Noble gases in the Finero phlogopite-peridotites, western Italian Alps

Takuya Matsumoto a,*, Tomoaki Morishita b, Jun-ichi Matsuda a, Toshiyuki Fujioka a,1, Masamichi Takebe c,2, Koshi Yamamoto c, Shoji Arai b

aDepartment of Earth and Space Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan
bGraduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan
cDepartment of Earth and Planetary Sciences, Graduate School of Environmental Studies, Nagoya University, Chikusa, Nagoya, 464-8602, Japan

Received 21 January 2005; received in revised form 16 June 2005; accepted 3 July 2005
Available online 10 August 2005
Editor: K. Farley

Abstract

Here we report results from an investigation of noble gases in a specimen with layers of very fine-grained apatite and orthopyroxene from the Finero ultramafic complex, western Italian Alps. We have also examined fresh olivine grains separated from phlogopite-harzburgites without an apatite layer. Fluid inclusions of these olivine separates appeared rich in radiogenic components such as 3He, 21Ne and 40Ar, suggesting the derivation of fluids from a crust-like reservoir. Such a crust-like component also appeared to be contained in the samples with the apatite-opx layer, however, an additional isotopically distinct component is necessary to explain progressive increases in 3He concentration and decreases in 40Ar/36Ar ratios observed approaching the apatite-rich layer. High 3He contents and low 40Ar/36Ar ratios are consistent with the signature expected for slab-derived metasomatic fluids. There is a clear mixing trend defined in a 3He/36Ar vs. 40Ar/36Ar diagram with crustal and slab-derived fluids as end-member compositions, suggesting that the complex was metasomatized by fluids derived from geochemically distinct regions and distinct geotectonic settings. The parent melt or fluids responsible for the formation of the apatite-rich layer should be derived from the slab-derived component, which is consistent with the notion that the Finero mantle was once in the mantle wedge. An in situ component produced in the previously

* Corresponding author. Tel./fax: +81 6 6850 5541.
E-mail addresses: matsumoto@ess.sci.osaka-u.ac.jp (T. Matsumoto), moripta@kenroku.kanazawa-u.ac.jp (T. Morishita), matsuda@ess.sci.osaka-u.ac.jp (J. Matsuda), toshiyuki.fujioka@anu.edu.au (T. Fujioka), takebe@matsue-ct.jp (M. Takebe), hamchans@nagoya-u.jp (K. Yamamoto), ultrasa@kenroku.kanazawa-u.ac.jp (S. Arai).
1 Current address: Research School of Earth Science, The Australian National University, Canberra, ACT0200, Australia.
2 Current address: Department of Sciences, Matsue National College of Technology, 14-4, Nishi-ikuma-cho, Matsue, Shimane, 690-8518, Japan.

0012-821X/S - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2005.07.005
1. Introduction

Increasing interest in the noble gas compositions of the lithospheric part of the upper mantle has stimulated many investigations of peridotite xenoliths in alkali basalts or of orogenic peridotites (e.g., [1, 13]). These studies have identified the subcontinental lithospheric mantle (SCLM) reservoir as a unique reservoir in which diverse noble gas elemental and isotopic components distinct from those in the sub-lithospheric reservoirs have been built up reflecting processes over a long term isolation from the mantle convection. Previous studies on mantle-derived xenoliths from Australia identified two distinct noble gas components in the SCLM. The first is a trapped component which is often stored in fluid inclusions with \( {^3}\text{He}/ {^4}\text{He} \) ratios being indistinguishable from those of the convecting upper mantle (8 ± 1 Ra; (e.g., [14]); Ra denotes the atmospheric \( {^3}\text{He}/ {^4}\text{He} \)). The second is a radiogenic and/or nucleogenic component produced in situ as a result of cryptic or modal metasomatism which re-fertilized the SCLM. This component is recognized most clearly in the crystal structure of metasomatic minerals which often host noble gas producing radioactive parents such as U, Th and K. However, some xenoliths, especially those from the central European lithospheric mantle, are reported to show significant enrichments in radiogenic noble gases in fluid inclusions with characteristically low \( {^3}\text{He}/ {^4}\text{He} \) ratios of 6.3 ± 0.4 Ra. This necessitates the fluxing of fluids that had already been enriched in radiogenic noble gases derived from some homogeneous sub-continental reservoirs. Even lower \( {^3}\text{He}/ {^4}\text{He} \) ratios are found in xenoliths from far eastern Russia indicating addition of fluids with a very low \( {^3}\text{He}/(\text{U}+\text{Th}) \) ratios associated with dehydration of a subducting plate [10]. The SCLM is also suggested to be a storage for the heavier atmospheric noble gases (e.g., Ar) recycled by subduction of a hydrated oceanic plate and its sedimentary cover [7,10] Thus, it is becoming clear that the sources and processes responsible for developing peculiar noble gas signatures of the SCLM reservoir are diverse and these issues need to be clarified.

As to the fundamental process of noble gas introduction to the SCLM, there is no doubt that the fluxing of metasomatising melts or fluids through the SCLM play a key role in modifying its noble gas compositions [1,4,12]. Ineffective diffusive movement of noble gases within the mantle [15] as well as the occurrence of noble gases in fluid inclusions of mantle minerals (e.g., [10]), requires advection of melt charged with noble gas through the mantle. These melts should also be responsible for causing modal or cryptic metasomatism with such evidence usually found in mantle xenoliths and orogenic peridotites (e.g., [16,17]). However, there has been only limited direct evidence found so far for metasomatic introduction of noble gases to the SCLM (e.g., [5,8]).

