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Spatial controls on the generation of low-δ^{18}O basalts on São Miguel, Azores

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ABSTRACT

Volcanism in the Azores is generally accepted to result from the decompression melting in the upper mantle associated with the Azorean plume. Basalts on the island of São Miguel have been previously recognised as having δ^{18}O values lower than MORB with different authors ascribing this low-δ^{18}O signature to either a component within the plume itself or as the result of assimilation of crustal materials at shallow level. Here we assess these contrasting models by using a suite of samples that are both geographically and temporally spread. We find that while low-δ^{18}O mafic magmas (reaching 4.98 ‰) do occur on São Miguel, they are spatially restricted to the Picos fissure system, between the central volcanoes of Sete Cidades and Fogo. Basalts of similar age from outside this restricted region return δ^{18}O values that are similar to MORB. This spatial constraint argues that the source of the observed low-δ^{18}O signature is within the crust rather than a component of the plume. Previous studies on mafic to intermediate rocks of the Picos fissure system have identified the assimilation of broadly syenitic lithologies, which were found as co-erupted lithic clasts at the Fogo volcano and may have δ^{18}O values as low as 2.6 ‰. However, trace element geochemistry indicates that these lithologies have not been assimilated within our low-δ^{18}O samples, a more likely assimilant is altered oceanic crust or mafic lavas within the island edifice.

1. Introduction

Mantle plume magmatism has occurred in a punctuated fashion throughout Earth's history. Such events have been fundamental in shaping the evolution of our planet in many ways, including controlling continental rifting, global climate, and even mass extinctions (Koppers et al., 2021). The volcanic provinces resulting from plume magmatism may persist for tens of millions of years, typically with brief periods of high-volume extrusion (e.g. Storey et al., 1995) but considerable variability in their expressions exists related to the properties of the mantle upwelling and the crustal rocks upon which it impinges. Gaining clarity on the physical and compositional properties of these upwellings or plumes remains a challenge. Geophysical studies have made significant progress in imaging thermal anomalies within the mantle, with a range of structures observed persisting to various depths in the mantle (many studies well summarised by Koppers et al., 2021). Complementing these findings, a range of geochemical studies have addressed the mineralogical makeup of mantle plumes and their sources (e.g. Barker et al.,

2023; Hauri, 1996; Sobolev et al., 2005). Isotopic systems have also been employed to address questions such as inputs to the plume itself (e.g. Béguelin et al., 2017), temporal changes in the magma source (Abouchami et al., 2005; Cousens et al., 1993) or provinciality within a single upwelling (Shorttle et al., 2013).

With such a range of potential behaviours and settings, investigating end-member types has clear benefit, particularly when magmatic systems are still active. The Azores mantle upwelling represents one such end-member with a high inferred water content, relatively muted excess temperatures, and low ^{3}He values (Beier et al., 2012; Métrich et al., 2014; Moreira et al., 2012). In addition, magmas in the Azores exhibit large ranges in radiogenic isotopic compositions for ocean island settings, often with coherent variations across the archipelago (e.g. Moreira et al., 1999; Elliott et al., 2007; Millet et al., 2009). Many of these isotopic studies have identified an ancient component (estimated as >2.5 Ga) as a notable constituent within the Azores plume (Béguelin et al., 2017; Beier et al., 2007; Elliott et al., 2007; Schaefer et al., 2002).

Oxygen isotope compositions of the Azores magmas have also been

used to provide constraints on the componentry of the plume. Some studies, focussing on O isotopes, have suggested that the Azores plume itself is low-δ^{18}O (Turner et al., 2007; Widom and Farquhar, 2003) while others have suggested that the low-δ^{18}O signature is inherited in the shallow crust (Genske et al., 2013). Similar differing interpretations exist for other light stable isotopes with Turner et al. (2007) attributing variable B isotopes to a plume source, while Genske et al. (2014) suggest variations in B and Li isotopes originate from shallow assimilation.

On a smaller scale, it has been noted that there may be considerable variability on a single island, particularly the case for São Miguel, which is the focus of this study (Widom et al., 1997; Haase and Beier, 2003; Elliott et al., 2007;). Haase and Beier (2003) found distinct Sr isotopic compositions from basalts erupted in 'the waist zone' (also known as the Picos fissure system) between Sete Cidades and Água de Pau (Fogo) volcanoes (Fig. 1). They attributed these variations to small-scale heterogeneities being sampled due to the tectonic structure of the lithosphere underneath the island. Similarly, using Fe isotopes, Ruttor et al. (2022) concluded that the heavier Fe isotopic compositions found in western São Miguel were the result of addition of a MORB-like component to an initial OIB-like basalt due to overprinting within the active Terceira Rift.

Despite the known spatial isotopic variability in São Miguel samples, the vast majority of samples previously studied for δ^{18}O that could be reliably located were taken from the centre-west of the island, the Picos fissure system (Fig. 1). With this work we expand the existing dataset from São Miguel both in terms of geographic and temporal spread of samples, and by the analysis of multiple mineral phases per sample. With this approach, we aim to investigate whether deeper or shallower processes control δ^{18}O values on São Miguel.

2. Geological background

The Azores archipelago (North Atlantic Ocean) consists of nine islands (Fig. 1 inset) straddling the Mid-Atlantic Ridge. Its complex geodynamic setting results from the interaction between the triple junction of the North American, Eurasian, and Nubian lithospheric plates and a mantle melting anomaly, often referred to as the Azores mantle plume (e.g. Cannat et al., 1999; Storch et al., 2020). All the islands are of volcanic origin and seven of them have active volcanic systems, most of which have erupted in historical times, that is within the last 500 years. Overall, volcanic rocks of the Azores islands show a full range of compositions from basanite to trachyte and more rarely rhyolite (Larrea et al., 2018).

The island of São Miguel, the largest and most populated of the Azores is the site of this study. Some 60 km long and 12 km wide, São Miguel hosts seven volcanic systems: three active central volcanoes with calderas (Sete Cidades, Fogo, – also known as Água de Pau, and Furnas) linked by two active fissure systems (Picos and Congro), and two extinct volcanic systems (Povoação and Nordeste) in the eastern part of the island (Gaspar et al., 2015) (Fig. 1). This study focuses on the most prominent regions of basaltic volcanism, which are briefly described below.

Sete Cidades volcano, the westernmost of the three active central volcanoes of São Miguel, is a low-relief edifice (845 m a.s.l.) characterised by a 5 km wide sub-circular caldera with steep-sided walls 30–400 m high. Its lower volcanic pile dates back to >210 ka (Moore, 1990) and is predominantly formed by basaltic and a few trachytic lavas alternating with pyroclastic deposits. The upper sequence (< 36 ka) includes three major trachytic pyroclastic deposits at 36 ka, 29 ka, and 16 ka (Queiroz et al., 2015) related to different phases of formation of the caldera, which are intercalated with subordinate trachytic and basaltic products. Rocks of intermediate compositions are less common. The recent, < 5 ka, products comprise trachytic pumice deposits from 17 intra-caldera eruptions (Pepom tephras, Fig. 2A) and basaltic lavas and scoriae from 12 flank eruptions (Queiroz et al., 2015).

Picos fissure system also known as 'the waist zone' is, at 7.5 to 12 km wide, the narrowest part of the island linking Sete Cidades in the west to Fogo in the east. This low-lying area (up to 485 m a.s.l. in the central part) is characterised by two sub-parallel volcanic ridges of scoria cones, whose lavas gently slope to the north and south coasts. The Picos fissure system is the youngest volcanic area of São Miguel, the age of the oldest products is poorly constrained to >30 ka (Moore, 1990). The older volcanism was widespread across the entire fissure system, while the recent activity (< 5 ka) has been concentrated in the two main ridges,
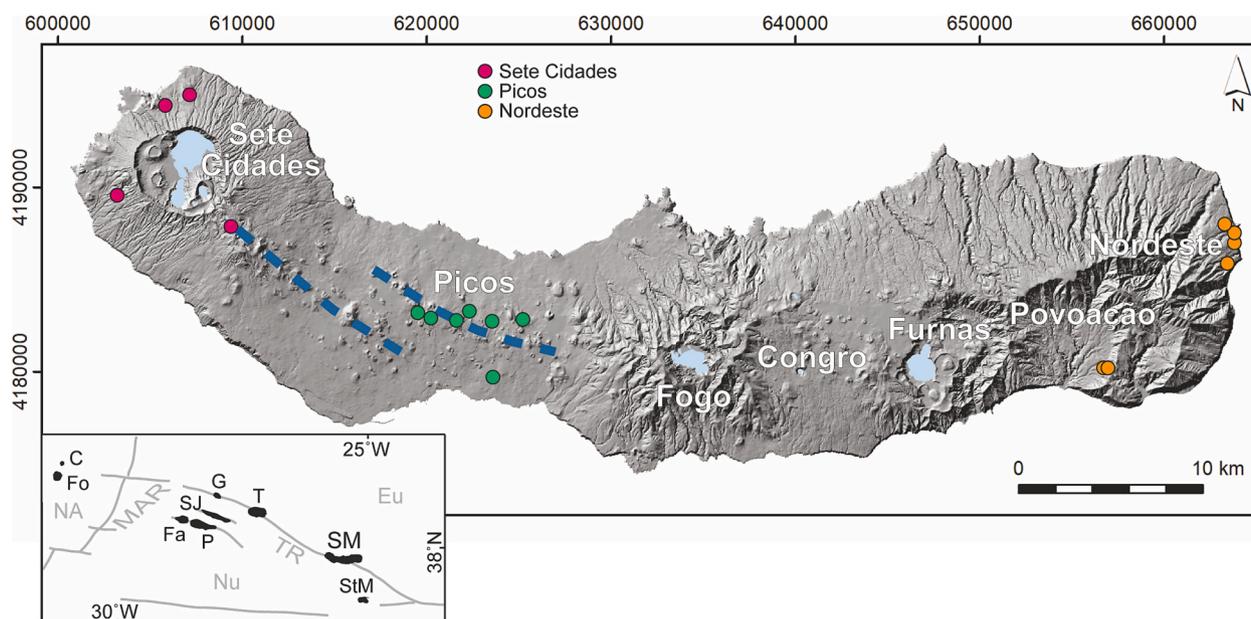

