6.5	[17]
266-33	9.11	104.23	D	0.64	0.70244	45.8	0.02	0.02	2	0.03	7.3	50.7	2.6	8.3	[17]
265-05	9.11	104.24	D	0.64	0.70243	53.9	0.05	0.02	2	0.06	7.0	51.0	2.7	9.2	[17]
265-88	9.13	104.21	D	0.71	0.70251*	51.6	0.04	0.03	3	0.05	6.7	50.9	2.4	10.3	[18]
265-82	9.13	104.21	D	0.61	0.70248*	53.0	0.04	0.04	2	0.05	6.9	50.8	2.3	9.9	[18]
<i>East Pacific Rise</i>															
2737-8	9.85	104.30	D	0.63	0.70246*	58.6	0.04	0.03	2	0.06	8.6	49.3	2.8	7.1	PetDB
2359-4	9.89	104.30	D	0.65	0.70248*	63.9	0.05	0.00	2	0.07	7.9	50.4	2.7	9.4	PetDB
Replicate ^e							0.06	0.04	3	0.08					
2746-14	9.82	104.31	N	0.59	0.70277*	71.2	-0.03	0.03	4	-0.04	7.2	50.4	2.8	8.8	PetDB
2746-9	9.82	104.29	N	0.60	0.70250*	72.3	0.03	0.00	2	0.04	8.5	50.2	2.8	8.4	PetDB
2392-9	9.85	104.32	N	0.55	0.70249*	74.8	0.06	0.01	2	0.08	8.5	50.1	2.7	7.3	PetDB
2368-4	9.85	104.29	D	0.68	0.70247*	70.0	0.05	0.04	2	0.07	8.6	50.0	2.7	7.3	PetDB
<i>Mid-Atlantic Ridge</i>															
AH0127 D7-2	34.35	37.10	N	0.55	0.70276	93.3	-0.01	0.02	2	-0.01	8.9	52.3	2.8	10.0	[16]
AH0127 D9-10	35.21	34.77	E	3.65	0.70368	102.6	0.08	0.00	2	0.11	6.7	47.6	2.7	453.3	[16]
Replicate ^e							0.08	0.00	2	0.10					
AH0127D40-4	35.78	34.22	E	1.03	0.70394	116.3	-0.01	0.01	3	-0.02	8.0	51.3	2.2	35.5	[16]
AH0127D44-1	35.33	34.86	E	3.84	0.70404	111.2	0.03	0.05	4	0.03	7.7	48.2	2.9	435.3	[16]
AH0127D45-3	35.33	34.86	E	2.94	0.70366	114.3	0.04	0.05	4	0.05	8.4	50.2	2.2	144.2	[16]

(To be continued on the next page)

(Continued)

Sample name	Latitude (N)	Longitude (W)	Type	(La/Sm) _N ^a	⁸⁷ Sr/ ⁸⁶ Sr	Ba/Th	$\delta^{137}\text{Ba}$ (‰)	$\delta^{138}\text{Ba}$ (‰)	MgO (wt%)	SiO ₂ (wt%)	Na ₈ (wt%)	Ba (µg/g)	References
AI10127 D46-7	35.24	34.82	E	3.38	0.70344	88.8	0.06	0.08	7.5	50.6	2.3	207.0	[16]
<i>Gakkel Ridge</i>													
HLY0102-008-011	82.90	6.24	N	0.67	0.70311	169.2	-0.01	-0.02	7.9	50.8	3.0	46.0	[16]
Replicate ^e					0.70312		0.01	0.01					
HLY0102-026-020	84.46	-2.57	N	0.63	0.70291	120.3	0.07	0.10	8.3	49.8	3.1	21.5	[16]
HLY0102-027-029	84.48	-2.75	N	0.43	0.70287	89.0	0.08	0.10	9.1	49.1	3.1	6.9	[16]
HLY0102-038-029	85.31	-12.69	E	1.15	0.70300	159.3	-0.05	-0.06	7.6	50.8	3.2	93.4	[16]
HLY0102-073-012	86.96	-57.36	N	0.86	0.70263	91.9	0.02	0.03	8.5	49.8	3.4	18.3	[16]
<i>South East Indian Ridge</i>													
VEM0033-1-001-002	-50.41	-131.01	E	1.07	0.70264	68.3	0.03	0.04	9.0	48.8	3.5	25.0	[16]
<i>Lau Basin</i>													
KLM0417-004-001	-19.34	-176.16			0.70320	81.4	0.04	0.05	7.5	51.2	2.4	5.9	[16]
KLM0417-005-001	-19.45	-175.96			0.70322	88.2	0.01	0.01	8.2	51.0	2.3	5.5	[22]
KLM0417-007-001	-19.80	-176.03			0.70296	97.0	0.03	0.04	8.1	49.1	2.7	7.2	[22]
Replicate ^e					0.04		0.01	0.05					
KLM0417-016-001	-22.19	-176.62			0.70332	247.8	0.06	0.08	2.7	58.5	1.2	112.3	[16]
KLM0417-034-002	-21.57	-176.41			0.70315	210.9	0.02	0.03	3.4	57.5	1.6	75.3	[16]
<i>Reference material</i>													
NBS-987					0.710257								
BCR-2					0.705025		0.05						
GSP-2							0.01						

