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Barium isotope evidence of a fluid-metasomatized mantle component in the source of Azores OIB

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ABSTRACT

This study presents Ba isotope compositions of ocean island basalts (OIB) from the Azores Archipelago to investigate the origin of the enriched components within their mantle sources. These samples have large variations in radiogenic Sr-Nd-Pb-Hf isotope compositions, indicating that they tap highly heterogeneous mantle sources. They display two types of Ba isotope characteristics. Samples from the Faial, Pico, São Jorge, and São Miguel Islands exhibit homogeneous and MORB-like Ba isotope compositions, whereas samples from Terceira Island have variable Ba isotopes. The $\delta^{138/134}$Ba values of the Terceira samples range from -0.03 to $+0.24$‰, extending to values significantly higher than those of the other islands.

The MORB-like Ba isotope composition of the São Jorge samples indicates that the enriched HIMU/FOZO material in the Azores mantle plume source has a homogeneous and MORB-like Ba isotope composition. In contrast, the Terceira samples are characterized by heavy Ba isotope compositions, which are likely inherited from subducted altered oceanic crust (AOC) and may reflect the presence of a shallower enriched source beneath Terceira. As the Azores archipelago is located at a triple junction far from any active subduction zone, the signature of subducted AOC must be an ancient feature, potentially derived from a recycled fluid-metasomatized mantle component now present beneath the Azores archipelago. The negative correlation between $\delta^{138/134}$Ba and ^{206}Pb/^{204}Pb and the positive correlation between $\delta^{138/134}$Ba and Ba/Th among selected Terceira samples likely reflect mixing between the mantle plume and shallower, recycled, fluid-metasomatized mantle components enriched in heavy Ba isotopes.

1. Introduction

Ocean island basalts serve as effective probes for deciphering the compositional variability and evolution of the mantle. Enriched geochemical signatures relative to the depleted upper mantle, observed in many OIB, can potentially be explained by the addition of recycled materials (e.g., Zindler and Hart, 1986). Various element/element ratios (e.g., Nb/Zr, La/Sm, and Sm/Zr; Workman and Hart, 2005) and radiogenic isotopes (e.g., Sr, Pb and Nd; White, 1985; Hart and Hauri, 1992) have been used to identify different enriched components, but distinguishing the origins of these components remains a challenge. With the recent development of analytical methods, a growing diversity of metal stable isotopes have been used to identify the different components of subducted slabs and to constrain the mechanism of crustal recycling in the mantle (e.g., Teng et al., 2017).

Barium is a fluid-mobile element during slab dehydration (Kessel et al., 2005), which makes it a sensitive indicator for fluid-rock reactions and to track fluids in subduction zones. Barium is also highly incompatible during mantle partial melting, so crustal materials usually have much higher Ba abundances than the mantle (Sun and McDonough, 1989; Rudnick and Gao, 2003). Seawater and crustal materials (e.g., oceanic/continental crust and glacial diamictites) show much larger Ba

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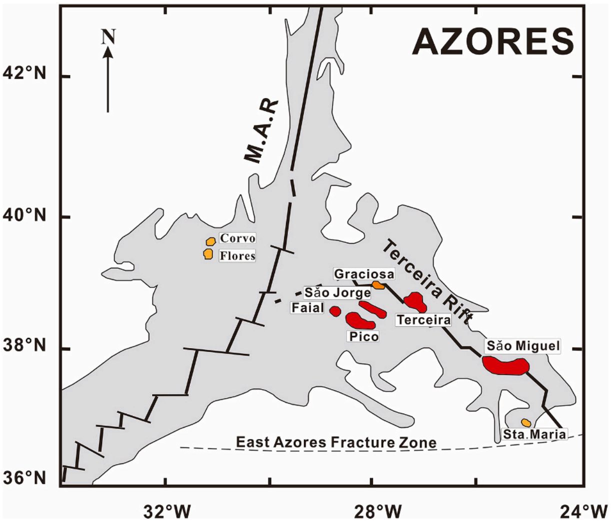

Fig. 1. Map of the Azores archipelago (modified after Moreira et al., 1999).

isotope variations ($\delta^{138/134}$Ba of −0.63 to +0.95‰) than MORB and the upper mantle ($\delta^{138/134}$Ba of +0.03 to +0.14‰) (e.g., Horner et al., 2015; Nan et al., 2018, 2022; Nielsen et al., 2018; Li et al., 2020; Deng et al., 2021). Although the Ba isotope signatures of most marine sediments are similar to the average of MORB, the altered oceanic crust (AOC) exhibits a large variation in $\delta^{138/134}$Ba (−0.23 to +0.40‰; Nan et al., 2017; Nielsen et al., 2018; Wu et al., 2020). Therefore, the addition of different components from subducted slabs could produce distinct Ba isotope signatures in the mantle.

Barium isotopes have been applied to discern the contribution of different recycled components in subduction zones (Wu et al., 2020; Gu et al., 2021). Tonga arc lavas exhibit a positive correlation between Ba isotope ratios and Ba/Th, indicating the contribution of a fluid-dominated source with heavy Ba isotopes (Wu et al., 2020). High-pressure veins and retrograded amphibolites from the Dabie orogen, central China, have large variations in $\delta^{138/134}$Ba (−0.17 to +0.46‰), further supporting that metasomatic fluids resulting from dehydration of different subduction components may have distinct Ba isotope signatures (Gu et al., 2021). Nielsen et al. (2020) proposed that the addition of subducted sediments and AOC could produce variable $\delta^{138/134}$Ba values (−0.07 to +0.11‰) in the Aleutian and Ryukyu arc lavas. If these enriched components were subducted and recycled into the mantle source of the OIB, they could be recorded by Ba isotope signatures. In this study, we applied Ba isotopes to investigate the origin of enriched components in the mantle sources of the Azores archipelago. The results of this study provide important insights into using Ba isotopes to trace subduction related materials in the mantle.

2. Geological setting and samples

The Azores archipelago is a group of nine islands located between ~37–40°N and ~24–32°W in the vicinity of the Mid-Atlantic Ridge (MAR) and the triple junction between the North American, African and Eurasian plates (Fig. 1). Two islands, Corvo and Flores, lie to the west of the ridge; the other seven islands, including Faial, Graciosa, Pico, São Miguel, São Jorge, Santa Maria, and Terceira, lie to the east of the ridge. To the east of the ridge is the Terceira Rift, a spreading center along which three islands, Graciosa, São Miguel and Terceira, are aligned. The other four islands, including Faial, Pico, São Jorge, and Santa Maria, are to the south of this rift. Based on their relative geographic proximity, the nine islands of the Azores archipelago can be divided into three groups: the Occidental Group, including the Corvo and Flores Islands; the Central Group, including Faial, Graciosa, Pico, São Jorge and Terceira; and the Oriental Group, including São Miguel and Santa Maria. The samples analyzed in this study are from five islands located to the east of MAR, including four from the Central Group (Faial, Pico, São Jorge, and Terceira) and one from the Oriental Group (São Miguel) (Fig. 1).

Previous studies suggest that the Terceira Rift magmas were produced by low degrees of partial melting (<5%) of a mantle plume with low excess temperature and buoyancy flux (Bourdon et al., 2005). Seismic tomography data and noble gas isotope signatures indicative of a relatively undegassed source (high ^{3}He/^{4}He and ^{20}Ne/^{22}Ne) in select Central Group samples have led to the interpretation that the Azores mantle plume is likely situated beneath Terceira, Faial or São Jorge (e.g., Moreira et al., 1999; Moreira and Allègre, 2002; Madureira et al., 2005; Jean-Baptiste et al., 2009).

Azores OIB exhibit extreme heterogeneity in radiogenic isotopes at both the archipelago-wide and the intra-island scales (e.g., Turner et al., 1997; Widom et al., 1997; Beier et al., 2007, 2008; Elliott et al., 2007; Millet et al., 2009; Waters et al., 2020; Fig. 2). In addition to the Azores mantle plume component, which is considered to be a source common to all Azores islands (e.g., White et al., 1976), each island also taps its own unique enriched component. These additional components are typically inferred to reside in the mantle, and many models have been proposed to explain their geochemical characteristics. It has been proposed that ancient suboceanic lithospheric mantle was in the source of Faial and Pico, because some basalts from these two islands had subchondritic ^{187}Os/^{188}Os ratios (Schaefer et al., 2002). For São Jorge, samples from different formations can be separated into different groups based on elemental and Pb and Sr isotope systematics, which has been attributed to multiple enriched source components that are dispersed in the shallow mantle/lithosphere (Millet et al., 2009). The mantle source of

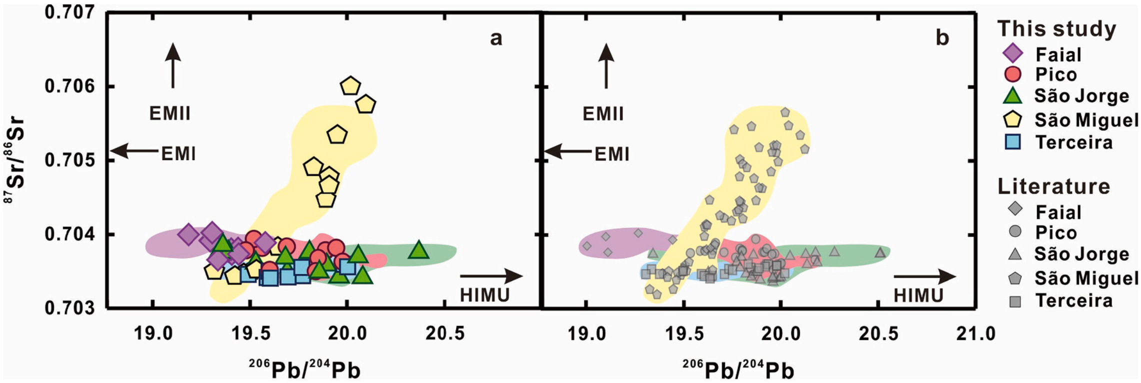

Fig. 2. Plot of ^{87}Sr/^{86}Sr and ^{206}Pb/^{204}Pb of Azores samples of (a) this study and (b) reported in previous literature. The color designates the isotope variations of samples from different islands. The literature data are from Turner et al. (1997), Widom et al. (1997), Beier et al. (2007, 2008), Elliott et al. (2007), Millet et al. (2009), Madureira et al. (2011), and Waters et al. (2020).