Fig. 1. Digital elevation model of São Miguel Island showing where samples in this study were taken from and identification of the volcanic systems (Sete Cidades volcano, Picos fissure system, Fogo volcano, also known as Água de Pau volcano, Congro fissure system, Furnas volcano, Povoação volcano, Nordeste volcanic system). Inset shows the location of the island of São Miguel (SM) within the Azores archipelago (StM – Santa Maria, T – Terceira, G – Graciosa, SJ – São Jorge, P – Pico, Fa – Faial, Fo – Flores, C – Corvo) in the North Atlantic and the main tectonic features of the region (Eu – Eurasian plate, Nu – Nubian plate, NA – North American plate, MAR – Mid-Atlantic Ridge, TR – Terceira Rift).
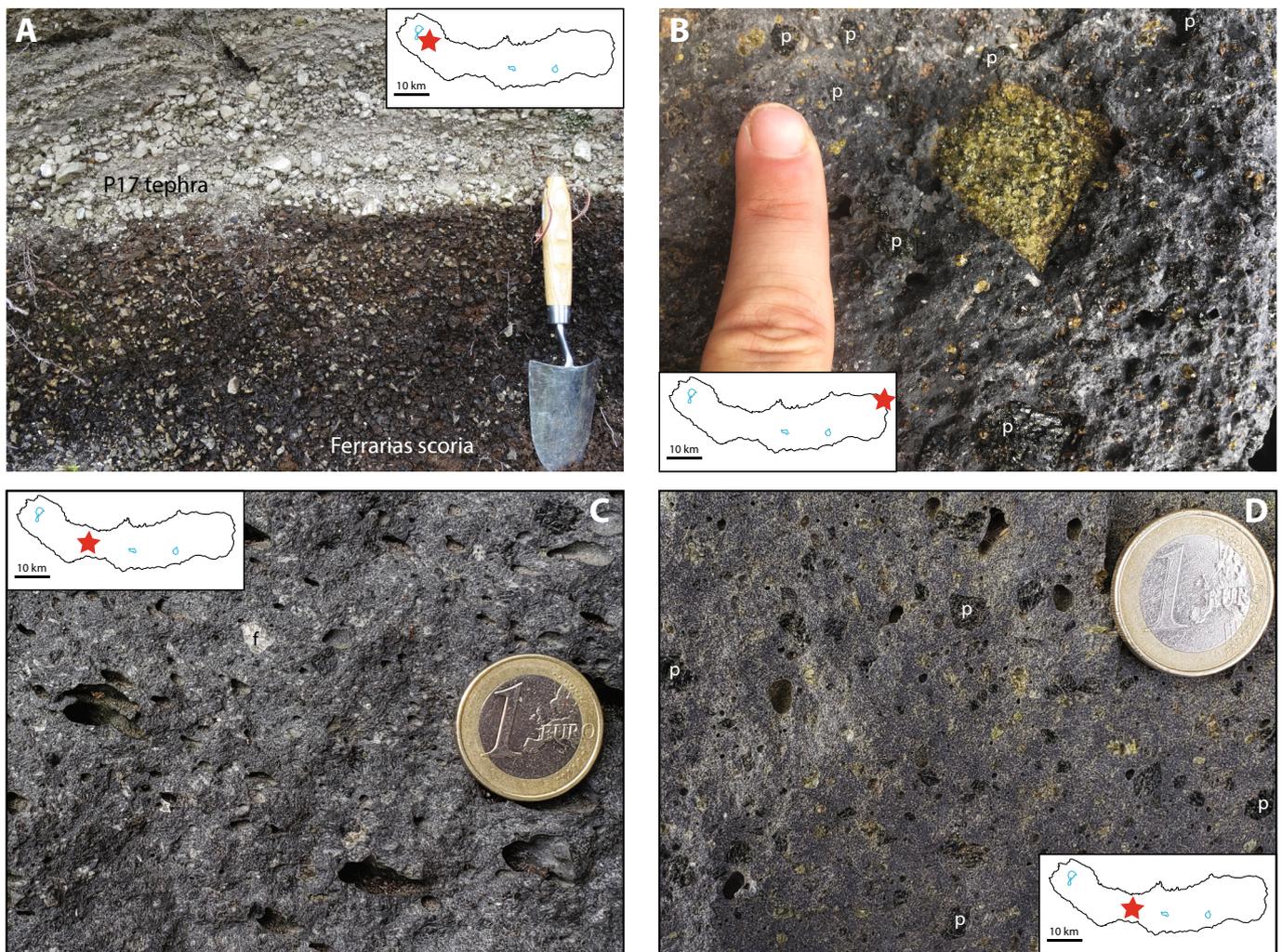
Fig. 2. Field appearance of samples in this study – A. Scoria layer (Ferrarias) intercalated within the Pepom tephra succession (between P15 and P17) at Sete Cidades volcano. B. Basaltic lavas in Nordeste containing abundant olivine-dominated clasts and large clinopyroxene crystals (p). C. Lava from the Picos fissure system (APAZ 22–19) with prominent feldspar (f). D. Lava from the Picos fissure system (APAZ 22–21) with prominent olivine and clinopyroxene (p) crystals.

where at least 30 predominantly basaltic eruptions have occurred (Ferreira et al., 2015) with subordinate volumes of hybrid magmas (Storey et al., 1989).

Nordeste volcanic system, reaching 1162 m a.s.l., corresponds to a highly eroded large shield volcano that constitutes the eastern end of São Miguel Island. It is the oldest ($>$ 878 ka; Johnson et al., 1998) volcanic edifice on the island and is predominantly formed by a sub-parallel stack of basaltic lavas. The older stratigraphy of this extinct shield volcano is poorly known, but the upper volcanic pile, 820 to 780 ka, is composed of ankaramitic and basaltic lavas (Fig. 2B), with a small volume of trachytic lavas found atop. Rocks of intermediate compositions are rare (Duncan et al., 2015).

3. Methodology

Fresh mafic volcanic products were sampled from across the island of São Miguel (Fig. 1) in an attempt to cover the spatial and temporal variability of mafic volcanic products. After removing any unwanted surficial material, samples were crushed with a vertical milled, then sieved for mineral separation and another aliquot being powdered for bulk rock analysis using agate mortars. Samples were prepared for X-ray fluorescence (XRF) at ETH Zürich following standard methods as described in Cortes-Calderon et al. (2022). Following XRF analyses, glass pills were broken and internal surfaces were analysed via laser

ablation inductively coupled plasma mass spectrometry (LA-ICPMS), also at ETH Zürich. Typical relative errors are $<$1% for the majority of major elements and $<$ 2% for Na$_2$O. For trace elemental analyses by laser ablation, uncertainties are typically $<$1 ppm for elements $<$10 ppm and $<$ 20 ppm for elements $<$1000 ppm based on multiple analyses of the BCR-2 reference material (Jochum et al., 2005). All new geochemical data are provided in the supplementary materials.

Where present olivine crystals were separated from the bulk samples to investigate crystal textures and compositions, particularly in light of earlier studies (e.g. Genske et al., 2013). Crystals were picked under a binocular microscope, mounted in epoxy and polished to 1 μm prior to carbon coating. Backscattered electron images using a JEOL JSM-6390 LA Secondary Electron Microscope (SEM) were obtained at ETH Zürich (a library of olivine images is provided in the supplementary data). Following zonation patterns as observed in backscatter electron imaging, olivine crystals were then analysed using a JEOL-JXA 8230 electron probe microanalyser (EPMA) equipped with five tuneable wavelength dispersive spectrometers hosted at ETH Zürich. Measurements were performed following methodology described in Ellis et al. (2022) at 15 kV acceleration voltage, 20 nA beam current and focused beam. The standards employed were rutile for Ti, pyrolusite for Mn, chromite for Cr, bunsenite for Ni, albite for Na and Si, forsterite for Mg, anorthite for Al and Ca, fayalite for Fe, and microcline for K. On-peak acquisition time was set to 30 s for all elements except Fe, Mn and Ni that were acquired

for 20 s.

Background was modelled using the mean atomic number (MAN) background fit correction for each element using standards that do not contain the analyte (Donovan and Tingle, 1996). Data was acquired and processed using probe for EPMA software (Donovan et al., 2021).

Other crystals, depending on the sample mineralogy, were also picked under a binocular microscope, typically from the 355 to 710 μm size fraction to be analysed for O isotopes by laser fluorination at the Department of Geological Sciences at the University of Cape Town, South Africa. Analyses typically involved 2–4 mg of material (2–5 crystals) and followed the methodology of Harris and Vogeli (2010) as modified in Ellis et al. (2022). The oxygen produced was converted to CO_2, the amount of gas was measured by reference to the mass 32 peak voltage to check for complete conversion and the isotopic ratios were measured using a DeltaXP gas-source mass spectrometer in dual-inlet mode at the University of Cape Town, South Africa.

We strived wherever possible to analyse two mineral phases per sample to allow testing for high-temperature equilibrium using well-established fractionation factors. In a number of cases we analysed the same samples in duplicate during different analytical sessions. Over the

course of the three years of analyses involved in this study the long-term average difference between duplicates of the Monastery garnet (MON GT) standard ($\delta^{18}O = 5.38$ ‰, Harris and Vogeli, 2010) was 0.12 ‰ (n = 393 pairs), corresponding to a 2σ value of 0.16 ‰.

4. Results

4.1. Bulk rock geochemistry

Mafic samples from São Miguel generally have higher and more variable crystal contents than the evolved lithologies. Some of the Nordeste mafic lavas have large and abundant olivine and clinopyroxene crystals occurring both as single grains and as nodules of cumulates (Fig. 2B).

