Helium isotopes in hydrothermal volcanic fluids of the Azores archipelago

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We present the first helium isotope data for thermal waters and gas emissions on the islands of Terceira, Graciosa, Faial, Pico and Flores, as well as new data for Sao Miguel. The results allow us to track current mantle degassing associated with the Azores hot spot, to delineate its spatial distribution and to discuss its possible origin. As a general rule, we find that free gases tend to display somewhat higher 3He/4He ratio than groundwater. We argue that this difference is likely due to radiogenic helium inputs to aquifers during water-rock interactions and, therefore, that gas phases are the fluid carriers with the most representative of mantle source signature. The measured 3He/4He ratios (normalized to the air ratio, R a) range from lower-than-MORB values (5.23–6.07 R a) on central Sao Miguel, to MORB values on Faial (8.53 R a) and Flores (8.04 R a) — located on either side of the Mid-Atlantic Ridge — and to plume-type values on Graciosa (11.2 R a) and Terceira (13.5 R a) where free gases also display ten times higher-than-MORB CO2/3He ratios (1.8–2.6×1010). Such a wide He isotopic range and its spatial distribution corroborate with available data for volcanic rocks, indicating that plume’s head presently underlies the central part of the archipelago. The plume-type 3He/4He ratios on Terceira and Graciosa agree with geochemical and seismic evidence of a deep-rooted mantle plume feeding the Azores hot spot. Our finding that high 3He/4He ratios correspond to low He concentrations and high (arc-type) CO2/3He values exclude a simple plume supply of 3He-rich primitive mantle. Instead, the simultaneity of both elevated CO2/3He and 3He/4He ratios is best explained by a 3He-rich contribution from the lower mantle diluted in a CO2-rich feeding plume that contains a recycled altered oceanic plate component. The alternative possibility of an enhanced time-integrated 3He/(U+Th) ratio in the Azores plume due to a greater compatibility of helium relative to U and Th during melting events is difficult to reconcile with the enriched pattern of volcanic rocks from the central islands. In any case, the Azores plume should derive from a mantle reservoir that could escape convective homogenization for a very long period of time, in agreement with sub-chondritic osmium isotopic ratios in volcanic rocks from the central islands of the archipelago.

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1. Introduction

The Azores archipelago, composed of nine active volcanic islands (Fig. 1), is the emerged part of a huge oceanic basaltic province (see Gente et al., 2003 for a recent review), located at the Triple Junction of the North American, the African and the Eurasian plates between 35° and 40°N. The Eurasian/African branch of the Triple Junction is a complex system of tectonic faults and ridges (Searle, 1980; Vogt and Jung, 2004). It forms a linear structure trending ESE-WNW on top of the North American, the African and the Eurasian plates between 35° and 40°N. The Eurasian/African branch of the Triple Junction is a complex system of tectonic faults and ridges (Searle, 1980; Vogt and Jung, 2004). It forms a linear structure trending ESE-WNW on top of

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volcanism is also evidenced by numerous persistent gas emissions and hydrothermal manifestations on the islands as well as on the seafloor (Jean-Baptiste et al., 2008).

The Azores intra-platonic oceanic basaltic (OIB) magmatism which developed close to the Mid-Atlantic Ridge, is a typical example of hotspot–ridge interaction (Schilling, 1975; Montagner and Ritsema, 2001). Although initially considered as a low 3He/4He hotspot (Tolstikhin et al., 1991; Kurz et al., 1982a), its basalts were subsequently found to display 3He/4He ratios both above and below the MORB domain (Moreira et al., 1999; Madeireira et al., 2005). Ocean island basalts worldwide show a wide range of 3He/4He values between ~5 R a and 50 R a — where R a is the atmospheric 3He/4He ratio (Kurz et al., 1982b; Farley and Neroda, 1998; Graham, 2002; Stuart et al., 2003), which sharply contrasts with the relative homogeneity (8±1 R a) of Mid-Ocean Ridge Basalts (MORB) derived from the upper mantle. Classically, high 3He/4He ratios have been attributed to plume uprise of primitive material supposedly residing in the lower mantle (Craig and Lupton, 1976; Lupton, 1983; Allègre et al., 1983; Allègre and Turcotte, 1985), whereas lower-than-MORB ratios are thought to reflect the
recycling of crustal material (sediments, oceanic crust or continental lithosphere) with high time-integrated (U + Th)/4He ratios (Kurz et al., 1982b; McKenzie and O’Nions, 1983; Hanyu and Kaneoka, 1997) or, in some cases, shallow crustal contamination during magma ascent and ponding (Zindler and Hart, 1986; Hilton et al., 1995). However, even the nature of the high 3He/4He OIB source itself remains controversial (e.g. Anderson, 1998). Recent advances in seismological studies (e.g. Van der Hilst et al., 1997; Grand, 2002) have shown that oceanic plates can be subducted down to the base of the lower mantle and, therefore, have raised new questions on the reality of the canonical two-layered mantle, opening the way to alternative scenarios. In particular, recent measurements of the partition coefficients of noble gases and U–Th during melting and crystallisation (Parman et al., 2005; Heber et al., 2007) have led to the alternative hypothesis that high 3He/4He ratios in OIB samples could track recycled upper mantle residues left behind with higher-than-MORB time-integrated 3He/(U + Th) ratios rather than primitive mantle reservoirs (Parman et al., 2005).

Here, we present new 3He/4He data for both hydrothermal gases and waters in the Azores archipelago. Up to now, only a few helium isotope data were available for fluids in Sao Miguel island (Tolstikhin et al., 1991). In addition to providing additional results for Sao Miguel, here we report the first He isotope data for hydrothermal fluids on five other islands: Terceira, Graciosa, Faial, Pico and Flores. The results allow us to characterize current mantle degassing across the Azores domain and, together with available He isotope data for the local volcanic rocks (Kurz, 1991; Moreira et al., 1999; Madureira et al., 2005), to delineate the horizontal extent of the mantle plume feeding the Azores hot spot.