This paper presents new noble gas data obtained from a unique specimen with a distinct apatite-rich layer in a phlogopite-peridotite matrix (Fig. 1). The specimen was from the Finero phlogopite-peridotite body in western Italy. The complex is famous for...
the occurrence of unweathered and unaltered orogenic peridotites, and is believed to be a highly metasomatised slice of mantle, indicated by the occurrence of ubiquitous phlogopite and other accessory metasomatic phases. The formation of the thin apatite-rich layer in the phlogopite-peridotite matrix is most likely associated with the infiltration of carbonatic metasomatizing fluids through the peridotitic body. Availability of such a sample enables us to directly investigate effects of metasomatism on noble gas signatures within the mantle lithosphere.

2. Sampling and analysis

The Finero mafic–ultramafic complex lies within the north-western, basal portion of the Ivrea zone of the Italian western Alps. The complex has been divided into four main units: (1) upper metagabbro, (2) amphibole-peridotite, (3) lower metagabbro, and (4) phlogopite-peridotite. They have been folded into a tight antiform. The peridotite units show different structural andgeochemical characteristics. In general, the phlogopite-peridotite consists of dunite and harzburgite, with small amounts of chromitite and clinopyroxenite. Platinum-group minerals and zircon are found within the chromitite. Zanetti et al. [24] reported that apatite and carbonate appear to be randomly distributed within the phlogopite-peridotite unit. The country rock of the Finero mafic–ultramafic complex is the Kinzigite Formation, which consists of metamorphic wackes, pelites, marbles and volcanic rocks.

In this study, noble gas isotopic compositions of a phlogopite-peridotite with an apatite-rich layer of <1 cm thickness was targeted. The sample was taken from a large boulder buried in river sediments, 0.7 × 0.4 × 0.3 m in size, from the Cannobino River to the west of Finero village. The thin layer consists of very fine-grained olivine, orthopyroxene, spinel, amphibole, phlogopite, sulfide minerals, and apatite, with small amounts of carbonate and clinopyroxene. In the apatite-rich layer, amphibole and carbonate minerals are more abundant than in the apatite-poor portion, suggesting that an alkali- and phosphate-rich carbonatic metasomatizing agent existed within the thin layer. A detailed petrological investigation of this specimen has already

<table>
<thead>
<tr>
<th>Element</th>
<th>FIN-OL1</th>
<th>FIN-OL2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Step-heating</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800 °C</td>
<td>1800 °C</td>
</tr>
<tr>
<td>[4He]</td>
<td>1.33</td>
<td>4.34</td>
</tr>
<tr>
<td>(×10^-6 cm^3 STP/g)</td>
<td>±0.14</td>
<td>±0.44</td>
</tr>
<tr>
<td>[3He]/[4He]</td>
<td>0.155</td>
<td>0.157</td>
</tr>
<tr>
<td>(R/Ra)</td>
<td>±0.007</td>
<td>±0.004</td>
</tr>
<tr>
<td>[22Ne]</td>
<td>16</td>
<td>4.9</td>
</tr>
<tr>
<td>(×10^-12 cm^3 STP/g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[20Ne]/[22Ne]</td>
<td>10.1</td>
<td>10.35</td>
</tr>
<tr>
<td>[21Ne]/[22Ne]</td>
<td>0.0682</td>
<td>0.0870</td>
</tr>
<tr>
<td>[36Ar]</td>
<td>5.8</td>
<td>5.9</td>
</tr>
<tr>
<td>(×10^-10 cm^3 STP/g)</td>
<td>±0.6</td>
<td>±0.6</td>
</tr>
<tr>
<td>[40Ar]/[36Ar]</td>
<td>1643</td>
<td>1904</td>
</tr>
<tr>
<td>168</td>
<td>±68</td>
<td>±79</td>
</tr>
<tr>
<td>[He]/[40Ar]</td>
<td>3.3</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Quoted errors (1σ) in Tables 1–3 include the uncertainties in the correction factors for mass discrimination and sensitivity determined by repeated analysis of the air-standard (Ne and Ar) and the helium standard of Japan (HESJ), as well as the uncertainties in the blank correction and interference correction in the case of Ne.
Table 2

Results of step-heating gas extraction on five samples sliced out of the Finero phlogopite-periodotite with apatite-opx veins