All of the samples considered in this study are mafic with recalculated anhydrous SiO_2 between 43.7 and 53.7 wt%, and total alkalis between 2.08 and 8.32 wt%. These values are consistent with the compositions that volumetrically dominate the island of São Miguel (Moore, 1990). Most notable are the samples from Nordeste that contain conspicuous accumulations of olivine and clinopyroxene (Fig. 3) that are
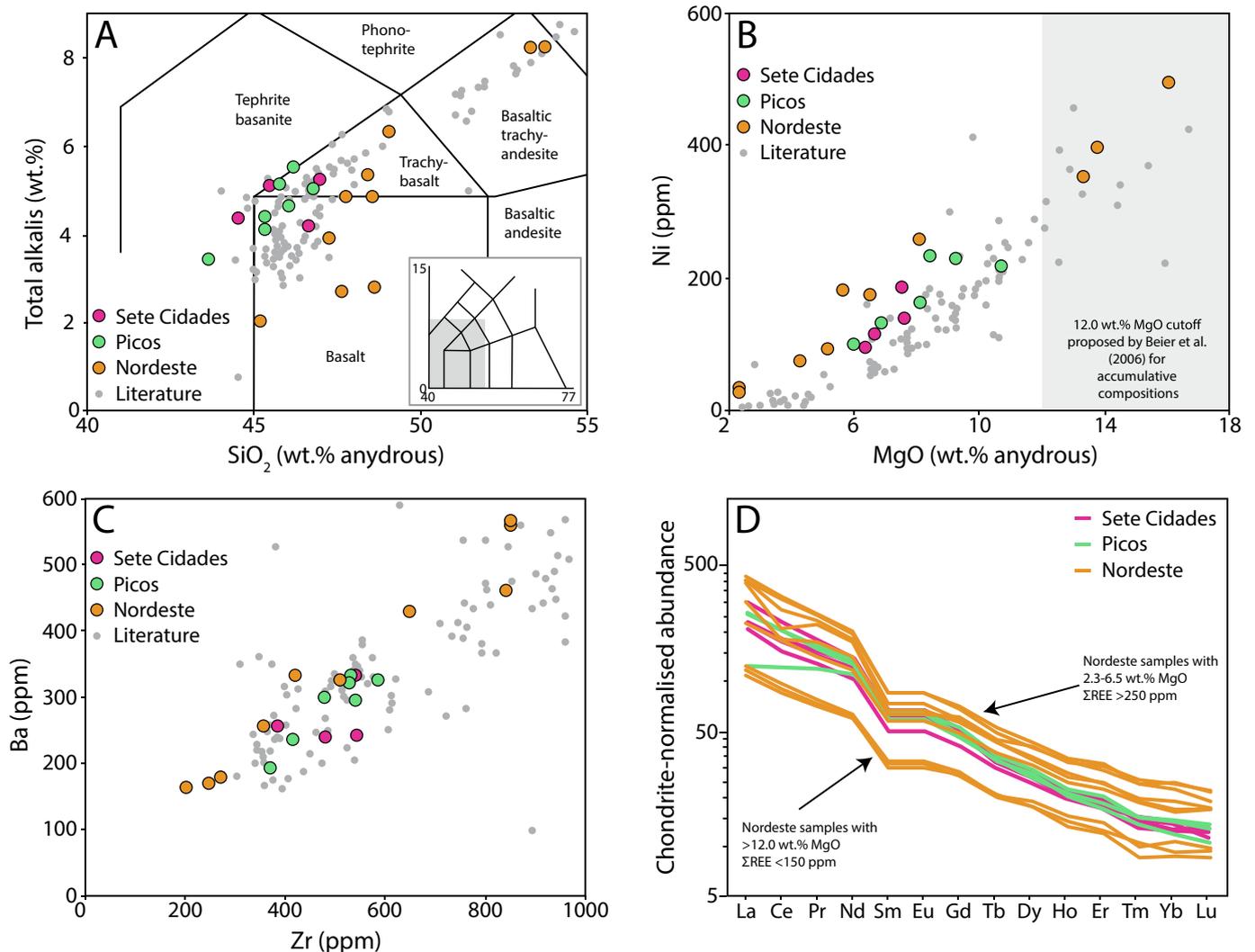

Fig. 3. Bulk rock compositions of São Miguel mafic rocks with our samples compared against literature data for São Miguel (Widom et al. 1996; Turner et al., 1997; Renzulli and Santi, 2000; Beier et al., 2006, 2007; Elliott et al., 2007; Prytulak et al., 2014) A. Total alkali vs. SiO_2 plot after Le Bas et al. (1986), B. MgO vs Ni showing the occurrence of three samples in the Nordeste suite that have MgO values >12 wt% which Beier et al. (2006) defined as accumulative in olivine. C. Ba vs Zr plot of two incompatible elements with the olivine accumulative samples having the lowest values D. Normalised REE plots using normalising data from McDonough and Sun (1995), showing similar trends between all samples from this study. The Nordeste accumulative samples show an overall decrease in REE due to the incorporation of olivine, but the pattern of the REE is the same as the other samples here.

observable in their lower total alkalis, elevated MgO contents (to nearly 16 wt%) and the high abundances of Ni and Sc, while simultaneously being depleted in elements that are incompatible in clinopyroxene and olivine such as Ba and Zr (Fig. 3). Following Beier et al. (2006) we use a cutoff point of 12 wt% MgO to distinguish between mafic samples without cumulate olivine addition and those that are accumulative in olivine and clinopyroxene, with Ubide et al. (2022) also suggesting a similar approach using a cutoff at 10 wt% MgO. The three compositions from Nordeste that are significantly above the Beier et al. (2006) cutoff (13.31, 13.78, and 15.97 wt% MgO) are those that show hand specimen evidence for the mechanical entrainment of mafic cumulates of olivine and clinopyroxene (Fig. 2B). Some lavas in the Picos fissure system (Fig. 2D) are also relatively high in MgO (9.32 wt%) and contain a prominent crystal cargo. Trace element ratios for the samples in this study are broadly similar to those described by Beier et al. (2006) with Ba/Rb higher for Sete Cidades and Picos samples than for Nordeste and the reverse true for Rb/Sr. Although we note that there is more variability in our samples than those of Beier et al. (2006). Chondrite-normalised REE plots (McDonough and Sun, 1995) have Eu/Eu* (Eu/Eu* = $Eu_{CN}/(Sm_{CN}*Gd_{CN})^{0.5}$) ranging between 1.02 and 1.14, consistent with the minimal role of plagioclase fractionation in this compositional range (Fig. 3) and a general enrichment in REE.

4.2. Olivine textures and compositions

Olivine is common in the mafic samples from the studied volcanic systems of São Miguel. In Nordeste, samples often contain cumulate nodules of olivine and clinopyroxene reaching 10 cm in diameter

(Fig. 2B) and with total crystallinity of the samples on the order 15–30%. In addition, the crystals found both as nodules and as single grains may reach prodigious size (1 cm or more). In contrast, some of the mafic samples from the Picos fissure system are almost aphyric. Olivine zonation styles vary within samples and examples are provided in Fig. 4 (and supplementary fig. 1). Even within a volcanic system the olivines can vary significantly. From the Sete Cidades volcano, olivines from the Ferrarias scoria (AE AZ 1918) intercalated within the Pepom tephras (Fig. 2A), have a distinctly brighter, sharply defined, 10–20 μm thick rim in BSE imaging while the other samples from Sete Cidades contain texturally homogeneous olivines (Fig. 4D).

São Miguel olivine compositions range between Fo_{65-88} and agree well with the range of Azores olivine compositions published by Sobolev et al. (2005), albeit with some of the Nordeste compositions more Ni-rich at a given Fo content. Overall, the olivines are normally zoned (Fig. 4A) with the largest intra-grain variation of Fo_{65-86}. The olivines from Sete Cidades are notably more homogeneous than those from the Picos or Nordeste systems and even within the Picos and Nordeste individual samples show variable zonation patterns (Figs. 4E-G). Few olivine compositions pass a classic equilibrium test (Fig. 4B) on a 'Rhodes diagram' (Roeder and Emslie, 1970). Overall, in any given sample the range of olivine compositions suggests a role for mixing between mafic magmas as previously suggested (Beier et al., 2006). The lack of equilibrium in the more mafic samples is likely a combined result of samples containing abundant cumulate crystals (e.g. Fig. 2) and the use of bulk rock compositions for the liquid rather than glass. The three samples from Nordeste that were suggested to be accumulative in olivine are those with the highest Mg-number and the fewest olivine
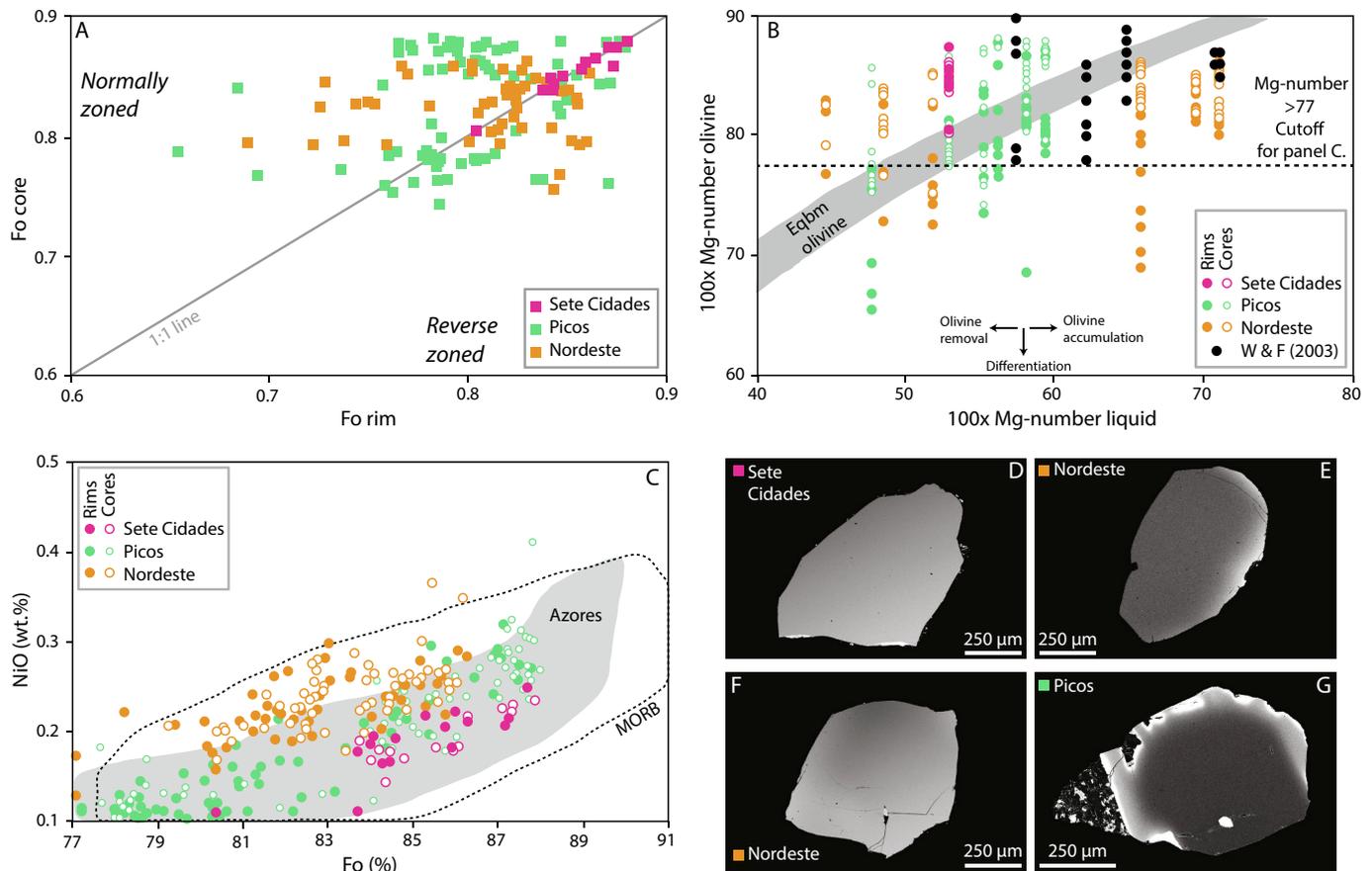

Fig. 4. Olivine backscattered electron images and compositions. A) Zonation within single olivine crystals showing that some olivines from Picos and Nordeste are significantly zoned while those from Sete Cidades are homogeneous. B) Rhodes diagram showing few olivine compositions would be in equilibrium with their co-existing whole rock with similar results from Widom and Farquhar (2003) shown in black and trajectories after Putirka (2008) C) Comparison of data from this study with those from Sobolev et al. (2005) shown in grey field. D) – G) Typical olivine appearance from the main regions studied here.

compositions that approach equilibrium (Fig. 4). We note that Widom and Farquhar (2003) found a similar range of olivine compositions overall and a comparable range within a single sample to those we report here. The two samples from Widom and Farquhar (2003) that overlap with the accumulative samples from Nordeste have MgO contents of 11.48 and 11.88 wt% and may also have 'excess' olivine.