### 2. Sample location and methods

Our study of the main hydrothermal features of the volcanic archipelago concerned twenty five sites on the islands of Sao Miguel, Terceira, Graciosa, Pico, Faial and Flores. In Sao Miguel, Terceira and Graciosa islands, the main hydrothermal manifestations and degassing fields occur on central volcanoes. The other islands are characterized by minor or more punctual degassing sites (Ferreira et al., 2005). Fluids were collected from natural manifestations (fumaroles, solfataras, thermal springs and pools, gas bubbles in water), geothermal production wells, and cold water wells (Fig. 2).

Water samples were taken in copper tubes equipped with metal clamps at both ends. The tubes were flushed with water prior to closure using a peristaltic pump connected with Tygon tubing, except for samples taken at geothermal well heads which were flushed directly by the water flow. Fumarolic and solfataric gases, as well as gas bubbles in water – including one submarine sample taken by scuba diving off the coast of Ribeira Quentes (Sao Miguel) – were collected in pre-evacuated glass bulbs with stopcocks using an inverted funnel. All gases are essentially composed of carbon dioxide (up to 99.7 vol.%), plus minor amounts of N2, CH4, and H2S in fumarolic gases (Pasquier-Cardin et al., 1999; Ferreira and Oskarsson, 1999; Ferreira et al., 2005).

The isotopic analyses were made at LSCE — Saclay (Jean-Baptiste et al., 1992). Helium and neon isotopes in the gas samples were directly measured on a MAP-215 mass spectrometer connected to a high-vacuum inlet system. Helium dissolved in the water samples was first extracted under vacuum into sealed glass tubes and then analysed on a VG–3000 mass spectrometer (neon was not measured on these samples due to Hall probe problems on the mass spectrometer at that time). Typical He blank for both spectrometers is due to Hall probe problems on the mass spectrometer at that time). Typical He blank for both spectrometers is due to Hall probe problems on the mass spectrometer at that time). Typical He blank for both spectrometers is due to Hall probe problems on the mass spectrometer at that time). The analytical uncertainty on measured 3He/4He ratios, calibrated against an atmospheric air standard, is better than 0.8%.

Helium concentrations and isotopic ratios in gas samples were corrected for possible air contamination using the measured 20Ne/4He ratios and considering a pure atmospheric origin for neon, as classically done, since magmatic 20Ne/4He ratios are very much lower than the atmospheric ratio (20Ne/4He) at Craig and Lupton (1976); Madureira et al. (2005). The air-corrected 3He/4He ratio, R, is thus obtained from the following equation:

\[
\frac{R_c}{R} = \frac{(R / R_a) - (20Ne / 4He) / (20Ne / 4He)_{a}}{1 - (20Ne / 4He) / (20Ne / 4He)_{a}}
\]

![Fig. 1. Bathymetry of the Azores Plateau and location map of the nine islands of the Azores archipelago (Lourenço et al., 1998).](image-url)
As no neon data are available for the water samples (except for sample 20 from Terceira which was sampled later and analysed on the MAP-215), the $^{3}\text{He}/^{4}\text{He}$ ratio ($R_m$) of the dissolved magmatic helium component is computed as follows:

The measured helium isotope concentrations can be divided in three components,

$$
^{4}\text{He}_{\text{hi}} = ^{4}\text{He}_{\text{sol}} + ^{4}\text{He}_{\text{a}} + ^{4}\text{He}_{\text{m}}
$$

$$
^{3}\text{He}_{\text{hi}} = ^{3}\text{He}_{\text{sol}} + R_a^{4}\text{He}_{\text{a}} + R_m^{4}\text{He}_{\text{m}}
$$

where $^{4}\text{He}_{\text{sol}}$ and $^{3}\text{He}_{\text{sol}}$ correspond to the solubility equilibrium at the temperature and salinity conditions of the waters (Weiss, 1971; Potter and Clynne, 1978), $^{4}\text{He}_{\text{a}}$ is a possible helium excess of atmospheric origin, and $^{4}\text{He}_{\text{m}}$ is the magmatic component. The air excess component is usually noted as $\\Delta/100 \times [^{4}\text{He}_{\text{sol}}]$, hence $R_m$ will be given by the following formula:

$$
R_m = \left( [^{4}\text{He}] - [^{4}\text{He}_{\text{sol}}] - R_a \Delta / 100 \times [^{4}\text{He}_{\text{sol}}] \right) \div \left( [^{4}\text{He}] - [^{4}\text{He}_{\text{sol}}] - \Delta / 100 \times [^{4}\text{He}_{\text{sol}}] \right).
$$

Eq. (3) shows that if the term $\\Delta/100 / ([^{4}\text{He}] / [^{4}\text{He}_{\text{sol}}] - 1)$ is much less than 1, $R_m$ and $R'_m$ tend to be identical. Practically, the value of the slope $R_m$ is strongly influenced by the samples with the highest helium content (corresponding in the present data set to $([^{4}\text{He}] / [^{4}\text{He}_{\text{sol}}] - 1)$ values between 2.8 (on Sao Miguel) and 34.2 (on Flores). For an air component excess in the upper range ($\\Delta = 5\%$) and the less favourable $([^{4}\text{He}] / [^{4}\text{He}_{\text{sol}}] - 1)$ value of 2.8, we thus calculate that the maximum difference between $R_m$ and $R'_m$ is on the order of 0.1 $R_a$. The reliability of this correction procedure is illustrated by sample 20 (for which the neon concentration is available) where there is a good agreement between the air-corrected $^{3}\text{He}/^{4}\text{He}$ ratio computed by the present procedure ($10.31 R_a$) and that based on the neon concentration ($10.36 R_a$).