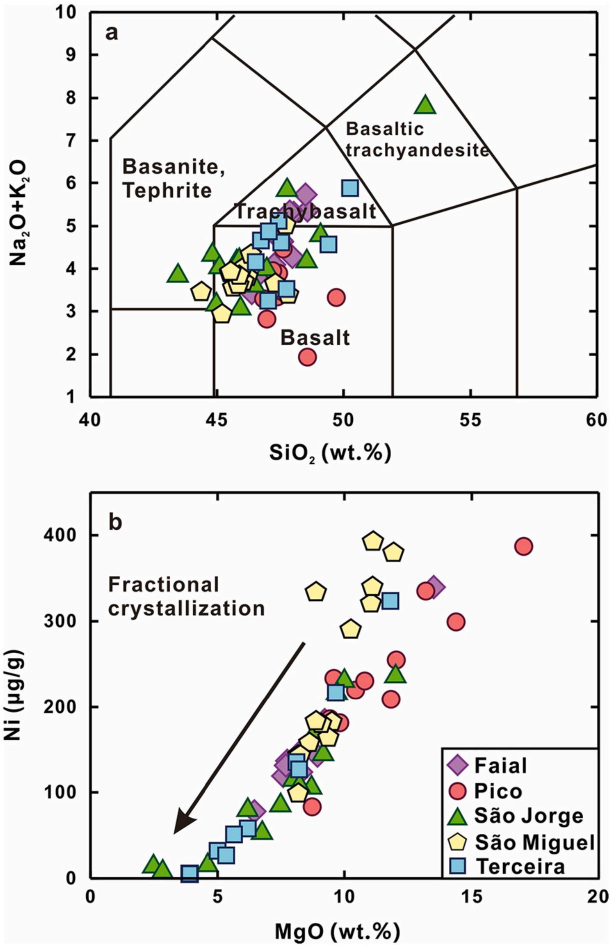

Fig. 3. (a) Total alkalis versus SiO_2 (wt%) and (b) plot of Ni (μg/g) versus MgO (wt%) of Azores OIB.

Terceira has been ascribed to both a HIMU-type component with radiogenic $^{206}Pb/^{204}Pb$ carried by the Azores plume and the contribution of delaminated sub-continental lithospheric mantle residing in the upper mantle with less radiogenic $^{206}Pb/^{204}Pb$, $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ (Madureira et al., 2011). São Miguel basalts exhibit an unusually enriched mantle (EM) component with highly radiogenic Sr and Pb isotope ratios (Fig. 2), which have been variously attributed to subcontinental lithospheric mantle, recycled sediment, or an ancient (~3 Ga) basaltic melt in oceanic lithospheric mantle (Widom and Shirey, 1996; Elliott et al., 2007; Turner et al., 2007; Genske et al., 2016).

In this study, we analyzed 59 samples from the Azores archipelago, including 11 from Faial, 11 from Pico, 14 from São Jorge, 14 from São Miguel, and 9 from Terceira (WAF/AF, WAP/AP, WASJ/ASJ, WASM, and WAT/AT series, respectively). These samples are mainly young (<4 Ma; Yu, 2011 and references therein), subaerial fresh basalts and trachybasalts (Fig. 3a), with variable crystal contents. Most Pico, São Miguel and Faial samples are olivine rich (>10% olivine), and most are also clinopyroxene (cpx) rich (>20% cpx). Samples from São Jorge and Terceira have lower crystal contents, with <10% by volume of olivine and cpx. In addition, most samples in this study have microcrystalline matrices, including feldspar microphenocrysts between ~50 and 250 μm. The textures of the Azores lavas are predominantly porphyritic with the major phenocryst phases (olivine and clinopyroxene) surrounded by microcrystalline matrix (Fig. S1).

3. Analytical methods

Barium purification procedures were performed in an ISO-Class 6 clean laboratory of the CAS Key Laboratory of Crust-Mantle Materials and Environments at the University of Science and Technology of China (USTC). The details of the purification procedure are described in Nan et al. (2018). All reagents used were high purity acids that were double-distilled and diluted with ultrapure 18.2 MΩ·cm water. Barium was purified from the matrix using AG50W-X12 (200–400 mesh, Bio–Rad, USA) cation exchange resin following established procedures (Nan et al., 2018). Sample powders containing ~0.5 μg Ba were dissolved in 7 ml Teflon® PFA screw-top beakers (Savillex®) using a 3:1 (v/v) mixture of concentrated HF and HNO_3. After drying and treating with aqua regia and HCl to remove fluorides, the samples were dissolved in 3 mol L^{-1} HCl for column separation. The sample solution was passed through the first column with 2 ml AG50W-X12 resin, and Ba was collected using 4 mol L^{-1} HNO_3 after eluting the matrix elements with 3 mol L^{-1} HCl. After that, an additional column with 0.5 ml AG50W-X12 resin was applied to further separate Ba from rare earth elements (e.g., Ce). The resin was conditioned with 3 ml 2 mol L^{-1} HNO_3, and the samples were loaded with 1 ml 2 mol L^{-1} HNO_3. Barium was finally collected in 16 ml 2 mol L^{-1} HNO_3 after matrix elements were eluted with 5 ml 2 mol L^{-1} HNO_3. The recovery of the purification process was >99%, and the total procedural blank was <5 ng.

Barium isotope compositions were analyzed using a multiple-collector inductively coupled plasma mass spectrometer (MC-ICP–MS, Thermo-Fisher Scientific Neptune-Plus) in the same laboratory at the USTC. A ^{135}Ba—^{136}Ba double-spike pair with the optimum ratio of 1.72 was used to correct the mass bias of instrumental fractionation. The sample/standard solution containing ~100 ng Ba was mixed with an appropriate amount of the ^{135}Ba—^{136}Ba spike solution such that the $^{135}Ba/^{134}Ba$ ratio in the mixture was approximately 23. An Aridus II desolvating nebulizer (CETAC Technologies) was used to obtain high sensitivity. ^{131}Xe, ^{134}Ba, ^{135}Ba, ^{136}Ba, ^{137}Ba, and ^{140}Ce were collected on Faraday cups L4, L2, L1, C-cup, H1 and H3, respectively. ^{131}Xe and ^{140}Ce were monitored for interferences of ^{134}Ba and ^{136}Ba. The fractionation factor β of Ce and Xe isotopes was assumed to be the same as that of Ba isotopes. Before the measurement, the sample solutions were diluted to 100 ng/g. The background signal for ^{137}Ba (<0.005 V) was negligible relative to the sample signals (~ 7 V). The long-term 2 SD precision of $\delta^{137/134}Ba$ ($\delta^{137/134}Ba = [(^{137/134}Ba_{sample})/(^{137/134}Ba_{SRM3104a})-1] \times 1000‰$) based on measurements of in-house standards of USTC-Ba and ICPUS-Ba is ±0.04‰ (Nan et al., 2018). Because most Ba isotope data reported in the literature are $\delta^{138/134}Ba$ values, we also report Ba isotope data as $\delta^{138/134}Ba$ here, which are recalculated as $\delta^{137/134}Ba \times 1.33$. The $\delta^{138/134}Ba$ values of the international reference materials BHVO-2 and BCR-2 agree well with published data, and all of the replicated samples are consistent within error (Table 1).

4. Results

The major element, trace element, $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$ data are from Yu (2011) (Table 1 and Table S1). The Azores samples have SiO_2 ranging from 43.5 to 53.2 wt% and MgO from 2.5 to 17.0 wt%, and exhibit a trend of decreasing Ni with decreasing MgO (Fig. 3b). The primitive magmas in the Azores have been inferred to have MgO contents of ~12 wt% (Beier et al., 2006). Samples with MgO > 12 wt% are considered to result from the accumulation of olivine and cpx, and samples with MgO < 12 wt% are considered to have been affected by fractional crystallization. Fig. 3b shows that most of the Pico samples have substantially higher MgO (up to 17.04 wt%) than the other samples, consistent with their high crystal contents (>20% olivine and cpx crystals).

Among the samples analyzed, those from São Miguel have large variations in both $^{87}Sr/^{86}Sr$ (0.703440 to 0.705996) and $^{206}Pb/^{204}Pb$ (19.319 to 20.095), and those from São Jorge and Terceira have HIMU and/or FOZO signatures with high $^{206}Pb/^{204}Pb$ ratios (19.339 to 20.367) and limited $^{87}Sr/^{86}Sr$ variation (0.703412 to 0.703857). Most Faial and Pico samples have lower $^{206}Pb/^{204}Pb$ (19.052 to 19.977) but

Table 1
Barium isotopes, ^{87}Sr/^{86}Sr and ^{206}Pb/^{204}Pb data of ocean island basalts from Azores archipelago.