4.3. Oxygen isotopic compositions

Measured $\delta^{18}O$ values range from 4.58 ‰ from an olivine from the Picos fissure system to 6.66 ‰ from a feldspar from a basaltic scoria from Sete Cidades (all new data in supplementary material and supplementary fig. 3). To estimate melt $\delta^{18}O$ values we make the following adjustments to mineral data: +0.4 ‰ for olivine (Genske et al., 2013), −0.2 ‰ for feldspar, and + 0.2 ‰ for clinopyroxene (Harris et al., 2000). Using these values return estimated magmatic $\delta^{18}O$ values of 4.98–6.46 ‰ (Fig. 5). Analyses of co-existing mineral phases from a single sample indicate that the O isotopic compositions reflect high-temperature equilibrium (Fig. 5) and multiple measurements of the same mineral phase from the same sample reproduce well (supplementary fig. 2), even allowing for the presence of small inclusions, particularly within the mafic phases. Where multiple mineral phases were analysed within a single sample, we take the magmatic value from the crystal phases in the following order olivine, clinopyroxene, feldspar. Where olivine and clinopyroxene have been analysed from the same sample, $\Delta^{18}O_{cpx-olivine}$ values range between −0.22 and 0.48 ‰ with the average 0.15 ‰, approximating analytical uncertainty. Across the dataset as a whole (i.e. including samples with analyses from only olivine or clinopyroxene in the average) the overall average magmatic value calculated from olivine is <0.02 ‰ higher than the average value calculated from clinopyroxene. Estimates from the literature for the $\Delta^{18}O_{cpx-olivine}$ are similar to our results, with estimates of ~0.40 ‰ (Mattey et al., 1994), between 0.3 and 0.4 ‰ (Chazot et al., 1997), between 0.04 and 0.29 ‰ (Dobosi et al., 1998), and between 0.24 and 0.40 ‰ (Day et al., 2012). We consider the 6.46‰ value from a scoria deposit feldspar with caution, as the other Sete Cidades samples analysed indicate magmatic values estimated from feldspar are somewhat higher than those from olivine and clinopyroxene (order 0.4–0.6 ‰).

5. Discussion

5.1. Low-$\delta^{18}O$ magmas on São Miguel

The O isotopic composition of a volcanic rock is the final aggregated result of all the processes having occurred during its generation and traverse of the crust (Bindeman, 2008; Rooyakers et al., 2023; Troch et al., 2017). It is widely accepted that closed-system fractional crystallisation induces a modest increase in $\delta^{18}O$ from the values of 5.4–5.9 ‰ generally assumed to reflect 'mantle' values (Bindeman, 2008; Eiler, 2001; Troch et al., 2020). To define a magma as low-$\delta^{18}O$, therefore depends upon establishing deviation from reference $\delta^{18}O$ trajectories resulting from closed-system behaviour. To do this, we follow the model of Troch et al. (2020) that summarises the various estimates of closed-system behaviour and places a lower limit on what 'normal-$\delta^{18}O$' magmas should be (Fig. 5A). Differentiation in Fig. 5 is evaluated by magma SiO_2 content. With our data being lavas or bulk juvenile tephra there is always the potential that some compositions may not reliably reflect melts when crystal contents are high. The Nordeste compositions suggest that they contain cumulate olivine and/or clinopyroxene, but such features are predominantly observed in trace element data rather than SiO_2 (Fig. 3).

The generation of a low-$\delta^{18}O$ magma is widely accepted to require the assimilation of a hydrothermally altered lithology that underwent alteration at high temperatures (Bindeman, 2008). The $\delta^{18}O$ imprint on the altered rocks will be further controlled by the $\delta^{18}O$ of the water involved. The variation in $\delta^{18}O$ of meteoric water can be significant at different regions across the globe. The meteoric water in the Azores is less negative (−4.1‰ to −5.2 ‰, Woitischek et al., 2017) than the values reported from areas known for recent low-$\delta^{18}O$ magmas (e.g. Yellowstone −19 ‰ Hildreth et al., 1984). Thus the potential to generate low-$\delta^{18}O$ magmas varies across settings.

A low-$\delta^{18}O$ signature in a magma could have a variety of potential origins, which can be broadly categorised as:

i) a primary signal of the mantle plume with the low-$\delta^{18}O$ values inferred to represent an addition of high-temperature hydrothermally altered slab material to the plume source (Turner et al., 2007; Widom and Farquhar, 2003).
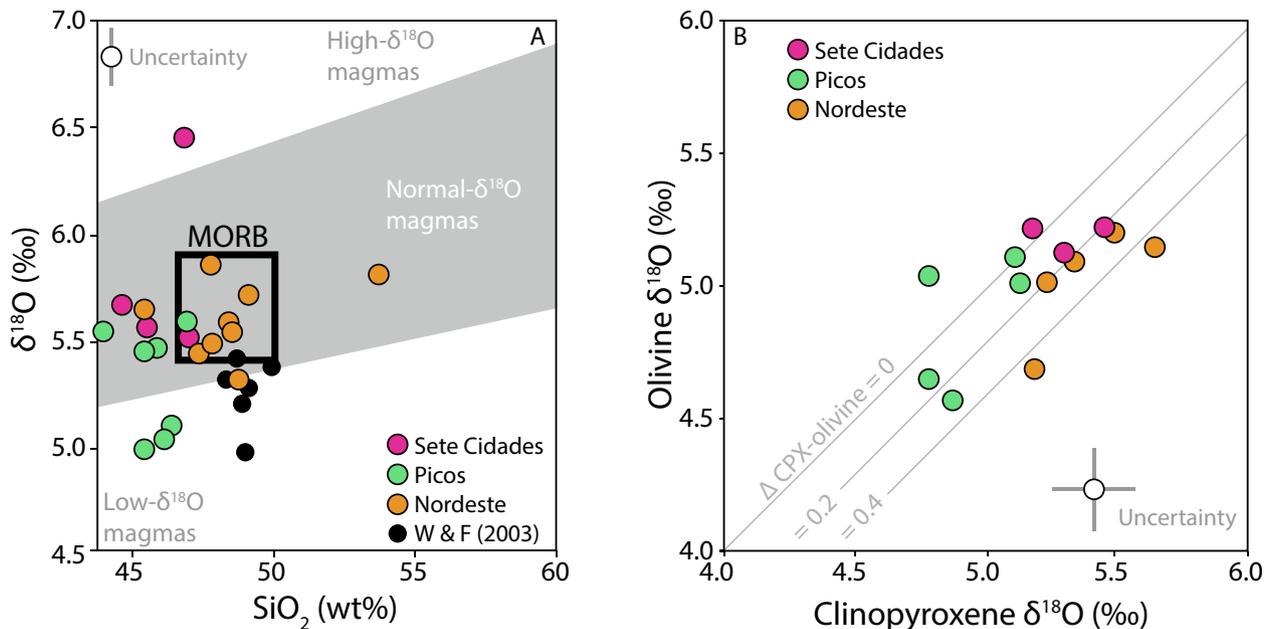

Fig. 5. Oxygen isotopes and magmatic evolution. A. Bulk rock composition (SiO_2 wt%) against $\delta^{18}O$ values for all samples in this study illustrating expected behaviour following the summary of Troch et al. (2020). The grey box reflects the composition of MORB. B. Mineral-mineral plot of samples containing both olivine and clinopyroxene indicating the minerals are in high-temperature equilibrium.

ii) a result of assimilation fractional crystallisation (AFC) processes either progressively during magmatic evolution (Genske et al., 2013), or as part of a two-stage processes where the evolved magmas assimilate low-δ^{18}O materials (Hampton et al., 2021).

iii) direct melting of hydrothermally altered rocks, either partially or totally, with the resultant melt then erupted (Bindeman and Valley, 2000). Where the low-δ^{18}O signature is observed in mafic magmas, the direct melting mechanism is problematic due to the requirements of melting an altered lithology while having the resultant melt be mafic. If the altered materials were initially mafic it is unlikely that they would melt as a result of mafic magma recharge (e.g. Ellis et al., 2023), while if alteration had changed the composition of the rock to something more readily 'meltable' then the resultant composition would be unlikely to be basaltic. Experimental petrology studies of hydrothermally altered mafic lithologies indicate that partial melts of such rocks typically produce silicic melts (Beard and Lofgren, 1991; France

et al., 2010). For these reasons we do not consider this option further.

5.2. A plume-related origin

Previous studies have produced conflicting views on the nature of the O isotopes within the Azores magmas. Widom and Farquhar (2003) and Turner et al. (2007) ascribed the low-δ^{18}O values they found predominantly from the Picos fissure system to a low-δ^{18}O component of the Azores mantle upwelling with the plume source estimated to have >10% of hydrothermally altered oceanic crust (Widom and Farquhar, 2003). Genske et al. (2013) however, found by coupling O isotopes and major elemental compositions of the same olivine crystals from samples across the Azores that lowering of the δ^{18}O tracked the decreasing Fo content of the olivines, i.e. lowering of the δ^{18}O occurred during magmatic evolution. Regressing this trend back to the most primitive compositions gave results similar to the typical 'mantle olivine' value of δ^{18}O of 5.2 ‰

