

Oxygen isotope signatures in olivines from São Miguel (Azores) basalts: implications for crustal and mantle processes

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Abstract

Oxygen isotope ratios were measured in olivines from eight São Miguel basalt lavas. With one exception (4.57‰), the olivines are indistinguishable from one another with an average $\delta^{18}\text{O}$ of $4.92 \pm 0.03\text{‰}$ (1σ). This value is slightly lower than that characteristic of upper mantle peridotite and MORB olivines ($5.2 \pm 0.2\text{‰}$). Assimilation of $\geq 10\text{--}20\%$ of high-temperature altered lower oceanic crust or $4\text{--}9\%$ hydrothermally altered volcanic edifice rocks could produce the low $\delta^{18}\text{O}$ signatures in the São Miguel olivines; both of these assimilation models are permitted by the trace element and radiogenic isotope variations in the São Miguel basalts. However, the limited variation in $\delta^{18}\text{O}$ despite eruption of the basalts through compositionally and tectonically variable lithosphere, and the lack of correlation of $\delta^{18}\text{O}$ with olivine forsterite content, are more easily explained if the olivine $\delta^{18}\text{O}$ signatures are inherited from their mantle source. If the $\delta^{18}\text{O}$ signatures reflect mantle source compositions, then the relatively low and uniform $\delta^{18}\text{O}$ signatures allow constraints to be placed on the origin of the mantle sources beneath São Miguel. Extreme variations in radiogenic isotope signatures have previously been attributed to two component source mixing between a predominant Azores plume source with mild HIMU-like characteristics, and an EMII-type mantle with very radiogenic Sr. The low $\delta^{18}\text{O}$ signatures in the São Miguel basalt olivines suggest that the predominant Azores plume source contains $>10\%$ hydrothermally altered recycled oceanic crust. The limited variation in $\delta^{18}\text{O}$ is consistent with a component of recycled sediment in the São Miguel EMII-type source, although, unlike the case for other EMII OIB (e.g. Samoa and Society), the relatively low $\delta^{18}\text{O}$ signatures in São Miguel restrict any involvement of recycled sediment to $<2\%$ of a relatively low $\delta^{18}\text{O}$ and very radiogenic Sr or high Rb/Sr sediment. Involvement of several percent metasomatized subcontinental lithospheric mantle could alternatively produce the EMII-type Sr–Nd–Pb isotope signatures without significantly affecting the plume-related low $\delta^{18}\text{O}$ signatures. The São Miguel $\delta^{18}\text{O}$ data are thus consistent with mixing between a low $\delta^{18}\text{O}$ Azores plume source with a component of subducted, hydrothermally altered lower oceanic crust, and either minor recycled sediment or localized EMII-rich delaminated subcontinental lithospheric mantle. The latter could have been introduced into the lithosphere or shallow asthenosphere during opening of the Atlantic ocean basin.

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1. Introduction

Heterogeneity of the Earth's mantle, recorded by variations in radiogenic isotope signatures of oceanic basalts, is generally considered to reflect the time-integrated effects of variable depletion due to melting and crust extraction, and variable enrichment due to recycling of lithosphere back into the convecting mantle (Zindler and Hart, 1986). Correlations in Sr–Nd–Pb isotope space indicate the existence in the Earth's mantle of several reservoirs that are isotopically distinct from the mid-ocean ridge basalt (MORB) source. These variably enriched mantle reservoirs (EMI, EMII, HIMU; Zindler and Hart, 1986) are most commonly attributed to subduction of oceanic crust \pm various types of sediment (e.g. Hofmann and White, 1982; Weaver, 1991; Hart et al., 1992). However, it is difficult to relate the observed variations in radiogenic isotopes to crustal recycling processes for a number of reasons. First, other geologic processes, including intra-mantle fluid metasomatism, can fractionate parent–daughter element pairs, such that with time isotopic signatures with crustal-like characteristics might develop. Second, there is insufficient information about the chemical and physical processes that occur during subduction metamorphism of oceanic crust and sediment to predict with certainty the isotopic composition that crustal material will acquire upon aging in the mantle. Finally, because time plays an important role in controlling the radiogenic isotope signatures, variable aging of crustal material at the Earth's surface and during and after subduction, will produce a range of isotopic signatures in the mantle, irrespective of any parent/daughter variability.

It has recently been recognized that the use of light stable isotope systems such as oxygen may overcome some of the limitations inherent in using radiogenic isotopes as tracers of crustal recycling processes (Woodhead et al., 1993; Eiler et al., 1995, 1996a, 1997; Harmon and Hoefs, 1995; Geist et al., 1998; Lassiter and Hauri, 1998; Skovgaard et al., 2001). Isotopic fractionation is far more significant at low temperatures than at high temperatures, and, as a result, crustal material is isotopically heterogeneous compared to mantle material; significant variations due to high temperature intra-mantle processes are unexpected. Subduction metamorphism apparently does not have a significant effect on the isotope

signature of the crustal material so that distinct crustal sources should remain recognizable (Garlick et al., 1971; Nadeau et al., 1993; Valley, 1986; Bebout and Barton, 1993; Putlitz et al., 2001). Finally, time does not affect the isotope signature of subducted material during aging in the mantle. For these reasons, oxygen isotopes can potentially be an important tracer of distinct types of recycled crustal material in the Earth's mantle.

The first extensive survey of oxygen isotopes in oceanic basalt lavas and glasses indicated a large degree of isotopic variability that was interpreted as evidence for pronounced mantle heterogeneity due to crustal recycling processes (Harmon and Hoefs, 1995). However, a subsequent survey study restricted to olivine phenocrysts concluded that there may be significantly less oxygen isotope variability in the mantle; $\delta^{18}\text{O}$ values for olivines in most ocean island basalts (OIB) are comparable to those of oceanic and continental peridotite and MORB olivine ($\delta^{18}\text{O} = 5.0$ – 5.4 ‰; Eiler et al., 1997). The implication of these results is that any contribution of recycled crustal material to most OIB mantle sources is minor ($\leq 1\%$; Eiler et al., 1997). Nevertheless, EMII-type OIB olivines were found to exhibit measurable isotopic variations with oxygen isotope signatures heavier than MORB mantle ($\delta^{18}\text{O} = 5.4$ – 6.1 ‰; average = 5.6 ‰), consistent with ~ 2 – 6% recycled sediment in the EMII OIB mantle sources (Eiler et al., 1997). In addition, olivines from some HIMU-type and low $^3\text{He}/^4\text{He}$ -type basalts are isotopically light relative to MORB mantle (average 5.03 and 4.87 ‰, respectively; Eiler et al., 1997). Low $\delta^{18}\text{O}$ signatures have been attributed to either recycled, subducted altered oceanic crust in the mantle plume source (e.g. Lassiter and Hauri, 1998; Skovgaard et al., 2001), or to shallow level crustal assimilation processes that may affect ascending basaltic magmas (e.g. Garcia et al., 1998; Gee et al., 1998; Eiler et al., 2000; Harris et al., 2000). In some cases, crustal recycling into the mantle can be distinguished from shallow level crustal contamination by the distinctive curvatures in the respective resulting lava suites on plots of $\delta^{18}\text{O}$ vs. radiogenic isotope ratios (e.g. James, 1981; Thirlwall et al., 1997; Skovgaard et al., 2001; Van Soest et al., 2002), or by comparisons of $\delta^{18}\text{O}$ signatures in olivine and matrix (Garcia et al., 1998); in other cases such a distinction is not possible (e.g. Eiler et al., 1996a, 1997).

In this paper, we report the results of oxygen isotope analyses of olivines from a suite of basalts from the island of São Miguel, Azores. These basalts exhibit extreme variability in Sr–Nd–Pb isotopic composition, indicative of two-component source mixing involving an EMII-type mantle source and a HIMU-type source characteristic of the predominant Azores plume (Hawkesworth et al., 1979; Davies et al., 1989; Widom et al., 1997). The measured oxygen isotope signatures in the São Miguel olivines (Table 1) are slightly lower than typical upper mantle, and are discussed with regard to possible shallow crustal assimilation processes and recycling of crustal material in the Azores mantle source region. The results from São Miguel highlight the difficulty in distinguishing between these processes geochemically.

2. Geological and geochemical setting

The Azores archipelago comprises a group of nine islands that straddle the Mid-Atlantic Ridge (MAR) between 37° and 40°N (Fig. 1). The islands emerge from the Azores platform, a topographic and gravity high located at the triple junction of the African, Eurasian and North American plates. The excess melting in this region of the MAR has been attributed to plume-ridge interaction based on geochemical differences between the tholeiitic basalts from the MAR along the Azores Platform, and tholeiites from normal ridge segments. The Azores Platform tholeiites exhibit

a greater degree of light rare earth element (LREE) enrichment than tholeiites from normal ridge segments, and there is a progressive increase in LREE enrichment as the Azores islands are approached (Schilling, 1975). The Azores platform tholeiites also exhibit correspondingly high concentrations of large-ion-lithophile elements (LILE) and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (White et al., 1976; White and Schilling, 1978), as well as high Pb- and low Nd-isotopic ratios (Dupré and Allègre, 1980, 1984; Ito et al., 1987; Dosso et al., 1996). These geochemical enrichments correlate with a topographic high and a positive gravity anomaly, consistent with a hotspot origin (Schilling, 1975), although the buoyancy flux of the Azores plume is estimated to be small ($\sim 1.1 \text{ Mg s}^{-1}$; Sleep, 1990). Higher concentrations of volatiles in the Azores Platform tholeiites indicate that the mantle beneath the Azores is also a “wet spot” (Schilling, 1975; Bonatti, 1990; Michael, 1995; Dixon et al., 1996), which likely contributes to the higher degrees of melting in this region of the MAR.