3. Results

He isotope results for water and free gas samples are respectively given in Tables 1 and 2. Fig. 3 shows scatterplots of $^{3}\text{He}$ versus $^{4}\text{He}$ concentrations when plotting $[^{4}\text{He}] - [^{4}\text{He}_{\text{sol}}]$ versus $[^{4}\text{He}] - [^{4}\text{He}_{\text{sol}}]$. Comparing Eqs. (1) and (2) leads to the following equation linking the true value $R_m$ and the approximate value $R_m'$:

$$
R_m / R_a = \left( R_m / R_a - \Delta / 100 / \left( [^{4}\text{He}] / [^{4}\text{He}_{\text{sol}}] - 1 \right) \right) \div \left( 1 - \Delta / 100 / \left( [^{4}\text{He}] / [^{4}\text{He}_{\text{sol}}] - 1 \right) \right).
$$

Fig. 2. Fluid sample locations on the islands of Flores, Graciosa, Faial, Terceira, Pico and Sao Miguel islands.
3.1. Sao Miguel

Sao Miguel, located 400 km east of the Mid-Atlantic-Ridge (MAR) is the largest island of the Azores archipelago. It has three active stratovolcanoes (Furnas, Agua de Pau, and Sete Cidades), with summit calderas partially filled by a lake, which have a long record of both effusive and explosive eruptions (Booth et al., 1978). The last eruption in Furnas caldera, in 1650 AD, caused about 200 casualties. Whereas Sete Cidades volcano has been at rest for quite a long (unknown) time, both Furnas and Agua de Pau volcanoes display intense hydrothermal manifestations along their main volcano-tectonic structures, tapping active hydrothermal systems at depth. All thermal springs and emitted gases are CO2-dominated (Ferreira and Oskarsson, 1999; Cruz et al., 1999; Ferreira et al., 2005). CO2 is also released through widespread diffuse soil emanations across Furnas caldera’s floor (Pasquier-Cardin et al., 1999) and fogo’s northern slopes (Ferreira et al., 2005). Carbon is typically mantle-derived, with a mean δ13C value of −4% (Ferreira and Oskarsson, 1999). We collected water and/or gas samples with temperature ranging from 17.6 °C to 99.4 °C at ten sites in the southeastern and central parts of the island (Fig. 2). Gas samples were obtained from fumaroles, mud pools, and bubbling springs or pools. In addition, we could collect submarine bubbling gas at ten meters depth off the coast of Ribeira Quente (sample no. 7).

All gas samples display a narrow 4He/3He range, between 5.23 and 6.07 Ra (Fig. 3). These values are higher than those (4.06–4.9 Ra) initially reported by Tolstikhin et al. (1991) for three sites (Furnas Caldera, Caldeira Vehla and Ribeira Grande), but the latter were uncorrected for air contamination. In the water samples, dissolved helium in excess of the solubility equilibrium has a 4He/3He ratio lower than the

<table>
<thead>
<tr>
<th>Island Sample number</th>
<th>Sample location Type of manifestation</th>
<th>T (°C)</th>
<th>Conductivity (μS/cm)</th>
<th>pH</th>
<th>R/Ra (uncorrected)</th>
<th>[4He]/[3He] (10−8 cm³ STP/g)</th>
<th>[4He]sub (10−8 cm³ STP/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sao Miguel 1</td>
<td>Lagoa das Furnas/North Boiling pool</td>
<td>98.7</td>
<td>4680</td>
<td>2.0</td>
<td>3.36</td>
<td>3.84</td>
<td>0.31</td>
</tr>
<tr>
<td>2</td>
<td>Lagoa das Furnas/East Bubbling waters</td>
<td>17.6</td>
<td>146.4</td>
<td>6.0</td>
<td>2.65</td>
<td>7.20</td>
<td>4.50</td>
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<tr>
<td>3</td>
<td>Furnas/Terra Nostra Bubbling waters</td>
<td>18.3</td>
<td>323</td>
<td>6.4</td>
<td>3.82</td>
<td>16.94</td>
<td>4.49</td>
</tr>
<tr>
<td>4</td>
<td>Ribeira Quente Submarine bubbling waters</td>
<td>18.5</td>
<td>6900</td>
<td>7.8</td>
<td>2.73</td>
<td>2.32</td>
<td>2.15</td>
</tr>
<tr>
<td>5</td>
<td>Fogo/Ribeira Grande Geothermal plant CL3</td>
<td>86.1</td>
<td>23,200</td>
<td>7.9</td>
<td>1.0</td>
<td>2.32</td>
<td>2.16</td>
</tr>
<tr>
<td>Flores 11</td>
<td>Lagoa do Povo North Geothermal plant CL3</td>
<td>39.9</td>
<td>0.71</td>
<td>2.2</td>
<td>1.89</td>
<td>5.50</td>
<td>3.88</td>
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<td>12</td>
<td>Baia dos Homiciados Hot spring/bubbles</td>
<td>15.6</td>
<td>167</td>
<td>8.2</td>
<td>0.98</td>
<td>5.37</td>
<td>4.14</td>
</tr>
<tr>
<td>13</td>
<td>Varadouro Well</td>
<td>29.2</td>
<td>7900</td>
<td>7.1</td>
<td>2.83</td>
<td>6.21</td>
<td>4.28</td>
</tr>
<tr>
<td>Pico 14</td>
<td>Silveira Well</td>
<td>15.6</td>
<td>167</td>
<td>8.2</td>
<td>0.98</td>
<td>5.37</td>
<td>4.14</td>
</tr>
<tr>
<td>15</td>
<td>Silveira Well</td>
<td>15.6</td>
<td>2560</td>
<td>6.6</td>
<td>4.45</td>
<td>8.80</td>
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<tr>
<td>Terceira 17</td>
<td>Ladeira do Povo/Fontinhas Well</td>
<td>22.9</td>
<td>7900</td>
<td>7.2</td>
<td>6.02</td>
<td>20.11</td>
<td>4.22</td>
</tr>
<tr>
<td>18</td>
<td>Pico do Capelo Well</td>
<td>25.2</td>
<td>1701</td>
<td>7.2</td>
<td>6.02</td>
<td>20.11</td>
<td>4.42</td>
</tr>
<tr>
<td>19</td>
<td>Juncal/Praia de Vitoria Well</td>
<td>25.2</td>
<td>1701</td>
<td>7.2</td>
<td>6.02</td>
<td>20.11</td>
<td>4.42</td>
</tr>
<tr>
<td>20</td>
<td>Terra Cha Well</td>
<td>25.2</td>
<td>1701</td>
<td>7.2</td>
<td>6.02</td>
<td>20.11</td>
<td>4.42</td>
</tr>
<tr>
<td>Graciosa 21</td>
<td>Baia dos Homicidados Bubbling hot spring</td>
<td>58.0</td>
<td>81,000</td>
<td>5.9</td>
<td>5.57</td>
<td>4.14</td>
<td>3.44</td>
</tr>
<tr>
<td>22</td>
<td>Furna do Enxofre Subterranean lake</td>
<td>14.7</td>
<td>729</td>
<td>6.7</td>
<td>7.68</td>
<td>52.3</td>
<td>4.54</td>
</tr>
<tr>
<td>23</td>
<td>Furo Pontal Well</td>
<td>25.2</td>
<td>1152</td>
<td>8.4</td>
<td>4.48</td>
<td>8.85</td>
<td>4.40</td>
</tr>
<tr>
<td>24</td>
<td>Furo Pontal Well</td>
<td>25.2</td>
<td>1152</td>
<td>8.4</td>
<td>4.48</td>
<td>8.85</td>
<td>4.40</td>
</tr>
<tr>
<td>25</td>
<td>Termas do Carapacho Hot spring</td>
<td>41.4</td>
<td>16,300</td>
<td>6.3</td>
<td>7.08</td>
<td>18.77</td>
<td>4.09</td>
</tr>
</tbody>
</table>

