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The Ne isotopic signature of Terceira lavas (Azores): evidence for Ne recycling?

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ABSTRACT: The available noble gas database shows that the presence of an atmospheric component in oceanic basalts is common. Several models have been considered and will be discussed here in order to explain the Ne isotopic data obtained for olivine phenocrysts sampled in Terceira lavas. Analysed samples are porphyritic olivine+clinopyroxene±plagioclase bearing lavas that were erupted from the Fissural and Santa Bárbara eruptive vents. Different incompatible element ratios (e.g. Ba/Nb, La/Nb) were obtained for lavas from these two volcanic systems, which can be related with the presence of crustal recycled components in the Terceira mantle source. Ne isotopic ratios are also distinct for Fissural and Santa Bárbara olivine crystals, the later being invariably similar to air. Indirect barometric data from clinopyroxene-liquid equilibrium point to olivine crystallisation at mantle depths, thus precluding the existence of direct atmospheric contamination during magma ascent and cooling. Alternatively, we argue for a recycled origin of atmospheric Ne in accordance with geochemical data.

KEYWORDS: Noble gas, Neon, Recycling, Olivine, Azores.

1. INTRODUCTION

Systematic Ne isotopic analyses of oceanic basalts have shown the ubiquitous presence of an atmospheric component. The linear trends obtained in the three Ne isotope diagram has been commonly interpreted as a consequence of magma contamination by air or seawater during lava emplacement or by hydrothermally altered oceanic crust during magma ascent (e.g. Sarda et al., 1988; Patterson et al., 1990; Honda et al., 1993). More recently, Sarda (2004) and Holland & Ballentine (2006) argued for recycling of noble gases into the mantle. Our contribution is focused on the Ne isotopic data obtained for lavas of the Terceira Island (Azores archipelago) by Madureira et al. (2005) and will be discussed considering those hypotheses.

2. GEOLOGICAL SETTING

Terceira Island is one of the nine Islands of the Azores archipelago, which is located close to the triple junction between the American, Euro-Asiatic and Nubia lithospheric plates (inset Fig. 1).



Figure 1 – Volcanic systems interpreted from the Terceira exposed lavas (adapted from Nunes, 2000). CPC – Cinco Picos Caldera; GMC – Guilherme Moniz Caldera; SBC; Santa Barbara Caldera; PAV – Pico Alto Volcano; AC – Algar do Carvão. The samples locations are shown by white dots inside the Island. Inset – Geologic and Geographic setting of the Azores archipelago; Am, EA, Nu – American, Euro-Asiatic and Nubia litospheric plates respectively.

The island morphology and the volcanic deposits exposed at the surface allow the recognition of five main volcanic systems (Fig. 1): Cinco Picos, Guilherme Moniz, Pico Alto, Santa Barbara and a Fissural system composed by lavas erupted from the Terceira fissure zone. Historical lavas result from subaerial and submarine eruptions along the fissure zone. Nevertheless, Santa Barbara and Pico Alto volcanic systems are also considered to be active. Trace element and noble gas isotopic data used in this study were obtained from lavas belonging to the Fissural (F) and Santa Barbara (SB) volcanic systems (Madureira et al., 2005; Madureira 2006). From the radiometric ages obtained by Calvert et al. (2006) for Terceira Island, the studied lavas are not older than 100 ka and most samples should be younger than 35 ka (see also Self, 1976 and Féraud et al., 1980).

3. PETROGRAPHY AND GEOCHEMISTRY OF TERCEIRA LAVAS

Fissural and Santa Bárbara mafic lavas are predominantly porphyritic to seriate and the major phenocryst phases correspond to olivine, clinopyroxene and plagioclase, the later being dominant in Santa Bárbara lavas. For the less evolved lavas, olivine phenocrysts are characterized by the absence of mineral inclusions other than cromite (Fissural lavas) or titanomagnetite (Santa Bárbara lavas). Petrograhic observations led us to consider olivine as the first crystallizing silicate phase, lately joined by clinopyroxene and plagioclase in the more evolved samples. Phenocrysts are invariably surrounded by a microcrystalline matrix dominated by plagioclase and opaque minerals that include minor olivine and clinopyroxene.