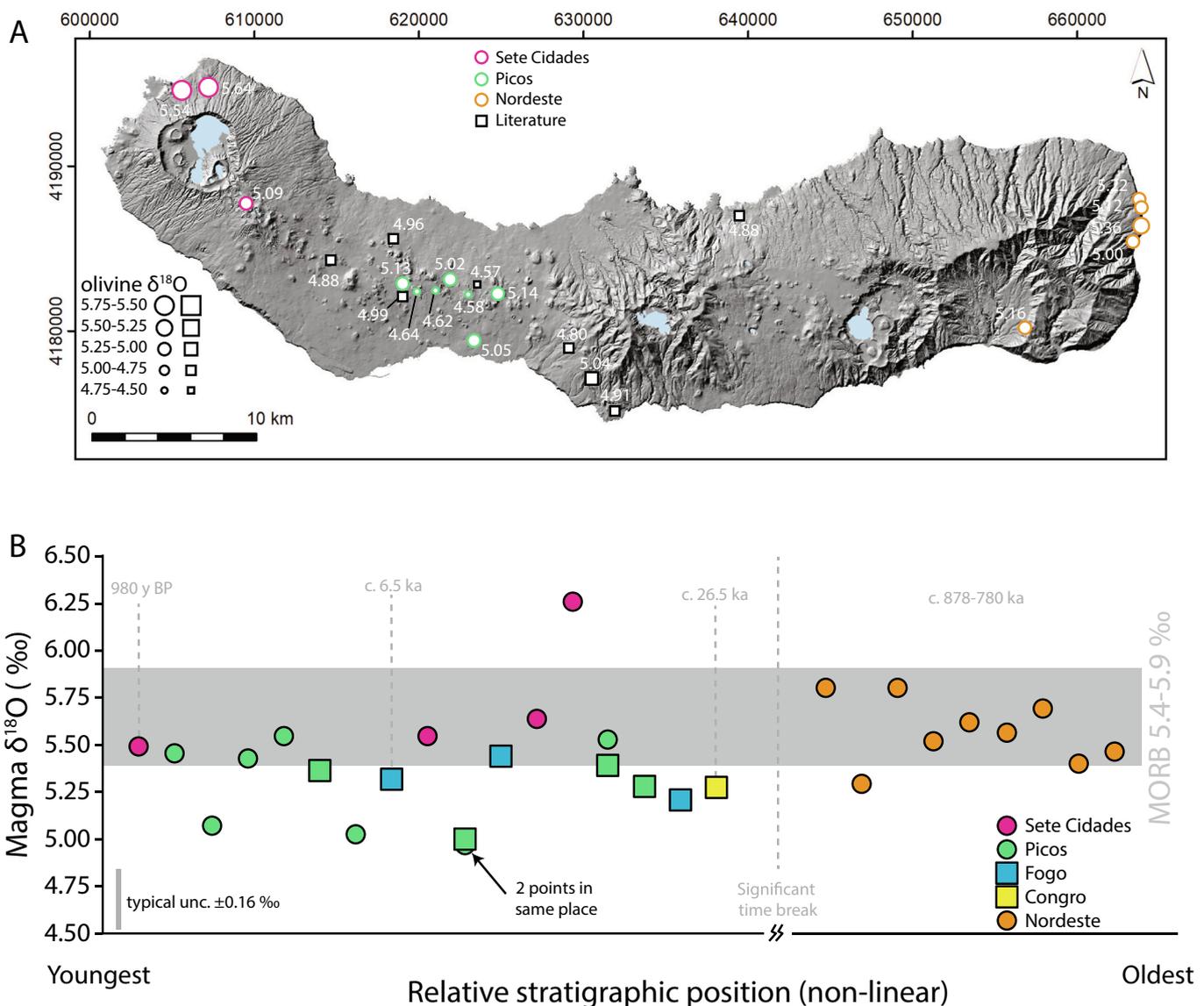**Fig. 6.** δ^{18}O values from São Miguel as a function of A. location for just olivine analyses, and B. sample age (for magmas calculated from mineral analyses as described in the text) based on the geochronology of Moore (1990) and relative field stratigraphy. In cases of the Widom and Farquhar (2003) samples we have superimposed sample locations in their map to the geological map of Moore (1991) to try and estimate which unit was sampled. Where samples lie on a vertical line, we believe these samples are of the same unit, and the agreement of the data between the two studies supports this. Geochronology for the Nordeste samples remains imperfect but the best ages for this group of samples place them in the 878–780 ka bracket.

([Eiler, 2001](#)).

Olivine $\delta^{18}O$ values from this study range from 4.58 to 5.36 ‰ ($n = 18$) almost identical to the published olivine values of 4.57 to 5.28 ‰ ([Fig. 6](#)). However, when plotted by location, for samples that could be reasonably located, it is notable that the lowest $\delta^{18}O$ values cluster within the Picos fissure system ([Fig. 6](#)A) the central region of the island dominantly sampled by [Widom and Farquhar (2003)](#). Our Picos olivine values average 4.85 ± 0.25 ‰, 1 std. dev., $n = 8$ in good agreement with the overall average of [Widom and Farquhar (2003)](#) of 4.87 ± 0.15 ‰, 1 std. dev., $n = 8$. In the east and west sectors of the island however, olivines tend to have $\delta^{18}O$ values closer to accepted mantle values (5.2 ± 0.2 ‰, [Eiler, 2001](#)). Taking all olivine analyses in [Table 1](#), including repeats from a single unit, Sete Cidades olivine averages 5.14 ± 0.12 ‰, 1 std. dev., $n = 6$ and Nordeste olivine averages 5.17 ± 0.13 ‰, 1 std. dev., $n = 5$. The variability in the $\delta^{18}O$ of the mafic magmas reported here may reflect a number of potential processes. A first possibility is that the assimilant required to lower the $\delta^{18}O$ in the mafic magmas simply does not exist under the central volcanoes. A second option is that the mafic rocks in the fissure systems reflect a relatively earlier stage of the magmatic life of that system. In this scenario, the assimilant is progressively exhausted (similar to the progressive inhibited crustal assimilation model of [Meade et al., 2014](#)) and therefore the young mafic magmas erupted from the central volcanoes have a lower potential for assimilation. To distinguish between these hypotheses would require access to the older mafic rocks of the central volcanoes, which are typically poorly exposed if at all due to the frequent resurfacing at these active centres. However, we do note that in the Nordeste system where we have samples throughout the stratigraphy, there is no correlation between $\delta^{18}O$ value and stratigraphic position.

In contrast to the spatial relationship observed in magma $\delta^{18}O$ values, there is little to no relationship in terms of age. Shown in [Fig. 6](#)B are the olivine $\delta^{18}O$ values plotted as a function of sample age. This includes both our data and those from the literature where samples as located in the original work have been attributed to map units of [Moore (1991)](#). Where samples have the same position on the X-axis on this diagram they are thought to be from the same unit, with good agreement with earlier work. While the samples from Nordeste are significantly older (on the order of hundreds of thousands of years), the eruption of low-$\delta^{18}O$ and normal-$\delta^{18}O$ magmas from Picos and Sete Cidades contemporaneously indicates the $\delta^{18}O$ character is unrelated to the age of the sample and is unlikely to reflect a source characteristic.

In terms of composition, there is no relationship between magma

$\delta^{18}O$ values and bulk indicators of compositional evolution, with $\delta^{18}O$ ranges of 0.6 ‰ at a given SiO_2 content ([Fig. 5](#), [Fig. 7](#), Sup. [Fig. 3](#)). This indicates that the lowering of $\delta^{18}O$ is not readily tracked by bulk composition, a similar finding as reported from other settings (e.g. Yellowstone, [Hildreth et al., 1984](#), [Bindeman, 2008](#), [Troch et al., 2017](#); Calabozos, [Grunder, 1987](#); Lebombo, [Harris and Erlank, 1992](#); Kilauea, [Garcia et al., 1998](#); Gran Canaria, [Cortes-Calderon et al., 2022](#)).

[Haase and Beier (2003)](#) noted that the Sete Cidades and the Fogo volcanoes were isotopically distinct despite being only some 20 km apart, with Sete Cidades having $^{87}Sr/^{86}Sr < 0.7038$ while Fogo-related lavas have $^{87}Sr/^{86}Sr > 0.7040$. They interpreted these differences as reflecting separate magmatic systems fed by different mantle sources. However, when plotting the [Widom and Farquhar (2003)](#) $^{87}Sr/^{86}Sr$ data against $\delta^{18}O$ it is clear that variations in $\delta^{18}O$ occur independently from the radiogenic isotope composition of a sample (Sup. [Fig. 4](#)). On a mineral-scale, [Genske et al. (2013)](#) showed a relationship between Fo content of the olivine (as a proxy of magmatic evolution) and $\delta^{18}O$ from the Azores archipelago, suggesting that assimilation occurred as evolution progressed. Our results are broadly in agreement with this (Sup. [Fig. 5](#)) but our lowest $\delta^{18}O$ values are off the trend presented by [Genske et al. (2013)](#). However, given that potential assimilants could vary widely in their $\delta^{18}O$ values, a similar extent of AFC could result in very different $\delta^{18}O$ values for a given Fo content.

5.3. The role of the crust

At the Sete Cidades caldera system, the youngest trachytes, the Pepom tephras, have magma $\delta^{18}O$ values mostly between 5.03 and 5.80 ‰ with a single value extending down to 4.13 ‰ ([Ellis et al., 2022](#)). These values are lower than the young mafic magmas in the same system, some of which are intercalated within the trachytic Pepom tephra stratigraphy ([Figs. 2, 8](#)). While models ([Bindeman et al., 2004](#); [Bucholz et al., 2017](#); [Harris et al., 2000](#)) differ in the extent of the increase in $\delta^{18}O$ during closed-system fractionation leading to a silicic magma, all models agree that this process causes an increase in $\delta^{18}O$. Thus, assuming that the mafic products intercalated with the silicic deposits at Sete Cidades reflect suitable parental magmas for the trachytes, this drop in $\delta^{18}O$ occurs during magmatic evolution and likely within the island crust.

Similarly, the spatial restriction of mafic, low-$\delta^{18}O$ values in the Picos fissure system also implies a role for crustal assimilation. The Picos fissure system, or the 'waist zone', was shown by [Storey et al. (1989)](#) to

Table 1
All measured O isotopic compositions from minerals.