^a ⁸⁷Sr/⁸⁶Sr values of the samples with asterisks were measured in this study.

^b La/Sm was normalized to CI-chondrite^[31].

^c *n* represents the number of repeated measurements of the population of *n* repeat measurements of a sample solution.

^d Data were calculated from the measured $\delta^{137}\text{Ba}$ values, as described in the text.

^e Replicate = repeat sample dissolution, purified column chemistry, and MC-ICP-MS analysis.

PetDB= the Petrological Database website (<http://www.earthchem.org/petdb>).

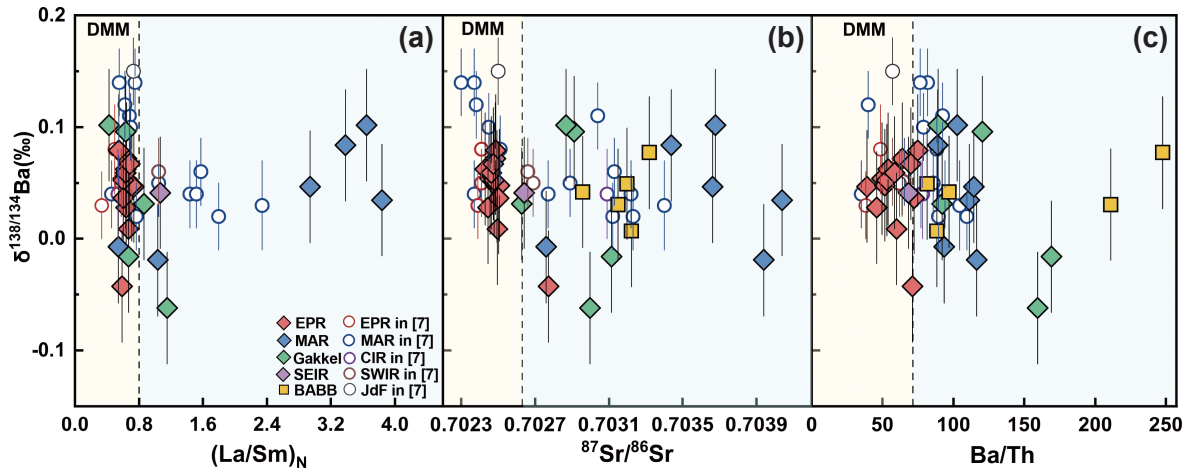


Fig. 1. Correlations between $\delta^{138/134}\text{Ba}$ and (a) $(\text{La}/\text{Sm})_N$, (b) $^{87}\text{Sr}/^{86}\text{Sr}$, and (c) Ba/Th for the mid-ocean ridge basalt (MORB) and back-arc basin basalt (BABB) samples in our study and MORB samples analyzed by Nielsen et al.^[7]. Data are from Table 1. Error bars represent 2SD uncertainties. The vertical dotted lines present the defined average $(\text{La}/\text{Sm})_N$ ^[16], $^{87}\text{Sr}/^{86}\text{Sr}$ ^[23], and Ba/Th ^[28] of the depleted MORB mantle. Samples in the orange shade are marked as depleted MORB, and those in the blue shade are marked as normal-type MORB or enriched-type MORB.

