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# LETTERS

# Boron and oxygen isotope evidence for recycling of subducted components over the past 2.5 Gyr

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**Evidence for the deep recycling of surficial materials through the Earth's mantle and their antiquity has long been sought to understand the role of subducting plates and plumes in mantle convection. Radiogenic isotope evidence for such recycling remains equivocal because the age and location of parent–daughter fractionation are not known. Conversely, while stable isotopes can provide irrefutable evidence for low-temperature fractionation, their range in most unaltered oceanic basalts is limited and the age of any variation is unconstrained. Here we show that $\delta^{18}O$ ratios in basalts from the Azores are often lower than in pristine mantle. This, combined with increased Nb/B ratios and a large range in $\delta^{11}B$ ratios, provides compelling evidence for the recycling of materials that had undergone fractionation near the Earth's surface. Moreover, $\delta^{11}B$ is negatively correlated with $^{187}Os/^{188}Os$ ratios, which extend to subchondritic values[1], constraining the age of the high Nb/B, $^{11}B$-enriched endmember to be more than 2.5 billion years (Gyr) old. We infer this component to be melt- and fluid-depleted lithospheric mantle from a subducted oceanic plate, whereas other Azores basalts contain a contribution from ∼3-Gyr-old melt-enriched basalt[2]. We conclude that both components are most probably derived from an Archaean oceanic plate that was subducted, arguably into the deep mantle, where it was stored until thermal buoyancy caused it to rise beneath the Azores islands ∼3 Gyr later.**

The dynamics of the Earth reflect its internal heat but the nature and timescales of mantle convection remain poorly constrained. Over the past decade tomography data have provided spectacular images of seismically fast material inferred to be cool zones of downwelling associated with subducting plates and suggest that these can extend beyond the 670 km discontinuity into the deep mantle, ponding at the core–mantle boundary[3]. Conversely, a significant component of return flow is associated with mantle plumes, many of which, including the Azores, appear to rise from the core–mantle boundary[4]. Thus, there has been much interest in developing independent evidence for entrainment of subducted material from the composition of ocean island basalts erupted above plumes. Radiogenic isotopes have long been used in this search because of their potential to constrain the timescales of recycling and many ocean island basalts have indeed been found to have signatures distinct from those of mid-ocean ridge basalts (MORB)[5] that sample the upper mantle. However, although such signals undoubtedly reflect the time-integrated effects of fractionated parent–daughter element ratios, the age and extent of this fractionation can rarely be deconvolved. Even if this is possible, the parent–daughter fractionation is not restricted to processes occurring near the Earth's surface and could instead reflect intra-mantle metasomatism[6,7]. In contrast, fractionation of isotopes of light elements such as O, B and Li results from low-temperature processes near the Earth's surface, and significant variations in the stable isotope ratios of MORB and ocean island basalts could provide unambiguous evidence for contributions from recycled material[8]. However, the range of O and B isotope ratios observed in MORB and ocean island basalts has generally been rather restricted and observed variations are often attributed to shallow-level assimilation of altered oceanic crust[8–14]. Furthermore, stable isotopes cannot be used to constrain the timescales of recycling.

Recent Os isotope analyses found that seven basalts from the Azores had subchondritic Os isotope ratios and here we supplement those data with new subchondritic Os data from a picrite from Faial which has 14% MgO, 0.117 p.p.b. Os and a $^{187}Os/^{188}Os$ ratio of 0.12559. These require a contribution from a component which must be at least 2.5 Gyr in age[1] and in Table 1 we report the first B and O isotope data from a subset of these well characterized samples[15,16].