<table>
<thead>
<tr>
<th></th>
<th>A1 (0.721 g)</th>
<th>B1 (0.934 g)</th>
<th>C1 (1.088 g)</th>
<th>D1 (1.042 g)</th>
<th>E1 (1.248 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800</td>
<td>1300</td>
<td>1800</td>
<td>Total</td>
<td>800</td>
</tr>
<tr>
<td>$^3$He (10$^{-6}$ cm$^3$ STP/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3$He/$^4$He</td>
<td>1.4 ± 0.1</td>
<td>7.5 ± 0.8</td>
<td>4.5 ± 0.5</td>
<td>13.5 ± 0.9</td>
<td>0.49 ± 0.05</td>
</tr>
<tr>
<td>$^{20}$Ne/$^{22}$Ne (10$^{-12}$ cm$^3$ STP/g)</td>
<td>3.8 ± 0.95</td>
<td>1.18 ± 0.65</td>
<td>1.03 ± 0.96</td>
<td>0.99 ± 0.57</td>
<td>0.87 ± 0.80</td>
</tr>
<tr>
<td></td>
<td>9.26 ± 0.70</td>
<td>10.6 ± 0.9</td>
<td>12.5 ± 4.9</td>
<td>9.7 ± 1.6</td>
<td>8.5 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>0.0626 ± 0.0052</td>
<td>0.0657 ± 0.0062</td>
<td>0.103 ± 0.041</td>
<td>0.065 ± 0.006</td>
<td>0.078 ± 0.013</td>
</tr>
<tr>
<td>$^3$He/$^4$He</td>
<td>11.7 ± 2.7</td>
<td>4.3 ± 0.6</td>
<td>8.1 ± 1.3</td>
<td>17.5 ± 1.5</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>$^{38}$Ar (10$^{-6}$ cm$^3$ STP/g)</td>
<td>1.6 ± 0.06</td>
<td>4.9 ± 0.15</td>
<td>6.4 ± 0.42</td>
<td>8.0 ± 0.23</td>
<td>1.8 ± 0.6</td>
</tr>
<tr>
<td>$^{36}$Ar/$^{38}$Ar (10$^{-4}$ cm$^3$ STP/g)</td>
<td>320 ± 8.49</td>
<td>1153 ± 34</td>
<td>2192 ± 96</td>
<td>349 ± 135</td>
<td>2498 ± 33</td>
</tr>
<tr>
<td>$^4$He/$^{38}$Ar*</td>
<td>0.125 ± 0.6</td>
<td>2.5 ± 0.2</td>
<td>1.8 ± 0.7</td>
<td>3.8 ± 2.5</td>
<td>2.5 ± 0.5</td>
</tr>
</tbody>
</table>

Notes:
- All values are given in parts per million (ppt).
- Errors represent 1σ uncertainties.
- STP: Standard Temperature and Pressure (0°C, 1 atm).
- $^3$He, $^4$He, $^{20}$Ne, $^{21}$Ne, $^{36}$Ar, $^{38}$Ar, $^{4}$He are noble gases.
- $^{38}$Ar* is Ar isotopic ratio.
- The table includes results for five samples sliced from the Finero phlogopite-periodotite with apatite-opx veins.
been carried out [28] and a geochemical study of major and trace element composition is being undertaken (e.g., [29]). For the noble gas analysis, the sample was first sliced to a thin slab (~1 cm thick) perpendicular to the thin layer. The slab was then cut into ~1 cm intervals parallel to the direction of the thin layer. Finally, these were cut into small, ~1 cm³ blocks (Fig. 1). Part of these blocks was subjected to major and trace element analysis [29].

One of the blocks contained the apatite-rich layer (A1) and other four (B1, C1, D1 and E1) were from host peridotites containing phlogopite. As shown in the Appendix, abundances of REE’s (and U, Th and Sr) in A1 are greater than those in other blocks taken from the host phlogopite-peridotite, indicating that phases associated with the apatite-rich layer host these trace elements as well. Note that host peridotites (B1 to E1) also showed enriched LREE patterns, with smaller La/Yb than A1. These geochemical and petrological results suggest that the apatite-layer was locally formed from a fractionated metasomatizing agent after the main silicate metasomatism recorded in the phlogopite-peridotite [28].

In addition to the sample with the apatite-rich layer, we also examined noble gas compositions of two olivine separates (FIN-OL1 and FIN-OL2) from Finero phlogopite-peridotites without an apatite layer. These two samples were extremely fresh, with abundant fluid or melt inclusions. They form cross-cutting arrays of differing orientations, with isolated inclusions being rare. Thus, most of fluid inclusions are of secondary origin and likely to be remnants of fluxed fluids. Arrays of fluid inclusions are also abundant in olivines of the peridotite containing the apatite-rich layer.

Noble gas isotope analysis was carried out using the VG5400 noble gas mass spectrometer at Osaka University. Noble gases were extracted from the samples either by step-heating or crushing. For the phlogopite-peridotite with the apatite layer (A1 to E1), we loaded blocks of ca. 1 gram without making mineral separates, due to the difficulty of separating a sufficient amount of minor and fine-grained apatite or other constituents for noble gas analysis. Details of analyses (including sample preparation, cleaning, gas purification and noble gas analysis) are essentially the same as those described previously (e.g., [7]).

3. Results and discussion: characterization of noble gases associated with apatite vein and host peridotite

Two suites of samples were analysed for He, Ne and Ar isotopic compositions. One suite consists of olivine separates from two phlogopite-peridotites without an apatite-rich layer (“unveined” peridotites). The other suite consists of five slices prepared from a phlogopite-peridotite with an apatite-rich layer (the “veined” peridotite). The analyses were carried out on a whole rock basis for the latter suite. Table 1 lists the results obtained from two olivine separates (FIN-OL1 and -OL2) from the unveined peridotites. Noble gas data from the veined peridotite obtained by step-heating and by crushing are listed in Tables 2 and 3, respectively. Uncertainties in noble gas elemental and isotopic compositions listed in tables (and shown in figures) are 1 sigma. Neon isotopic ratios obtained by crushing and at some temperature steps during step-heating were not reported here, due to the relatively small neon release and consequently large CO₂⁻⁻⁻⁻⁻⁻ interference corrections applied for ²²Ne peaks lead to >100% uncertainties in isotopic ratios (shown as “-” in Table 1). In this section, we will demonstrate that the sample with the apatite-rich vein (A1) has a distinct noble gas signature compared with other parts of the sample (B1 to E1). It will also be shown that the unveined peridotites have noble gas signatures distinct from those expected for mantle derived samples.