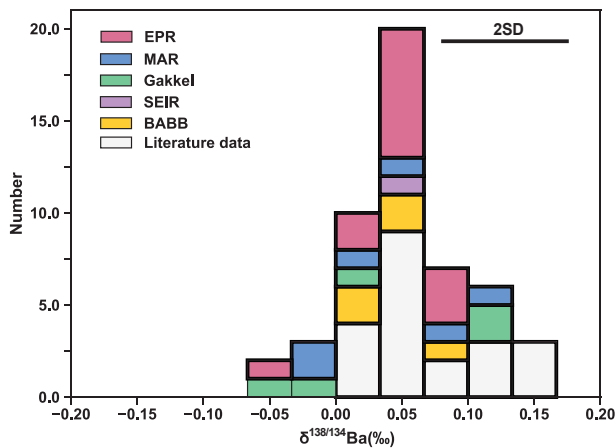


Fig. 2. The histogram of Ba isotope compositions of MORBs and BABBs investigated in this study. Literature data of MORBs are from Nielsen et al.^[7]. Data are from Table 1.

positions. The inconsistent Ba isotope data between this study and that in Nielsen et al.^[7] could not reflect the different degrees of rock alteration because all these samples are fresh. Interlaboratory bias is also not considered as Ba isotope analyses of the igneous rock standards in our and their studies

display consistent results within error^[7,24]. The most probable explanation is that this difference is due to practical Ba isotope variations among global MORBs.

Barium isotope variation in MORBs can potentially be induced by magmatic differentiation during the formation of these basalts or mantle heterogeneity. Fig. 3 shows that no observable correlations exist between $\delta^{138/134}\text{Ba}$ and the indicators of magmatic differentiation (MgO and SiO_2) or degree of partial melting (Na_8)^[27]. In addition, as has been verified previously^[7], Ba is highly incompatible with the bulk distribution coefficient $D_{\text{solid/melt}}$ of 0.00012 during mantle melting^[28], and ~99% of Ba tends to enter the melt after 1% partial melting. MORBs represent degrees of melting between 6% and 20%^[29], as a result, Ba isotope fractionation between the starting mantle composition and these basaltic melts is negligible. Therefore, the Ba isotope compositions of the MORBs principally reflect variations in the $\delta^{138/134}\text{Ba}$ values of their mantle sources.

Together, all the MORB data sets in this study and the literature^[7] (51 samples, including BABB samples) provide a range of $\delta^{138/134}\text{Ba}$ of -0.06‰ to $+0.15\text{‰}$, with an average of $+0.05\text{‰} \pm 0.09\text{‰}$ (2SD, $n = 51$).