The alkali basalts of the Azores islands also exhibit evidence of the elemental and isotopic enrichments observed in the Azores Platform tholeiites. São Miguel in particular is distinguished among the Azores islands by the extremity of its geochemical enrichments. Of the nine islands, São Miguel is the most potassic (Schmincke and Weibel, 1972; Schmincke, 1973), displays the most radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (White et al., 1979), and is among the most LREE-enriched (Flower et al., 1976). Another unusual feature of São Miguel is the strong intra-island heterogeneity, evi-

Table 1
Oxygen isotope data for São Miguel olivine

Sample	MgO (%)	$\delta^{18}\text{O}$ small	<i>n</i>	$\delta^{18}\text{O}$ large	<i>n</i>	$\delta^{18}\text{O}$ average	<i>n</i>	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{206}\text{Pb}/^{204}\text{Pb}$
SMB-5	9.12	4.88 (0.14)	2			4.88 (0.14)	2	0.703464	19.489
ASM36	11.48	5.02 (0.21)	2	4.83	1	4.96 (0.14)	3	0.703522	19.518
SMB-6	11.88			4.99 (0.06)	4 (2 and 2*)	4.99 (0.06)	4	0.703532	19.653
SMB-8	7.37	4.58 (0.06)	2	4.57	1	4.57 (0.03)	3	0.704447	19.638
SMB-3	9.58	4.98	1	4.72 (0.02)	2	4.80 (0.09)	3	0.704911	19.827
SM88-14	11.4			5.04 (0.08)	3*	5.04 (0.08)	3	0.705475	20.040
SMB-1	8.91	4.88 (0.14)	2	4.98	1	4.91 (0.09)	3	0.705181	19.890
SM88-49	5.5			4.88 (0.00)	2*	4.88 (0.00)	2	0.705114	19.977

São Miguel samples are listed according to geographic location across the island from west to east. The $\delta^{18}\text{O}$ values are reported as averages for small and large grains, and as averages for all grains from each sample. Samples were analyzed by CO_2 and excimer laser fluorination (excimer data designated with *). Measured ratios were normalized to San Carlos olivine $\delta^{18}\text{O} = 5.20\text{‰}$ (measured average for San Carlos = $5.14 \pm 0.11\text{‰}$ by CO_2 , and $5.28 \pm 0.03\text{‰}$ by excimer). Errors are reported as ± 1 standard error (1σ). MgO and radiogenic isotope data for whole-rock samples from Widom et al. (1997).

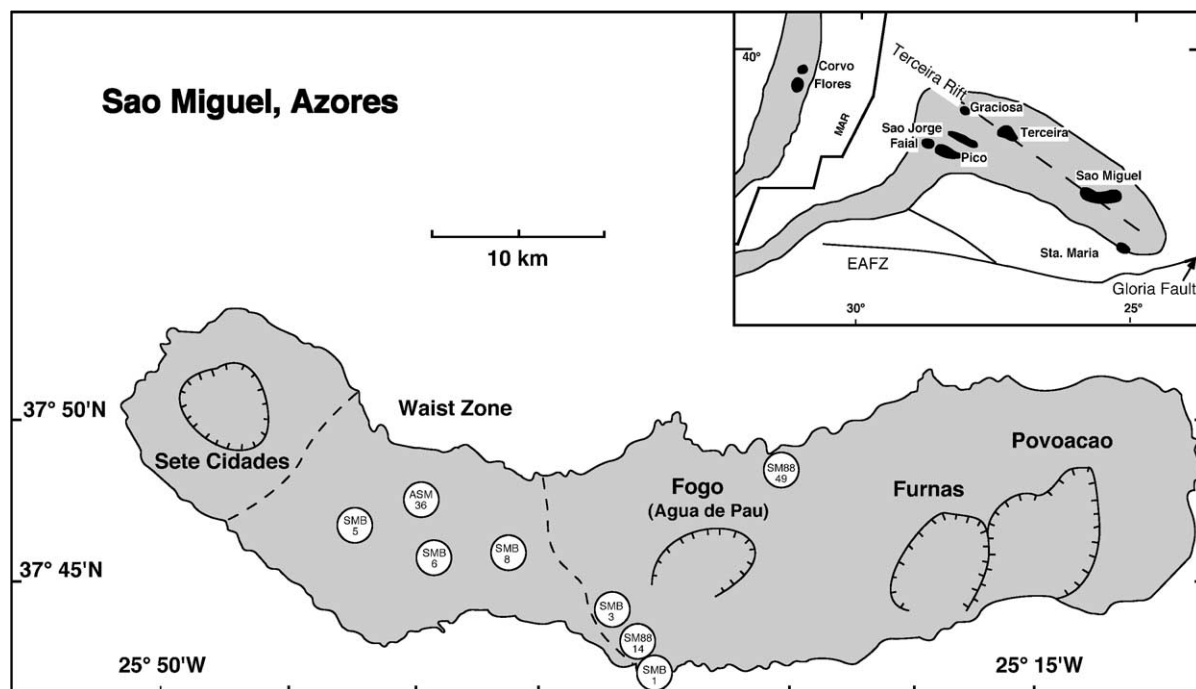


Fig. 1. Map of São Miguel, showing locations of samples for which $\delta^{18}\text{O}$ measurements were made. Trachytic stratovolcanoes and the “waist zone” are identified for reference (after Moore, 1990; Widom et al., 1997). The “waist zone” is an extensional region with NW–SE trending en echelon faults, which represents the location of the Terceira Rift. Inset illustrates the Azores archipelago and associated tectonic features.

denced by large variations in Sr, Nd, Pb, Th and He isotopic signatures (Hawkesworth et al., 1979; Davies et al., 1989; Kurz, 1991; Widom et al., 1997; Moreira et al., 1999). These isotopic variations are correlated with one another and with geographic location across the island, such that basalts become progressively more radiogenic in Sr and Pb isotope signatures from west to east.

In addition to being distinctive in its geochemical characteristics, the island of São Miguel is cut by a plate boundary. The active Terceira Rift, which is thought to be the locus of the present-day Eurasian–African plate boundary, passes through the western side of the island, and is thought to pass through the “waist zone” (Fig. 1), an area of NW–SE trending fissures (Booth et al., 1978) that has been the most volcanically active part of São Miguel during the Holocene (Moore, 1990). Most of the isotopic variations in São Miguel occur within the western two-thirds of the island, and largely within the waist zone.

The isotopic variations in São Miguel have been interpreted as two-component mixing trends, involv-

ing the predominant Azores plume source that contributes to the enrichment of the Azores Platform tholeiites, and a source with a strong EMII-type character (Fig. 2; Widom et al., 1997). There is, however, no consensus as to the origins of either of the two mantle sources. The origin of the predominant Azores plume source has been attributed to recycled oceanic crust plus entrained lower mantle based on both Os–Pb and He–Pb isotopic systematics (Widom and Shirey, 1996; Moreira et al., 1999); or alternatively to recycled lithospheric mantle based on the trace element and apparent low Fe characteristics of the inferred plume source (McKenzie and O’Nions, 1995; Turner et al., 1997). Similarly, the EMII-type source beneath São Miguel has been variously attributed to recycled upper crustal sediment (Hawkesworth et al., 1979; Davies et al., 1989; Turner et al., 1997; Moreira et al., 1999) or delaminated, metasomatized subcontinental lithospheric mantle (Hawkesworth et al., 1979; Davies et al., 1989; McKenzie and O’Nions, 1995; Widom et al., 1997). In this study, we analyzed oxygen isotopes in

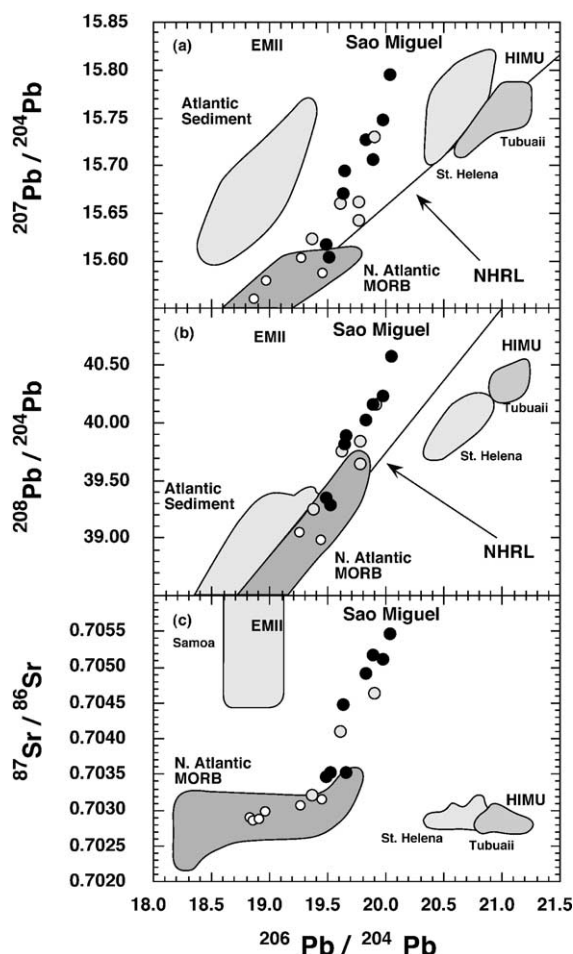


Fig. 2. $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ for São Miguel basalts (black and gray filled circles). The black circles are those samples for which $\delta^{18}\text{O}$ measurements were made. The linear trends exhibited by the São Miguel basalts are indicative of two-component mixing involving a component that falls within the enriched end of the MORB field, similar to the Azores Platform tholeiites (APT; unfilled circles), and an enriched component with a strong EMII-type signature ($^{87}\text{Sr}/^{86}\text{Sr} \geq 0.7055$). Data for MORB, including Azores Platform tholeiites, from Dupré and Allègre (1980), Ito et al. (1987), and Shirey et al. (1987); data for OIB from Chaffey et al. (1989), Hauri and Hart (1993), Reisberg et al. (1993), Vidal et al. (1984), and Zindler and Hart (1986); and data for sediment from Ben Othman et al. (1989), and Plank and Langmuir (1998).

olivine phenocrysts from a suite of São Miguel basalts with the intent that combined oxygen-radioisotopic data might better constrain the origins of the São Miguel mantle sources.