Samples	$\delta^{137/134}$Ba	2SD	n	$\delta^{138/134}$Ba[#]	^{87}Sr/^{86}Sr	^{206}Pb/^{204}Pb	Ba (μg/g)
WASM1	0.02	0.03	2	0.03	0.704478	19.892	363
WASM1a	0.01	0.04	2	0.02			363
WASM5	0.01	0.04	2	0.02	0.705751	20.095	326
WASM5-R	0.01	0.02	2	0.02			
WASM7	−0.01	0.03	2	−0.02	0.705343	19.951	378
WASM10	0.03	0.01	2	0.04	0.705996	20.019	477
WASM16	0.04	0.01	2	0.05	0.704662	19.907	320
WASM17	0.00	0.03	2	0.00	0.703827	19.642	410
WASM19	0.04	0.01	2	0.05	0.703505	19.319	391
WASM22	0.05	0.03	2	0.06	0.703506	19.509	378
WASM23	0.04	0.04	3	0.05	0.703462	19.465	384
WASM24	0.00	0.04	2	0.00	0.703518	19.533	378
WASM28	0.02	0.00	2	0.02	0.703440	19.424	402
WASM29	0.00	0.04	2	0.00	0.703468	19.469	393
WASM32	0.01	0.02	2	0.01	0.704910	19.828	433
WASM33	0.01	0.04	2	0.01	0.704784	19.908	484
WAF1a	0.01	0.02	2	0.02	0.703885	19.579	227
WAF3	0.02	0.05	2	0.03	0.703735	19.407	311
WAF10	0.02	0.03	2	0.03	0.703780	19.387	288
WAF11	0.03	0.03	2	0.05	0.703735	19.443	322
WAF15	0.03	0.02	2	0.04	0.703807	19.436	319
WAF24	0.00	0.00	2	0.01	0.704021	19.307	454
WAF25	0.02	0.04	4	0.02	0.703921	19.299	484
WAF30	0.00	0.05	2	0.01	0.703912	19.299	291
WAF31	0.02	0.01	2	0.02	0.703662	19.336	615
AF4	0.01	0.02	4	0.01	0.704011	19.052	440
AF4-R	0.00	0.04	2	0.00			
AF15	0.00	0.04	4	0.00	0.704000	19.185	422
WAP3	0.03	0.00	2	0.04	0.703833	19.687	220
WAP6	0.02	0.03	2	0.03	0.703817	19.563	347
WAP8	0.04	0.04	2	0.06	0.703632	19.977	225
WAP9	0.01	0.03	3	0.02	0.703935	19.519	285
WAP9-R	0.02	0.04	2	0.03			
WAP10	0.04	0.03	2	0.05	0.703780	19.887	112
WAP25	0.03	0.03	2	0.04	0.703819	19.943	194
WAP28	0.04	0.01	2	0.05	0.703683	19.851	266
WAP30	0.02	0.04	2	0.02	0.703788	19.888	318
WAP33a	0.02	0.03	2	0.02	0.703784	19.478	261
AP4	0.03	0.04	2	0.03	0.703501	19.836	240
AP14	0.03	0.03	2	0.04	0.703519	19.601	149
WASJ3	0.03	0.01	2	0.04	0.703857	19.363	380
WASJ5	0.04	0.05	4	0.05	0.703420	20.081	265
WASJ7	0.03	0.01	2	0.03	0.703431	19.960	245
WASJ13	0.04	0.02	2	0.05	0.703593	19.895	236
WASJ14	0.01	0.02	2	0.01	0.703680	19.683	289
WASJ15	0.02	0.01	2	0.03	0.703759	19.393	227
WASJ16	0.06	0.01	2	0.08	0.703619	19.531	513
WASJ17	0.03	0.01	2	0.04	0.703702	20.056	347
WASJ18	0.02	0.00	2	0.03	0.703495	19.691	289
WASJ19	0.01	0.00	2	0.01	0.703745	19.339	293
WASJ20	0.00	0.03	4	0.00	0.703759	19.804	303
WASJ21	0.01	0.03	2	0.02	0.703758	20.367	230
WASJ21-R	0.03	0.00	2	0.04			
WASJ27	0.01	0.00	2	0.01	0.703493	19.855	200
WASJ29	0.03	0.00	2	0.04	0.703477	19.794	249
WAT1	0.00	0.02	2	0.01	0.703599	19.982	340
WAT3	0.00	0.04	3	0.00	0.703443	19.768	270
WAT3-R	0.01	0.01	2	0.01			
WAT4	0.05	0.02	2	0.07	0.703555	19.766	289
WAT5	−0.02	0.02	2	−0.03	0.703503	19.598	419
WAT8	0.10	0.04	2	0.13	0.703412	19.603	737
WAT11	0.04	0.02	2	0.05	0.703568	20.002	397
WAT15	0.18	0.01	3	0.23	0.703467	19.492	576
WAT15-R1	0.19	0.03	2	0.25			
WAT15-R2	0.18	0.00	2	0.24			
WAT18	0.09	0.03	2	0.12	0.703430	19.694	607
AT30	0.18	0.02	2	0.23	0.703418	19.589	663

(*continued on next page*)

Table 1 (*continued*)

Samples	$\delta^{137/134}$Ba	2SD	n	$\delta^{138/134}$Ba$^{\#}$	^{87}Sr/^{86}Sr	^{206}Pb/^{204}Pb	Ba (μg/g)
BHVO-2	0.05	0.04	3	0.06			
	0.05[a]	0.03[a]	22[a]	0.07[a]			
BCR-2	0.04	0.02	2	0.05			
	0.05[a]	0.04[a]	13[a]	0.07[a]			

$\delta^{138/134}$Ba$^{\#}$ is calculated by $\delta^{137/134}$Ba × 1.33.
^{87}Sr/^{86}Sr and ^{206}Pb/^{204}Pb data are from Yu (2011).
R is replicated sample.
[a] Data from Nan et al. (2015).

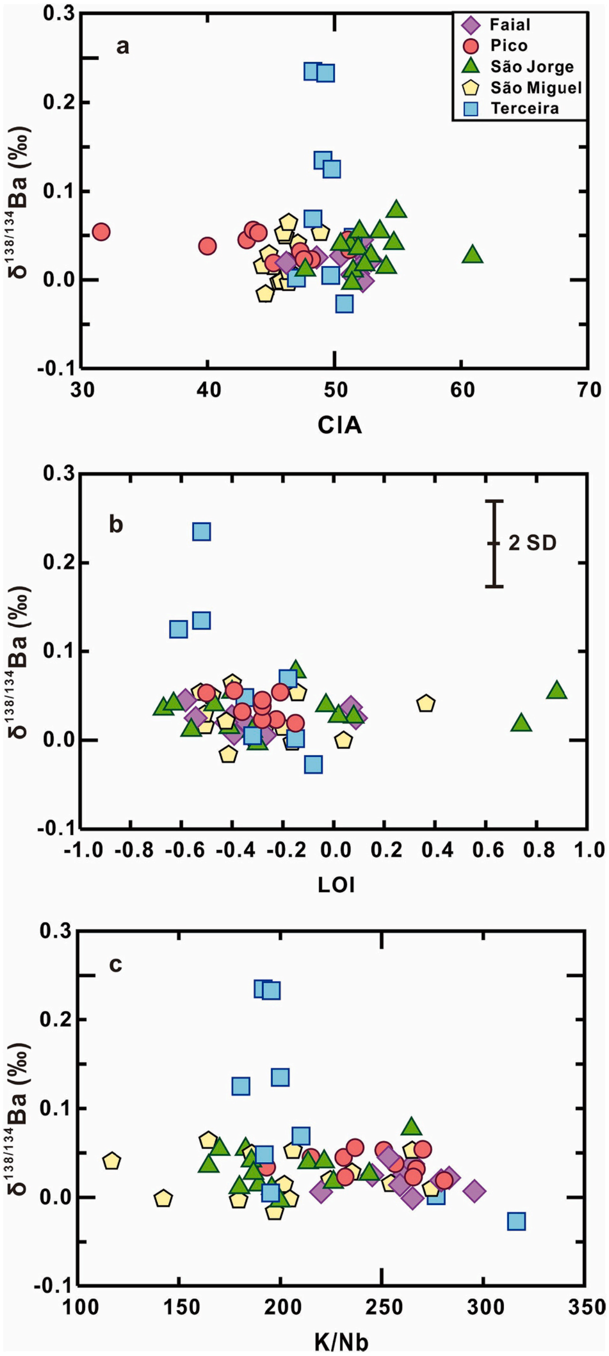

Fig. 4. Plots of $\delta^{138/134}$Ba versus (a) CIA, (b) LOI and (c) K/Nb.

slightly higher ^{87}Sr/^{86}Sr ratios (0.703501 to 0.704021) than the São Jorge and Terceira samples (Fig. 2).

Most Azores samples, with the exception of those from Terceira, have homogeneous $\delta^{138/134}$Ba (−0.02‰ to +0.08‰) despite heterogeneous radiogenic isotope signatures. In contrast, the Terceira samples have variable $\delta^{138/134}$Ba values, from −0.03‰ to +0.24‰.

5. Discussion

5.1. *Potential effects of partial melting, fractional crystallization, crustal assimilation, and post-eruptive processes on Ba isotopes*

5.1.1. *The effect of weathering processes on Ba isotopes*

The potential effects of any source-to-surface and weathering processes on the Ba isotope compositions of the Azores samples should be considered before using Ba isotopes to constrain mantle signatures. Strong chemical weathering can fractionate Ba isotopes (Gong et al., 2019). All Azores samples analyzed in this study are very fresh, and any visible weathered surfaces were removed during sample collection and/or by sawing prior to crushing. There is no evidence of secondary mineral phases in these samples. Although some Azores samples have a chemical index of alteration (CIA) higher than that of unweathered basalts (30 to 45, Nesbitt and Young, 1982), there is no correlation between Ba isotope ratios and CIA (Fig. 4a). The samples with high CIA (e.g., São Jorge samples) have homogeneous Ba isotope compositions, indicating that the Ba isotope signatures of these samples were not significantly affected by weathering.