**Table 1 | $\delta^{11}B$ and $\delta^{18}O$ data for Azores basalts**

| Sample number | Island | MgO (%) | Nb (p.p.m.) | B (p.p.m.) | $\delta^{11}B$ (‰) | ± 1 s.e.m. | Number of analyses, *n* | $\delta^{18}O$ (‰) | ± 1 s.e.m. | *n* |
|---|---|---|---|---|---|---|---|---|---|---|
| S1 | Sao Miguel | 7.76 | 70.7 | 5.4 | −6.0 | 0.5 | 1 | 4.88 | 0.058 | 3 |
| S3 | Sao Miguel | 8.34 | 77.9 | 6.2 | −6.8 | 0.1 | 2 | Not analysed | | |
| S10 | Sao Miguel | 8.33 | 68.8 | | 5.0 | 0.5 | 2 | 5.10 | 0.007 | 2 |
| S19 | Sao Miguel | 6.38 | 87.5 | 5.9 | −7.4 | 0.2 | 1 | 5.28 | 0.028 | 2 |
| SJ26 | Sao Jorge | 4.71 | 90.9 | 5.4 | −3.3 | 0.1 | 2 | 5.14 | 0.047 | 3 |
| SJ30 | Sao Jorge | 9.70 | 49.1 | 3.1 | −4.7 | 0.3 | 1 | 4.94 | 0.057 | 2 |
| T6 | Terceira | 8.70 | 40.8 | | Not analysed | | | 4.87 | 0.070 | 3 |
| T18 | Terceira | 7.94 | 41.5 | 3.4 | −6.0 | 0.2 | 2 | 4.88 | 0.030 | 2 |
| P5 | Pico | 9.63 | 37.6 | 2.4 | −3.6 | 0.2 | 1 | 5.10 | 0.048 | 2 |
| P25 | Pico | 8.24 | 43.1 | 3.8 | −3.5 | 0.3 | 1 | 5.02 | 0.014 | 2 |
| P29 | Pico | 8.16 | 52.4 | 3.7 | −4.1 | 0.2 | 1 | 5.14 | 0.070 | 3 |
| FCA-6 | Faial | 9.73 | 35.0 | 2.6 | −3.3 | 0.5 | 2 | 5.02 | 0.014 | 2 |
| FCA-24 | Faial | 13.99 | 30.2 | 5.9 | −2.1 | 0.4 | 2 | 5.14 | 0.014 | 3 |
| FCP-18 | Faial | 7.83 | 46.0 | 4.4 | −7.6 | 0.5 | 2 | 5.09 | 0.057 | 2 |

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The majority were measured in duplicate or triplicate. $^{18}O/^{16}O$ data were obtained by high-precision $CO_2$ laser fluorination and mass spectrometry[17] on separated olivine phenocrysts. Analyses were performed at the Universities of Wisconsin and Oregon using standards of garnet and mantle San Carlos olivine and similarly low $\delta^{18}O$ olivine values were obtained in both laboratories. The range of $\delta^{18}O$ values (5.14‰ to 4.87‰) exceeds analytical error and extends below the value (5.2 ± 0.2‰) value inferred for pristine mantle[9]. A comparable $\delta^{18}O$ range, extending down to 4.57, was also found in a recent study of olivine phenocrysts from Sao Miguel[18]. Similarly, MORB glass data[10] from 38–40° N along the mid-Atlantic ridge, across the centre of the Azores platform, range from 5.2‰ to 5.7‰ which is equivalent to 4.7‰ to 5.2‰ in olivine. Thus, $\delta^{18}O$ values below that of pristine mantle do appear to occur in the Azores[18] (Fig. 1). Such low $\delta^{18}O$ values are characteristic of the layer-3 gabbros and altered peridotites from the oceanic lithosphere ($\delta^{18}O = 3$–5) but are unlike altered oceanic crust ($\delta^{18}O = 5$–9) or pelagic sediments ($\delta^{18}O = 15$–25)[9]. Subcontinental lithospheric mantle is expected to have MORB-like $\delta^{18}O$ and so the presence of low $\delta^{18}O$ supports models of recycling of oceanic rather than subcontinental lithospheric mantle[1,19].