3. Samples and analytical methods

Oxygen isotopes were measured in olivines separated from eight São Miguel basalt lavas that were chosen to represent the observed range in whole-rock Sr and Pb isotopic compositions (Fig. 2). The lavas are young (<5 to 26.5 ka) alkali olivine basalts, that were erupted from distinct vents in the extensional waist zone and the flanks of the trachytic Fogo volcano (Fig. 1). The samples analyzed in this study are free of any crustal or mantle xenoliths (Widom and Shirey, 1996; Widom et al., 1997).

Olivine separates were handpicked from crushed and sieved basalt lavas and examined with a binocular microscope, in order to eliminate grains that contained inclusions, cracks or alteration. Two grain size populations (>2-mm diameter and <1-mm diameter) with a range in forsterite contents were processed for analysis in order to document potential differences in $\delta^{18}\text{O}$ of distinct crystal populations.

CO_2 laser fluorination analyses were made using a 25-W Synrad Laser with BrF_5 as the fluorinating agent (Sharp, 1990; Rumble and Hoering, 1994; Valley et al., 1995). Whole mineral grains of 1.4- to 3.7-mg mass were weighed and loaded into sample cups of a stainless steel sample holder, which was loaded into the reaction chamber. The reaction chamber was degassed and prefluorinated overnight. The samples were fluorinated by heating the grains with the laser after the chamber was filled with 30–35 torr of BrF_5 . Laser focus and power were manipulated to heat and melt the grains in a controlled manner without sample spattering. The process was monitored through a sapphire window and binocular microscope. The fluorination reaction produces MgF_2 liquid, SiF_4 gas, FeF_2 crystals and O_2 gas. The O_2 gas was purified cryogenically and transferred to the inlet of a gas source mass spectrometer using sample tubes containing 4–6 mesh molecular sieve substrate with 5-Å pore diameter. Analyte oxygen was expanded into the inlet of the mass spectrometer with the molecular sieve heated to 80–100 °C. $\delta^{18}\text{O}$ was determined by conventional gas source mass spectrometry techniques using a Finnigan MAT 252 at the Geophysical Laboratory. Five CO_2 laser fluorination analyses of San Carlos olivine made over the course of the study yielded $\delta^{18}\text{O} = 5.14 \pm 0.11\text{‰}$ (1 σ), which is comparable to laser fluorination values for San Carlos

olivine measured previously at the Geophysical Lab (5.0–5.2‰; Rumble et al., 1997) and in other labs (4.9 ± 0.1 ‰ 1σ , Matthey et al., 1994 and Chazot et al., 1997; 5.25 ± 0.05 ‰ 1σ , Eiler et al., 1996b).

Olivine grains from a few samples were analyzed using KrF excimer laser ablation (Lambda Physik Compex 110 laser) with F_2 as the fluorinating agent (see Wiechert and Hoefs, 1995; Rumble et al., 1997; Farquhar and Rumble, 1998). Olivine grain samples were weighed and mounted into stainless steel sample holders with set screws. The sample holder was loaded into a reaction chamber that was outgassed and pre-fluorinated following procedures outlined in Farquhar and Rumble (1998). Laser ablation was accomplished by focusing the laser beam to a 400×800 - μm spot on the sample surface. Fluorination occurs by reaction of the plume of ablated material in a 30–40-torr atmosphere of fluorine gas. Product O_2 was purified by reacting residual F_2 with 110 °C KBr and condensing other gaseous contaminants into liquid nitrogen cooled traps. O_2 was frozen directly into the inlet of the Finnigan MAT 252 for mass spectrometric analysis using 4–6 mesh 5-Å pore diameter molecular sieve. Four KrF excimer laser ablation analyses of San Carlos olivine made over the course of the study yielded $\delta^{18}O = 5.28 \pm 0.03$ ‰ (1σ).

In order to best compare samples measured by CO_2 and KrF excimer laser fluorination, all $\delta^{18}O$ values reported in Table 1 are normalized to San Carlos olivine = 5.20‰. Results for sample SMB-6, for which olivines were analyzed by both CO_2 and KrF excimer, indicate excellent agreement between the techniques ($\delta^{18}O = 4.96 \pm 0.14$ and 5.03 ± 0.03 , respectively). All measurements in this study were repeated and uncertainties are estimated to be better than ± 0.15 ‰ (1σ).

4. Results

Olivines of two crystal size populations (larger grains >2 mm and smaller grains <1 mm diameter) were analyzed for most of the samples, and the results are reported in Table 1. Electron microprobe analyses of the smaller and larger olivine populations in five of the samples for which oxygen isotope analyses were performed indicate that, in general, the larger olivines have higher forsterite (Fo) contents than the smaller

olivines (Fig. 3). With the exception of one sample (SMB-3), the $\delta^{18}O$ values measured in the two crystal size populations for each analyzed sample are within 1σ of one another, and there is no apparent bias towards ^{18}O enrichment or ^{18}O depletion for the smaller vs. larger grain size populations (Table 1). Average values for each sample are also reported in Table 1.

The measured oxygen isotope ratios range from $\delta^{18}O = 4.57$ ‰ to 5.04‰, but, with the exception of one sample (4.57‰; SMB-8), are indistinguishable from one another at the 1σ level, and have an average $\delta^{18}O = 4.92 \pm 0.03$ ‰ (1σ). The measured $\delta^{18}O$ values for the São Miguel olivines were systematically lower than those measured in the San Carlos olivine standard during the time period of sample analysis, and are lower than the average of mantle olivines from 76 peridotite xenolith samples (5.18 ± 0.14 ‰ 1 standard deviation [S.D.]; Matthey et al., 1994) and the average of six MORB-related olivine samples (5.16 ± 0.09 ‰ 1σ ; Eiler et al., 1997). The $\delta^{18}O$ signatures of the São Miguel olivines are relatively uniform despite the

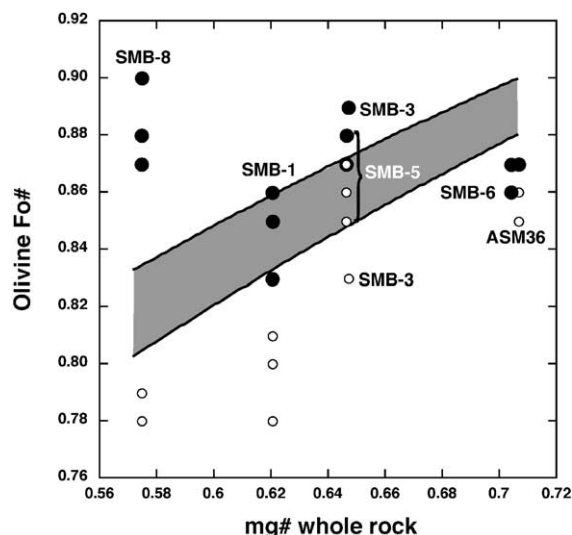


Fig. 3. Forsterite contents (mole fraction) of olivine cores vs. mg# of São Miguel basalt whole rocks ($mg\# = [(Mg^{2+}/(Fe^{2+} + Mg^{2+}))]; Fe^{2+}$ is calculated as 90% of total Fe; Moore, 1991). Filled circles represent the larger (>2 mm) olivine population, and open circles represent the smaller (<1 mm) olivine population. The larger olivines have higher Fo than smaller olivines for any given sample. Shaded field represents equilibrium field for olivines and basaltic magmas assuming $K_d(Fe/Mg) = 0.3 \pm 0.03$ (Roeder and Emslie, 1970).