5.1.2. *The effect of seawater alteration on Ba isotopes*

Seawater has heavy Ba isotopes ($\delta^{138/134}$Ba ≈ +0.3 to +0.6‰) compared with MORB (Horner et al., 2015; Nielsen et al., 2018; Nan et al., 2022), so seawater alteration could produce high $\delta^{138/134}$Ba in the AOC after a low-temperature reaction (up to +0.4‰, Nielsen et al., 2020). However, as opposed to submarine AOC, all Terceira basalts and the samples from other islands in this study were collected from subaerial eruptions. Photomicrographs show that the Azores samples have fresh, centimeter-sized, euhedral to sub-euhedral olivine and clinopyroxene crystals (Fig. S1), and no secondary minerals formed by seawater alteration have been observed. Seawater alteration would produce high LOI and high K/Nb ratios in altered basalts, because of the addition of water and K (but not Nb) during the formation of secondary minerals (Liu et al., 2021). The Azores samples analyzed in this study have a low LOI (loss on ignition) (< 1 wt%, Table S1, Fig. 4), and much lower K/Nb ratios (120 to 320) than those of AOC (300 to 1800; Zhong et al., 2017) (Fig. 4), also indicating that these samples did not experience strong seawater alteration. Seawater alteration could also increase Ba contents and produce a positive correlation between Ba contents and LOI (Zhang and Smith-Duque, 2014). However, there is no correlation between Ba isotopes or Ba contents and LOI (Figs. 4 and S2), arguing against the effects of seawater alteration on Ba contents and the Ba isotope signature of the Azores samples.

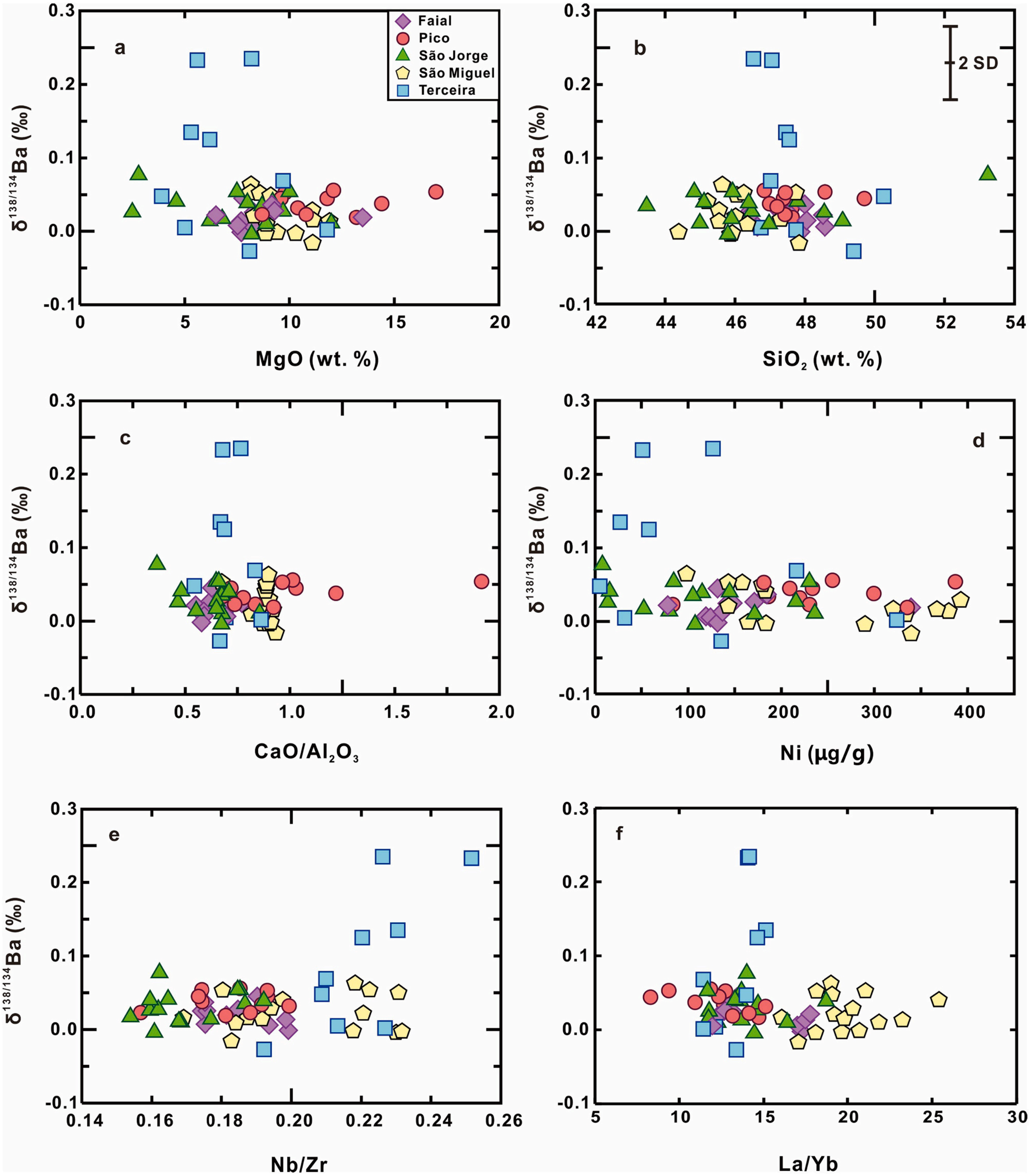

Fig. 5. Plots of $\delta^{138/134}$Ba versus (a) MgO (wt%), (b) SiO$_2$ (wt%), (c) CaO/Al$_2$O$_3$, (d) Ni (μg/g), (e) Nb/Zr, and (f) La/Yb.

5.1.3. The effect of partial melting and fractional crystallization processes on Ba isotopes

Major and trace element compositional variations among the Azores samples from each island have been attributed to variable degrees of partial melting and fractional crystallization (e.g., Bourdon et al., 2005; Beier et al., 2008) (Figs. 3b and 5). The large variations in CaO/Al$_2$O$_3$ and Ni contents reflect the variable degrees of fractional crystallization in the Azores samples. The lack of correlation of Ba isotope ratios with MgO (wt%), SiO$_2$ (wt%), CaO/Al$_2$O$_3$ or Ni contents (Fig. 5) confirms that fractional crystallization does not control the Ba isotope signatures of these samples. Variable degrees of partial melting will yield variations in Nb/Zr and La/Yb ratios due to the different compatibilities of these trace elements. The Azores samples have variable Nb/Zr and La/Yb ratios, but there is no correlation between $\delta^{138/134}$Ba and Nb/Zr or La/Yb ratios (Fig. 5), indicating that partial melting did not produce Ba isotope fractionation in these samples. These observations indicate that neither partial melting nor fractional crystallization impacted the Ba isotope compositions of the Azores samples.

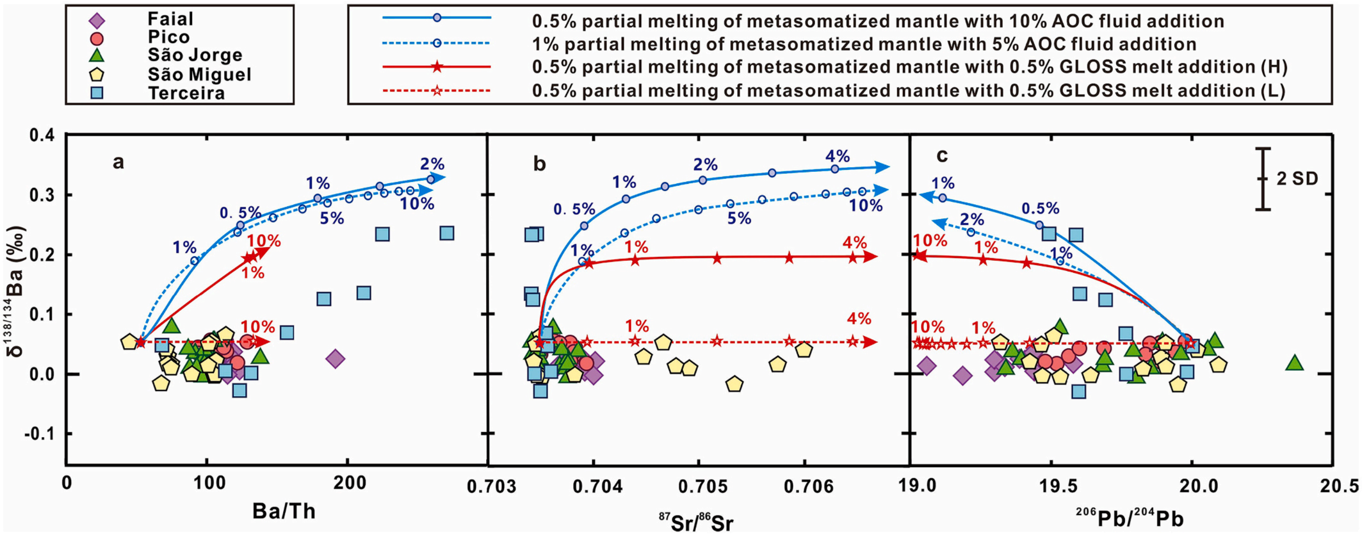

Fig. 6. Plots of $\delta^{138/134}$Ba versus (a) Ba (μg/g), (b) Ba/Th, (c) ^{206}Pb/^{204}Pb, and (d) ^{87}Sr/^{86}Sr. The calculated results show the mixing trends (red and blue curves) between melts from recycled metasomatized mantle components and melts from mantle plume. The recycled metasomatized mantle components either reacted with fluids dehydrated from subducted AOC or with subducted sediment-derived melts that have different Ba isotope compositions. Both the dehydration degree of oceanic crust and the partial melting degree of GLOSS sediments are set as 5% in the modeling. The $\delta^{138/134}$Ba values of sediments are chosen as +0.05‰ (L-light) and +0.20‰ (H-heavy). These mantle components may have been recycled into the Azores mantle sources and partially melted. The melts mixed with an ascending mantle plume to produce basaltic magmas. The numbers beside the curves are the percentage of melts from different recycled metasomatized mantle components that contribute to the magmas. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5.1.4. *The effect of crustal assimilation on Ba isotopes*