Major and trace element data was obtained from ICP and ICP-MS (Activation Laboratories, Canada) on aphyric and porphyritic mafic samples with a proportion of phenocrysts generally less than 10% in volume (Madureira 2006). Fissural and Santa Bárbara lavas are alkaline to mildly alkaline, ranging between basalts and benmoreites. Concerning trace elements, all lavas display enrichment in incompatible elements and a REE fractionated profile with La/Ybn ratios ranging between 7.4-11.3. Spiderdiagrams constructed for Fissural and Santa Bárbara lavas are

presented in Fig. 2. Most Fissural lavas are enriched in Ba, Ta, Nb and LREE, while Santa Bárbara samples display Nb and Ta enrichments relatively to LILE and LREE. According to Weaver (1991) and Willbold & Stracke (2006), these patterns can be considered as reflecting the presence of recycled components in the mantle source, i.e. the EM I and HIMU mantle components respectively. The same interpretation result from the position of the samples in the plot La/Nb versus Ba/Nb, with Fissural lavas plotting close to the enriched components and/or primitive mantle. Nevertheless, despite the common association of Ba anomaly with sediment recycling (EM components, e.g. Willbold & Stracke, 2006), existing isotopic data on Fissural lavas have been also interpreted with the presence of the HIMU component in Terceira mantle source (Turner et al., 1997).



Figure 2 – A) Spiderdiagrams constructed for Fissural and Santa Barbara lavas. The typical patterns of EM and HIMU components as proposed by Weaver (1991) are shown for comparison (see text). Black lines represent basalt samples from Terceira Island. Values for normalization were taken from McDonough & Sun (1995); B) Fissural and Santa Barbara lavas plotted in the Ba/Nb vs. La/Nb diagram (adapted from Mata et al., 1998).

4. Ne ISOTOPIC DATA

Ne isotopic data was obtained from olivine crushing using the ARESIBO I mass spectrometer housed at IPGP and the experimental procedure and running conditions presented by Madureira et al. (2005). The olivine concentrates were collected from lavas erupted at Terceira Island from the Fissural volcanic system and Santa Bárbara volcano.

As shown by Madureira et al. (2005), in the three neon isotope diagram some Fissural samples plot clearly above the atmospheric end-member defining a trend that point to the contribution of a relatively undegassed/primitive mantle component to its source (Fig. 3). This component, being also evident from the He isotopic signatures (see also Moreira et al. 1999) endorses a lower mantle origin for the Azores mantle plume (which is also not contradicted by the La/Nb *versus* Ba/Nb plot, see Fig. 2). However, for Terceira lavas, the proportion of atmospheric component is always higher than 50%, as evidenced even by the sample with the higher 20 Ne/ 22 Ne if we consider a 20 Ne/ 22 Ne ratio of 12.6 for the mantle end-member (Trieloff et al., 2000). This is strengthened by the Ne isotopic data obtained for Santa Bárbara olivines, which are invariably similar to air (at the 1 σ uncertainty level).



Figure 3 – Ne isotopic data obtained from Terceira olivines (adapted from Madureira et al., 2005). mfl – "mass fractionation line".

The presence of the atmospheric component is usually interpreted as a consequence of magma contamination by air or hydrothermally altered oceanic crust during its ascent to the surface. However, this hypothesis must be confronted with estimates of olivine crystallisation depth. Considering the extent of widespread hydrothermal alteration in oceanic crust (2-3 km; e.g. Nicolas, 1990), crystallisation depths higher than 3 km preclude the possibility of direct surface-derived atmospheric contamination of melt or fluid inclusions trapped in the olivine. In the following section we will use the chemical composition of clinopyroxene phenocrysts from representative F and SB samples to constrain the upper limit of olivine crystallisation depth. Clinopyroxene phenocrysts are used since petrographic data point to their nucleation during or after olivine crystallisation and because equilibrium crystallisation of jadeite component is pressure-dependent.

5. GEOBAROMETRY

Clinopyroxene phenocrysts were analysed with a JEOL JCXA 733X electron microprobe in Centro de Geologia at Lisbon University. The microprobe operated with a 5 mµ beam diameter, a beam current of 25 nA and an accelerating voltage of 15 kV. Precision, as indicated by replicate determinations on an in-house standard, is better than 2% for major elements. The depth of clinopyroxene crystallization can be estimated by converting barometric data obtained from the thermobarometer developed by Putirka et al. (1996). The calibration of Putirka et al. (2003) was considered since it can be applied to non-primitive and hydrated magmas, which can be relevant for the Azores lavas (Asimow et al., 2004). The method uses the composition of clinopyroxene and coexisting residual magma to determine the temperature and pressure at which these two phases were last in equilibrium. The equilibrium condition is constrained by the Kd_{Fe/Mg} partition coefficient, using the range between 0.23 and 0.3 following the works of Thompson (1974), Green et al. (1979) and Sisson & Grove (1993). It must be stressed that the equilibrium pre-requisite is more difficult to constrain for SB lavas due to the abundance of