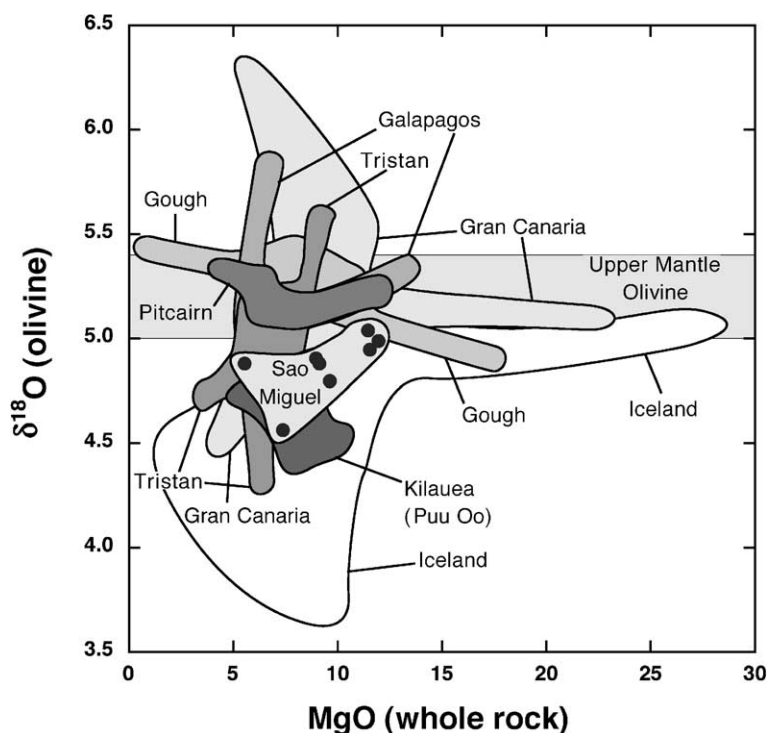


Fig. 4. $\delta^{18}\text{O}$ of olivine (or “olivine equivalent”) vs. whole rock MgO for São Miguel and other OIB. A rough positive correlation of $\delta^{18}\text{O}$ vs. MgO is observed for the São Miguel olivines, but is not apparent if the one anomalously low $\delta^{18}\text{O}$ sample is excluded. The São Miguel olivine $\delta^{18}\text{O}$ values exhibit a relatively limited range compared to many other OIB, especially those for which the $\delta^{18}\text{O}$ signatures have been attributed to crustal assimilation (Iceland, Gran Canaria-Canary Islands, Tristan da Cunha, and Kilauea-Puu Oo). Literature data are from the following sources: Gough and Tristan da Cunha (Harris et al., 2000); Galapagos (Geist et al., 1998); Pitcairn (Eiler et al., 1995); Iceland (Gee et al., 1998); Gran Canaria (Thirlwall et al., 1997); Kilauea-Puu Oo (Garcia et al., 1998). All $\delta^{18}\text{O}$ values were measured on olivines except for the Gran Canaria data, for which clinopyroxene data have been converted to “olivine equivalents” assuming $\Delta\text{cpx-ol}=0.51$ (Mattey et al., 1994).

significant range in whole-rock radiogenic isotope compositions ($^{87}\text{Sr}/^{86}\text{Sr}=0.7035$ to 0.7055 , and $^{206}\text{Pb}/^{204}\text{Pb}=19.49$ to 20.04 ; Table 1), and no correlations of $\delta^{18}\text{O}$ with radiogenic isotope signatures are apparent. MgO contents in the whole rock lavas range from 5.5 to 11.9 wt.% (Table 1), and there is a rough positive correlation of $\delta^{18}\text{O}$ vs. MgO (Fig. 4); however, this correlation is only present because of the one anomalously low $\delta^{18}\text{O}$ sample (SMB-8).

5. Discussion

The measured $\delta^{18}\text{O}$ for São Miguel olivines are slightly but systematically low (average $\delta^{18}\text{O}=4.9\text{‰}$) relative to continental and oceanic mantle ($5.2 \pm 0.1\text{‰}$ 1σ ; Mattey et al., 1994; Eiler et al., 1997). The $\delta^{18}\text{O}$

data for São Miguel olivines are also relatively homogeneous despite the large variations in whole-rock radiogenic isotope signatures.

5.1. Origin of the low $\delta^{18}\text{O}$ signature

Low $\delta^{18}\text{O}$ signatures might be ascribed either to an inherent low $\delta^{18}\text{O}$ composition of the Azores mantle plume source due to lithospheric recycling, or to assimilation by the basaltic magmas of low $\delta^{18}\text{O}$ lithosphere. Relatively low $\delta^{18}\text{O}$ signatures, ranging in values to as low as 2.0‰ in some cases, are known to characterize portions of lower oceanic crust and serpentinized uppermost oceanic mantle that have interacted with seawater at high temperature (Muehlenbachs, 1986; Hart et al., 1999). Significantly lower $\delta^{18}\text{O}$ signatures are found in some oceanic island

volcanic edifices, where high temperature exchange with isotopically light local circulating meteoric water has occurred (Guatason and Muehlenbachs, 1998). Values of $\delta^{18}\text{O} \leq 0.1\text{‰}$ are inferred to exist within the Icelandic crust (Hemond et al., 1993), and values as low as -1‰ have been measured in plutonic samples from the basal complex of Fuerteventura, Canary Islands (Javoy et al., 1986). Below we consider in more detail the various processes that might be responsible for the low $\delta^{18}\text{O}$ signatures in the São Miguel olivines.

5.1.1. Assimilation of oceanic lithosphere

The island of São Miguel is built on 38–49 Ma oceanic lithosphere (Krause and Watkins, 1970). Assimilation of the lower sections of such lithosphere, including gabbros or serpentinites, could potentially produce the low $\delta^{18}\text{O}$ values found in the São Miguel olivines. The minimum amount of assimilation of oceanic lithosphere necessary to lower the $\delta^{18}\text{O}$ signature of the Azores olivines from a typical upper mantle value of 5.2‰ to the lowest measured value of 4.57‰ (SMB-8) and to the average value for the other samples (4.92‰), can be estimated by assuming that the lithosphere beneath São Miguel has a $\delta^{18}\text{O}$ signature comparable to the lowest values found in altered oceanic lithosphere (2‰ ; Hart et al., 1999). Given these constraints, a *minimum* of 10–20% bulk assimilation of oceanic lithosphere would be necessary to explain the São Miguel olivine $\delta^{18}\text{O}$ data. Similar amounts of assimilation of high temperature altered oceanic crust have been suggested to explain low $\delta^{18}\text{O}$ signatures in olivines from Mauna Kea, Hawaii, and it was argued that this would have little effect on the major and trace element and Sr–Nd–Pb isotopic signatures of the erupted lavas (Eiler et al., 1996a).

The significant amounts of assimilation of oceanic lithosphere required to produce the low $\delta^{18}\text{O}$ signatures of the São Miguel olivines ($\geq 10\text{--}20\%$) would also be expected to significantly alter the Os isotope signatures of the host basalts, due to the high sensitivity of the Os isotope system to lithospheric assimilation (e.g. Widom, 1997; Widom et al., 1999). For a suite of related magmas with a common assimilant, one might predict a negative relationship between $^{187}\text{Os}/^{188}\text{Os}$ and $\delta^{18}\text{O}$ for assimilation of gabbroic oceanic crust (high $^{187}\text{Os}/^{188}\text{Os}$ and low $\delta^{18}\text{O}$), and

a positive or negative relationship for assimilation of serpentinized oceanic mantle (low or high $^{187}\text{Os}/^{188}\text{Os}$ and low $\delta^{18}\text{O}$). Although no $^{187}\text{Os}/^{188}\text{Os}$ or $\delta^{18}\text{O}$ analyses of the oceanic crust beneath the Azores presently exist, analyses of MORB-related gabbros from ODP hole 735B (Hart et al., 1999), Hawaii (Lassiter and Hauri, 1998) and the Canary Islands (Widom and Neumann, unpublished data) provide estimates of the composition of lower oceanic crust over a broad geographic and crustal age range (Indian Ocean, 11–12 Ma; Pacific Ocean, ~ 100 Ma; and Atlantic Ocean, $\sim 160\text{--}180$ Ma, respectively). $^{187}\text{Os}/^{188}\text{Os}$ ratios in these samples range from 0.142 to 0.439, with Os concentration ranging from 3 to 838 ppt, and $\delta^{18}\text{O}$ from 2.0‰ to 6.2‰ .

The $^{187}\text{Os}/^{188}\text{Os}$ signatures in the São Miguel basalts (Widom and Shirey, 1996) do not correlate with $\delta^{18}\text{O}$ signatures (Fig. 5), suggesting that a simple assimilation model like the one described cannot explain the low $\delta^{18}\text{O}$ signatures in the São Miguel olivines. Nevertheless, mixing models (Fig. 5) indicate that the observed ranges of $\delta^{18}\text{O}$ and $^{187}\text{Os}/^{188}\text{Os}$ in the São Miguel basalts are consistent with assimilation of significant percentages (up to $\sim 25\%$) of altered oceanic crust with ranges in Os concentration and $^{187}\text{Os}/^{188}\text{Os}$ and $\delta^{18}\text{O}$ compositions that are well within the range found in MORB gabbros.

Assimilation of the ultramafic portion of the oceanic lithosphere, which is also typically characterized by low $\delta^{18}\text{O}$, is difficult to reconcile with all of the São Miguel data (Fig. 5, curves ‘c’ and ‘d’). Because of the relatively high Os abundances in most mantle peridotite compared to basalts, such assimilation will generally have a significant effect on the resulting basalt $^{187}\text{Os}/^{188}\text{Os}$ signatures, with little effect on the $\delta^{18}\text{O}$. Fig. 5 (curve ‘c’) illustrates that assimilation of oceanic mantle with low $\delta^{18}\text{O}$ but average “minimally altered” abyssal peridotite $^{187}\text{Os}/^{188}\text{Os}$ signatures (0.1246; Snow and Reisberg, 1995) will produce basalts with unradiogenic Os isotope signatures, unlike the observed data. Our data therefore rule out assimilation of typical mantle peridotite with subchondritic Os isotope signatures. Some abyssal peridotites, however, have lower Os abundances and are more radiogenic than their less altered counterparts (Standish et al., 2002). Modeling of assimilation of such altered peridotites suggests that this process can produce O–Os isotope signatures similar to those of