Crustal assimilation could affect the geochemical compositions of the Azores basalts. A linear positive correlation between forsterite content and δ^{18}O in single olivine crystals in some Azores samples supports that assimilation and fractional crystallization (AFC) processes can produce low δ^{18}O values in Azores samples (Genske et al., 2013). However, δ^{18}O is particularly sensitive to crustal assimilation due to the very large differences between the δ^{18}O signatures of AOC and sediment versus that of the mantle. The potential effect of AFC on Ba isotopes has been estimated by modeling based on the equation of DePaolo (1981). All parameters used in the modeling are listed in Table S2, and are summarized as follows: The degree of magmatic differentiation (F) is varied from 0.9 to 0.3, the solid/liquid partition coefficient (D) is varied from 0.0005 to 0.075 based on the D values of crystallizing mineral phases (Blundy and Wood, 1991; Adam and Green, 2006), and the rate of assimilation to crystallization (r) is set to 0.25 following the oxygen isotope model of Genske et al. (2013). In this modeling, the Ba content of the original magma is set to 350 μg/g, which is the average Ba content of OIB (Sun and McDonough, 1989); and the $\delta^{138/134}$Ba of the original magma is set to +0.04‰, which is the $\delta^{138/134}$Ba of most Azores samples. The Ba contents of the oceanic crust used are 183 μg/g and 268 μg/g, which are the average Ba content and the highest Ba content of basalts from MAR (White and Schilling, 1978), respectively. To evaluate the maximum potential effect of crustal assimilation on Ba isotopes, the $\delta^{138/134}$Ba of wall-rock (MAR) used in the calculation is +0.4‰, which is the highest $\delta^{138/134}$Ba of AOC reported in the literature (Nielsen et al., 2018). The results suggest that even using the highest Ba content and Ba isotope value for oceanic crust in the modeling, the $\delta^{138/134}$Ba of magma would increase only from +0.04‰ to +0.09‰ by the point that only 30% of the original magma remains, assuming an r value of 0.25 (Genske et al., 2013). Based on the modeling, the AFC process could not modify the Ba isotope ratios of OIB lavas in the Azores sufficiently to produce the highest $\delta^{138/134}$Ba (+0.24‰) observed in Terceira samples. Thus, the heavy Ba isotopes of Terceira samples are more likely due to source heterogeneity.

5.2. *The origin of the heavy Ba isotope signature in basalts from Terceira Island*

The relatively constant $\delta^{138/134}$Ba values of samples from Faial, Pico, São Jorge and São Miguel indicate that their mantle sources, potentially dominated by the Azores mantle plume, have a relatively homogeneous Ba isotope composition similar to those of most MORB and mantle-derived carbonatites (Nielsen et al., 2018; Li et al., 2020; Nan et al., 2022). In contrast, the Ba isotope variations among Terceira samples imply that their mantle source contains other enriched material with heavy Ba isotope signatures.

The high ^{206}Pb/^{204}Pb (~19.5 to 20.0) and elevated ^{3}He/^{4}He and ^{20}Ne/^{22}Ne ratios of some Terceira samples have been attributed to a source component with recycled oceanic crust and lower mantle in the Azores mantle plume (e.g., Moreira et al., 1999; Madureira et al., 2005; Stracke et al., 2005). The high ^{3}He/^{4}He and ^{20}Ne/^{22}Ne suggest that Terceira is fed by a mantle plume containing a relatively undegassed reservoir from the deep mantle, and the radiogenic Pb isotopes are attributed to recycled oceanic crust, which lost soluble Pb during subduction, resulting in high U/Pb and Th/Pb and, with time, radiogenic Pb isotope signatures. However, the samples with the highest ^{206}Pb/^{204}Pb in the Azores (including São Jorge and some of the Terceira samples) have mantle-like $\delta^{138/134}$Ba (Fig. 6), suggesting that the inferred HIMU/FOZO mantle plume component beneath the Azores is not characterized by heavy Ba isotope compositions, despite an inferred subducted oceanic crust component.

Previous studies from several different IODP sites have reported differing findings regarding the variability of Ba isotope signatures in AOC (Nan et al., 2017; Nielsen et al., 2018). For example, $\delta^{138/134}$Ba in AOC samples from IODP 1256 are highly variable (−0.23 to +0.40‰; Nan et al., 2017), whereas in IODP 504B the variations in $\delta^{138/134}$Ba for AOC samples were quite limited (−0.09 to +0.15‰) and similar to mantle values (Nielsen et al., 2018). Therefore, any subducted oceanic crust incorporated in the Azores HIMU/FOZO mantle plume may either have lacked distinctive Ba isotope compositions, or may have lost its distinctive Ba isotope signatures during dehydration. In either case, mixing between the Azores plume and an additional enriched component with low ^{206}Pb/^{204}Pb but high $\delta^{138/134}$Ba is needed to explain the

Terceira data. As the mantle has a relatively homogeneous Ba isotope composition compared with crustal materials, and neither partial melting nor fractional crystallization can produce melts with heavy Ba isotope signatures (Li et al., 2020; Nielsen et al., 2020; Wu et al., 2020; Nan et al., 2022), the relatively high $\delta^{138/134}$Ba values of the Terceira samples are most likely inherited from subducted crustal materials.

Slab-derived fluids can have heavy Ba isotope signatures (Wu et al., 2020; Gu et al., 2021). Hydrous fluid released from a subducted slab is expected to have both high Ba abundances and high Ba/Th, because Ba is highly fluid mobile, whereas Th is fluid immobile, and these two elements will be strongly fractionated during slab dehydration (Kessel et al., 2005). Therefore, a positive correlation between $\delta^{138/134}$Ba and Ba/Th may suggest the contribution of slab-derived hydrous fluids. For example, Tonga arc lavas show a positive correlation between $\delta^{138/134}$Ba and Ba/Th, which was interpreted to reflect the addition of Ba-rich slab-derived fluids with high $\delta^{138/134}$Ba to their mantle wedge sources (Wu et al., 2020). In addition, high-pressure veins within the Hualiangting eclogites and the nearby amphibolites, formed by subduction-zone fluid metasomatism, have much higher $\delta^{138/134}$Ba values (up to +0.47‰) than the average mantle and wall-rock eclogites (Gu et al., 2021), further supporting that deep subduction-related fluid metasomatism can produce heavy Ba isotope signatures in the mantle. Therefore, a mantle component metasomatized by fluid enriched in heavy Ba isotopes, if present beneath Terceira, could produce Terceira basalts with high $\delta^{138/134}$Ba and high Ba/Th.

It is notable that marine sediments can also have high Ba abundances (up to 1.94 wt%) and high Ba/Th ratios (up to 7000, Plank and Langmuir, 1998). Although most marine sediments have MORB-like Ba isotope signatures, few of them have high $\delta^{138/134}$Ba (up to +0.20‰) (Bridgestock et al., 2018, 2019; Crockford et al., 2019). Thus, subduction-modified mantle components metasomatized by sediment-derived melt, which has high Ba contents, high Ba/Th and high $\delta^{138/134}$Ba, could be another candidate. However, there is no evidence from trace elements or radiogenic isotopes (e.g., Sr isotopes), indicating that the mantle source of Terceira contains a significant amount of subducted sediments (Moreira et al., 1999; Madureira et al., 2011).

5.3. Involvement of fluid-metasomatized mantle in Azores OIB by plume-mantle interaction

Given that there is no active subduction in the vicinity of the Azores Archipelago (Fig. 1), any mantle source with a subducted AOC signature beneath Terceira must be an ancient heterogeneity that has persisted in the mantle. Previous research has revealed the presence of mantle with high carbon and water contents and arc-like trace element signatures indicative of carbonated subduction-modified mantle components in the upper mantle beneath the Atlantic Ocean basin (Hauri et al., 2018). These subduction-modified mantle components may be related to metasomatism by AOC-derived fluids from prior episodes of Iapetus subduction in the Silurian (~420 Ma ago) during the accretion of Neoproterozoic arc terranes to Laurussia (Nance et al., 2010). Such subduction-modified mantle components may have been widely distributed in the Atlantic upper mantle, leading to their presence beneath the Azores.

Interaction between the Azores mantle plume and such metasomatized mantle components could explain the heavy Ba isotope signatures of the Terceira samples. A mass balance modeling of such a process is demonstrated in Fig. 6. In this model, we evaluate contributions from both fluids released from subducted AOC and melts derived from subducted sediment, assuming that both the degree of subducted crust dehydration and the degree of partial melting of marine sediment were ~ 5%. Because the AOC is the primary component of the subducted slab and recycled sediment involved in OIB sources is generally less than a few percent (Chauvel et al., 2007; Jackson et al., 2007), our modeling assumes the addition of ~5–10% AOC-derived hydrous fluid or 0.5% sediment-derived melt to the mantle wedge. The $\delta^{138/134}$Ba value for the AOC end-member is defined as +0.40‰, which is the highest value reported in a previous study (Nielsen et al., 2018). Given that some marine sediments may have extremely high Ba contents, even a minor sediment contribution can significantly affect the Ba isotope compositions of the mixture. A previous study inferred that there is Ba isotope fractionation between melts and sediment residue, and partial melting could produce melt with lighter Ba isotopes ($\Delta^{138}/^{134}\text{Ba}_{\text{melt/residue}} \sim -0.12$ to -0.15‰, Nielsen et al., 2020). Because the present model is not concerned with the origin of light Ba isotopes, the $\delta^{138/134}$Ba values for the sediment end-member are defined as +0.05 or +0.20‰ for simplicity, spanning the range of most marine sediments. Other parameters used in modeling are listed in Table S3.

The resulting metasomatized mantle component, subject to convection in the upper mantle, is assumed to have been recycled into the region beneath Terceira through mantle convection and above the ascending Azores mantle plume. The modeling results suggest that mixtures of melts from the Azores plume and melts from the shallow metasomatized mantle component, in variable relative proportions, can explain the compositional range of the Terceira samples. However, it is important to note that only the model involving AOC-derived fluid can explain the Terceira data, because the partial melting of the mantle component metasomatized by sediment melt cannot produce the full range of Ba isotope signatures in the Terceira samples.