<table>
<thead>
<tr>
<th></th>
<th>A1</th>
<th>B1</th>
<th>C1</th>
<th>D1</th>
<th>E1</th>
</tr>
</thead>
<tbody>
<tr>
<td>[⁴He]</td>
<td>0.75</td>
<td>0.54</td>
<td>1.48</td>
<td>0.28</td>
<td>0.18</td>
</tr>
<tr>
<td>(10⁻⁵ cm³)</td>
<td>± 0.08</td>
<td>± 0.05</td>
<td>± 0.15</td>
<td>± 0.03</td>
<td>± 0.02</td>
</tr>
<tr>
<td>STP(g)</td>
<td>0.472</td>
<td>0.689</td>
<td>0.655</td>
<td>0.609</td>
<td>0.525</td>
</tr>
<tr>
<td>(R/Ra)</td>
<td>± 0.014</td>
<td>± 0.023</td>
<td>± 0.016</td>
<td>± 0.034</td>
<td>± 0.014</td>
</tr>
<tr>
<td>[³⁸Ar]</td>
<td>0.6</td>
<td>0.8</td>
<td>2.8</td>
<td>0.4</td>
<td>0.38</td>
</tr>
<tr>
<td>(10⁻¹⁰ cm³)</td>
<td>± 0.1</td>
<td>± 0.1</td>
<td>± 0.3</td>
<td>± 0.1</td>
<td>± 0.04</td>
</tr>
<tr>
<td>STP(g)</td>
<td>840</td>
<td>1209</td>
<td>1883</td>
<td>1595</td>
<td>1396</td>
</tr>
<tr>
<td>[⁴⁰Ar]</td>
<td>± 24</td>
<td>± 28</td>
<td>± 10</td>
<td>± 108</td>
<td>± 11</td>
</tr>
<tr>
<td>[⁴He]/[⁴⁰Ar]</td>
<td>± 3.9</td>
<td>± 1.2</td>
<td>± 0.5</td>
<td>± 1.1</td>
<td>± 0.6</td>
</tr>
</tbody>
</table>
3.1. He and Ar of unveined samples

Helium isotope ratios in the unveined samples (FIN-OL1 and OL2) are 0.15 Ra and are significantly lower than the atmospheric ratio. The two olivine samples yielded quite consistent helium isotopic ratios in gases released at both 800 and 1600 °C, as well as by crushing. This consistency clearly indicates that helium with 0.15 Ra is from a single component trapped in fluid inclusions within the olivines.

Moderately high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of 2000–3000 are observed in the olivine separates and are plotted against $^{3}\text{He}/^{4}\text{He}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios being significantly more radiogenic than mantle-derived samples, including orogenic peridotites from Horoman, northern Japan [7]. The ranges of ratios are consistent with a reservoir having significantly higher time-integrated U+Th/$^{3}\text{He}$ and K/$^{36}\text{Ar}$ ratios than in the mantle. Such a signature is generally expected for a crustal environment [30]. An important issue here is that these quasi-crustal noble gases are released from fluid inclusions in olivine grains, so the radiogenic component is not an in situ component; thus the radiogenic component would have been obtained by the fluids before being trapped in inclusions.

3.2. He in the veined samples

Helium isotopic ratios measured from the samples prepared from the veined sample also yielded $^{3}\text{He}/^{4}\text{He}$ ratios lower than those commonly expected for mantle-derived samples. The range of $^{3}\text{He}/^{4}\text{He}$ ratios of between 0.4 and 1.2 Ra were observed in helium released by step-heating extraction. The helium released at lower temperature steps (see Table 2) yielded consistently lower $^{3}\text{He}/^{4}\text{He}$ ratios than those released at higher temperatures. This indicates a preferential release of in situ radiogenic $^{4}\text{He}$ from the samples (note that we subjected the whole rock samples for the analysis of this suite of samples, with U, Th, K-bearing minerals included in the analysed fractions). Even with an apparent contribution of radiogenic $^{4}\text{He}$, nominal $^{3}\text{He}/^{4}\text{He}$ ratios released by step-heating were actually higher than the 0.15 Ra observed in the two olivine separates from the unveined specimen, indicating the contribution of a helium component with a $^{3}\text{He}/^{4}\text{He}$ ratio higher than the highest value observed (1.2 Ra) in the veined samples.

The high $^{3}\text{He}/^{4}\text{He}$ component appears to be focused in the apatite-rich layer. This is shown in Fig. 3(a,b) in which the profiles of $^{3}\text{He}$ and $^{3}\text{He}/^{4}\text{He}$ ratios are shown. As reported by Morishita et al. [29] (and in Appendix), a metasomatic component with LREE and U–Th enrichments is significantly enriched.
in A1 relative to adjacent host peridotite blocks (B1 to E1) (see Fig. A in Appendix for a gradual decrease in total REEs from A1 to E1). In terms of helium composition, a progressive increase in $^3\text{He}$ contents and correspondingly high $^3\text{He}/^4\text{He}$ ratios towards sample A1 was observed. Concentrations of U and Th are also highest in A1 due to the presence of modal apatite (locally up to 10% of mode; [28]), gradually decreasing from A1 to E1. It is expected that the contribution of in situ radiogenic $^4\text{He}$ would be most significant in A1, and $^3\text{He}/^4\text{He}$ ratios should therefore be lowest in A1. However, as shown in Fig. 3b, the highest $^3\text{He}/^4\text{He}$ ratios were in fact observed in the highest temperature fraction of the sample A1.