Helium solubility was calculated at water in situ temperature and conductivity conditions using the solubility data from Weiss (1971) in the range 0–40 °C and from Potter and Clynne (1978) above 40 °C.
gas phase, with a mean value of $4.5 \pm 0.8 R_a$, but share comparable He isotopic ratios with the local volcanic rocks for which post-eruptive radiogenic helium contamination was invoked (Moreira et al., 1999). We have shown in Section 2 that the residual influence of the air contribution upon the air-corrected $^3$He/$^4$He value is $\leq 0.1 R_a$ and so, cannot explain the isotopic difference with the gas phase. Therefore,

![Fig. 3. Scatter diagrams of $^3$He versus $^4$He content in free gas phases and $[^3\text{He}]-[^4\text{He}]$ versus $[^3\text{He}]-[^4\text{He}]$ in water samples. Scales for water and gas results are in black and red respectively. Data of Moreira et al. (1999) for volcanic rocks have been plotted for comparison (“+” symbols). For convenience, we use the same scale for water samples (in cm$^3$ STP/g of water) and rock samples (in cm$^3$ STP/g of rock). Therefore, rock concentrations were multiplied by 4 for Sao Miguel and Terceira and by 100 for Graciosa.](image)
since the $^{3}$He/$^{4}$He ratio of the gas phase more faithfully represents the local magmatic end-member, as we argue in Section 4.1, this isotopic discrepancy suggests a significant (~20%) radiogenic $^{4}$He input to the groundwaters from the host volcanic rocks during water–rock interactions.

3.2. Terceira

The most active volcanic site on Terceira, Furnas de Enxofre, is a solfataric field located in the central part of the island. It consists of numerous small fumaroles distributed along fissures and cracks with sulphur deposits, cutting a highly altered soil. Two gas samples collected from the most active fumaroles reveal plume-type $^{3}$He/$^{4}$He ratios of 13.53 ± 0.7 $R_o$ and 12.79 ± 0.25 $R_o$ (Table 2 and Fig. 3b). These ratios are even higher than the values (up to 11.4 $R_o$) reported for Terceira volcanic rocks by Moreira et al. (1999) and Madureira et al. (2005), with the exception of a value of 14.8 $R_o$ in one He-poor sample for which the authors did not exclude a cosmogenic $^{3}$He contribution. Therefore, our results strengthen the idea that plume-type mantle He degassing is actively occurring through Terceira Island. This is confirmed by the higher-than-MORB $^{3}$He/$^{4}$He ratios in our water samples (up to 10.3 $R_o$ in sample 20), in spite of their partial contamination by radiogenic helium during water–rock exchange, as previously observed on Sao Miguel.

3.3. Graciosa

The main hydrothermal manifestations occur in the Caldeira volcano (southeastern part of the island), and particularly inside the huge (150 m wide, 80 m high) Furna do Enxofre lava cave located in the caldera, where a bubbling mud pool releases steam and gases. This leads to the accumulation of deadly (~15%) CO$_2$ concentrations at the bottom of the cave, filled by a cold water subterranean lake. Two gas samples collected from this bubbling mud pool give comparably high $^{3}$He/$^{4}$He ratios of 10.7 $R_o$ and 11.2 $R_o$, which again suggest a plume-type contribution (Table 2 and Fig. 3). In contrast with these relatively high ratios, helium dissolved in the subterranean lake located in the same cave (Table 1: samples 22a and 22b) displays a surprisingly more radiogenic $^{3}$He/$^{4}$He value (8.3–8.4 $R_o$). This ratio closely matches that of all other waters collected on Graciosa, which define a quite homogeneous air-corrected $^{3}$He/$^{4}$He signature (mean value = 8.31 $R_o$) comparable to the value of (8.1 ± 0.2) $R_o$ measured on one olivine sample by Moreira et al. (1999). This strongly suggests that the subterranean lake waters are outcropping groundwaters directly connected to the underlying aquifer and little influenced by the nearby gas bubbling. An intermediate value of 8.9 $R_o$ is observed in the gas phase of the Baia dos Homiciados seashore hydrothermal system (sample 21).