The $^{11}B/^{10}B$ isotope ratios and B concentrations were measured by thermal ionization mass spectrometry at Pisa using the di-caesium, meta-borate method[20] following alkali carbonate fusion and ion exchange separation[21]. Sample S10, which had visible evidence for alteration along cracks, yielded a $\delta^{11}B$ ratio of +5.02, providing strong evidence for seawater ($\delta^{11}B = +39$) contamination for this one sample. For the remaining samples, $\delta^{11}B$ data show a large range from −3.3 to −7.6‰. B concentrations vary from 2.4 to 6.2 p.p.m. and the samples with the lowest B concentrations have the highest B isotope ratios. Also, with the exception of one sample (FCP-18), B and O isotopic compositions are positively correlated, ranging from compositions within the normal range for oceanic basalts to low $\delta^{11}B$ and $\delta^{18}O$ (Fig. 2a). These relationships are in contrast to the effects of seawater contamination and thus the data are likely to reflect magmatic signatures. The source of MORB has $^{87}Sr/^{86}Sr \approx 0.7025$, an average $\delta^{11}B$ of −4.6‰ (refs 11–13) and Nb/B ≈ 3 (ref. 22), whereas the Azores samples have higher $^{87}Sr/^{86}Sr$ and Nb/B = 5–17 (Fig. 2b, c). These observations, in combination with the inverse relationship between B and $\delta^{11}B$ and the O isotope data, strongly suggest that the basalts sample a source that has been modified. The O and B isotope data implicate recycled material that had undergone fractionation at relatively low temperatures in the near-surface environment. Conversely, the absence of any strongly elevated $\delta^{11}B$ and $\delta^{18}O$ ratios, in conjunction with the observation that those samples with the highest $^{87}Sr/^{86}Sr$ also have the lowest $\delta^{18}O$ ratios, indicates that the magmas did not significantly interact with the local mid-Atlantic oceanic crust through which they ascended.

The nature of the recycled material is explored further on a plot of Nb/B versus $\delta^{11}B$ (Fig. 2b). Nb and B have very similar partitioning behaviour in mantle minerals and are unlikely to be fractionated significantly during melting or crystallization[22,23]. Instead, B is strongly fluid-mobile compared with Nb[22,24] and so Nb/B is mainly sensitive to fluid transfer and/or mixing processes, which will be linear on Fig. 2b. MORB and their source have a Nb/B ratio of 3–3.5 (refs 22, 25) whereas the Nb/B ratios in the Azores and many other ocean island basalts are all significantly higher than this (Fig. 2b), suggesting a source strongly depleted in B by fluid removal[22,24]. Fluids preferentially mobilize $^{11}B$ in the low-temperature environment[26] and so the source of the basalts must have had higher $\delta^{11}B$ than their measured values before fluid extraction of B. This suggests that their source originally had $\delta^{11}B > -2$, which is similar to that of oceanic lithosphere that has been altered by interaction with sea water. Subsequent fluid loss, such as that attending subduction, would raise the Nb/B ratios and lower $\delta^{11}B$; that is, in a manner consistent with the observed decrease in $\delta^{11}B$ downward

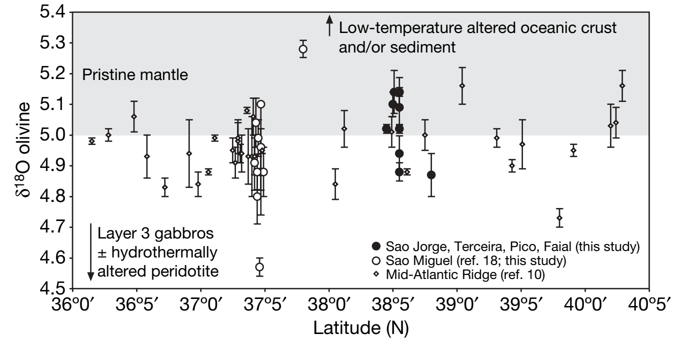


**Figure 1 | Oxygen isotope variation across the Azores platform.** Plot of $\delta^{18}O$ (±1σ) versus latitude. Data from this study, and refs 10 and 18. Vectors indicate the sense of displacement during hydrothermal alteration[9].