5.2 Estimation of the Ba isotope composition of DMM

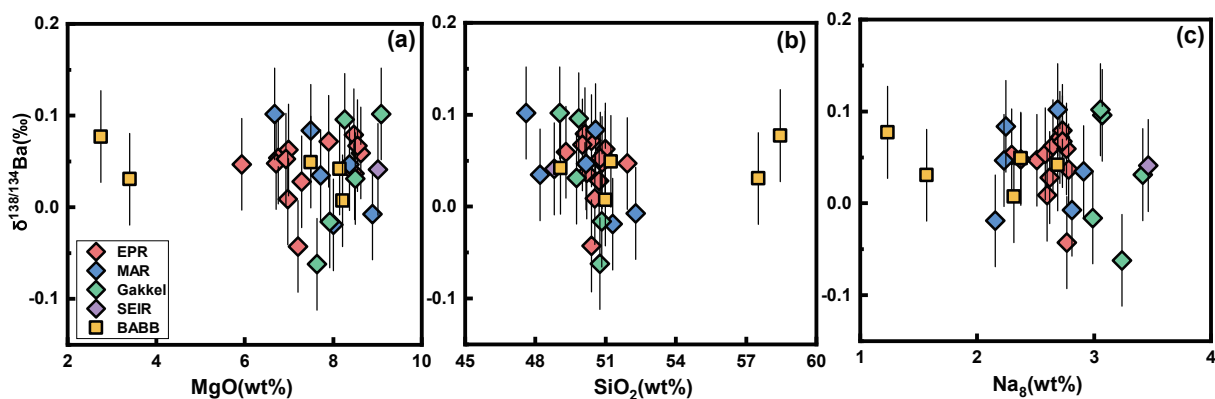


Fig. 3. $\delta^{138/134}\text{Ba}$ versus (a) MgO , (b) SiO_2 and (c) Na_8 for MORBs and BABBs. $\text{Na}_8 = \text{Na}_2\text{O} + 0.373 \times \text{MgO} - 2.98$ (from Ref. [27]). Data are from Table 1. The error bars represent the 2SD uncertainties.

According to the previous definition of N-MORB [19], 70% of the MORB samples in PetDB are categorized as N-MORB, displaying a considerable range of major and trace element compositions [2]. Only the most depleted samples were representative of the DMM. Therefore, we estimated the $\delta^{138/134}\text{Ba}$ of DMM based on the most depleted MORB (D-MORB) data. The selected 10 D-MORB samples showed typical depleted compositions with $(\text{La}/\text{Sm})_{\text{N}} < 0.8$ [16]. We also used $^{87}\text{Sr}/^{86}\text{Sr} < 0.70263$ and $\text{Ba}/\text{Th} < 71.3$, which are lower than the average DMM [28], as the criteria for recognizing the D-MORBs (Figs. 1b and 1c). Along with the D-MORB samples measured in the literature [7], the average $\delta^{138/134}\text{Ba}$ of DMM was estimated to be $+0.05\text{‰} \pm 0.05\text{‰}$ (2SD, $n = 16$). The JdF sample ($+0.15\text{‰}$) in Nielsen et al. [7] is beyond the average $\delta^{138/134}\text{Ba}$ of all MORBs ($+0.05\text{‰} \pm 0.09\text{‰}$, 2SD, $n = 51$) and was thus precluded when calculating the average DMM value. To avoid artificial bias in different laboratories, we also calculated a mean $\delta^{138/134}\text{Ba}$ solely based on our data of $+0.05\text{‰} \pm 0.04\text{‰}$ (2SD, $n = 10$). Our estimation of $\delta^{138/134}\text{Ba}$ of DMM is significantly lower than that reported by Nielsen et al. [7] ($\sim +0.14\text{‰}$).

It is necessary to evaluate different estimates of the average $\delta^{138/134}\text{Ba}$ values of the DMM. The estimation of the DMM by Nielsen et al. [7] may be problematic for two reasons. First, the DMM and E-MORB mantle (EMM) were defined using only three MORB samples with the lowest and highest $^{87}\text{Sr}/^{86}\text{Sr}$ respectively. The limited sample size leads to a lack of representativeness for the samples that estimate the DMM. Second, as pointed out by Wu et al. [11], using only $^{87}\text{Sr}/^{86}\text{Sr}$ is not sufficient to choose appropriate samples to define the DMM. In fact, both the DMM and EMM reservoirs span a large range of radiogenic isotope ratios. In this case, the D-MORBs with $^{87}\text{Sr}/^{86}\text{Sr} < 0.7024$ exhibited a large $\delta^{138/134}\text{Ba}$ range ($+0.03\text{‰}$ to $+0.14\text{‰}$), overlapping with the $\delta^{138/134}\text{Ba}$ range ($+0.02\text{‰}$ to $+0.11\text{‰}$) of the MORBs with $^{87}\text{Sr}/^{86}\text{Sr} > 0.7030$. Therefore, one should rigorously choose MORB samples to estimate the average DMM. Based on all Ba isotope data for the D-MORBs, our study provides a more reliable estimate for the average $\delta^{138/134}\text{Ba}$ of the DMM ($+0.05\text{‰} \pm 0.05\text{‰}$, 2SD, $n = 16$), which leads to new constraints on the nature of the E-MORB source.