| Sample	System	Unit name	Bulk rock MgO (wt%)	Olivine $\delta^{18}O$ (‰)	Olivine Repeat (‰)	CPX $\delta^{18}O$ (‰)	CPX Repeat (‰)	Feldspar $\delta^{18}O$ (‰)
AEAZ1918	Sete Cidades	Ferrarias	6.36	5.24	4.94	5.17		6.41
AEAZ1931	Sete Cidades	Mafra	7.61	5.14	5.05, 5.23	5.30		
AEAZ1932	Sete Cidades	CN11 Lagoa do Pilar	6.65	5.24		5.45		6.20
APAZ2207	Sete Cidades	CN4 Pico da Varzea	7.56					6.66
APAZ2211	Picos	Lava of Pico do Paio	6.94	5.05		4.78		
APAZ2218	Picos	Lava S of Pico do Bispo	10.75	5.13		5.11		
APAZ2219	Picos	Lava of Pico do Cascalho	6.08	4.66	4.62	4.78	4.66	5.22
APAZ2220	Picos	Lava E of Coroa da Furna	8.17	5.02		5.23		
APAZ2221	Picos	Lava of Pico de Água	9.32	4.58		4.87		
APAZ2222	Picos	Lava of Pico de Engenho	8.15	4.62		4.97		
BE AZ 22 8	Picos	Lava N of Pico de João Ramos	8.46	5.14				
BE AZ 22 2	Nordeste	n/a	6.45	5.16		5.64		
BE AZ 22 3	Nordeste	n/a	4.30			5.49		
BE AZ 22 9	Nordeste	n/a	2.34					
BE AZ 22 10	Nordeste	n/a	2.32			5.60		
BE AZ 22 11	Nordeste	n/a	13.78			5.08		
BE AZ 22 12	Nordeste	n/a	15.97	5.36		5.16	5.13	
BE AZ 22 13	Nordeste	n/a	5.12	5.12		5.34		
BE AZ 22 14	Nordeste	n/a	13.31	5.22		5.49		
BE AZ 22 15	Nordeste	n/a	8.08	5.0		5.24		
BE AZ 22 16	Nordeste	n/a	5.65			5.26		
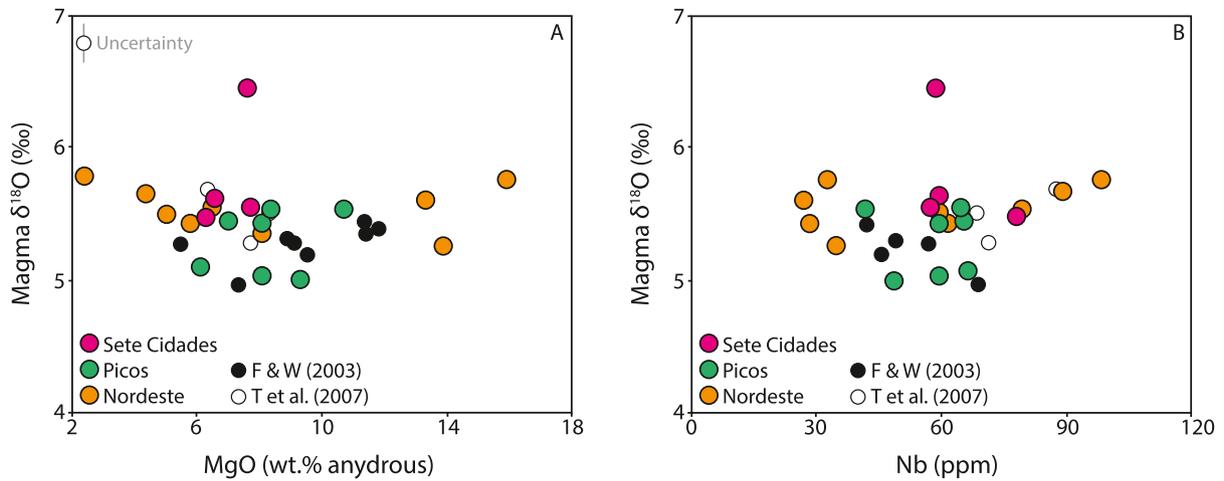
Fig. 7. Diagram showing the lack of relationship between $\delta^{18}O$ values and *A. major* elements – MgO and B. trace elements – Nb.
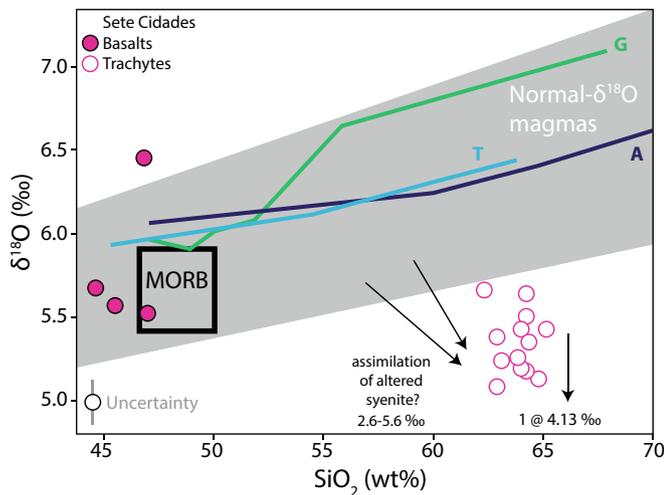

Fig. 8. O isotopic compositions of the youngest products of the Sete Cidades volcano (with trachyte data from Ellis et al., 2022). Notably the trachytes are lower in $\delta^{18}O$ than the intercalated mafic rocks indicating that assimilation, and the lowering of $\delta^{18}O$, occurred during magmatic evolution likely within the crust. Reference trajectories for closed-system fractionation are shown from other oceanic island settings: G – Galapagos (Muehlenbachs and Byerly, 1982.); T- Tristan da Cunha (Harris et al., 2000); A – Ascension (Sheppard and Harris, 1985).

contain numerous 'hybrid' mafic lavas with partially resorbed anorthoclase crystals. These hybrid lavas are readily identified in bulk geochemistry by their elevated K/Zr at a given Ti/Zr (Storey et al., 1989; Fig. 9) that results from the assimilation of syenites / alkali feldspar-dominated cumulates. The low-$\delta^{18}O$ values we identify in some of the Picos basalts cannot, however, be attributed to this process as their compositions plot on a standard fractionation trend (Fig. 9). Rather, we hypothesise that the structural features of the Terceira Rift running roughly NW-SE through São Miguel's western half (Fig. 1), which controlled the eruption of the mafic magmas in the Picos fissure system, may have played an important role. This relationship implies that suitable assimilants may occur in zones across the island as a whole (as suggested in other regions e.g. Iceland, Hampton et al., 2021), rather than being restricted to the central volcanoes where present-day hydrothermal activity is observed.

5.4. Potential assimilants

While some syenite lithics that were erupted within the Fogo A Plinian event are visibly hydrothermally altered and have low-$\delta^{18}O$ values (2.6 to 5.6 ± 0.30 ‰ Snyder et al., 2004), the Ti/Zr vs K/Zr relations (as shown in Fig. 9) rule out such evolved compositions from playing a significant role in petrogenesis of the Picos low-$\delta^{18}O$ basalts. Rather, we suggest that the assimilant is likely to be altered oceanic crust (AOC), or other mafic lithologies within the island edifice. While the upper oceanic crust may have elevated $\delta^{18}O$ compared to mantle-derived melts
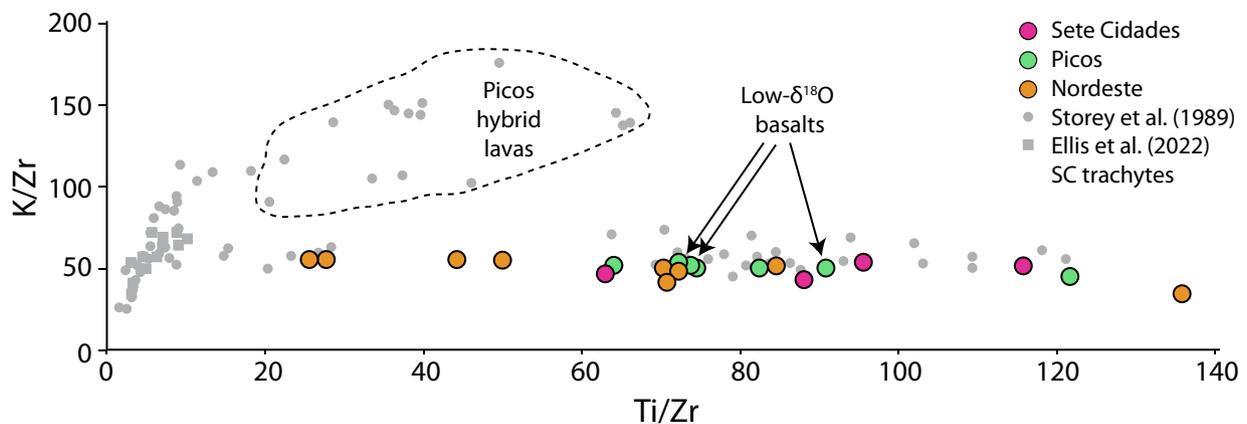

Fig. 9. Compositions of the samples in this study using a K/Zr and Ti/Zr plot (modified after Storey et al., 1989). This diagram shows that the low-$\delta^{18}O$ samples in our study (highlighted) do not have elevated K/Zr as the hybrid lavas of the Picos fissure system. Thus the assimilation of syenitic or alkali feldspar cannot be used to explain the low-$\delta^{18}O$ nature of these samples.

(typically 7–15 ‰, Eiler, 2001), values in the altered lower crustal gabbros may reach values as low as 0 ‰ (Gregory and Taylor, 1981; Muehlenbachs, 1986; Staudigel et al., 1995). Other studies of ocean islands with low-δ^{18}O mafic rocks have suggested a source within the volcanic edifice itself (e.g. Eiler et al., 1997; Garcia et al., 1998; Thirlwall et al., 1997) with recovered drillcore from the HGP-A well on the Big Island of Hawaii returning bulk δ^{18}O values reaching as low as 3.2‰ (Garcia et al., 1998). Perhaps the most suitable potential assimilants are the rocks of altered layer 3 ocean crust (i.e. gabbros) from around the Canary Islands (Hansteen and Troll (2003), another mid-Atlantic ocean island chain whose AOC δ^{18}O values range from 3.3 to 5.1 ‰. The occurrence of intrusive gabbroic bodies (8–12 km depth) is also reported for Pico Island in the Azores central group (Zanon et al., 2020), thus making it plausible that such rocks are present underneath São Miguel at similar depths. Taking a mid-point of the δ^{18}O values range from the Canary Islands of 4.2 ‰ would imply a ~ 20 % contribution from such lithologies to produce the lowest δ^{18}O magmas found in the Picos fissure system using simple binary mixing (Sup. Fig. 6). This estimate is very much in line with that of Widom and Farquhar (2003) who suggested a hydrothermally altered component within the plume of 10–20 %. The key difference with the interpretation of Widom and Farquhar (2003) is that our larger dataset highlights the spatial control on the low-δ^{18}O mafic magmas and thus we prefer a shallow rather than deeper source for the assimilation.

6. Conclusions

This work represents the first detailed multi-mineral study of the oxygen isotopic composition of the mafic products of the island of São Miguel, Azores. From our new bulk rock, mineral, and isotopic data we can conclude:

i) Analyses of olivine (4.58–5.36 ‰) and clinopyroxene (4.66–5.64 ‰) crystals indicate that these minerals are consistent with high-temperature equilibrium. Our results indicate that low-δ^{18}O mafic magmas exist on São Miguel (as suggested in previous studies) but the majority of analysed samples are similar to MORB.

ii) There exists little relationship between sample composition (e.g. MgO content, Ba, Zr, Ni, Th) and the δ^{18}O values of mafic magmas on São Miguel. Nor is there a temporal relationship with both the highest and lowest-δ^{18}O magmas erupted within the last few thousand years.

iii) A spatial relationship is however found, with the low-δ^{18}O magmas concentrated in the Picos fissure system while those from the east (Nordeste) and west (Sete Cidades) sectors of São Miguel have higher values. This implies a local control on the δ^{18}O of the mafic magmas rather than this being a deeper characteristic of the Azorean plume.

iv) The Picos fissure system contains mafic magmas that have assimilated abundant alkali feldspar from syenitic cumulates (Storey et al., 1989). The bulk compositions of our low-δ^{18}O samples indicate that limited, if any, syenite cumulate involvement occurred and thus altered syenitic lithologies are unlikely responsible for the low-δ^{18}O values. Rather, we suggest that altered oceanic crust materials are assimilated to decrease the δ^{18}O of Picos basalts.