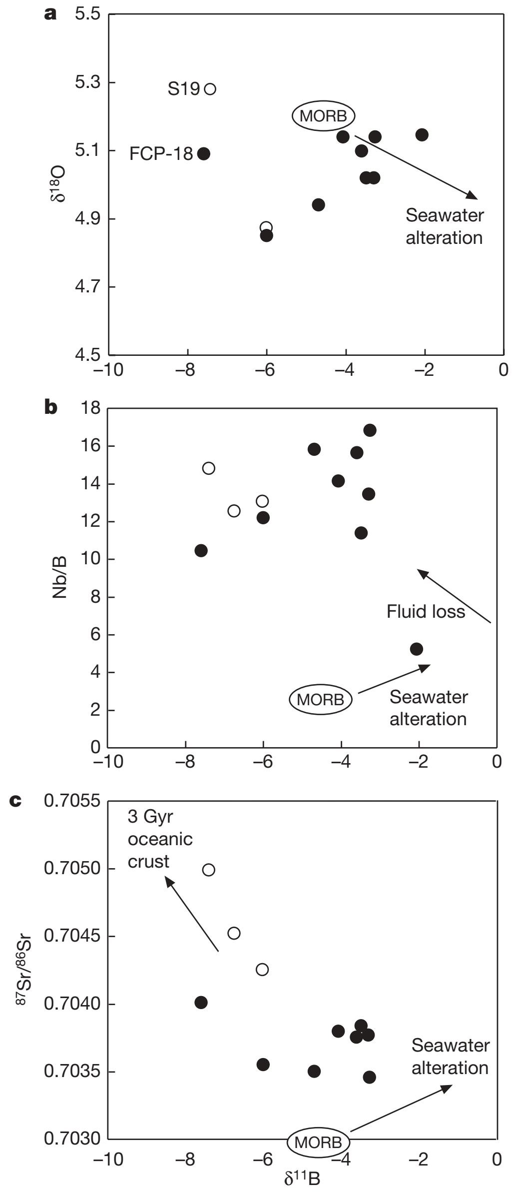


**Figure 2 | Variation of B isotopes with other geochemical indices in the Azores.** Plots of $\delta^{11}B$ versus $\delta^{18}O$ (**a**), Nb/B (**b**) and $^{87}Sr/^{86}Sr$ (**c**). Vectors indicate the effects of fluid loss[9]. Average MORB value was compiled from refs 11–13, 22, 25 and 30 and the subducted sediment value is taken from ref. 31. Sample numbers in **a** refer to Table 1. Open symbols identify data from Sao Miguel that have been argued to have increased $^{87}Sr/^{86}Sr$ owing to recycling of ~3 Ga oceanic basalts[2].



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from altered oceanic crust into the underlying gabbros and peridotites in oceanic lithosphere[26] or decreasing $\delta^{11}B$ in volcanic rocks from cross-arc transects[27]. This could produce a component with $\delta^{11}B \approx -3$ and $Nb/B \approx 17$ observed in our samples on Fig. 2b. Other Azores basalts, especially those from Sao Miguel, which trend towards lower $\delta^{11}B$ and Nb/B in Fig. 2b, could reflect involvement of recycled oceanic crust[2].

Although the B and O isotope data unambiguously seem to implicate the presence of recycled components in the Azores plume they do not by themselves constrain the age of these components. However, Fig. 3 shows that there are broad negative correlations of B concentration, Nb/B and $\delta^{11}B$ with $^{187}Os/^{188}Os$ and the observation that the high-Nb/B endmember extends to subchondritic Os isotope ratios uniquely constrains the age of this endmember to exceed 2.5 Gyr (ref. 1). Furthermore, the Sao Miguel rocks bearing evidence for involvement of recycled oceanic crust have high $^{187}Os/^{188}O$ and $^{87}Sr/^{86}Sr$ ratios and recent modelling of Hf–Nd isotope systematics suggests that this component is recycled, melt-enriched oceanic crust which could be as ancient as 3 Gyr (ref. 2). These combined observations provide compelling evidence for both the age and origin of material in a mantle plume.