5.3 The origin of the enriched source of E-MORB

There are long-term debates on how the mantle source of E-MORB was formed, i.e., melting of the enriched lower mantle [30, 31], and recycling crustal materials into the mantle (e.g., crustal rocks, metamorphic fluids, and sediments) [3, 13, 15, 32]. Because Ba isotope compositions are unlikely to be modified during mantle melting and fractional crystallization from basaltic melt, Ba isotope variation in MORBs should reflect the introduction of recycled, Ba-rich crustal components into the mantle.

Based on the early estimates of average DMM data, Nielsen et al. [7] proposed that Ba isotope variation in MORBs is derived from pervasive mixing between isotopically heavy DMM and light EMM reservoirs. However, different insights into the formation of the EMM may be gained if the new DMM estimation is applied. The E-MORBs and BABBs show a slightly larger range of $\delta^{138/134}\text{Ba}$ (-0.06‰ to $+0.11\text{‰}$) relative to D-MORBs. The $\delta^{138/134}\text{Ba}$ does not show a simple

trend with increasing $(\text{La}/\text{Sm})_{\text{N}}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and Ba/Th (Fig. 1), which is inconsistent with previously observed hyperbolic mixing relationships [7]. Nielsen et al. [7] attributed the isotopically light Ba signature of EMM ($\approx +0.03\text{‰}$) to the pervasive addition of sedimentary materials to DMM ($\approx +0.14\text{‰}$), as they proposed that sediments have a narrow range of $\delta^{138/134}\text{Ba}$ ($0.01\text{‰} \pm 0.04\text{‰}$, 2SD) and are similar to the E-MORB ($+0.03\text{‰} \pm 0.02\text{‰}$, 2SD). However, if the new estimation is applied, the $\delta^{138/134}\text{Ba}$ values of such sediments will be similar to the DMM value ($+0.01\text{‰}$ vs. $+0.05\text{‰}$). Considering the observations of the MORBs and sediments together, it is unreasonable to infer that the Ba isotope signatures of E-MORBs are derived from pervasive recycled sediments in their mantle source. Additionally, the $\delta^{138/134}\text{Ba}$ observed in this study did not show a simple trend, but became more scattered with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ and Ba/Th (Figs. 1b and 1c).

Significant variations in $\delta^{138/134}\text{Ba}$ for crustal materials, such as marine sediments (-0.11‰ to $+0.10\text{‰}$) [7–9], AOC (-0.09‰ to $+0.33\text{‰}$) [7], and diamicrites [6] have been reported, which are much wider than the range used by Nielsen et al. [7]. Although the AOC does not have much higher Ba content and $^{87}\text{Sr}/^{86}\text{Sr}$ relative to the sediment, a study of the Tonga arc revealed that the addition of AOC-derived fluid to the mantle wedge is the most probable source of the high $\delta^{138/134}\text{Ba}$ in the arc lavas (up to $+0.16\text{‰}$) [11]. In addition, Hao et al. [33] identified the contribution of bulk AOC, aside from the sediment components, to the formation of the Fushui mafic rocks using Ba isotopes. Therefore, we suggest that subduction of sediments and AOC can account for the variation of $\delta^{138/134}\text{Ba}$ in the E-MORBs (-0.06‰ to $+0.11\text{‰}$). However, Ba isotopes can be considerably fractionated during subduction-zone fluid processes, resulting in a metamorphic fluid with much higher $\delta^{138/134}\text{Ba}$ than the subducted materials [34]. Therefore, evaluating the contributions of different crustal components to the source of mantle-derived igneous rock requires careful consideration.