Declaration of Competing Interest

Ben Ellis reports financial support was provided by Swiss National Science Foundation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lithos.2023.107440.

References

Abouchami, W., Hofmann, A.W., Galer, S.J.G., Frey, F.A., Eisele, J., Feigenson, M., 2005. Lead isotopes reveal bilateral asymmetry and vertical continuity in the Hawaiian mantle plume. Nature 434 (7035), 851–856.

Barker, A.K., Magnusson, E., Troll, V.R., Harris, C., Mattsson, H.B., Holm, P.M., Perez-Torrado, F.J., Carracedo, J.C., Deegan, F.M., 2023. Disequilibrium in historic volcanic rocks from Fogo, Cape Verde traces carbonatite metasomatism of recycled ocean crust. Lithos 456-457, 107328.

Beard, J.S., Lofgren, G.E., 1991. Dehydration melting and water-saturated melting of basaltic and andesitic greenstones and amphibolites at 1, 3, and 6.9 kb. J. Petrol. 32, 365–401.

Béguelin, P., Bizmis, M., Beier, C., Turner, S., 2017. Rift–plume interaction reveals multiple generations of recycled oceanic crust in Azores lavas. Geochim. Cosmochim. Acta 218, 132–152.

Beier, C., Haase, K.M., Hansteen, T.H., 2006. Magma evolution of the Sete Cidades volcano. São Miguel, Azores. J. Petrol. 47, 1375–1411. https://doi.org/10.1093/petrology/egl014.

Beier, C., Strake, A., Haase, K.M., 2007. The peculiar geochemical signatures of Sao Miguel (Azores) lavas: metasomatised or recycled sources? Earth Plan. Sci. Lett. 259, 186–199.

Beier, C., Haase, K.M., Turner, S.P., 2012. Conditions of melting beneath the Azores. Lithos 144-145, 1–11.

Bindeman, I.N., 2008. Oxygen isotopes in mantle and crustal magmas as revealed by single crystal analysis. Rev. Mineral. Geochem. 69, 445–478.

Bindeman, I.N., Valley, J.W., 2000. Formation of low-δ^{18}O rhyolites after caldera collapse at Yellowstone, Wyoming, USA. Geology 28, 719–722.

Bindeman, I.N., Ponomareva, V.V., Bailey, J.C., Valley, J.W., 2004. Volcanic arc of Kamchatka: a province with high-δ18O magma sources and large-scale ^{18}O/^{16}O depletion of the upper crust. Geochim. Cosmochim. Acta 68, 841–865.

Bucholz, C.E., Jagoutz, O., VanTongeren, J.A., Setera, J., Wang, Z., 2017. Oxygen isotope trajectories of crystallizing melts: Insights from modeling and the plutonic record. Geochim. Cosmochim. Acta 207, 154–184.

Cannat, M., Briais, A., Delpus, C., Escartín, J., Georgen, J., Lin, J., Mercouriev, S., Meyzen, C., Muller, M., Pouliquen, G., Rabain, A., da Silva, P., 1999. Mid-Atlantic Ridge–Azores hotspot interactions: along-axis migration of a hotspot-derived event of enhanced magmatism 10 to 4 Ma ago. Earth Plan. Sci. Lett. 173, 257–269. https://doi.org/10.1016/S0012-821X(99)00234-4.

Chazot, G., Lowry, D., Menzies, M., Mattey, D., 1997. Oxygen isotopic composition of hydrous and anhydrous mantle peridotites. Geochim. Cosmochim. Acta 61, 161–169.

Cortes-Calderon, E.A., Ellis, B.S., Harris, C., Mark, D., Neukampf, J., Wolff, J.A., Ulmer, P., Bachmann, O., 2022. Generation and field relations of low-δ^{18}O silica-undersaturated and mildly saturated alkaline magmas: a case study from the Fataga Group, Gran Canaria. J. Petrol. 63 (9), 1–22. https://doi.org/10.1093/petrology/egac090.

Cousens, B.L., Spera, F.J., Dobson, P.F., 1993. Post-eruptive alteration of silicic ignimbrites and lavas, Gran Canaria, Canary Islands: Strontium, neodymium, lead, and oxygen isotopic evidence. Geochim. Cosmochim. Acta 57 (3), 631–640.

Day, J.M.D., Macpherson, C., Lowry, D., Pearson, D.G., 2012. Oxygen isotope heterogeneity of the mantle beneath the Canary Islands: a discussion of the paper of Gurenko et al. Contrib. Mineral. Petrol. 164, 177–183.

Dobosi, G., Downes, H., Mattey, D., Embey-Iszyin, A., 1998. Oxygen isotope ratios of phenocrysts from alkali basalts of the Pannonian basin: evidence for an O-isotopically homogeneous upper mantle beneath a subduction-influenced area. Lithos 42, 213–223.

Donovan, J.J., Tingle, T.N., 1996. An improved mean Atomic Number Background Correction for Quantitative Microanalysis. Microsc. Microanal. 2 (1), 1–7.

Donovan, J.J., Allaz, J.M., Von Der Handt, A., Seward, G.G., Neill, O., Goemann, K., Chouinard, J., Carpenter, P.K., 2021. Quantitative WDS compositional mapping using the electron microprobe. Am Min: J Earth Planet Mater 106 (11), 1717–1735. https://doi.org/10.2138/am-2021-7739.

Duncan, A.M., Guest, J.E., Wallenstein, N., Chester, D.K., 2015. The older volcanic complexes of São Miguel, Azores: Nordeste and Povoação. In: Gaspar, J.L., Guest, J. E., Duncan, A.M., Barriga, F.J.A.S., Chester, D.K. (Eds.), Volcanic Geology of São

Miguel Island (Azores Archipelago), Geological Society, London, Memoirs, vol. 44, pp. 147–153. https://doi.org/10.1144/M44.11.

Eiler, J.M., 2001. Oxygen Isotope Variations of Basaltic Lavas and Upper Mantle Rocks. Rev. Mineral. Geochem. 43 (1), 319–364.

Eiler, J.M., Farley, K.A., Valley, J.W., Hauri, E., Craig, H., Hart, S.R., Stolper, E.M., 1997. Oxygen isotope variations in ocean island basalt phenocrysts. Geochim. Cosmochim. Acta 61, 2281–2293.

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

Ellis, B.S., Pimentel, A., Wolff, J.A., Cortes-Calderon, E.A., Harris, C., Mark, D.F., Neukampf, J., Bachmann, O., 2022. Geochemistry of the Pepom tephra deposits: the most recent intracaldera volcanism of Sete Cidades volcano, São Miguel, Azores. J. Volcanol. Geotherm. Res. 432, 107673 https://doi.org/10.1016/j.jvolgeores.2022.107673.

Ellis, B., Wolff, J.A., Szymanowski, D., Forni, F., Cortes-Calderon, E.A., Bachmann, O., 2023. Cumulate recycling in igneous systems: the volcanic record. Lithos 456-457, 107284.

Ferreira, T., Gomes, A., Gaspar, J.L., Guest, J., 2015. Distribution and significance of basaltic eruptive centres: São Miguel, Azores. In: Gaspar, J.L., Guest, J.E., Duncan, A. M., Barriga, F.J.A.S., Chester, D.K. (Eds.), Volcanic Geology of São Miguel Island (Azores Archipelago), Geological Society, London, Memoirs, vol. 44, pp. 135–146. https://doi.org/10.1144/M44.10.

France, L., Koepke, J., Ildefonse, B., Cichy, S.B., Deschamps, F., 2010. Hydrous partial melting in the sheeted dike complex at fast spreading ridges: experimental and natural observations. Contrib. Mineral. Petrol. 160, 683–704.

Garcia, M.O., Ito, E., Eiler, J.M., Pietruszka, A.J., 1998. Crustal contamination of Kilauea volcano magmas revealed by oxygen isotope analysis of glass and olivine from Puu Oo eruption lavas. J. Petrol. 39, 803–817.

Gaspar, J.L., Guest, J.E., Queiroz, G., Pacheco, J., Pimentel, A., Gomes, A., Marques, R., Felpeto, A., Ferreira, T., Wallenstein, N., 2015. Eruptive frequency and volcanic hazards zonation in São Miguel Island, Azores. In: Gaspar, J.L., Guest, J.E., Duncan, A.M., Barriga, F.J.A.S., Chester, D.K. (Eds.), Volcanic Geology of São Miguel Island (Azores Archipelago), Geological Society, London, Memoirs, vol. 44, pp. 155–166. https://doi.org/10.1144/M44.12.

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

Genske, F.S., Turner, S.P., Beier, C., Chu, M.F., Tonarini, S., Pearson, N.J., Haase, K.M., 2014. Lithium and boron isotope systematics in lavas from the Azores islands reveal crustal assimilation. Chem. Geol. 373, 27–36.

Gregory, R.T., Taylor, H.P., 1981. An oxygen isotope profile in a section of cretaceous oceanic crust, Samail ophiolite, Oman: evidence for δ^{18}O buffering of the oceans by deep (>5 km) seawater-hydrothermal circulation at mid-ocean ridges. J. Geophys. Res. 86, 2737–2755.

Grunder, A.L., 1987. Low δ^{18}O silicic volcanic rocks at the Calabozos Caldera complex southern Andes. Contrib. Mineral. Petrol. 95, 71–81.

Haase, K.M., Beier, C., 2003. Tectonic control of ocean island basalt sources on São Miguel, Azores? Geophys. Res. Lett 30 (16), 1856.

Hampton, R.L., Bindeman, I.N., Stern, R.A., Coble, M.A., Rooyakkers, S.M., 2021. A microanalytical oxygen isotopic and U-Th geochronologic investigation and modeling of rhyolite petrogenesis at the Krafla Central Volcano, Iceland. J. Volcanol. Geotherm. Res. 414, 107229.

Hansteen, T.H., Troll, V.R., 2003. Oxygen isotope composition of xenoliths from the oceanic crust and volcanic edifice beneath Gran Canaria (Canary Islands): consequences for crustal contamination of ascending magmas. Chem. Geol. 193, 181–193.

Harris, C., Erlank, A.J., 1992. The production of large-volume, low-δ^{18}O rhyolites during the rifting of Africa and Antarctica: the Lebombo Monocline, southern Africa. Geochim. Cosmochim. Acta 56, 3561–3570.

Harris, C., Vogeli, J., 2010. Oxygen isotope composition of garnet in the Peninsula Granite, Cape Granite Suite, South Africa: constraints on melting and emplacement mechanisms. S. Afr. J. Geol. 113, 401–412.