3.4. Pico

The island is dominated by the 2300 m high and steep cone of the Pico volcano, which last erupted in 1718–1720. At present, surface hydrothermal manifestations are scarce on the island. A single water well, sampled on the southern coast in the Silveira area, gives a MORB-type $^{3}$He/$^{4}$He ratio of 8.5 ± 0.5 $R_o$ (Fig. 3). This value plots at the lower side of the He isotopic range measured by Moreira et al. (1999) for Pico lavas (9.4 ± 0.9 $R_o$).

3.5. Faial

The main hydrothermal activity on Faial is located on the outer western flank of the central caldera, in the vicinity of the Capelinhos volcano which started erupting under seawater in 1957 then subaerially throughout 1957–1958. No gas sample could be collected in this area, fuming activity on Capelinhos being too residual. Instead, water samples (12 and 13) could be collected using hydrological sampling bottles from two wells located at Capelo (180 m deep) and Varadouro (6 m deep).

Both waters have similar He isotopic ratio, 8.53 $R_o$, in good agreement with the data of Moreira et al. (1999) for Faial volcanic rocks (Fig. 3).

3.6. Flores

The island of Flores is one of the two islands of the Azores group located on the western side of the MAR. The sole geothermal feature that we were able to find, thanks to the help of local people, is located in a very remote place (Punta Negra) on the seashore close to Lajedo. It consists in a tiny thermal pool, a few tens of liters in size only, hidden at the base of a highly fractured rock. The pool is fed from beneath by a small inflow of warm water (29 °C). Gas bubbles also escape from a small fissure at the bottom of the pool. Lying one and a half meter only above sea level, the pool is regularly submerged by waves especially at high tide. In spite of the difficult access and of the very small size of this geothermal feature, the results are quite interesting: both water and gas samples show a spectacularly high helium content (6300 ppm for gas bubbles), which suggests gas separation and concentration from a deeper thermal aquifer, and display a similar $^{3}$He/$^{4}$He ratio (8.04 $R_o$ – Fig. 3). Such a value points to a pure MORB origin for helium. No comparison is possible with volcanic rocks on Flores, as no He isotopic data are yet available for this island.

4. Discussion

4.1. Representativity of the analysed samples with respect to the helium isotope signature of the mantle source

Noble gas isotope composition of olivine phenocrysts in volcanic rocks is widely used in geochemistry and considered as representative of mantle sources, even though different processes (e.g., partial melting, crystal-melt-bubble partitioning, outgassing, crustal contamination, etc.) can potentially affect the noble gas composition of silicate liquids and solid products (Dymond and Hogan, 1978; Honda and Patterson, 1999 and references therein). Noble gases can also be tracked from the magma-derived gas phase, which carries the vast majority of the initial gas content of the magma. As a matter of fact, there is a general good agreement worldwide between $^{3}$He/$^{4}$He ratios measured in volcanic rocks samples (phenocrysts) and in emitted volcanic gases, as illustrated by the results for mid-ocean ridge submarine volcanism (Graham, 2002; Schlösser and Winckler, 2002) and for subaerial volcanoes such as Mount Etna (Allard et al., 1997), Pantelleria (Parello et al., 2000), and the Roman Comagmatic Province in Italy (see Fig. 7 in Martelli et al., 2004).

In the Azores, our helium isotopic data set for hydrothermal fluids offers a consistent picture with that for volcanic rocks (Moreira et al., 1999; Madureira et al., 2005), but also shows locally some discrepancies between gas, water and rock results. In particular, the most intense thermal gas emissions from central vents on Sao Miguel, Terceira and Graciosa volcanic islands tend to display higher $^{3}$He/$^{4}$He ratio than thermal and cold groundwaters and, in some cases, than volcanic rocks themselves. Therefore, the origin of these isotopic discrepancies needs first to be understood if one wants to correctly characterize the He isotopic signature of the underlying magmatic source. Two main classes of processes may potentially be involved:

(i) Kinetic fractionation of helium isotopes during either magma degassing processes or gas transport through aquifers, which, due to the mass difference between the two isotopes, can enrich the gas phase in $^{4}$He relative to $^{3}$He. Such a fractionation may principally occur during diffusion processes (Graham law) and can generate significant changes in the $^{3}$He/$^{4}$He ratio of the emitted and residual phases if Raleigh-type gas distillation affects a reservoir of limited size.

(ii) Contribution of radiogenic $^{4}$He produced by U and Th decay in both the ~23 My old oceanic crust (Searle, 1980) and the volcanic rocks of the Azores Plateau, which would preferentially affect
hydrothermal aquifers and possibly ponding magma bodies (and some of their erupted products).

Below we briefly outline a series of observations which support the idea of a limited bearing (if any) of kinetic fractionation of He isotopes onto the measured $\text{He}/^{4}\text{He}$ ratios of Azores gas phases and, instead, a significant contribution of radiogenic $^{4}\text{He}$ to the local groundwaters.