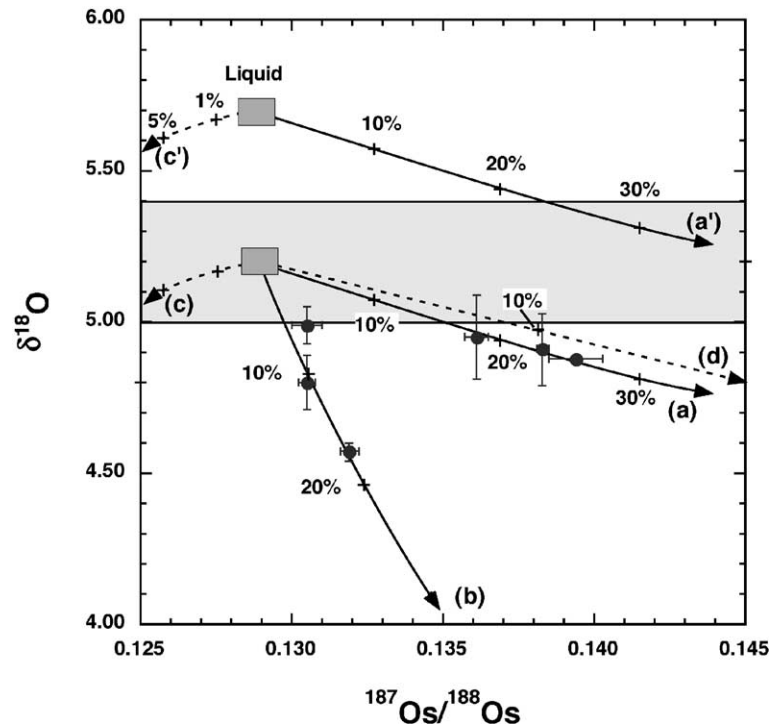


Fig. 5. $\delta^{18}\text{O}$ vs. $^{187}\text{Os}/^{188}\text{Os}$ showing isotopic composition of São Miguel samples (data points are olivine $\delta^{18}\text{O}$ and whole-rock $^{187}\text{Os}/^{188}\text{Os}$ values). Shaded band shows the average $\delta^{18}\text{O}$ value of 5.2 ± 0.2 ‰ for mantle olivine based on peridotite xenoliths and MORB olivine (Mattey et al., 1994; Eiler et al., 1997). The São Miguel olivines have $\delta^{18}\text{O}$ values slightly lower than the average mantle. Mixing curves show the expected effects of assimilation of altered lower oceanic crust (solid curves) and altered oceanic mantle lithosphere (dashed curves) by basaltic magmas. All models involve basalts that start with a MORB-like $\delta^{18}\text{O}$ signature of 5.7 ‰ and $^{187}\text{Os}/^{188}\text{Os}=0.129$ (a minimum value for the least radiogenic OIB; Widom, 1997). Models 'a' and 'b' involve assimilation of altered oceanic crust with higher and lower Os abundances, respectively. Models 'c' and 'd' illustrate assimilation of altered abyssal peridotites with minimally and strongly altered Os isotope signatures, respectively. Curves (a') and (c') show the liquid evolution paths that produce the olivines representing paths (a) and (c), respectively. Mixing parameters are as follows: Basalt magma: Os = 50 pg/g, $^{187}\text{Os}/^{188}\text{Os}=0.129$, $\delta^{18}\text{O}=5.7$ ‰; altered lower oceanic crust (curve 'a'): Os = 25 pg/g, $^{187}\text{Os}/^{188}\text{Os}=0.2$, $\delta^{18}\text{O}=4.4$ ‰; altered lower oceanic crust (curve 'b'): Os = 10 pg/g, $^{187}\text{Os}/^{188}\text{Os}=0.2$, $\delta^{18}\text{O}=2.0$ ‰; altered oceanic peridotite (curve 'c'): Os = 3.3 ng/g, $^{187}\text{Os}/^{188}\text{Os}=0.1246$ (Snow and Reisberg, 1995), $\delta^{18}\text{O}=4.4$ ‰; altered oceanic peridotite (curve 'd'): Os = 0.120 ng/g, $^{187}\text{Os}/^{188}\text{Os}=0.1725$ (Standish et al., 2002), $\delta^{18}\text{O}=3.2$ ‰.

some but not all of the São Miguel basalts. Fig. 5 (curve 'd') illustrates this process using the extreme example of a low Os, highly radiogenic dunite assimilant (120 ppt Os; $^{187}\text{Os}/^{188}\text{Os}=0.1725$; Standish et al., 2002), and assuming the lowest $\delta^{18}\text{O}$ signature found in the altered ultramafic portion of the oceanic lithosphere (3.2 ‰; Muehlenbachs, 1986). Although the O–Os isotope signatures of the more radiogenic Os samples from São Miguel can be reproduced by this model with a little more than 10% assimilation, the other São Miguel samples cannot be explained by this process using the compositions of any known abyssal peridotites.

5.1.2. Assimilation of volcanic edifice

Hydrothermally altered volcanic edifice rocks are potentially even more effective agents of contamination of $\delta^{18}\text{O}$ signatures in basalts than is oceanic crust, due to the extremely low $\delta^{18}\text{O}$ signatures that can develop in volcanic edifice rocks that have interacted with low $\delta^{18}\text{O}$ meteoric water. Extreme examples are the plutonic gabbros and syenites from the basal complex of Fuerteventura, Canary Islands, which reach $\delta^{18}\text{O}$ values as low as -1 ‰ (Javoy et al., 1986). If such extreme $\delta^{18}\text{O}$ signatures characterize hydrothermally altered volcanics in São Miguel, then as little as 4–9% assimilation would be required

produce the lowest São Miguel olivine $\delta^{18}\text{O}$ value of 4.57‰ and the average value for the other samples of 4.92‰, respectively. In São Miguel, possible volcanic edifice assimilants include basalts and intermediate differentiates (benmoreite–mugearite), and highly evolved trachytes and their intrusive equivalents, syenites (Muecke et al., 1974; Moore, 1990; Widom et al., 1992, 1993).

Evolved volcanic and plutonic rocks in São Miguel are generally very strongly enriched relative to the basalts in highly incompatible trace elements such as Nb and Zr. The relatively tight correlation of Nb/Zr vs. $^{206}\text{Pb}/^{204}\text{Pb}$ for the São Miguel basalts (Widom et al., 1997; Fig. 6) should thus represent one of the most sensitive constraints as to permissible amounts of assimilation of evolved volcanic edifice. For example, São Miguel basalt sample SMB-4, which erupted

through the western flank of the trachytic/syenitic Sete Cidades volcano (Fig. 1) and exhibits petrographic and other geochemical evidence of interaction with syenite (Widom et al., 1997), falls distinctly off the Nb/Zr vs. $^{206}\text{Pb}/^{204}\text{Pb}$ correlation line (Fig. 6). However, mixing calculations indicate that as much as 5–15% assimilation of average composition trachyte or syenite could be accommodated even within the limited scatter of the basalts in the Nb/Zr– $^{206}\text{Pb}/^{204}\text{Pb}$ correlation (Fig. 6). As discussed above, such amounts of assimilation are sufficient to produce the low $\delta^{18}\text{O}$ signatures in the São Miguel olivines.

Assimilation of hydrothermally altered basaltic edifice lavas would be even more difficult to detect geochemically. Given the young age of São Miguel island (1–4 Ma; Feraud et al., 1981; Moore, 1990), the radiogenic isotope signatures of even the oldest

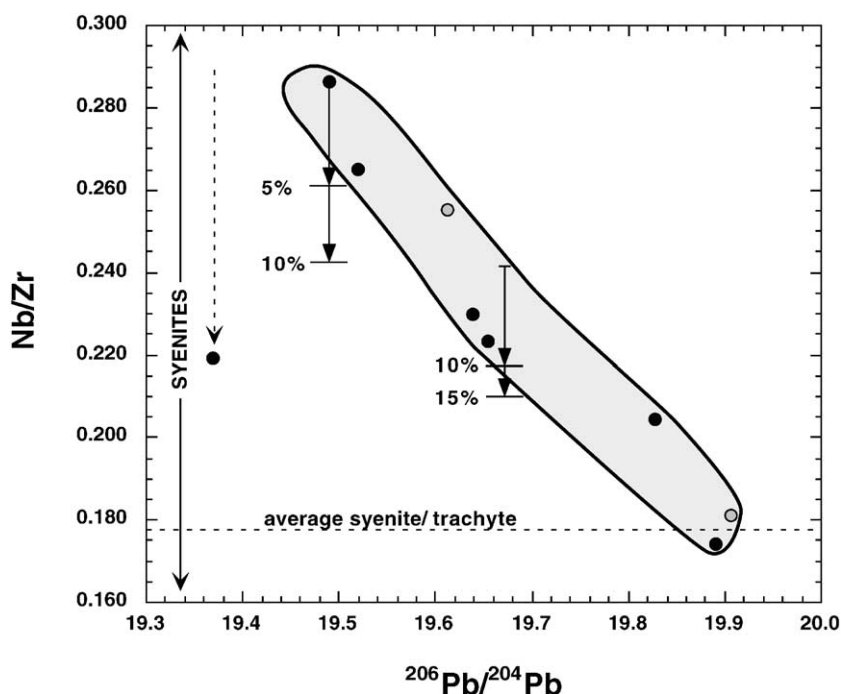


Fig. 6. Nb/Zr vs. $^{206}\text{Pb}/^{204}\text{Pb}$ variations in São Miguel basalts (black circles are those for which olivine $\delta^{18}\text{O}$ has been measured). Despite the large range of Nb/Zr in syenite nodules from Fogo volcano (0.10 to 0.37 with an average 0.178; Widom et al., 1993), and the ~5–10-fold higher concentrations of these elements in the syenites compared to the basalts, a significant amount of crustal assimilation is permissible. One São Miguel basalt that erupted through the flanks of Sete Cidades volcano and that displays clear petrographic evidence of syenite assimilation (sample SMB-4; Widom et al., 1997) falls significantly below this otherwise linear trend (designated by dashed arrow). However, mixing calculations indicate that as much as 5–15% assimilation of average composition trachyte or syenite could be accommodated even within the limited scatter of the basalts in the Nb/Zr– $^{206}\text{Pb}/^{204}\text{Pb}$ correlation. Solid arrows with percentages represent amount of assimilant, assuming evolved rocks with the same $^{206}\text{Pb}/^{204}\text{Pb}$ compositions as the parental basalts, and Nb/Zr of 0.178 (Widom et al., 1992, 1993). Such amounts of assimilation are sufficient to produce the observed low $\delta^{18}\text{O}$ signatures in the São Miguel olivines.

potential basaltic assimilants would likely be very similar to recently intruding basalts. The most significant compositional difference between the oldest, hydrothermally altered island basalts and the recently erupted basalts is likely to be the low $\delta^{18}\text{O}$ signatures presumed to characterize the former. Assimilation of altered, basaltic edifice lavas has been proposed to explain variable low $\delta^{18}\text{O}$ signatures and olivine–host lava oxygen isotope disequilibria in basalts from Puu Oo (Kilauea); these basalts, nevertheless, exhibit no evidence of crustal assimilation based on Sr–Nd–Pb isotope or major or trace element systematics (Garcia et al., 1998).