Furthermore, the combined Ba and Sr isotope signatures of the Terceira samples may reflect a low degree of partial melting (0.5% or 1%) of the recycled enriched mantle component. Although both Ba and Sr are incompatible during mantle partial melting, Ba has a much lower partition coefficient (D) than Sr (0.00012 for Ba and 0.025 for Sr, Workman and Hart, 2005). Melts formed by low degrees of partial melting would have high Ba contents and high Ba/Sr. Thus, mixing of melts from the metasomatized mantle component with low degrees of partial melting could result in elevated $\delta^{138/134}$Ba without a significant change in Sr isotope ratios (Fig. 6b). If the recycled enriched mantle component is younger than 420 Ma, it would have lower ^{87}Sr/^{86}Sr ratios than the ratios used in the model. Therefore, mixing with a younger recycled mantle would increase $\delta^{138/134}$Ba more rapidly without disturbing Sr isotopes.

Collectively, we propose that the high $\delta^{138/134}$Ba component in the mantle source of Terceira is most likely to be a recycled mantle component, which was dominantly metasomatized by subducted AOC-derived fluids. Similar arc geochemical-isotope signatures have been observed in MORB suites. For example, the geochemical signatures of MORB from the Western Gakkel Ridge region in the Arctic Ocean reflect that the upper mantle underneath this area is heterogeneous, and the origin of this heterogeneity was subduction-modified mantle without deep mantle cycling (Richter et al., 2020). In addition, the highly depleted heavy rare earth element (HREE) and Ti concentrations of clinopyroxene (Cpx) from 16°N abyssal peridotites from the Mid-Atlantic Ridge indicate that hydrous melting was required to form such depleted compositions without exhausting Cpx (Urann et al., 2020). Low-density and buoyant refractory harzburgitic parcels, which formed in arc-mantle wedge settings and recycled from subduction zones to mid-ocean ridges, are likely ubiquitous mantle components (Shorttle et al., 2014; Urann et al., 2020). A recent study also found that water-rich basalt glasses from the Southwestern Indian Ocean Ridge (SWIR), which is located far from any recent subduction zone, have higher H_2O/Ce ratios, heavier H isotopes and lower Ce/Pb ratios than global MORBs (Liu et al., 2022). The low La/Sm, Ce/Yb, and Sm/Yb ratios of these glasses are different from those of the other ridge basalts affected by the mantle plume, indicating that their high H_2O/Ce ratios and heavy H isotope compositions are likely inherited from mantle wedge residue recycling into the upper asthenosphere (Liu et al., 2022). These examples provide evidence that the mantle wedge residue could remain in the shallow position of the mantle.

Terceira samples with high $\delta^{138/134}$Ba have high Ba/Nb, Ba/Th, and Nb/U ratios (Fig. 6 and Fig. S3). This is consistent with previous

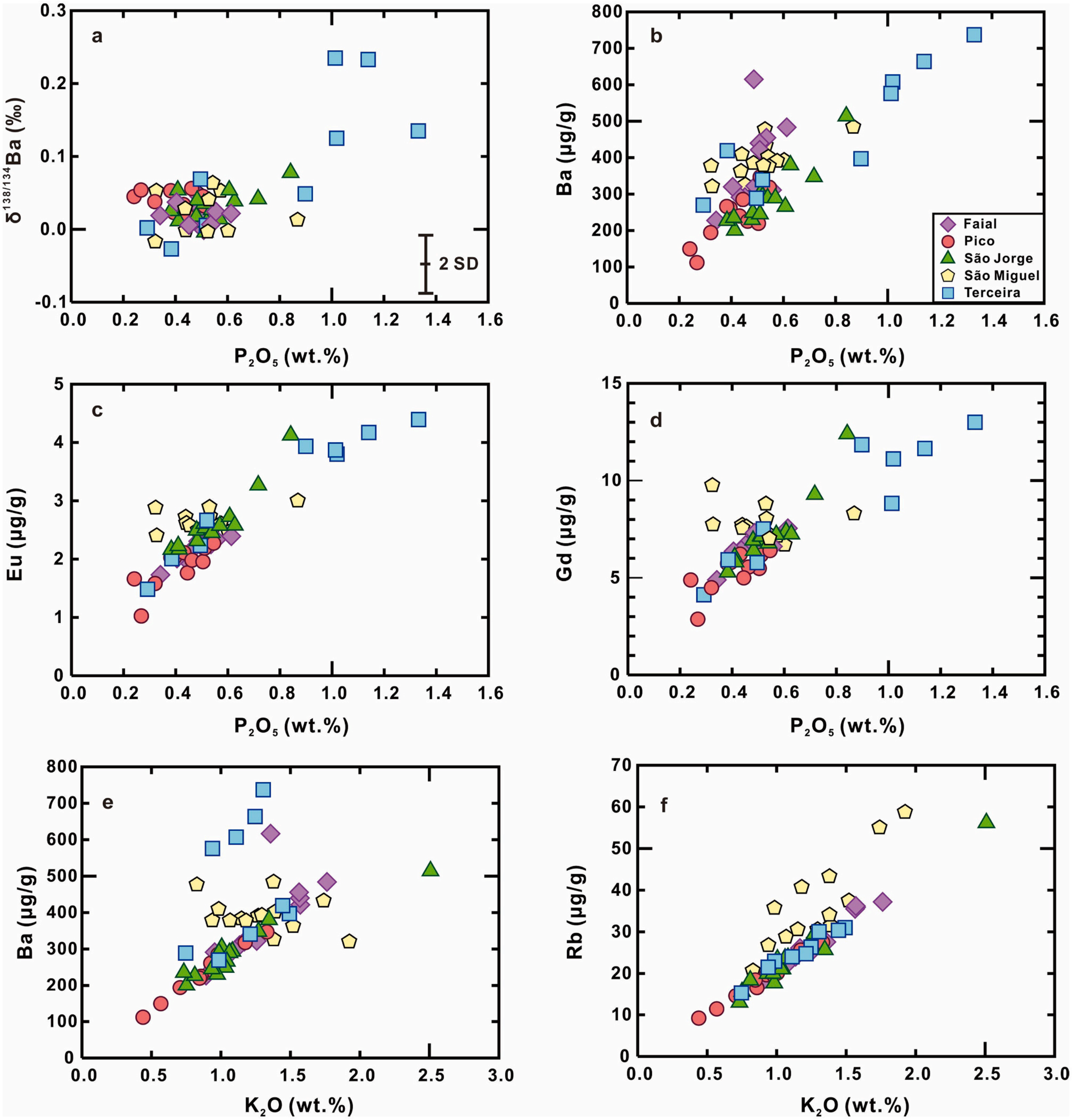

Fig. 7. Variation in $\delta^{138/134}$Ba and selected trace elements vs P_2O_5 and K_2O. P_2O_5 vs (a) $\delta^{138/134}$Ba, (b) Ba, (c) Eu, (d) Gd, and K_2O vs (e) Ba and (f) Rb. Ba, Eu and Gd are positively correlated with P_2O_5, which is consistent with melting of a metasomatized apatite-bearing mantle source. The Ba and K_2O of Terceira samples are not correlated, indicating that the compositions of Terceira samples were not controlled by phlogopite melting.

observations that some basalts from the Fissural volcanic system of Terceira Island have high Ba/Nb, Ba/Th, Nb/U, and Nb/Zr and less radiogenic ^{206}Pb/^{204}Pb (Madureira et al., 2011). Their ^{206}Pb/^{204}Pb ratios were negatively correlated with Nb/U ratios, which is also observed in this study (Fig. S3). Madureira et al. (2011) suggested that the source of Fissural volcanic samples may contain amphibole-rich domains in the upper mantle beneath Terceira, accounting for the high Ba/Nb, Ba/Th, Nb/U, and Nb/Zr ratios. These Terceira samples with high $\delta^{138/134}$Ba also have high P_2O_5 contents, indicating a phosphate-rich origin. A previous study showed that the orthopyroxene (Opx) grains of abyssal peridotites from the SWIR hosted mineral inclusions of primarily diopside associated with apatite and other minerals, implying that the suboceanic asthenosphere reacted with phosphate-rich melts (Seyler et al., 2004). In addition, Proterozoic gabbros in eastern Canada are enriched in P_2O_5 and K_2O and are most consistent with the melting of subcontinental lithospheric mantle, that has been metasomatized by melts of phosphate-rich components (Rogers et al., 2019). It is highly possible that the recycled mantle wedge beneath Terceira was an apatite-bearing mantle, and partial melting of this mantle could produce magma with high Ba, Eu, Gd, and P_2O_5 contents and high $\delta^{138/134}$Ba (Fig. 7). Besides apatite, the mantle source of Proterozoic gabbros in eastern Canada also contained phlogopite, which contributed high K_2O, Ba, and Rb contents (Rogers et al., 2019). However, Terceira samples with high $\delta^{138/134}$Ba do not have high K_2O contents. There is no positive