Harris, C., Smith, H.S., le Roex, A.P., 2000. Oxygen isotope composition of phenocrysts from Tristan da Cunha and Gough Island lavas: variation with fractional crystallization and evidence for assimilation. Contrib. Mineral. Petrol. 138, 164–175.

Hauri, E.H., 1996. Major-element variability in the Hawaiian mantle plume. Nature 382, 415–419.

Hildreth, W., Christiansen, R.L., O'Neil, J.R., 1984. Catastrophic isotopic modification of rhyolitic magma at times of caldera subsidence, Yellowstone Plateau Volcanic Field. J. Geophys. Res. 89, 8339.

Jochum, K.P., Willbold, M., Raczek, I., Stoll, B., Herwig, K., 2005. Chemical Characterisation of the USGS Reference Glasses GSA-1G, GSC-1G, GSD-1G, GSE-1G, BCR-2G, BHVO-2G and BIR-1G using EPMA, ID-TIMS, ID-ICP-MS and LA-ICP-MS. Geostand. Geoanal. Res. 29 (3), 285–302. https://doi.org/10.1111/j.1751-908X.2005.tb00901.x.

Johnson, C.L., Wijbrans, J.R., Constable, C.G., Gee, J., Staudigal, H., Tauxe, L., Forjaz, V. H., Salgueiro, 1998. ^{40}Ar/^{39}Ar ages and paleomagnetism of São Miguel lavas, Azores. Earth Plan. Sci. Lett. 160, 637–649.

Koppers, A.P., Becker, T.W., Jackson, M.G., Konrad, K., Dietmar, Muller R., Romanowicz, B., Steinberger, B., Whittaker, J.M., 2021. Mantle plumes and their role in earth processes. Nat. Rev. Earth Env. 2, 382–401.

Larrea, P., França, Z., Widom, E., Lago, M., 2018. Petrology of the Azores Islands. In: Kueppers, U., Beier, C. (Eds.), Volcanoes of the Azores - Revealing the Geological Secrets of the Central Northern Atlantic Islands, Active Volcanoes of the World Series. Springer, pp. 197–249. https://doi.org/10.1007/978-3-642-32226-6_10.

Le Bas, M.J., Le Maitre, R.W., Streckeisen, A., Zanettin, B., 1986. A Chemical Classification of Volcanic Rocks based on the Total Alkali-Silica Diagram. J. Petrol. 27, 745–750.

Mattey, D., Lowry, D., Macpherson, C., 1994. Oxygen isotope composition of mantle peridotite. Earth Plan. Sci. Lett. 128, 231–241.

McDonough, W.F., Sun, S.S., 1995. The composition of the Earth. Chem. Geol. 120, 223–253.

Meade, F.C., Troll, V.R., Ellam, R.M., Freda, C., Font, L., Donaldson, C.H., Klonowska, I., 2014. Bimodal magmatism produced by progressively inhibited crustal assimilation. Nat. Commun. 5, 4199. https://doi.org/10.1038/ncomms5199.

Métrich, N., Zanon, V., Creon, L., Hildenbrand, A., Moreira, M., 2014. Is the 'Azores hotspot' a wetspot? Insights from the geochemistry of fluid and melt inclusions in olivine of Pico basalts. J. Petrol. 55, 377–393.

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.

Moore, R., 1990. Volcanic geology and eruption frequency. São Miguel, Azores. Bull. Volcanol. 52, 602–614. https://doi.org/10.1007/BF00301211.

Moore, R.B., 1991. Geologic map of São Miguel, Azores. United States Geological Survey, Miscellaneous Investigations Series, map I-2007, scale 1:50 000.

Moreira, M., Doucelance, R., Kurz, M., Dupre, B., Allegre, C.J., 1999. Helium and lead isotope geochemistry of the Azores Archipelago. Earth Plan. Sci. Lett. 169, 189–205.

Moreira, M., Kanzari, A., Madureira, P., 2012. Helium and neon isotopes in São Miguel island basalts, Azores Archipelago: New constraints on the "low 3He" hotspot origin. Chem. Geol. 322-323, 91–98.

Muehlenbachs, K., 1986. Alteration of the oceanic crust and the ^{18}O history of seawater. Rev. Mineral. 16, 425–444.

Muehlenbachs, K., Byerly, G., 1982. ^{18}O-enrichment of silicic magmas caused by crystal fractionation at the Galapagos Spreading Center. Contrib. Mineral. Petrol. 79, 76–79.

Prytulak, J., Avanzinelli, R., Koetsier, G., Kreissig, K., Beier, C., Elliott, T., 2014. Melting versus contamination effects on ^{238}U–^{230}Th–^{226}Ra and ^{235}U–^{231}Pa disequilibria in lavas from São Miguel, Azores. Chem. Geol. 381, 94–109.

Putirka, K.D., 2008. Thermometers and barometers for volcanic systems. Rev. Mineral. Geochem. 69, 61–120.

Queiroz, G., Gaspar, J.L., Guest, J.E., Gomes, A., Almeida, M.H., 2015. Eruptive history and evolution of Sete Cidades Volcano, São Miguel Island, Azores. In: Gaspar, J.L., Guest, J.E., Duncan, A.M., Barriga, F.J.A.S., Chester, D.K. (Eds.), Volcanic Geology of São Miguel Island (Azores Archipelago), Geological Society, London, Memoirs, vol. 44, pp. 87–104. https://doi.org/10.1144/M44.7.

Renzulli, A., Santi, P., 2000. Two-stage fractionation history of the alkali basalt-trachyte series of Sete Cidades volcano (São Miguel, Azores). Eur. J. Mineral. 12, 469–494. https://doi.org/10.1127/0935-1221/2000/0012-0469.

Roeder, P.L., Emslie, R.F., 1970. Olivine-Liquid Equilibrium. Contrib. Mineral. Petrol. 29, 275–289.

Rooyakers, S.M., Chambefort, I., Faure, K., Wilson, C.J.N., Barker, S.J., Mortimer, N., Elms, H.C., Troch, J., Charlier, B.L.A., Leonard, G.S., Farsky, D., 2023. Absence of low-δ^{18}O magmas despite widespread assimilation of altered crust in a large magmatic and hydrothermal province. Geochim. Cosmochim. Acta 355, 195–209.

Ruttor, S., Nebel, O., Williams, H., Beier, C., Richter, M., Nebel-Jacobsen, Y., Romer, R.H. W., Turner, S.P., Soderman, C.R., 2022. Iron isotope evidence in ocean island basalts for plume- and plate-controlled melting, São Miguel, Azores. Geochim. Cosmochim. Acta 335, 111–123.

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

Sheppard, S.M., Harris, C., 1985. Hydrogen and oxygen isotope geochemistry of Ascension Island lavas and granites: variation with crystal fractionation and interaction with seawater. Contrib. Mineral. Petrol. 91, 74–81.

Shorttle, O., Maclennan, J., Piotrowski, A.M., 2013. Geochemical provincialism in the Iceland plume. Geochem. Cosmochim. Acta 122, 363–397.

Snyder, D.C., Widom, E., Pietruszka, A., Carlson, R.W., 2004. The role of open-system processes in the development of silicic magma chambers: a chemical and isotopic investigation of the Fogo A trachyte deposit, São Miguel, Azores. J. Petrol. 45, 723–738.

Sobolev, A., Hofmann, A.W., Sobolev, S.V., Nikogosian, I.K., 2005. An olivine-free mantle source of Hawaiian shield basalts. Nature 434, 590–597.

Staudigel, H., Davies, G.R., Hart, S.R., Marchant, K.M., Smith, B.M., 1995. Large-scale isotopic Sr, Nd and O isotopic anatomy of altered oceanic crust- DSDP/ODP sites 417/418. Earth Planet. Sci. Lett. 130, 169–185.

Storch, B., Haase, K.M., Romer, R.H.W., Beier, C., Koppers, A.A.P., 2020. Rifting of the oceanic Azores Plateau with episodic volcanic activity. Sci. Rep. 10, 19718. https://doi.org/10.1038/s41598-020-76691-1.

Storey, M., Wolff, J.A., Norry, M.J., Marriner, G.F., 1989. Origin of hybrid lavas from Agua de Pau volcano, São Miguel, Azores. In: Saunders, A.D., Norry, M.J. (Eds.), Magmatism in the Ocean Basins: Geological Society of London Special Publication, 42, pp. 161–180.

Storey, M., Mahoney, J.J., Saunders, A.D., Duncan, R.A., Kelley, S.P., Coffin, M.F., 1995. Timing of Hot Spot-Related Volcanism and the Breakup of Madagascar and India. Science 267, 852–855.

Thirlwall, M.F., Jenkins, C., Vroon, P.Z., Mattey, D.P., 1997. Crustal interaction during construction of ocean islands: Pb-Sr-Nd-O isotope geochemistry of the shield basalts of Gran Canaria. Chem. Geol. 135, 233–262.

Troch, J., Ellis, B.S., Mark, D.F., Bindeman, I.N., Kent, A.J.R., Guillong, M., Bachmann, O., 2017. Rhyolite generation prior to a Yellowstone supereruption: insights from the Island Park-Mount Jackson rhyolite series. J. Petrol. 0, 1–24.

Troch, J., Ellis, B.S., Harris, C., Bachmann, O., Bindeman, I.N., 2020. Low-δ^{18}O magmas on Earth: a review. Earth Sci. Rev. 208, 103299.

Turner, S., Hawkesworth, C.J., Rodgers, N.W., 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.N., 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. https://doi.org/10.1038/nature05898.

Ubide, T., Larrea, P., Becerril, L., Gale, C., 2022. Volcanic plumbing filters on ocean-island basalt geochemistry. Geology 50, 26–31.

Widom, E., Farquhar, J., 2003. Oxygen isotope signatures in olivines from São Miguel (Azores) basalts: implications for crustal and mantle processes. Chem. Geol. 193, 237–255.

Widom, E., Carlson, R.W., Gill, J.B., Schmincke, H.U., 1997. Th–Sr–Nd–Pb isotope and trace element evidence for the origin of the São Miguel, Azores, enriched mantle source. Chem. Geol. 140 (1–2), 49–68.

Woitischek, J., Dietzel, M., Inguaggiato, C., Bottcher, M.E., Leis, A., Virgilo Cruz, J., Gehre, M., 2017. Characterisation and origin of hydrothermal waters at São Miguel (Azores) inferred by chemical and isotopic composition. J. Volcanol. Geotherm. Res. 346, 104–117.

Zanon, V., Pimentel, A., Auxerre, M., Marchini, G., Stuart, F.M., 2020. Unravelling the magma feeding system of a young basaltic oceanic volcano. Lithos 352, 105325. https://doi.org/10.1016/j.lithos.2019.105325.