5.1.3. Summary and implications of assimilation models

The models presented in the previous sections were designed to test possible assimilation processes using the most sensitive available geochemical indicators. It is expected that many other geochemical indicators will be less sensitive to crustal assimilation, and thus (if heat budgets allow) assimilation of 10–20% oceanic lower crust or 4–9% hydrothermally altered volcanic rocks could explain the low $\delta^{18}\text{O}$ signatures in the São Miguel olivines without disturbing other geochemical relationships amongst the São Miguel basalts. These results highlight the difficulty in recognizing basalts that have experienced crustal assimilation, and provide further support for the suggestion that caution must be used in firmly attributing low $\delta^{18}\text{O}$ signatures in oceanic basalts to mantle source characteristics, unless assimilation of hydrothermally altered crust can be categorically ruled out (Eiler et al., 1997; Garcia et al., 1998).

A corollary to the conclusion that geochemical signatures of basalts are often relatively insensitive to crustal assimilation is that it can be very difficult to document that crustal contamination has occurred. The existence of olivines with low $\delta^{18}\text{O}$ signatures is not sufficient evidence that crustal assimilation has occurred, since low $\delta^{18}\text{O}$ signatures in basalts can also result from melting low $\delta^{18}\text{O}$ mantle sources. In this regard, it is important to consider some additional aspects of the São Miguel data set, and the respective implications for crustal assimilation models.

One important consideration is the magnitude of the variation observed in the $\delta^{18}\text{O}$ signatures of the São Miguel olivines ($<0.5\text{‰}$), which is limited

relative to other ocean island basalts for which oxygen isotopes have been measured in phenocrysts and for which deviations from mantle values have been attributed to crustal assimilation. For example, $\delta^{18}\text{O}$ values in phenocrysts from Iceland, Gran Canaria (Canary Islands) and Tristan da Cunha span ranges of 2.2‰, 1.8‰ and 1.3‰, respectively (Fig. 4). Although the limited variation in olivine $\delta^{18}\text{O}$ observed in the São Miguel basalts might relate in part to the small number of samples analyzed, fewer samples were analyzed for Tristan, yet they span a significantly larger range in $\delta^{18}\text{O}$. Puu Oo (Kilauea) olivines, with low $\delta^{18}\text{O}$ signatures attributed to crustal assimilation (Garcia et al., 1998), display only a marginally larger variation in $\delta^{18}\text{O}$ than the São Miguel olivines. However, the Puu Oo basalts erupted over a restricted range in time (14 years) and a restricted geographic area (~ 3 km), and are thought to emanate from a common magma reservoir (Garcia et al., 1998), which may limit the potential for significant variations in extent and variety of crustal assimilation. In contrast, the São Miguel basalts for which $\delta^{18}\text{O}$ values were measured erupted over more than 26,000 years, across an ~ 40 -km length of the island, and through two distinct volcanic “provinces” that are characterized by significant compositional and tectonic differences (Moore, 1991; Widom and Shirey, 1996). Basalts from the western side of the island erupted within the extensional regime of the “waist zone” (Fig. 1), an area of NW–SE trending fissures related to the active Terceira Rift. The waist zone is almost exclusively basaltic and ankaramitic in composition (Moore, 1990), and some waist zone basalts contain spinel lherzolites, suggesting rapid ascent from mantle depths. In contrast, those samples to the east of the waist zone erupted through the flanks of Fogo volcano, a trachytic stratovolcano known to have an extensive syenitic intrusive complex, and a very active hydrothermal system (Muecke et al., 1974). Furthermore, the large variation in radiogenic isotope signatures of the São Miguel basalts, which correlate with geographic location on the island, requires that the magmas evolved in distinct plumbing systems, rather than emanating from a common, homogenized magma chamber. Thus, if the low $\delta^{18}\text{O}$ signatures in the São Miguel olivines are due to crustal assimilation, then the assimilation process must result in a very restricted range of magmatic

$\delta^{18}\text{O}$ signatures despite the significant variations in tectonic and volcanic provinces in which the basalts are generated and stored prior to eruption.

Another important consideration is the relationship between the $\delta^{18}\text{O}$ signatures of the larger, higher Fo and smaller, lower Fo olivine populations in the São Miguel basalts (Table 1 and Fig. 3). If assimilation (or assimilation-fractional crystallization) of low $\delta^{18}\text{O}$ hydrothermally altered crust was important in the petrogenesis of the São Miguel basalts, it might be expected that higher Fo olivines crystallized out of more mafic magmas should have higher $\delta^{18}\text{O}$ signatures than lower Fo olivines crystallized from more evolved magmas that have experienced greater amounts of assimilation. However, no clear difference is apparent in the $\delta^{18}\text{O}$ composition of the smaller (lower Fo) vs. larger (higher Fo) olivine populations in the São Miguel basalts. Although one can generate scenarios in which such a relationship between olivine populations would not be required (e.g. Eiler et al., 1996a), the lack of such a correlation is consistent with the low $\delta^{18}\text{O}$ signatures in the São Miguel olivines reflecting the mantle source composition rather than crustal assimilation processes. This possibility is also consistent with correlations in São Miguel basalts between $^3\text{He}/^4\text{He}$ in olivines and whole-rock radiogenic isotope ratios, an observation that has been used to argue against shallow-level assimilation processes affecting the recent São Miguel basalts (Kurz, 1991; Moreira et al., 1999).

In summary, although assimilation of hydrothermally altered oceanic crust or volcanic edifice rocks can explain the low $\delta^{18}\text{O}$ signatures in the São Miguel olivines, we find that there are compelling reasons to consider the alternative possibility that the low $\delta^{18}\text{O}$ signatures (excluding the anomalous sample with $\delta^{18}\text{O}=4.57\text{‰}$) were inherited from the São Miguel mantle source region.

5.1.4. Subduction of oceanic lithosphere

The only known mechanism by which a mantle source region might develop a low $\delta^{18}\text{O}$ signature is through processes related to subduction of high temperature altered lower oceanic crust or serpentinized peridotite (Eiler et al., 1997). The existence of subducted oceanic crust in many mantle plume sources is suggested by radiogenic Pb and Os isotope signatures, as well as distinctive major and trace element abun-

dance patterns, particularly in HIMU-type mantle sources (Hofmann and White, 1982; Zindler and Hart, 1986; Weaver, 1991; Hauri and Hart, 1993). Fig. 7 illustrates the O–Sr–Nd–Pb isotope relationships in the São Miguel samples, as well as other OIB for which it has been suggested that phenocryst $\delta^{18}\text{O}$ signatures represent mantle source compositions. The low $\delta^{18}\text{O}$ signatures in São Miguel are similar to those found in Mauna Kea (Eiler et al., 1996a), which have been attributed to recycling into the mantle of subducted, hydrothermally altered oceanic crust (Lassiter and Hauri, 1998). The São Miguel olivines are also similar in $\delta^{18}\text{O}$ to HIMU samples from Guadalupe and St. Helena, which have O–Sr–Nd–Pb isotopic compositions consistent with recycling of altered oceanic crust (Eiler et al., 1997).

If the low $\delta^{18}\text{O}$ signatures in the São Miguel olivines ($\sim 4.92\text{‰}$) are the result of a recycled, altered oceanic crust component in the Azores plume source, $\geq 10\%$ of the recycled component ($\delta^{18}\text{O} \geq 2\text{‰}$; Hart et al., 1999) would be required. This process is qualitatively consistent with the relatively radiogenic Pb, but moderate Sr isotope signatures relative to average N-MORB, of the Azores Platform tholeiites and the less radiogenic alkali basalts from the western end of São Miguel (Fig. 2); recycled altered oceanic crust would be expected to have high U/Pb but only moderately elevated Rb/Sr relative to unaltered MORB (Hart and Staudigel, 1989; Hart et al., 1999). Although it is difficult to constrain the amount of recycled oceanic crust indicated by radiogenic isotopes since the subduction process can have a profound effect on the resulting U/Pb and Rb/Sr ratios of subducted material (Tatsumi et al., 1986; Ayers, 1998; Becker et al., 2000), Re/Os ratios are apparently less strongly affected by subduction (Becker, 2000), and $^{187}\text{Os}/^{188}\text{Os}$ ratios more radiogenic than MORB mantle in most OIB are consistent with large percentages ($>10\%$) of recycled oceanic crust in OIB sources (Hauri and Hart, 1993; Widom and Shirey, 1996; Widom, 1997). Some trace element characteristics of the Azores Platform tholeiites and the less radiogenic alkali basalts from the western end of São Miguel are similar to those of HIMU OIB, which have been interpreted to come from mantle sources with a component of recycled, altered oceanic crust (Weaver, 1991). In particular, low ratios relative to N-MORB of some large ion lithophile element and light rare earth