We note that the observed $^3\text{He}/^4\text{He}$ ratios in this suite of samples are not explained by a nucleogenic $^3\text{He}$ production by the reaction $^6\text{Li}(n,\alpha)^3\text{H}(\beta^-)^3\text{He}$. This reaction only significantly increases $^3\text{He}/^4\text{He}$ ratios of minerals rich in Li and poor in U and Th [31]. Apatite is highly enriched in U and Th and is virtually devoid of Li [32]. Concentrations of Li in other constituent minerals of Finero peridotites are also reported to be less than a few ppm [33]. It has been demonstrated experimentally and theoretically that $^3\text{He}_\text{nucleogenic}/^4\text{He}_\text{radiogenic}$ ratios for minerals containing a few ppm of Li and U and Th are typically on the order of $10^{-7}$ or lower [31]. Therefore, it is unlikely that a helium component concentrated in the apatite-rich part of the sample is related to the in situ nucleogenic production; rather the $^3\text{He}/^4\text{He}$ ratio higher than air implies a contribution of mantle-He.

Helium analysis by crushing, however, did not show a clear mantle-He signature (Fig. 4). This is most likely due to the release of radiogenic $^4\text{He}$ by crushing as previously observed in similar experiments on mafic minerals with significant radiogenic $^4\text{He}$ [34,35]. This notion is supported by consistently higher $^4\text{He}/^{40}\text{Ar}^*$ ratios ($^{40}\text{Ar}^*$ is a non-atmospheric component of $^{40}\text{Ar}$) measured by crushing than those obtained by step-heating, indicating preferential release of radiogenic $^4\text{He}$ (Tables 2 and 3). Nevertheless, it is important to note that the range of $^3\text{He}/^4\text{He}$ ratios measured by crushing is higher than 0.6 Ra, thus higher than the value of 0.15 Ra obtained from the olivine. Thus the $^3\text{He}/^4\text{He}$ ratio of inclusion-trapped helium in the veined sample should be higher than in the unveined samples.
3.3. Ar in veined sample

Argon isotopic ratios measured by heating extraction show a systematic trend (Fig. 3c). The $^{40}$Ar/$^{36}$Ar ratios gradually increase from 840 (total) in A1 to 2400 in E1. In situ radiogenic $^{40}$Ar should contribute to the high $^{40}$Ar/$^{36}$Ar ratios observed in the samples, since ubiquitous phlogopite [28] hosts the largest proportion of the parental K in the samples [36]. In a $^{40}$Ar/$^{36}$Ar vs. $^{40}$K/$^{36}$Ar plot (Fig. 5), samples

![Graph showing Ar isotopic ratios](image1)

**Fig. 4.** $^{3}$He/$^{4}$He and $^{40}$Ar/$^{36}$Ar ratios of A1 to E1 measured by crushing extraction.

![Graph showing Ar isotopic ratios](image2)

**Fig. 5.** $^{40}$K/$^{36}$Ar vs. $^{40}$Ar/$^{36}$Ar ratios. A linear regression line is based on four data (except for A1 with bracket) with its slope yielded an isochron age of 240 ± 41 Ma. K concentrations are listed in the Appendix.
B1 to E1 show a clear linear trend, this can be regarded as an isochron. A1 lies off the trend due to heterogeneous K contents. The slope of this isochron corresponds to an age of 240 ± 41 Ma with an initial \( ^{40} \text{Ar} / ^{36} \text{Ar} \) ratio of 1220 ± 90. This age is consistent with a reported Sm–Nd whole rock age of 270 ± 57 Ma from Finero amphibole-peridotites \([37]\) a Pb isotope zircon age of 225 ± 12 Ma from syenite pegmatite dikes in the Finero phlogopite-peridotite body \([38]\) and a 215 ± 35 Ma age determined by SHRIMP on apatites from the present sample (e.g., \([29]\)). The significance of these ages are still controversial and will be discussed in a later publication, but we stress that the focusing of ages as determined by different radiometric methods most likely suggests continuous and rapid cooling of the Finero ultramafic body during late stage exhumation.

The gas released by crushing in samples B1 to E1 yielded \( ^{40} \text{Ar} / ^{36} \text{Ar} \) ratios lower than those measured by heating experiments on the same samples (Figs. 3c and 4b), and are less variable (1200 to 1900) compared to the variation of \( ^{40} \text{Ar} / ^{36} \text{Ar} \) ratios by crushing. These indicate that argon can be regarded as a mixture of a trapped components in fluid inclusions and a radiogenic component accumulated in mineral matrix sites. This is also supported by the similarity between the initial \( ^{40} \text{Ar} / ^{36} \text{Ar} \) ratio of the isochron (∼1200) and the range of \( ^{40} \text{Ar} / ^{36} \text{Ar} \) ratios by crushing extraction (it will be shown later that the inclusion trapped argon is likely to be a mixture of two isotopically distinct components, and this binary mixing is responsible for some variation in \( ^{40} \text{Ar} / ^{36} \text{Ar} \) ratios by crushing). It is also important to note that the lowest \( ^{40} \text{Ar} / ^{36} \text{Ar} \) ratio found in the A1 implies the lowest argon component, as was the case for helium isotopic compositions.