6 Conclusions

This study presents the Ba isotope compositions of a wide range of MORBs and BABBs from different localities, with variable $\delta^{138/134}\text{Ba}$ ranging from -0.06‰ to $+0.11\text{‰}$. Based on the D-MORB samples, we re-estimated the average $\delta^{138/134}\text{Ba}$ of the DMM as $+0.05\text{‰} \pm 0.05\text{‰}$ (2SD, $n = 16$). Because of the similar $\delta^{138/134}\text{Ba}$ values of sediments and the DMM, it is unreasonable to conclude that Ba isotope signatures of E-MORBs are attributed to pervasive sediment recycling in the upper mantle. Instead, the Ba isotope data of the E-MORBs indicate that the EMM could reflect the incorporation of subducted AOC and/or sediments, depending on the Ba isotope composition and other geochemical information of the local mantle.

Supporting information

The supporting information for this article can be found online at <https://doi.org/10.52396/JUSTC-2021-0276>.

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Conflict of interest

The authors declare that they have no conflict of interest.

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References

- [1] Rudnick R L, Gao S. Composition of the continental crust. In: Holland H D, Turekian K K, editors. *Treatise on Geochemistry*. Amsterdam: Elsevier, 2003, 3: 659.
- [2] Plank T, Langmuir C H. The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chemical Geology*, **1998**, *145*: 325–394.
- [3] Sun S S, McDonough W F. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geological Society, London, Special Publications*, **1989**, *42*: 313–345.
- [4] Kessel R, Schmidt M W, Ulmer P, et al. Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120–180 km depth. *Nature*, **2005**, *437*: 724–727.
- [5] Eugster O, Tera F, Wasserburg G J. Isotopic analyses of barium in meteorites and in terrestrial samples. *Journal of Geophysical Research*, **1969**, *74* (15): 3897–3908.
- [6] Nan X Y, Yu H M, Rudnick R L, et al. Barium isotopic composition of the upper continental crust. *Geochimica et Cosmochimica Acta*, **2018**, *233*: 33–49.
- [7] Nielsen S G, Horner T J, Pryer H V, et al. Barium isotope evidence for pervasive sediment recycling in the upper mantle. *Science Advances*, **2018**, *4* (7): eaas8675.
- [8] Nielsen S G, Shu Y, Auro M, et al. Barium isotope systematics of subduction zones. *Geochimica et Cosmochimica Acta*, **2020**, *275*: 1–18.
- [9] Bridgestock L, Hsieh Y-T, Porcelli D, et al. Controls on the barium isotope compositions of marine sediments. *Earth and Planetary Science Letters*, **2018**, *481*: 101–110.
- [10] Li W-Y, Yu H-M, Xu J, et al. Barium isotopic composition of the mantle: Constraints from carbonatites. *Geochimica et Cosmochimica Acta*, **2020**, *278*: 235–243.
- [11] Wu F, Turner S, Schaefer B F. Mélange versus fluid and melt enrichment of subarc mantle: A novel test using barium isotopes in the Tonga-Kermadec arc. *Geology*, **2020**, *48*: 1053–1057.
- [12] White W M, Klein E M, Holland H D, et al. Composition of the oceanic crust. In: Holland H D, Turekian K K, editors. *Treatise on Geochemistry*. 2nd ed. Amsterdam: Elsevier, 2014, 4: 457–496.
- [13] Hofmann A W. Sampling mantle heterogeneity through oceanic basalts: Isotopes and trace elements. In: Holland H D, Turekian K K, editors. *Treatise on Geochemistry*. 2nd ed. Amsterdam: Elsevier, 2014, 3: 67–101.
- [14] Hofmann A W. Mantle geochemistry: the message from oceanic volcanism. *Nature*, **1997**, *385*: 219–229.
- [15] Eiler J M, Schiano P, Kitchen N, et al. Oxygen-isotope evidence for recycled crust in the sources of mid-ocean-ridge basalts. *Nature*, **2000**, *403*: 530–534.