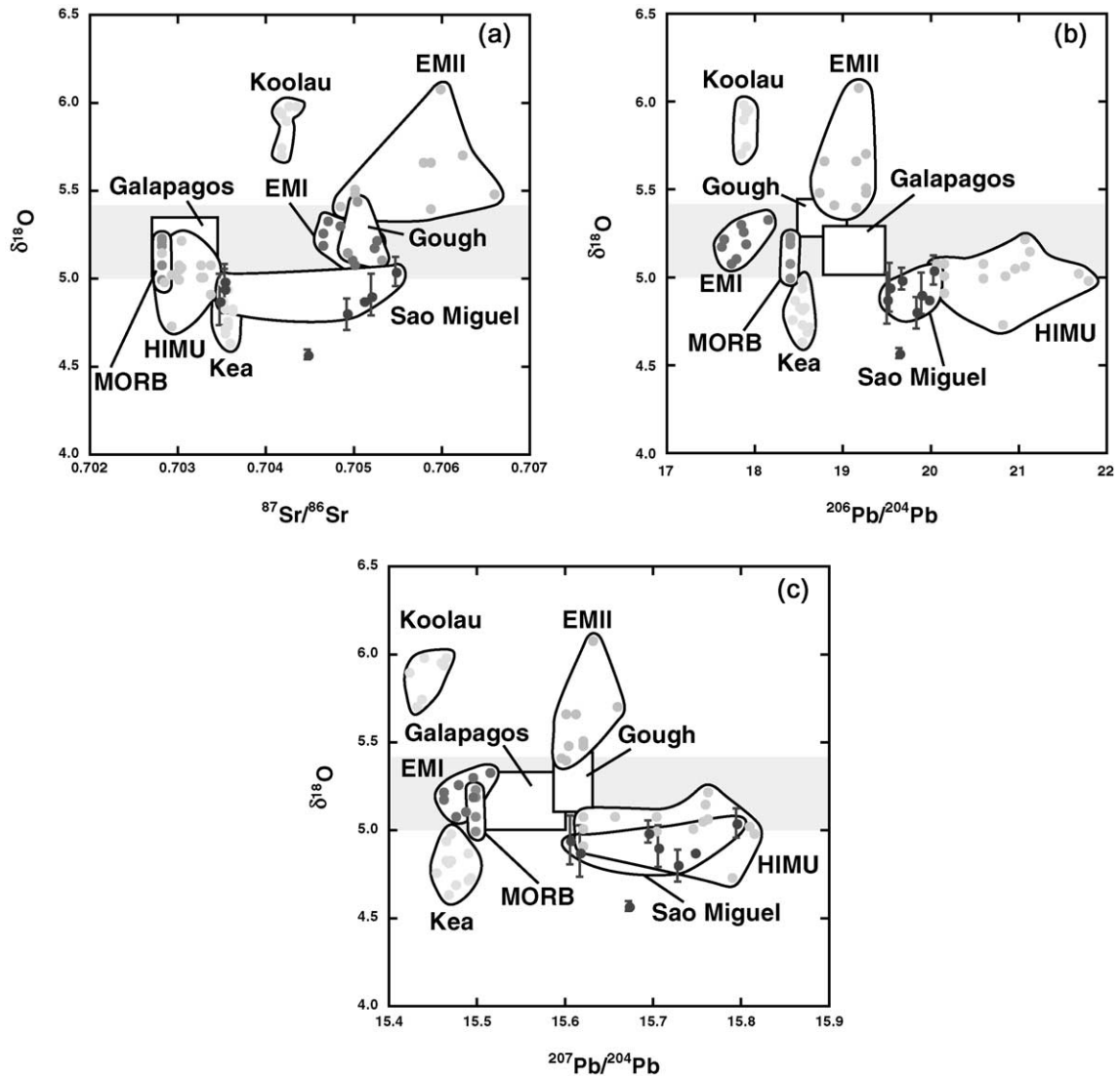


Fig. 7. $\delta^{18}\text{O}$ (olivines) vs. $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, and $^{207}\text{Pb}/^{204}\text{Pb}$ (whole rocks) for São Miguel and other OIB for which $\delta^{18}\text{O}$ signatures are thought to reflect mantle source compositions. São Miguel olivine $\delta^{18}\text{O}$ signatures are slightly lower than the normal upper mantle (shaded field), and similar to olivines from Mauna Kea and HIMU basalts from St. Helena and Guadalupe. Literature data are from the following sources: Hawaii-Mauna Kea and Koolau (Eiler et al., 1996a); EMI-Pitcairn (Eiler et al., 1995, 1997); EMII-Samoa and Societies (Eiler et al., 1997); HIMU-Guadalupe, St. Helena, Tubuaii, Mangaia, Rurutu and Raivavae (Eiler et al., 1997); MORB (Eiler et al., 1997); Galapagos (White et al., 1993; Reynolds and Geist, 1995; Geist et al., 1998; Kurz and Geist, 1999; Geist, personal communication); and Gough (Harris et al., 2000).

element to Nb ratios (e.g. K/Nb and La/Nb) are consistent with a recycled oceanic crust component in the Azores plume source.

Anomalously high ratios of Ba/Nb and low Fe abundances in these basalts, however, are uncharac-

teristic of HIMU OIB, and have led Turner et al. (1997) to propose that the Azores plume contains a component of delaminated SCLM. However, the oxygen isotope data (if mantle source-related) require a low $\delta^{18}\text{O}$ component in the Azores plume, which is

not easily explained with SCLM. Although relatively low $\delta^{18}\text{O}$ signatures have recently been measured in some metasomatic clinopyroxenes from SCLM peridotite xenoliths (Deines and Haggerty, 2000; Zhang et al., 2000), olivine and orthopyroxene from strongly metasomatized SCLM are characterized by normal mantle $\delta^{18}\text{O}$ signatures (Mattey et al., 1994; Chazot et al., 1997; Deines and Haggerty, 2000; Zhang et al., 2000), and whole-rock oxygen isotopic compositions should thus be close to unmetasomatized values.

We therefore conclude that the low $\delta^{18}\text{O}$ signatures in the São Miguel olivines, if a reflection of their mantle source, are best explained by a component of recycled, altered lower oceanic crust in the Azores mantle plume. Because such crust has low Os abundances relative to mantle peridotite, incorporation of ~10% of such crust in the plume source can easily be accommodated without producing unreasonably radiogenic Os isotope signatures (Widom and Shirey, 1996; Widom, 1997). Recent evidence for high $^3\text{He}/^4\text{He}$ ratios in the Azores plume (Moreira et al., 1999) is consistent with this model, and suggests that, in addition to a possible component of recycled, altered oceanic crust, the Azores plume contains a relatively undegassed component, most likely derived from the lower mantle.

5.2. Limited variation in São Miguel $\delta^{18}\text{O}$

If the limited variation in olivine $\delta^{18}\text{O}$ signatures reflects limited variation of $\delta^{18}\text{O}$ in the São Miguel mantle source (Fig. 7), then constraints can be placed on the nature and extent of recycling of lithospheric material into the mantle beneath São Miguel. The large variations in radiogenic isotope signatures of São Miguel basalts have previously been interpreted to result from two-component mixing between the predominant Azores plume mantle and a more enriched EMII-type component, the latter residing either within the plume or located more shallowly within the oceanic mantle beneath São Miguel (Turner et al., 1997; Widom et al., 1997; Moreira et al., 1999). The very radiogenic Sr and Pb isotopic composition of this EMII-type component has been attributed to either delaminated SCLM or recycled sediment (Hawkesworth et al., 1979; Davies et al., 1989; McKenzie and O'Nions, 1995; Turner et al., 1997; Widom et al., 1997; Moreira et al., 1999). The lack of correlation

between $\delta^{18}\text{O}$ and radiogenic isotope signatures in the São Miguel basalts has the potential to constrain the origin of the São Miguel EMII-type mantle component, because sediment is characterized by very heavy $\delta^{18}\text{O}$ signatures (15–25‰; Eiler et al., 1997), whereas SCLM, even when strongly fluid-metasomatized, generally retains MORB mantle-like $\delta^{18}\text{O}$ characteristics (5.18 ± 0.14 ‰, 1 S.D.; Mattey et al., 1994).

5.2.1. Subduction of sediment

The expected isotopic effects of mixing recycled sediment into the Azores mantle plume source can be modeled using the isotopic and trace element composition estimated for the predominant Azores plume source ($\delta^{18}\text{O} = 4.92$ ‰, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7032$, Sr = 24 ppm; Widom et al., 1997) and typical marine sediment. In Fig. 8, curves 'a' and 'b' illustrate the effect of peridotite-sediment mixing involving sediment with average pelagic and terrigenous $\delta^{18}\text{O}$ signatures (25‰ and 15‰, respectively; Eiler et al., 1997), and an average terrigenous sediment strontium composition ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710$, Sr = 237 ppm; Ben Othman et al., 1989). These models can nicely reproduce the $\delta^{18}\text{O}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ characteristics of some EMII-type OIB (e.g. Samoa and Society Islands; Eiler et al., 1997) with approximately 3–8% sediment incorporation. The origin of the São Miguel EMII-type mantle must differ from that of Samoa and Society, given that the former is characterized by significantly lower $\delta^{18}\text{O}$, as illustrated in Fig. 7. Any sediment component in the São Miguel EMII-type mantle must be significantly more Sr-rich and/or more radiogenic in order to produce the large variation in $^{87}\text{Sr}/^{86}\text{Sr}$ without the concomitant increase in $\delta^{18}\text{O}$. An estimate of the composition of average global subducting sediment (GLOSS) indicates that a more typical subducted sediment may indeed be more radiogenic and Sr-rich than the sediment in models 'a' and 'b' (GLOSS Sr = 350 ppm and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7173$; Plank and Langmuir, 1998). Fig. 8, curves 'c' and 'd' show the expected mixing trends involving GLOSS with $\delta^{18}\text{O}$ of 25‰ and 15‰, respectively. These results indicate that incorporation into the Azores mantle plume source of a little over 1% GLOSS-like sediment could produce a large variation in $^{87}\text{Sr}/^{86}\text{Sr}$ with only a very small increase in $\delta^{18}\text{O}$, as long as the sediment is characterized by $\delta^{18}\text{O} \leq 15$ ‰. However,