### 3.4. Neon isotopes

Helium and argon results suggest the present samples contain a significant radiogenic component, from either in situ production or entrapment as fluid inclusions. Neon isotopic ratios of the present samples also suggest that there is a significant nucleogenic neon component in addition to air-Ne and mantle-Ne. This is shown in Fig. 6 in which the neon results are plotted with expected mixing trends between possible end-members. All neon ratios plot above the air-nucleogenic mixing line, and to the right of the MORB-air mixing line, suggesting that these three components are required to explain the observed ratios. In the case of the present samples (especially with the apatite-vein), a nucleogenic neon component should include F-derived \( ^{22} \text{Ne} \) \((^{19} \text{F(α,n)} ^{22} \text{Ne})\) as well.

---

**Fig. 6.** Neon isotopic ratios of Finero phlogopite-peridotites. Arrows show directions of mixing trends with MORB-source or air and nucleogenic neon component expected in the average crustal composition \([39]\) and in the apatite of present samples (see text).
as $^{21}\text{Ne}$ produced from an $^{18}\text{O}(\alpha,\text{n})$ reaction. These arrows labeled as “nucleogenic Ne in apatite” in Fig. 6 show directions of mixing trends between air or MORB-Ne and the nucleogenic neon component expected for the apatite estimated from the chemical composition $^{22}\text{Ne}/^{21}\text{Ne}$ ratios with an empirical relationship found between $F/O$ and nucleogenic $^{22}\text{Ne}/^{21}\text{Ne}$ ratios.  Also, the presence of a significant $^{21}\text{Ne}$ excess in the crushing extraction on FIN-OL1 suggests that the component trapped in fluid inclusions is also enriched in nucleogenic neon. This is consistent with He and Ar observations. However, as most of the neon data are taken by step-heating, and because the difference between the crustal neon and in situ nucleogenic neon produced in the apatite are small compared with the uncertainties with each data point, it is impossible to discuss if there is a difference in neon isotopic composition between the olivine separates and the veined peridotites. Thus, hereafter we will concentrate in He and Ar results to further discuss the noble gas signatures of the present samples and some geochemical implications.

3.5. A binary mixing trend in He and Ar components of veined and unveined samples

As noted above, there are two distinct helium and argon components trapped in the present samples. These are: (1) a component having a relatively low $^{40}\text{Ar}/^{36}\text{Ar}$ ratio, concentrated in the apatite-rich part of the sample and (2) a component with a highly radiogenic argon component similar to the signature observed in the two olivine separates from the unveined samples. $^{3}\text{He}/^{36}\text{Ar}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios released from inclusion sites form a linear trend with the ratios from A1 and FIN-OL1 plotting at either end of the trend. The $^{3}\text{He}/^{36}\text{Ar}$ ratio of FIN-OL2 is not on the same line and actually plots out the range of Fig. 7 ($-0.014$). This is due to elemental fractionation favoring helium over argon in this sample, also supported by a fractionated $^{4}\text{He}/^{40}\text{Ar*}$ ($-50$) compared with the expected unfractionated production ratio of $-2$ to $5$ $^{40}\text{Ar}$. As noted earlier, the high $^{4}\text{He}/^{40}\text{Ar*}$ ratio of A1 is most likely due to a crush release of radiogenic $^{4}\text{He}$ from apatite, thus the process should not affect the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of A1. Also, there is no significant elemental fractionation implied for the rest of the samples, as their $^{4}\text{He}/^{40}\text{Ar}$ ratios are within the expected range. Thus, an interpretation of possible disturbance in the observed $^{3}\text{He}/^{36}\text{Ar}$ ratios caused by elemental fractionation is limited for data presented in Fig. 7. This suggests that the observed co-variation of $^{3}\text{He}/^{36}\text{Ar}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios is a result of binary mixing between two components. The fact that data from A1 plot at the end of the correlation line is particularly important as this block contains a significant apatite-rich layer, thus the observed noble gas signature in this part of the sample should be the
closest representative of a true end-member component; which should directly be associated with the apatite-forming metasomatic agent.

3.5.1. Identity and origin of noble gas component in the apatite-rich layer and implications to the mantle metasomatism affected the Finero complex

As discussed in Morishita et al. [28], the apatite-rich layer was formed as a result of introduction of metasomatic fluids within the mantle [28], which also resulted in significant refertilization in incompatible elements such as LREE, U and Th [28] (also shown in Appendix). This is shown in Fig. A1 in which the LREE enrichment is the most significant in sample A1 compared with the blocks separated from the host peridotite (i.e., B1 to E1). It is important to note that LREE contents gradually decrease from B1 to E1, thus the addition of a metasomatic component associated with the formation of the apatite-rich layer affected the host peridotite to some extent. However, there is a gradual increase in abundances of these incompatible elements from sample E1 to A1, suggesting that A1 is the most enriched in the component added by the introduction of the infiltrating metasomatic fluid. This is consistent with the helium and argon signatures noted above, as samples B1 to E1 are more significantly affected by He and Ar of the other component than in sample A1 (see Fig. 7).

From petrographic evidence, the apatite-rich layer formed during late stage silicate metasomatism of the Finero massif [28]. Indeed the apatite in the present samples is chlorapatite, with >2% Cl and <1 wt.% F, indicating a metasomatic origin [43]. The observation that the metasomatic apatite hosts a distinct noble gas component implies a genetic association between the apatite-forming metasomatic agent and its noble gases. Indeed, it has been previously postulated that the fluxing and entrainment of metasomatic fluids is responsible for introducing noble gases into the lithospheric part of the mantle which had lost its original noble gas component during earlier melting events (e.g., [4]). A clear link found between the petrographic evidence for the fluxing of metasomatic fluids (i.e., the apatite-rich vein) and the distinct noble gas component (especially the mantle-He) provides more evidence in support of arguments proposed as a result of previous xenolith studies.