- [16] Gale A, Dalton C A, Langmuir C H, et al. The mean composition of ocean ridge basalts. *Geochemistry, Geophysics, Geosystems*, **2013**, *14*: 489–518.
- [17] Wanless V D, Perfit M R, Ridley W I, et al. Dacite petrogenesis on mid-ocean ridges: Evidence for oceanic crustal melting and assimilation. *Journal of Petrology*, **2010**, *51*: 2377–2410.
- [18] Wanless V D, Perfit M R, Ridley W I, et al. Volatile abundances and oxygen isotopes in basaltic to dacitic lavas on mid-ocean ridges: The role of assimilation at spreading centers. *Chemical Geology*, **2011**, *287*: 54–65.
- [19] Arevalo Jr R, McDonough W F. Chemical variations and regional diversity observed in MORB. *Chemical Geology*, **2010**, *271*: 70–85.
- [20] Perfit M R, Wanless V D, Ridley W I, et al. Lava geochemistry as a probe into crustal formation at the East Pacific Rise. *Oceanography*, **2012**, *25* (1): 89–93.
- [21] Wanless V D, Perfit M R, Klein E M, et al. Reconciling geochemical and geophysical observations of magma supply and melt distribution at the 9°N overlapping spreading center, East Pacific Rise. *Geochemistry, Geophysics, Geosystems*, **2012**, *13* (11): Q11005.
- [22] Bézou A, Escrib S, Langmuir C H, et al. Origins of chemical diversity of back-arc basin basalts: A segment-scale study of the Eastern Lau Spreading Center. *Journal of Geophysical Research: Solid Earth*, **2009**, *114* (B6): B06212.
- [23] Chen F, Li X H, Wang X L, et al. Zircon age and Nd–Hf isotopic composition of the Yunnan Tethyan belt, southwestern China. *International Journal of Earth Sciences*, **2007**, *96*: 1179–1194.
- [24] Nan X Y, Wu F, Zhang Z F, et al. High-precision barium isotope measurements by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, **2015**, *30*: 2307–2315.
- [25] Weis D, Kieffer B, Maerschalk C, et al. High - precision isotopic characterization of USGS reference materials by TIMS and MC-ICP-MS. *Geochemistry, Geophysics, Geosystems*, **2006**, *7*: Q08006.
- [26] Deng G X, Kang J T, Nan X Y, et al. Barium isotope evidence for crystal-melt separation in granitic magma reservoirs. *Geochimica et Cosmochimica Acta*, **2021**, *292*: 115–129.
- [27] Klein E M, Langmuir C H. Global correlations of ocean ridge basalt chemistry with axial depth and crustal thickness. *Journal of Geophysical Research: Solid Earth*, **1987**, *92* (B8): 8089–8115.
- [28] Workman R K, Hart S R. Major and trace element composition of the depleted MORB mantle (DMM). *Earth and Planetary Science Letters*, **2005**, *231*: 53–72.
- [29] Hofmann A W. Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. *Earth and Planetary Science Letters*, **1988**, *90*: 297–314.
- [30] Schilling J G, Zajac M, Evans R, et al. Petrologic and geochemical variations along the Mid-Atlantic Ridge from 29°N to 73°N. *American Journal of Science*, **1983**, *283* (6): 510–586.
- [31] Taylor R N, Thirlwall M F, Murton B J, et al. Isotopic constraints on the influence of the Icelandic plume. *Earth and Planetary Science Letters*, **1997**, *148*: E1–E8.
- [32] Elliott T, Thomas A, Jeffcoate A, et al. Lithium isotope evidence for subduction-enriched mantle in the source of mid-ocean-ridge basalts. *Nature*, **2006**, *443*: 565–568.
- [33] Hao L L, Nan X Y, Kerr A C, et al. Mg-Ba-Sr-Nd isotopic evidence for a mélange origin of early Paleozoic arc magmatism. *Earth and Planetary Science Letters*, **2022**, *577*: 117263.
- [34] Gu X-F, Guo S, Yu H-M, et al. Behavior of barium isotopes during high-pressure metamorphism and fluid evolution. *Earth and Planetary Science Letters*, **2021**, *575*: 117176.