plagioclase phenocrysts in some samples. This difficulty arises from petrographic observations pointing to a possible cotetic crystallization of clinopyroxene and plagioclase. In fact, despite the maintenance of the previous Fe/Mg ratio of magma after plagioclase crystallization, its occurrence can reduce significantly the Na concentration of the liquid in equilibrium with clinopyroxene. Accordingly, as shown by Mordick & Glazner (2006), the whole-rock compositions used in thermobarometric calculations will be enriched in Na, resulting in lower than real pressures and temperatures being determined. A similar effect is expected to occur as a result of plagioclase accumulation. Conversely, for magmas affected by plagioclase removal after clinopyroxene crystallization, the whole-rock composition will be depleted in Na and the thermobarometric data overestimated. The existence of plagioclase accumulation or fractionation in phorphyritic SB lavas can be evaluated plotting Eu anomalies (given by Eu/Eu* = $Eun/\sqrt{[(Sm_n).(Gd_n)]}$, Taylor & McLennan, 1985) against the Sr/Nd ratio (Fig. 4). The positive correlation between these two ratios (with Eu/Eu* ratios higher than 1) support the plagioclase accumulation hypothesis in SB lavas. However, correction of this effect is a difficult task and can introduce systematic errors in thermobarometric calculations. We opted to maintain noncorrected whole-rock compositions and to consider the thermobarometric data obtained for SB clinopyroxenes as lower limits for clinopyroxene (and olivine) crystallization.



Figure 4 – Eu anomalies *versus* the Sr/Nd ratio obtained for Santa Bárbara lavas. The positive covariation support the existence of plagioclase accumulation.

The range of pressure estimates for F and SB clinopyroxenes are presented in table 1. The data suggest that clinopyroxene crystallisation in F magmas occurred at higher pressure than in SB lavas. This is also supported by the more evolved character of SB lavas, which can be interpreted as the result of crystallisation and magmatic evolution processes inside a magma chamber.

Volcanic system	P (kbar)	Depth (km)
Fissural	4.5 - 8.7	15.0 - 29.0
Sta Bárbara	3.2 - 4.5	10.7 - 15.0

Table 1 – Estimated pressure for clinopyroxene crystallisation (in equilibrium with whole rock composition) following the method of Putirka et al. (1996, 2003). The depth values were converted from pressure considering a mean density of 3 g/cm³ for the oceanic lithosphere in the vicinity of mid-oceanic ridges.

6. CONCLUSIONS

Although subduction zones has been considered as a barrier to the recycling of noble gases (e.g. Staudacher & Allègre, 1988), the possibility of noble gas recycling was reinforced by recent studies (Sarda, 2004; Holland & Ballentine, 2006). The validity of the recycling model to explain the atmospheric component trapped in Terceira olivines is endorsed by: 1) crystallization of olivines deeper than the Moho at the Azores (\cong 12 km, Luis & Neves, 2006); and 2) the HIMU isotopic signature of Terceira lavas. Indeed, while the crystallization of olivine in the mantle makes difficult the acceptance of the occurrence of atmospheric contamination directly dependent on surface processes, for the HIMU mantle component has been assigned an origin by recycling of oceanic crust \pm lithosphere (e.g. Chauvel et al., 1992; Moreira & Kurz, 2001).

We reported that lavas from the Santa Bárbara volcanic system, displaying a typical elemental and isotopic HIMU signature, are also those with a stronger atmospheric component. The HIMU component is usually considered as resulting from the recycling of altered oceanic crust. Consequently at the inception of subduction zones the HIMU precursors shall be highly enriched in atmospheric component characterized by low ²⁰Ne/²²Ne and ²¹Ne/²²Ne. The portion of this component trapped on low temperature alteration minerals and/or pore water is thought to be removed during processing at subduction zones. However, the atmospheric noble gas component can also be stored in melt inclusions, which were derived from seawater contaminated magma trapped in crystalline lattices formed during crust formation at mid-ocean ridges. Considering the relatively low diffusivity of Ne, we suggest that this component would not be easily removed unless extensive melt of the subducting slab occurs, which is very rare.

In conclusion, the atmospheric neon isotopic signatures of the Santa Bárbara olivines are interpreted as the result of atmospheric Ne recycling to the deep mantle. Conversely, for Fissural lavas the Ne isotopic ratios point to a higher contribution from the relatively undegassed mantle, probably sampled by the Azores plume.

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