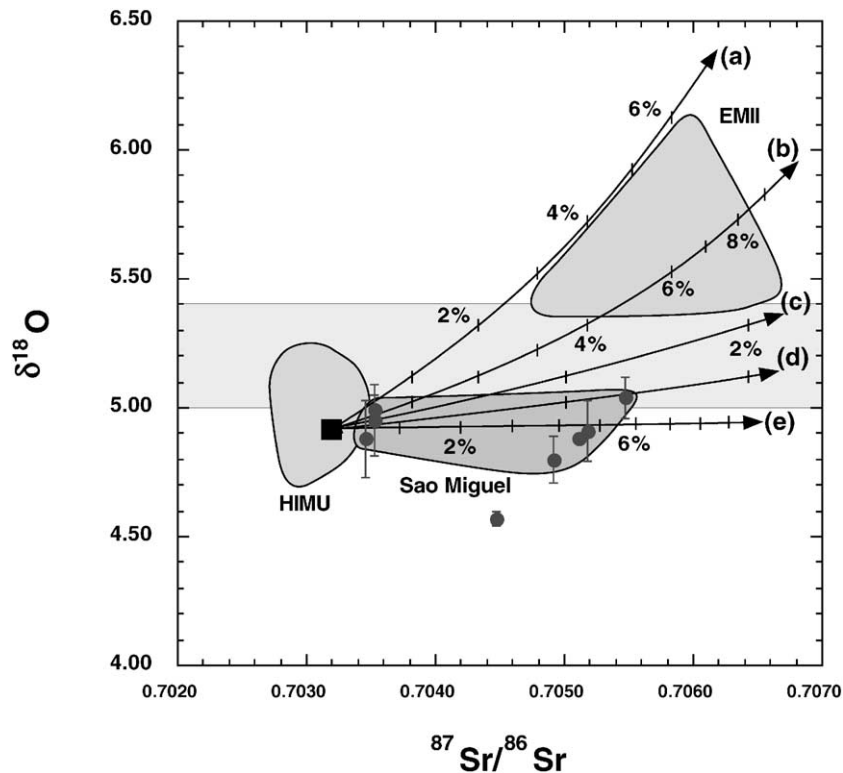


Fig. 8. $\delta^{18}\text{O}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ variations in São Miguel basalts, illustrating the effects of mixing recycled sediment and SCLM into the Azores mantle plume source. Two estimates of sediment composition are used, including average terrigenous sediment from Ben Othman et al. (1989) and GLOSS from Plank and Langmuir (1998). The following parameters are used in the calculations—predominant Azores plume source: $\delta^{18}\text{O}=4.92\text{‰}$, $^{87}\text{Sr}/^{86}\text{Sr}=0.7032$, $\text{Sr}=24\text{ ppm}$ (Widom et al., 1997); average terrigenous sediment: $^{87}\text{Sr}/^{86}\text{Sr}=0.710$, $\text{Sr}=237\text{ ppm}$ (Ben Othman et al., 1989), $\delta^{18}\text{O}=25\text{‰}$ (curve 'a') and $\delta^{18}\text{O}=15\text{‰}$ (curve 'b') (Eiler et al., 1997); GLOSS $\text{Sr}=350\text{ ppm}$ and $^{87}\text{Sr}/^{86}\text{Sr}=0.7173$ (Plank and Langmuir, 1998), $\delta^{18}\text{O}=25\text{‰}$ (curve 'c') and $\delta^{18}\text{O}=15\text{‰}$ (curve 'd'). These models can reproduce the $\delta^{18}\text{O}$ – $^{87}\text{Sr}/^{86}\text{Sr}$ characteristics of the Samoa and Society Islands EMII-type OIB with approximately 3–8% incorporation of the average 'terrigenous' sediment. The São Miguel data are marginally consistent with recycling of a more radiogenic and/or Sr-rich sediment like GLOSS, and with $\delta^{18}\text{O}<15\text{‰}$. Low Rb/Sr ratios in GLOSS, however, may produce relatively unradiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signatures in ancient recycled sediment. Mixing of the predominant Azores plume mantle source and strongly metasomatized SCLM ($\text{Sr}=200\text{ ppm}$, $^{87}\text{Sr}/^{86}\text{Sr}=0.710$, $\delta^{18}\text{O}=5.18\text{‰}$; Erlank et al., 1987; Matthey et al., 1994) is illustrated by curve 'e'. Fields for HIMU and EMII are from Eiler et al. (1997).

the Rb/Sr ratio of GLOSS is only 0.175, a factor of 2 lower than that of average upper continental crust (0.350; Taylor and McLennan, 1985). GLOSS-like sediment subducted 1–2 Ga ago might therefore have distinctly less radiogenic present-day $^{87}\text{Sr}/^{86}\text{Sr}$ signatures, if the low Rb/Sr ratios persist through subduction zone processing of the sediment. Evidence from metasediments in the Catalina schist, which have experienced subduction zone metamorphism, is in fact suggestive of very low Rb/Sr ratios (0.07–0.29) in subduction zone modified sediment (Sorensen and Grossman, 1989).

5.2.2. Subcontinental lithospheric mantle

An alternative possibility, that the São Miguel EMII-type mantle component reflects a component of delaminated enriched SCLM, is consistent with the lack of correlation between $\delta^{18}\text{O}$ and radiogenic isotope signatures in the São Miguel basalts. Although the $\delta^{18}\text{O}$ composition of SCLM is likely slightly heavier than that of the São Miguel basalt olivines, the $\delta^{18}\text{O}$ signatures are similar enough that several percent mixing of SCLM into the Azores plume source could be easily accommodated without producing a significant increase in $\delta^{18}\text{O}$. Fig. 8 illustrates

that mixing between inferred Azores plume mantle and SCLM ($\delta^{18}\text{O}=4.92\text{‰}$ and 5.18‰ , respectively) could produce the observed increase in $^{87}\text{Sr}/^{86}\text{Sr}$ with no significant change in $\delta^{18}\text{O}$ (Fig. 8, curve 'e'), provided that the SCLM is highly metasomatized mantle with high Sr abundances, and a radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signature, similar to that found in some ancient cratonic mantle (Erlank et al., 1987; Hawkesworth et al., 1990). Trace element systematics in the EMII-rich São Miguel basalts, including enrichments of Rb, K and Zr relative to Ba, Nb and Ti, have been shown to be similar to the enrichment patterns in hydrous phlogopite–K–richterite peridotites (PKP; Widom et al., 1997). Source mixing involving only $\sim 4\%$ enriched PKP-type SCLM (Fig. 8) would have minimal effect on the Os isotope signature, consistent with the lack of correlation of $^{187}\text{Os}/^{188}\text{Os}$ with Sr–Nd–Pb isotope signatures in the São Miguel basalts (Widom and Shirey, 1996). Ancient, metasomatized SCLM from Africa or Iberia could have been introduced into the lithosphere or shallow asthenosphere in the region of the Azores archipelago during the opening of the Atlantic ocean basin.

6. Conclusions

Oxygen isotope signatures measured in olivines from eight São Miguel basalts range from $\delta^{18}\text{O}=4.57\text{‰}$ to 5.04‰ , but, with the exception of one sample, are indistinguishable from one another at the 1σ level, and have an average $\delta^{18}\text{O}=4.92\pm 0.03\text{‰}$ (1σ). The measured $\delta^{18}\text{O}$ values for the São Miguel olivines are slightly but systematically lower than those measured in the San Carlos olivine standard during the time period of sample analyses, and are lower than the average of olivines from upper mantle xenoliths and MORB.

The low $\delta^{18}\text{O}$ signatures could be explained by $\geq 10\text{--}20\%$ assimilation of oceanic crust that has interacted with seawater at high temperature, or assimilation of lesser amounts ($4\text{--}9\%$) of volcanic edifice material that has been hydrothermally altered by interaction with low $\delta^{18}\text{O}$ meteoric water. However, the limited variation in $\delta^{18}\text{O}$ despite eruption of the basalts through compositionally and tectonically variable lithosphere, and the lack of correlation of $\delta^{18}\text{O}$ with olivine forsterite content, are more easily

explained if the low $\delta^{18}\text{O}$ signatures reflect mantle source characteristics. Low $\delta^{18}\text{O}$ signatures in the mantle beneath São Miguel can be explained by $\geq 10\%$ recycled, high temperature altered oceanic crust in the Azores mantle plume.

The relatively limited variation of $\delta^{18}\text{O}$ despite large and correlated variations in Sr–Nd–Pb–Th–He isotopes also places constraints on the origin of the São Miguel EMII-rich mantle. The EMII-rich source could be attributed to a component of Sr-rich GLOSS-like recycled sediment as long as the sediment had only moderately heavy $\delta^{18}\text{O}$ ($\leq 15\text{‰}$) and sufficiently radiogenic Sr and high Rb/Sr ratios that were preserved during subduction zone processing. Alternatively, the São Miguel EMII-type mantle signatures could result from a component of delaminated, metasomatized SCLM. Mixing of Azores plume mantle with several percent metasomatized SCLM could produce the radiogenic Sr–Nd–Pb isotope signatures without a significant increase in $\delta^{18}\text{O}$.

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