4.1.1. Kinetic fractionation during magma degassing

Kinetic fractionation of $^{3}\text{He}$ may occur during Rayleigh gas distillation from descending magma batches (i.e. during helium diffusion from the melt into escaping gas bubbles), and was invoked to explain the transient $^{3}\text{He}/^{4}\text{He}$ variations (on the order of $\pm 0.5 R$) recorded in Mount Etna gas emissions at the onset of several magmatic events between 2001 and 2005 (Rizzo et al., 2006). However, eruptive activity in the Azores archipelago is much more occasional than on Etna, and the hydrothermal manifestations we studied correspond to steady state degassing taking place during the long repose intervals of Azores volcanoes. Moreover, as already discussed by Moreira et al. (1999) and Madureira et al. (2005), helium isotopic data for the Azores volcanic rocks show no or little dependency of $^{3}\text{He}/^{4}\text{He}$ ratios to the He content of olivine crystals. For instance, most of the rock samples from Faial and Terceira respectively display similar $R_{\text{He}}$ ratio, within analytical uncertainty, despite olivine’s $^{3}\text{He}$ contents that vary by as much as two orders of magnitude. These different observations, and the global consistency between the hydrothermal fluids and rocks data sets, argue against any significant He isotopic fractionation between magmas, phenocrysts and emitted gases in the Azores data set.

4.1.2. Kinetic fractionation during gas transport

In theory, kinetic fractionation of helium isotopes between gas and water can occur in aquifers during bubble formation and/or gas bubbling. However, field data published for steady-state hydrothermal systems with short water residence time (i.e., with no suspicion of radiogenic helium contamination) generally show an excellent agreement between helium isotopes ratios in the gas and the water phases (e.g. Allard et al., 1997; Parello et al., 2000), and hence show no sign of any such Rayleigh kinetic fractionation. In the Azores too, such a fractionation process is quite unlikely, especially for the most active thermal gas emissions in Sao Miguel, Graciosa and Terceira: these emanations, characterized by intense advective gas flow, are directly connected to the active conduits of the volcanic systems; their nearly pure $\text{CO}_2$-composition is consistent with a continuous gas supply from deep magmatic sources through $\text{CO}_2$-He oversaturated hydrothermal systems, allowing almost direct gas transit towards the surface. We thus consider their $^{3}\text{He}/^{4}\text{He}$ ratios as the least exposed to possible isotopic fractionation. Here we also emphasize that, at Furnas volcano, we find similar $^{3}\text{He}/^{4}\text{He}$ ratios for both intense fumarolic gas emissions (sample 1) and gentle gas bubbling across Furnas lake (sample 2; Table 2) or ponding waters (samples 4 and 5), although differing markedly in their temperature, He content and $\text{He}/\text{CO}_2$ ratio. Similarly, at Fogo volcano, we find identical $^{3}\text{He}/^{4}\text{He}$ ratios for both surface bubbling gas (Caldera Velha, sample 9) and overpressured gas from the 1.4 km deep Cl2 geothermal drill of Ribeira Grande (sample 10). Similar $^{3}\text{He}/^{4}\text{He}$ ratios in the gas phase and in corresponding water are also found on Flores. Such similarities thus suggest minor kinetic fractionation of He isotopes during gas transport across the studied aquifers. The most spectacular He isotopic contrast in our data set is between the subterranean cold water lake located at the bottom of the Furna do Enxofre lava cave (Graciosa) and nearby mud-pool bubbling gases (see Section 3.3), for which we provide an explanation below.

4.1.3. Crustal contamination of groundwaters

As shown above, helium dissolved in hot springs and groundwaters of the Azores archipelago tends to display lower $^{3}\text{He}/^{4}\text{He}$ ratios than the most intense gas emissions. Although little is known concerning the water residence time in the various sampled aquifers and concerning the radiogenic $^{4}\text{He}$ production rate in the host formations, the most straightforward explanation for this discrepancy is a contamination by radiogenic helium, as observed in many instances worldwide (Ballentine and Burnard, 2002; Kipfer et al., 2002). Lower $^{3}\text{He}/^{4}\text{He}$ ratios in groundwaters and/or remote gas emissions, due to increasing dilution of the magmatic component by radiogenic $^{4}\text{He}$ derived from host rocks, are also a common observation made at many volcanoes (Sano et al., 1984; Welhan et al., 1988; Marty et al., 1989; Sakamoto et al., 1992). On Sao Miguel, Moreira et al. (1999) evidenced a post-eruptive radiogenic ingrowth in bulk lavas, which would allow the transfer of $^{4}\text{He}$ to groundwaters during water–rock exchanges. This contamination process of groundwaters should be favoured by the long repose intervals of Azores volcanoes and by the strong alteration of host rocks at depth by acid gases of magmatic derivation, such as documented at Furnas volcano (Ferreira and Oskarsson, 1999; Cruz et al., 1999). Accepting this framework, groundwaters at both Furnas and Fogo volcanoes could contain $\sim 20\%$ radiogenic $^{4}\text{He}$ from host rocks. We interpret in the same way the lower $^{3}\text{He}/^{4}\text{He}$ ratio (8.3–8.4 $R_e$) for Graciosa groundwaters with respect to the free gases (up to 11.2 $R_e$). This interpretation extends to the subterranean lake located in the Furna do Enxofre lava cave of Graciosa’s caldera (Section 3.3), whose $^{3}\text{He}/^{4}\text{He}$ ratio markedly differs from that of the nearby bubbling mud-pool but is identical to that of the local aquifer, and which may thus consist of outcropping groundwaters directly connected to the underlying aquifer and little influenced by the nearby gas bubbling.

In conclusion, while helium dissolved in thermal and cold groundwaters of the Azores archipelago is likely affected to various extents by radiogenic contamination from the host rocks, we are quite confident that steady-state gas emissions from the most active vents in each island are reliable carriers of the helium isotope composition of the underlying magmatic end-member.

4.2. Regional He isotopic pattern

Our results on Azores hydrothermal fluids, together with He isotopic data for the volcanic rocks (Kurz, 1991; Moreira et al., 1999; Madureira et al., 2005), reveal not only a wide range but also a quite coherent spatial distribution of $^{3}\text{He}/^{4}\text{He}$ ratios across the Azores archipelago.

Sao Miguel is clearly distinct from the other islands, with $^{3}\text{He}/^{4}\text{He}$ ratios consistently lower than the MORB reference in both fluids and rocks. The hydrothermal gas phases from both Furnas and Agua de Pau volcanoes indicate a homogeneous magmatic end-member, with mean $^{3}\text{He}/^{4}\text{He}$ ratio of 5.54 ± 0.25 $R_e$ (Fig. 3), which points to a magmatic source with higher time-integrated (U + Th)/$^{4}\text{He}$ ratio relative to normal MORB material. Whether this ratio is representative of whole magmatism in Sao Miguel island however remains uncertain. In fact, Kurz (1991) reported more extreme $^{3}\text{He}/^{4}\text{He}$ values of 3.5 $R_e$ and 8.4 $R_e$ respectively, for rock samples from the northeastern (Nordeste Complex) and northwestern (Sete Cidades) volcanic complexes. We emphasize that Kurz’s data correlate with a westward decrease of radiogenic Sr and Pb in volcanic rocks across Sao Miguel island (Kurz, 1991), which thus strongly suggests a trend in the underlying mantle source. In terms of He isotopes, the magmatic source feeding furnas and Agua de Pau central volcanoes would then be intermediate between typical MORB to the west (Sete Cidades) and highly radiogenic under the easternmost part of the island. As a matter of fact, lavas from Sao Miguel have long been recognized to display highly radiogenic Sr and Pb isotopic ratios among OIBs (Hawkesworth et al., 1979; White et al., 1979), implying a crustal component in their source. It has been proposed that this crustal component could represent either a mantle contaminated by subducted terrigenous sediment (Hawkesworth et al., 1979; Turner et al., 1997) or delaminated subcontinental lithosphere left behind at the opening of the North Atlantic (Widom et al., 1997; Moreira et al., 1999). However, more recent data for Sr–Pb–Hf–Nd isotopes and...
trace elements (Elliot et al., 2007; Beier et al., 2007) rather suggest an enriched crustal source containing recycled oceanic crust, plus some subducted seamount (for the easternmost volcanism in Sao Miguel). He isotope study of volcanic fluids in eastern Sao Miguel would certainly be of interest in the future to discuss these various options.

The other islands of the Azores archipelago exhibit a helium isotopic signature varying from typical MORB values (Flores, Faial) to plume-type values at Terceira, Graciosa and Pico. This He isotopic pattern broadly parallels the variations of other isotopic markers in corresponding volcanic rocks (Fig. 4). In addition to the radiogenic component mentioned above, the observed isotopic variations require a mixing with at least two other mantle components: (i) normal MORB mantle (Moreira et al., 1999; Madureira et al., 2005), which constitutes almost 100% of the gas phase at all sites, such a trend directly translates into corresponding variations of the CO₂/³He ratios, which increase from an average of (9.3 ± 2.1) × 10⁹ on Sao Miguel to ~17.5 × 10⁹ on Graciosa and 22 ± 4 × 10⁹ on Terceira (Fig. 6b). These latter values are one order of magnitude higher than the average MORB CO₂/³He molar ratio (~2.2 × 10⁹; Marty and Tolstikhin, 1998). Therefore, the trends in Fig. 6a–b could reflect either a dilution of ³He by a CO₂-rich gas from a carbon enriched mantle plume or alternatively a lower-than-MORB ³He content of the mantle source.

A CO₂-rich Azores plume was previously inferred by Kingsley and Schilling (1995) who measured high CO₂ contents and higher-than-MORB CO₂/³He ratios (up to 4.8 × 10⁹) in submarine basaltic glasses from the Mid-Atlantic ridge at the latitude of the Azores and estimated a minimal C/³He molar ratio of ~10⁻² for the plume source. The co-variations of these ratios with both Sr and Nd isotopic ratios in the same basalts, and their independence from the degree of basalt degassing and/or CO₂ oversaturation (1.8 to 6.4), were taken as an evidence for ridge interaction with a mantle plume highly enriched in carbon dioxide (by a

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The origin of the Azores plume component is complex and still debated. Plume-related OIBs from the central Azores islands display geochemical evidence of mixed contributions from the lower mantle (Moreira et al., 1999; Madureira et al., 2005) and a recycled radiogenic component which, depending on the considered indicators, may consist of altered oceanic crust and sediments (Turner et al., 1997; Moreira et al., 1999) or delaminated oceanic mantle lithosphere of Archean age (Schaefer et al., 2002). Plume supply from a primitive lower mantle source is indicated by helium isotopic data for volcanic rocks and fluids from the central islands (Moreira et al., 1999; Madureira et al., 2005; this work) and by the lower-than-MORB ²¹Ne/²²Ne ratios in volcanic rocks from Terceira (Madureira et al., 2005). A deep derivation of the Azores plume is also supported by the very low (sub-chondritic) Os isotopic ratios in volcanic rocks from Terceira and especially Faial–Pico islands (Schaefer et al., 2002) and by the seismic tomography inversion of Montelli et al. (2004), which shows a well-resolved plume originating from near the bottom of the mantle. However, an interesting feature which arises from our data set is that the gas emissions with the highest ³He/⁴He ratios correspond to the lowest ³He concentrations; there is in fact a broad anti-correlation between both parameters in Azores gas phases when considering all islands (Fig. 6a). Moreover, because CO₂ constitutes almost 100% of the gas phase at all sites, such a trend directly translates into corresponding variations of the CO₂/³He ratios, which increase from an average of (9.3 ± 2.1) × 10⁹ on Sao Miguel to ~17.5 × 10⁹ on Graciosa and 22 ± 4 × 10⁹ on Terceira (Fig. 6b). These latter values are one order of magnitude higher than the average MORB CO₂/³He molar ratio (~2.2 × 10⁹; Marty and Tolstikhin, 1998). Therefore, the trends in Fig. 6a–b could reflect either a dilution of ³He by a CO₂-rich gas from a carbon enriched mantle plume or alternatively a lower-than-MORB ³He content of the mantle source.
factor 3.3 to 8.8 relative to depleted asthenosphere) and other volatiles such as H₂O and Cl (Kingsley and Schilling, 1995). The high CO₂/³He ratios (1.8–2.6 × 10¹⁰) combined with high ³He/³²He ratios we measured in gas emissions from Terceira and Graciosa further argue in support of a CO₂-rich mantle plume feeding the Azores. Carbon recycling in the mantle through oceanic plate subduction is the main process capable of explaining higher-than-MORB ³He/²He ratios in the products of arc-volcanism and, likely, of plume-related hot spots (e.g. Marty and Jambon, 1987; Trull et al., 1993; Marty and Tolstikhin, 1998). Hence, we rather favour the conclusion that the Azores plume material might result from two possible processes:

i) Previous degassing of the plume upon ascent. Such a process was invoked by Hilton et al. (1997) for explaining the helium–carbon isotope relationship at Kilauea volcano and, more recently, for explaining the differences in noble gas elemental ratios between MORB and OIB glasses (Gonnermann and Mukhopadhyay, 2007; Hopp and Tieloff, 2008). Note, however, that because carbon dioxide is less soluble than helium in the melt, plume pre-degassing would be expected to lower the CO₂/³He ratio of the plume, whereas we find particularly high ratios for the Azores;

ii) Fractionation of He and U–Th during partial melting events. Recent experimental results unexpectedly revealed that helium could be more compatible (i.e. less efficiently removed) than U and Th during partial mantle melting (Parman et al., 2005), thereby allowing enhanced ³He/⁴He ratio (less affected by radiogenic He ingrowth from U–Th decay) in ancient mantle reservoirs that, otherwise, have been depleted by successive melting events. These results thus offer a potential key to resolve the apparent helium paradox between plume-related OIBs and MORBs. This possibility also extends to other noble gases, since new results from Heber et al. (2007) show that the partition coefficients of noble gases in olivine are one to two orders of magnitude greater than for U and Th. Therefore, as far as helium is concerned, partial mantle melting could lead to preferential extraction of U and Th, leaving behind a residual reservoir with a higher-than-MORB time-integrated ³He/(U+Th) ratio. The only condition to get high ³He/⁴He ratios is that these U–Th-depleted mantle domains must have formed before these ratios in the evolving mantle have dropped too low, hence relatively early in the Earth history. Therefore this scenario, sometimes presented as the “whole mantle convection” alternative to the classic “layered mantle” model, equally requires that mantle domains with distinct geochemical signatures could escape convective homogenization for very long periods of time, something which is difficult to reconcile with the whole mantle convection assumption.

With regard to the Azores hot spot, in addition to explaining the negative trend between ³He concentrations and the ⁴He/³²He ratios (Fig. 6a), this “residual reservoir” scenario would support Schaeffer et al.’s (2002) conclusions based on osmium isotopes, that the Azores plume may derive from the deep subduction of a depleted Archean oceanic mantle lithosphere. We emphasize, however, that the Azores lava present enriched trace element patterns (Turner et al., 1997), suggesting that the source of the Azores hotspot is more enriched in incompatible elements such as U and Th than MORB. It seems therefore difficult to produce a lower-than-MORB ³He content in the Azores source whatever the relative incompatibilities of He and U–Th.

Hence, we rather favour the conclusion that the Azores plume material is highly enriched in CO₂ and other volatiles (rather than being depleted in ³He), and contains ancient altered oceanic material with high initial CO₂/³He ratio that was recycled deep in a ³He-rich lower mantle. Future systematic investigations of carbon dioxide and noble gases in both volcanic rocks and fluids of the Azores archipelago should provide further insight into this matter.

5. Conclusions

Helium isotope ratios measured in both thermal waters and gases of the Azores archipelago lead to the following main observations and conclusions:

— Hydrothermal gas emissions from the most active and central vents of the volcanic systems tend to display higher ³He/⁴He ratios than local groundwaters, and likely carry the most representative isotopic signature of the underlying mantle source. Thermal groundwaters rather share similar isotopic ratio with the host volcanic rocks.
— Hydrothermal fluids in central Sao Miguel island clearly distinguish from those in the other islands, with He/4He ratios of 5.23–6.07 R, much lower than the MORB reference. Such ratios, together with Sr–Nd–Pb–Hf–Os isotopic compositions and trace element patterns in corresponding volcanic rocks, imply the contribution of a crustal radiogenic component in the local degassing mantle source. The actual nature of this crustal component however remains a matter of debate (e.g. Elliot et al., 2007).

— Fluids on Faial and Flores islands, located closer to and on either side of the nearby Mid-Atlantic Ridge, actually display MORB-type He/4He ratios, indicating essentially pure upper mantle degassing.

— Instead, plume-type He/4He ratios characterize hydrothermal fluids on Terceira, Graciosa and, to a lesser degree, Pico islands. Similarly high ratios in corresponding volcanic rocks indicate no or little He isotopic fractionation during magma degassing. A deep mantle origin of helium in the analysed fluids is consistent with tomographic evidence of a deep-rooted plume beneath the Azores hot spot. The spatial distribution of He/4He ratios demonstrates that plum’s head is located beneath the central part of the archipelago.

— The highest He/4He ratios in Terceira and Graciosa islands correspond to the lowest 3He concentrations and highest C3He/C4He ratios. This observation is interpreted as indicative of a high CO2 content (and consequent He dilution) in the Azores plume material, in agreement with previous measurement of high C3He/He ratios in basaltic glasses from the nearby Mid-Atlantic Ridge (Kingsley and Schilling, 1995). This C2O2 enrichment of the Azores plume, associated with plume-type He/4He values, is consistent with other geochemical evidence for the recycling of ancient oceanic material in the lower mantle beneath the Azores.

References