Because the analysis on the A1 was carried out on the blocks (not on the mineral separates) containing both the apatite-rich part and the host peridotite, it would be reasonable to regard the observed He and Ar compositions as being affected by the radiogenic component. Thus, the end-member composition for the apatite-forming metasomatic agent should have $^{3}$He/$^{36}$Ar and $^{40}$Ar/$^{36}$Ar ratios extrapolated from the correlation line in Fig. 4 to higher and lower ratios, respectively. The $^{40}$Ar/$^{36}$Ar ratio of the apatite-rich layer, therefore, must be smaller than 800, indicating a possible involvement of an argon component with an air-like $^{40}$Ar/$^{36}$Ar ratio (~300). Likewise, it is conceivable that the observed $^{4}$He/$^{36}$He ratio in A1 is also affected by a helium component from the host peridotite, which is probably as low as the ratio found in two olivine separates from unviewed samples (0.15 Ra). This suggests that the apatite-rich layer should be characterized by a helium component with a $^{3}$He/$^{4}$He ratio higher than 1.2 Ra. Again, the presence of mantle-He is suggested for the apatite-rich layer (note that if the source of high $^{3}$He in the samples is radiogenic $^{3}$He, produced from a nuclear reaction on Li, $^{3}$He/$^{36}$Ar ratios are not necessarily inversely correlated with $^{40}$Ar/$^{36}$Ar ratios).

Apatite-forming metasomatic fluids should have a hybrid of air-like argon and mantle-derived helium. Such a noble gas composition is clearly distinguishable from that expected for any melt of fluid rising from a crustal reservoir, and the combination of mantle-He and air-Ar is characteristically found in samples associated with a subduction zone setting (i.e., orogenic and xenolithic ultramafic rocks from volcanic arc mantle [44], arc lava [45] and well gases [46,47]). As demonstrated by Staudacher and Allegre [48], fluids released from altered oceanic crust and sedimentary cover have isotopically air-like argon inherited from dissolved air in seawater. Such fluids then acquire mantle-derived helium during their passage through the mantle wedge, and have a homogeneous $^{3}$He/$^{36}$Ar ratio corresponding to a mantle-air mixing ratio. The helium and argon signature found within the apatite-rich part of the present sample is consistent with a signature expected for fluids associated with slab dehydration. Therefore, this signature provides an excellent record of metasomatism that occurred when the complex was in a mantle-wedge setting, during the Variscan. Phlogopite-forming
metasomatism was also taking place at this stage, by addition of a slab-derived hydrous silicate melt, which subsequently evolved to form apatite-forming carbonatic fluids that separated by liquid immiscibility from a SiO$_2$-rich (high CO$_2$/H$_2$O) melt [28]. It is likely that the entire peridotite body had once been metasomatised by the slab-derived fluids. The presence of the subduction-related component in the Finero ultramafic body is consistent with previous studies such as Cumming et al. [49], Hartmann and Wedepohl [36], Zanetti et al. [24] and Morishita et al. [28].

3.5.2. A highly radiogenic helium and argon component

In addition to the subduction-related noble gas signatures found in the apatite-rich layer of the samples, we found a crust-like noble gas component in the present set of the samples. This component was most clearly identifiable in the olivine samples from unveined peridotite, but also affected the noble gas composition of the blocks of host peridotite prepared from the veined samples. Thus, the crust-like noble gas component is an undoubtedly important and perhaps more widespread component that affected the Finero complex than subduction related noble gases.

One possible scenario accounting for the occurrence of the crust-like noble gases is that the fluid was derived from dehydration or partial melting of metamorphic rocks (i.e., the Kinzigite Formation) around the Finero mafic–ultramafic complex during various stages of its diapiric uplift through the upper mantle to its emplacement in the lower crust, and to associated crustal uplift. Such processes are recorded as a significant correlation between K$_2$O and $^{87}$Sr/$^{86}$Sr ratios of the external gabbro unit [50] but the effect is suggested to be smaller in the case of Finero ultramafic body. The alternative source for the crust-like noble gases in Finero phlogopite-peridotites is the postmetasomatic lithospheric mantle, with some radiogenic ingrowth. A common characteristic of noble gases in modally metasomatised mantle xenoliths is that they are enriched in radiogenic and nucleogenic noble gases (e.g., [4, 11, 12]). This is because metasomatic minerals, such as amphibole, apatite and mica often host the radioactive parents of noble gases. As these phases are generally less refractory than olivine, the radiogenic signature is easily incorporated into melts or fluids generated within the region or during infiltration through the mantle (e.g., [4, 51, 52]). Thus, the modally metasomatized lithospheric mantle has the potential to host a significant amount of radiogenic and nucleogenic noble gases. Noble gas analysis on the wider lithologies in the Finero and surrounding mafic–ultramafic complexes should help to distinguish between the two alternative sources for radiogenic noble gases in the present samples.