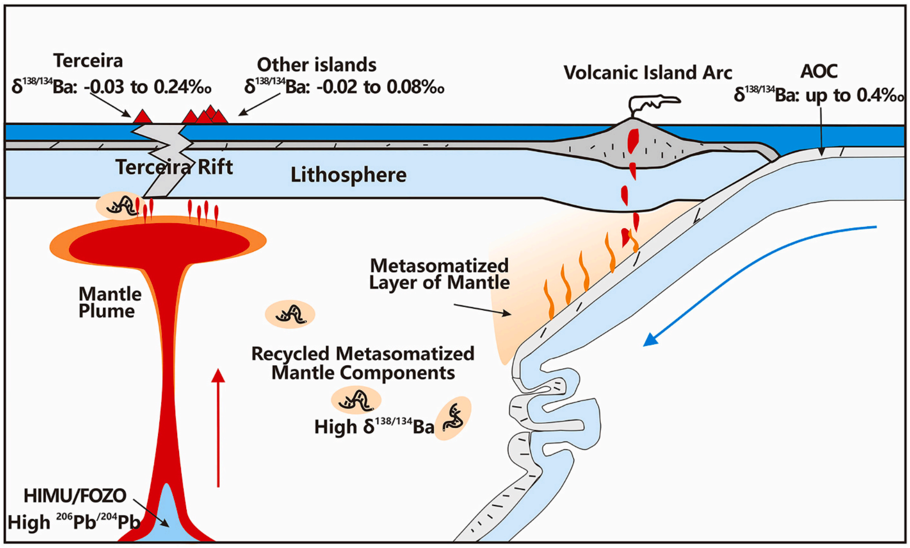

Fig. 8. Cartoon (not to scale) of the mantle source of the Azores OIB (modified after Donnelly et al., 2004). The OIB from all islands are related to the melting of a common heterogeneous mantle plume, but the Terceira magmatism involves an additional recycled metasomatized mantle component that inherited the signature of AOC-derived hydrous fluids.

correlation between Ba and K_2O contents, and at a given K_2O, Terceira samples with heavy Ba isotopes have higher Ba contents than the other samples (Fig. 7e), indicating phlogopite is not the source of Ba in Terceira samples. Therefore, melting of the metasomatized apatite-bearing mantle was pivotal in influencing the Ba contents and isotope compositions of Terceira samples.

Although the details of the metasomatized mantle component recycling process cannot be constrained with a unique model, a general scenario involving subduction-modified mantle beneath Terceira is viable (Fig. 8). A fluid metasomatized mantle component was dispersed by convection within the mantle and to the region beneath Terceira, which finally produced magmas on Terceira with heavy Ba isotope compositions. This enriched component contributes to magmas on Terceira and reflects a small, phosphate-rich, shallow mantle anomaly that resides only beneath Terceira. A recent 3-D numerical modeling suggests that plumes may be shaped like trees that branch toward the surface, producing volcanoes with multiple subparallel hot spot tracks, such as those observed in the Pacific and Atlantic Oceans (Liu and Leng, 2020). In this scenario, a plume branch may have incorporated a unique enriched, shallow, subduction-modified mantle component beneath Terceira to produce the distinctive Ba isotope compositions observed only in Terceira basalts.

This inferred subduction-modified mantle component would likely not exist only beneath Terceira Island, but could be dispersed more widely beneath the MAR. Likewise, a previous study proposed that there is mantle wedge residue recycled into the upper asthenosphere beneath the Indian Ocean Ridge (Liu et al., 2022). Therefore, it will be important to analyze Ba isotopes of basalt glasses from both the MAR and SWIR to provide further constraints on the potential existence of recycled metasomatized mantle components in the shallow position of the Atlantic and Indian mantle.

6. Conclusions

This study reports Ba isotope compositions for basalts from five islands (Faial, Pico, São Jorge, São Miguel, and Terceira) of the Azores archipelago. These samples have large variations in radiogenic Sr-Nd-Pb-Hf isotope compositions, reflecting that they have different enriched components in their mantle sources. Except for samples from Terceira, all samples from Faial, Pico, São Jorge, and São Miguel have homogeneous and MORB-like Ba isotopes, indicating that those enriched components in their mantle sources did not produce heterogeneous Ba isotope signatures. While the OIB from all of the Azores Islands might be related to melting of a common mantle plume, the MORB-like Ba isotope composition indicates that the Azores mantle plume has a homogeneous and MORB-like Ba isotope composition.

Terceira samples have variable Ba isotopes (from −0.03 to +0.24‰). The Ba isotope signatures indicate that an additional enriched component in the mantle source of Terceira formed via different processes from those of Faial, Pico, São Jorge, and São Miguel. The negative correlation between $\delta^{138/134}$Ba and ^{206}Pb/^{204}Pb and the positive correlation between $\delta^{138/134}$Ba and Ba/Th among select Terceira samples may reflect the signature of subduction-released fluids, with the heavy Ba isotopes inherited from subducted AOC. Because the Azores archipelago is far from any active subduction zone, the AOC-derived hydrous fluids could not be added into the mantle beneath Terceira directly. The fluid signature could potentially be derived from an ancient fluid-metasomatized mantle component with heavy Ba isotopes, which was transported by mantle convection to its present location beneath Terceira. This study thus highlights the potential utility of Ba isotopes for constraining different types of recycled materials and supports that recycled metasomatized mantle components could be dispersed in the shallow mantle.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2022.121097.

References

Adam, J., Green, T., 2006. Trace element partitioning between mica- and amphibole-bearing garnet lherzolite and hydrous basanitic melt: 1. Experimental results and the investigation of controls on partitioning behaviour. Contrib. Mineral. Petrol. 152, 1–17.

Beier, C., Haase, K.M., Hansteen, T.H., 2006. Magma evolution of the Sete Cidades volcano, São Miguel, Azores. J. Petrol. 47, 1375–1411.

Beier, C., Stracke, A., Haase, K.M., 2007. The peculiar geochemical signatures of São Miguel (Azores) lavas: metasomatized or recycled mantle sources? Earth Planet. Sci. Lett. 259, 186–199.

Beier, C., Haase, K.M., Abouchami, W., Krienitz, M.S., Hauff, F., 2008. Magma genesis by rifting of oceanic lithosphere above anomalous mantle: Terceira Rift, Azores. Geochem. Geophys. Geosyst. 9.

Blundy, J.D., Wood, B.J., 1991. Crystal-chemical controls on the partitioning of Sr and Ba between plagioclase feldspar, silicate melts, and hydrothermal solutions. Geochim. Cosmochim. Acta 55, 193–209.

Bourdon, B., Turner, S.P., Ribe, N.M., 2005. Partial melting and upwelling rates beneath the Azores from a U-series isotope perspective. Earth Planet. Sci. Lett. 239, 42–56.

Bridgestock, L., Hsieh, Y.-T., Porcelli, D., Homoky, W.B., Bryan, A., Henderson, G.M., 2018. Controls on the barium isotope compositions of marine sediments. E Earth Planet. Sci. Lett. 481, 101–110.

Bridgestock, L., Hsieh, Y.-T., Porcelli, D., Henderson, G.M., 2019. Increased export production during recovery from the Paleocene–Eocene thermal maximum constrained by sedimentary Ba isotopes. Earth Planet. Sci. Lett. 510, 53–63.

Chauvel, C., Lewin, E., Carpentier, M., Arndt, N.T., Marini, J.-C., 2007. Role of recycled oceanic basalt and sediment in generating the Hf–Nd mantle array. Nat. Geosci. 1, 64–67.

Crockford, P.W., Wing, B.A., Paytan, A., Hodgskiss, M.S., Mayfield, K.K., Hayles, J.A., Middleton, J.E., Ahm, A.-S.C., Johnston, D.T., Caxito, F., 2019. Barium-isotopic constraints on the origin of post-Marinoan barites. Earth Planet. Sci. Lett. 519, 234–244.

Deng, G., Kang, J., Nan, X., Li, Y., Guo, J., Ding, X., Huang, F., 2021. Barium isotope evidence for crystal-melt separation in granitic magma reservoirs. Geochim. Cosmochim. Acta 292, 115–129.

DePaolo, D.J., 1981. Trace element and isotopic effects of combined wallrock assimilation and fractional crystallization. Earth Planet. Sci. Lett. 53, 189–202.

Donnelly, K.E., Goldstein, S.L., Langmuir, C.H., Spiegelman, M., 2004. Origin of enriched ocean ridge basalts and implications for mantle dynamics. Earth Planet. Sci. Lett. 226 (3–4), 347–366.

Elliott, T., Blichert-Toft, J., Heumann, A., Koetsier, G., Forjaz, V., 2007. The origin of enriched mantle beneath Sao Miguel, Azores. Geochim. Cosmochim. Acta 71, 219–240.

Genske, F., Beier, C., Haase, K., Turner, S., Krumm, S., Brandl, P., 2013. Oxygen isotopes in the Azores islands: Crustal assimilation recorded in olivine. Geology 41 (4), 491–494.

Genske, F.S., Beier, C., Stracke, A., Turner, S.P., Pearson, N.J., Hauff, F., Schaefer, B.F., Haase, K.M., 2016. Comparing the nature of the western and eastern Azores mantle. Geochim. Cosmochim. Acta 172, 76–92.

Gong, Y., Zeng, Z., Zhou, C., Nan, X., Yu, H., Lu, Y., Li, W., Gou, W., Cheng, W., Huang, F., 2019. Barium isotopic fractionation in latosol developed from strongly weathered basalt. Sci. Total Environ. 687, 1295–1304.

Gu, X.F., Guo, S., Yu, H.M., Xu, J., Huang, F., 2021. Behavior of barium isotopes during high-pressure metamorphism and fluid evolution. Earth Planet. Sci. Lett. 575, 117176.

Hart, S., Hauri, E., 1992. Mantle plumes and entrainment: isotopic evidence. Science 256, 517.

Hauri, E.H., Maclennan, J., McKenzie, D., Gronvold, K., Oskarsson, N., Shimizu, N., 2018. CO_2 content beneath northern Iceland and the variability of mantle carbon. Geology 46, 55–58.

Horner, T.J., Kinsley, C.W., Nielsen, S.G., 2015. Barium-isotopic fractionation in seawater mediated by barite cycling and oceanic circulation. Earth Planet. Sci. Lett. 430, 511–522.

Jackson, M.G., Hart, S.R., Koppers, A.A.P., Staudigel, H., Konter, J., Blusztajn, J., et al., 2007. The return of subducted continental crust in Samoan lavas. Nature 448, 684–687.

Jean-Baptiste, P., Allard, P., Coutinho, R., Ferreira, T., Fourré, E., Queiroz, G., Gaspar, J., 2009. Helium isotopes in hydrothermal volcanic fluids of the Azores archipelago. Earth Planet. Sci. Lett. 281, 70–80.

Kessel, R., Schmidt, M.W., Ulmer, P., Pettke, T., 2005. Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120–180 km depth. Nature 437, 724–727.

Li, W.-Y., Yu, H.-M., Xu, J., Halama, R., Bell, K., Nan, X.-Y., Huang, F., 2020. Barium isotopic composition of the mantle: Constraints from carbonatites. Geochim. Cosmochim. Acta 278, 235–243.

Liu, H., Leng, W., 2020. Plume-tree structure induced by low-viscosity layers in the Upper Mantle. Geophys. Res. Lett. 47 (1) e2019GL086508.

Liu, H., Xue, Y.-Y., Zhang, G., Sun, W.-D., Tian, Z., Tuller-Ross, B., Wang, K., 2021. Potassium isotopic composition of low-temperature altered oceanic crust and its impact on the global K cycle. Geochim. Cosmochim. Acta 311, 59–73.

Liu, J., Tao, C., Zhou, J., Shimizu, K., Li, W., Liang, J., Liao, S., Kuritani, T., Deloule, E., Ushikubo, T., Nakagawa, M., Yang, W., Zhang, G., Liu, Y., Zhu, C., Sun, H., Zhou, J., 2022. Water enrichment in the mid-ocean ridge by recycling of mantle wedge residue. Earth Planet. Sci. Lett. 584, 117455.

Madureira, P., Moreira, M., Mata, J., Allègre, C.J., 2005. Primitive neon isotopes in Terceira Island (Azores archipelago). Earth Planet. Sci. Lett. 233, 429–440.

Madureira, P., Mata, J., Mattielli, N., Queiroz, G., Silva, P., 2011. Mantle source heterogeneity, magma generation and magmatic evolution at Terceira Island (Azores archipelago): constraints from elemental and isotopic (Sr, Nd, Hf, and Pb) data. Lithos 126, 402–418.

Millet, M.-A., Doucelance, R., Baker, J.A., Schiano, P., 2009. Reconsidering the origins of isotopic variations in Ocean Island Basalts: insights from fine-scale study of São Jorge Island, Azores archipelago. Chem. Geol. 265, 289–302.

Moreira, M., Allègre, C.-J., 2002. Rare gas systematics on Mid Atlantic Ridge (37–40°N). Earth Planet. Sci. Lett. 198, 401–416.

Moreira, M., Doucelance, R., Kurz, M.D., Dupré, B., Allègre, C.J., 1999. Helium and lead isotope geochemistry of the Azores Archipelago. Earth Planet. Sci. Lett. 169, 189–205.

Nan, Xiaoyun, Wu, Fei, Zhang, Zhaofeng, Hou, Zhenhui, Huang, Fang, Yu, Huimin, 2015. High-precision barium isotope measurements by MC-ICP-MS. J. Analyt. Atomic Spectro. 30 (11), 2307–2315.

Nan, X.Y., Yu, H.-M., Gao, Y.J., 2017. Barium isotope composition of altered oceanic crust from the IODP Site 1256 at the East Pacific rise: New Orleans, Louisiana. American Geophysical Union, Fall meeting supplement, abstract. V33C-0534.

Nan, X., Yu, H.-M., Rudnick, R.L., Gaschnig, R.M., Xu, J., Li, W.-Y., Zhang, Q., Jin, Z.-D., Li, X.-H., Huang, F., 2018. Barium isotopic composition of the upper continental crust. Geochim. Cosmochim. Acta 233, 33–49.

Nan, X., Yu, H., Kang, J., Huang, F., 2022. Re-visiting barium isotope compositions of mid-ocean ridge basalts and the implications. JUSTC 52 (3), 1. https://doi.org/10.52396/JUSTC-2021-0276.

Nance, R.D., Gutiérrez-Alonso, G., Keppie, J.D., Linnemann, U., Murphy, J.B., Quesada, C., Strachan, R.A., Woodcock, N.H., 2010. Evolution of the Rheic Ocean. Gondwana Res. 17, 194–222.

Nesbitt, H., Young, G., 1982. Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. Nature 299, 715–717.

Nielsen, S.G., Horner, T.J., Pryer, H.V., Blusztajn, J., Shu, Y., Kurz, M.D., Le Roux, V., 2018. Barium isotope evidence for pervasive sediment recycling in the upper mantle. Sci. Adv. 4, eaas8675.

Nielsen, S.G., Shu, Y., Auro, M., Yogodzinski, G., Shinjo, R., Plank, T., Kay, S.M., Horner, T.J., 2020. Barium isotope systematics of subduction zones. Geochim. Cosmochim. Acta 275, 1–18.

Plank, T., Langmuir, C.H., 1998. The chemical composition of subducting sediment and its consequences for the crust and mantle. Chem. Geol. 145, 325–394.

Richter, M., Nebel, O., Maas, R., Mather, B., Nebel-Jacobsen, Y., Capitanio, F.A., Dick, H. J.B., Cawood, P.A., 2020. An early cretaceous subduction-modified mantle underneath the ultraslow spreading Gakkel Ridge, Arctic Ocean. Sci. Adv. 6 (44), eabb4340.

Rogers, C., Cousens, B., Ernst, R.E., Söderlund, U., 2019. Phosphorus and potassium metasomatic enrichment in the mantle source of the c. 1450–1425 Ma Michael–Shabogamo gabbro of Eastern Laurentia. J. Petrol. 60 (1), 57–83.

Rudnick, R., Gao, S., 2003. Composition of the continental crust. Treatise Geochem. 3, 1–64.

Schaefer, B.F., Turner, S., Parkinson, I., Rogers, N., Hawkesworth, C., 2002. Evidence for recycled Archaean oceanic mantle lithosphere in the Azores plume. Nature 420, 304–307.

Seyler, M., Lorand, J.P., Toplis, M.J., Godard, G., 2004. Asthenospheric metasomatism beneath the mid-ocean ridge: evidence from depleted abyssal peridotites. Geology 32 (4), 301–304.

Shorttle, O., Maclennan, J., Lambart, S., 2014. Quantifying lithological variability in the mantle. Earth Planet. Sci. Lett. 395, 24–40.

Stracke, A., Hofmann, A.W., Hart, S.R., 2005. FOZO, HIMU, and the rest of the mantle zoo. Geochem. Geophys. Geosyst. 6.

Sun, S.-S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implication for mantle composition and processes. In: Saunders, A.D., Norry, M.J. (Eds.), Magmatism in the Ocean Basins, 42, pp. 313–345.

Teng, F.-Z., Watkins, J., Dauphas, N., 2017. Non-traditional stable isotopes. Rev. Mineral. Geochem. 82, 885p.

Turner, S., Hawkesworth, C., Rogers, N., King, P., 1997. U-Th isotope disequilibria and ocean island basalt generation in the Azores. Chem. Geol. 139, 145–164.

Turner, S., Tonarini, S., Bindeman, I., Leeman, W.P., Schaefer, B.F., 2007. Boron and oxygen isotope evidence for recycling of subducted components over the past 2.5 Gyr. Nature 447, 702–705.

Urann, B.M., Dick, H.J.B., Parnell-Turner, R., Casey, J.F., 2020. Recycled arc mantle recovered from the Mid-Atlantic Ridge. Nat. Commun. 11 (1), 1–9.

Waters, C., Day, J., Watanabe, S., Sayit, K., Zanon, V., Olson, K., Hanan, B., Widom, E., 2020. Sulfide mantle source heterogeneity recorded in basaltic lavas from the Azores. Geochim. Cosmochim. Acta 268, 422–445.

White, W.M., 1985. Sources of oceanic basalts: radiogenic isotopic evidence. Geology 13, 115–118.

White, W.M., Schilling, J.-G., 1978. The nature and origin of geochemical variation in Mid-Atlantic Ridge basalts from the Central North Atlantic. Geochim. Cosmochim. Acta 42, 1501–1516.

White, W.M., Schilling, J.G., Hart, S.R., 1976. Evidence for the Azores mantle plume from strontium isotope geochemistry of the Central North Atlantic. Nature 263, 659–663.

Widom, E., Shirey, S., 1996. Os isotope systematics in the Azores: implications for mantle plume sources. Earth Planet. Sci. Lett. 142, 451–465.

Widom, E., Carlson, R., Gill, J., Schmincke, H.-U., 1997. Th–Sr–Nd–Pb isotope and trace element evidence for the origin of the Sao Miguel, Azores, enriched mantle source. Chem. Geol. 140, 49–68.

Workman, R.K., Hart, S.R., 2005. Major and trace element composition of the depleted MORB mantle (DMM). Earth Planet. Sci. Lett. 231 (1), 53–72.

Wu, F., Turner, S., Schaefer, B.F., 2020. Mélange versus fluid and melt enrichment of subarc mantle: a novel test using barium isotopes in the Tonga-Kermadec arc. Geology 48 (11), 1053–1057.

Yu, H., 2011. Li, Hf and Os Isotope Systematics of Azores Basalts and a New Microwave Digestion Method for Os Isotopic Analysis. Miami University.

Zhang, G.L., Smith-Duque, C., 2014. Seafloor basalt alteration and chemical change in the ultra thinly sedimented South Pacific. Geochem. Geophys. Geosyst. 15, 3066–3080.

Zhong, Y., Chen, L.-H., Wang, X.-J., Zhang, G.-L., Xie, L.-W., Zeng, G., 2017. Magnesium isotopic variation of oceanic island basalts generated by partial melting and crustal recycling. Earth Planet. Sci. Lett. 463, 127–135.

Zindler, A., Hart, S., 1986. Chemical geodynamics. Annu. Rev. Earth Planet. Sci. 14, 493–571.