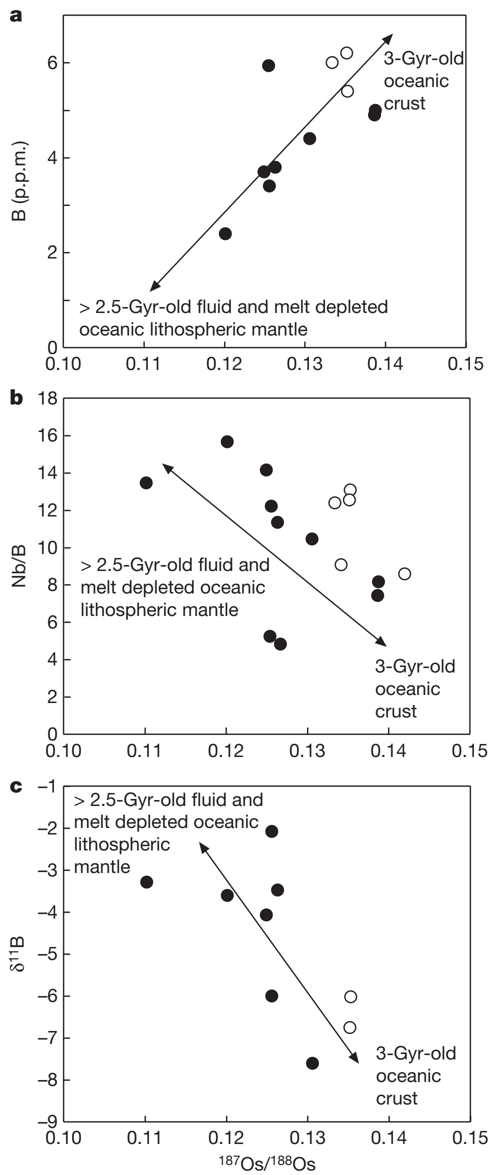


**Figure 3 | Variation of Os isotopes with other geochemical indices in the Azores.** Plots of $^{187}Os/^{188}Os$ versus B concentration (**a**), Nb/B (**b**) and $\delta^{11}B$ (**c**). Open symbols identify data from Sao Miguel.

Although the multi-stage, multi-component model precludes a unique quantitative treatment, the combined data may be interpreted in the following way. Large degree (≳20%) partial melting to produce Archaean oceanic crust also formed a refractory residual lithospheric mantle that was sufficiently depleted in Re to have a subchondritic Re/Os ratio. Hydrothermal or other surficial processes resulted in lowering of $\delta^{18}O$ and enrichment of B and $\delta^{11}B$ but, during later subduction, fluid loss from the lower gabbro and peridotite sections of the plate raised Nb/B ratios and lowered $\delta^{11}B$. Long-term storage of this material in the mantle resulted in the development of subchondritic Os isotopes while overlying, melt-enriched basalts developed their distinctive Hf-Nd isotope characteristics[2] and elevated $^{187}Os/^{188}O$. Later entrainment in a mantle plume brought these materials back to the shallow mantle, where decompression melting produced basaltic magmas that carry the integrated Os-O-B signal. Thus, the Azores basalts contain evidence for contributions from the two main components of an ancient oceanic plate and the broad symmetry and length scale observed in the isotope data[1] suggests that this component is intrinsic to the plume over 10–100 km. However, numerical fluid dynamic models suggest that subducted materials that remain in the mantle convection system will become highly attenuated and that the timescale for circulation through the mantle is likely to be of the order of 500 million years rather than many billions of years[28,29]. In contrast, recent seismic results suggest that some subducted plates may pile up at the core–mantle boundary[3], where they could remain stored for much longer periods of time. Seismic tomography suggests that the Azores plume is ascending from the core–mantle boundary[4] and so we suggest that this plume samples recycled material that was subducted to the core–mantle boundary and stored there since the Archaean era.

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