4. Concluding remarks: general implications for the noble gas reservoir in the SCLM

As discussed above, a significant concentration of $^3$He and air-Ar in the apatite-rich layer was observed. Clear correlations found between the noble gas signatures, LREE-enrichment and the occurrence of mineralogically distinct veining in the Finero peridotite is strong evidence in support of the importance of metasomatic fluids as a carrier of noble gases in the lithospheric part of the mantle. Also, the present results reinforce the view that the fluid derived from the subducting slab metasomatised the Finero phlogopite-peridotite body, as proposed by previous geochemical and petrological investigations of Finero samples.

Finally, we note that results from the present study provide some insight into the nature and origin of noble gas signatures in the SCLM. Enrichment of air-Ar in the metasomatised part of the mantle provide additional evidence to support the storage of recycled surface noble gases in the wedge mantle. It has been shown that some vestige of the metasomatically added noble gas component becomes obscured if the event occurred early enough for the production of an in situ radiogenic component to overwhelm inherited signatures. In the Finero phlogopite-peridotite complex, there have been a few hundreds of million of years for radiogenic noble gas components to accumulate. This is in contrast to the relatively short post-metasomatic history (a few tens of million years [53]) for Horoman complex. A highly radiogenic noble gas component has also been found in Jwaneng framesite diamonds from old SCLM [54] Very low $^3$He/$^4$He ratios of 0.3 Ra found in Siberian mantle xenoliths as well as 0.075 Ra found in Indonesian lavas [55] also require the presence of some helium reservoir.
enriched in radiogenic $^4$He. This suggests that the lithospheric mantle domains metasomatised through ancient subduction-related process have a potential to develop and preserve highly radiogenic crust-like noble gas signatures either by direct recycling of crustal material to the SCLM by subduction [54] or by the in situ production of radiogenic isotopes in the metasomatised part of the mantle (this study and [41]).

Absence of such an intense radiogenic signature in some part of the SCLM (especially that beneath Europe [11,12]) suggests that the traces of ancient metasomatism and its aging effect have been overwritten by some recent non-subduction related metasomatic agent with relatively uniform $^3$He/$^4$He ratios [12]. It is also possible that radiogenic noble gas components (and air-like heavy noble gases if affected by ancient subduction-related processes) have been removed from the SCLM by delamination of old, thick lithosphere. Examples of such processes are found in eastern China, where Cenozoic basalts yield MORB-like $^3$He/$^4$He ratios (7.4 to 8.4 Ra in five megacrysts) without an apparent radiogenic $^4$He signature expected for magma associated with the old SCLM [56,57]. This helium signature from the Chinese megacrysts is consistent with several independent (geophysical and geochemical) lines of evidence supporting the removal of an Archean keel of lithosphere, presumably by delamination, and effective replacement by “oceanic”-like mantle during the Cenozoic [58–60]. The fate of delaminated material, and its noble gas budget is far beyond the scope of present study, however it is quite likely that the delaminated materials have noble gas elemental and isotopic compositions distinct from those in sublithospheric reservoirs. Therefore, the scale and effect of recycling noble gases by such processes should be explored further to better understand the nature of noble gas reservoirs in the mantle.

Acknowledgements

The authors thank O. Vaselli, A. Tamura, K. Matsukage, N. Abe for their help in sampling rocks used for this study. This manuscript benefited from thoughtful and constructive reviews by P. Sarda and an anonymous reviewer. This work was supported by Grants-in-Aid from the Japan Society for the Promotion of Science (14740314 and 17684029) to TM.

Appendix. Major and REE compositions of the present samples

The detailed investigations on major and trace elemental compositions of the present samples will be discussed elsewhere. Here we present only part of the data relevant for the sake of the present contribution (bulk K$_2$O, P$_2$O$_5$, U, Th contents of samples A1 to E1 in Table A, and their REE abundance patterns in Fig. A). Details of analytical procedures for XRF and ICP-MS will be presented in Morishita et al., and are also available in previous publications [61,62].

![Fig. A. Chondrite-normalized REE patterns of each slice taken from the Finero phlogopite-peridotite with the apatite-rich layer. Chondrite values are from McDonough and Sun [59].](image)

Table A

<table>
<thead>
<tr>
<th></th>
<th>K$_2$O (wt.%)</th>
<th>P$_2$O$_5$ (wt.%)</th>
<th>Th (ppm)</th>
<th>U (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.01</td>
<td>0.43</td>
<td>5.24</td>
<td>1.24</td>
</tr>
<tr>
<td>B1</td>
<td>0.08</td>
<td>0.01</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>C1</td>
<td>0.08</td>
<td>0.01</td>
<td>0.36</td>
<td>0.51</td>
</tr>
<tr>
<td>D1</td>
<td>0.10</td>
<td>0.01</td>
<td>0.46</td>
<td>0.06</td>
</tr>
<tr>
<td>E1</td>
<td>0.09</td>
<td>0.01</td>
<td>0.35</td>
<td>0.06</td>
</tr>
</tbody>
</table>

K$_2$O and P$_2$O$_5$ were analyzed by XRF with fused glass beads. P$_2$O$_5$ of 0.01% is upper limit as it is the detection limit.
References


[41] H. Hünemohr, Edelgase in U-und Th-reichen Mineralen und die Bestimmung der $^{21}$Ne-Dicktarget-Ausbeute der $^{18}$O(a,n)$^{21}$Ne-Kernreaktion im Bereich 4.0–8.8 MeV, Ph.D., Johannes-Gutenberg-Universität, Mainz, 1989.


[60] X. Xu, S.Y. O’Reilly, W.L. Griffin, X. Zhou, X. Huang, The nature of the Cenozoic lithosphere at Nushan, eastern China, in: