New Olivine Reference Materials for Secondary Ion Mass Spectrometry Oxygen Isotope Measurements

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Abstract: To accurately analyze the oxygen isotope of olivine using secondary ion mass spectrometry (SIMS), appropriate standard materials are required to calibrate for matrix effects caused by chemical composition differences between the samples and the standard materials. In this study, we investigated the homogeneity of oxygen isotopes in two natural olivine minerals using a secondary ion mass spectrometer to evaluate their potential as standard materials. The two minerals, JAY03-3 and JAY02-4, with forsterite contents of 99.3% and 99.6%, respectively, were evaluated for homogeneity in oxygen isotope composition. The recommended oxygen isotope values were characterized using CO₂ laser fluorination, and the homogeneity was tested with in situ SIMS oxygen isotope measurements. Our results show that the δ¹⁸O value determined via CO₂ laser fluorination for JAY03-3 is 16.37 ± 0.22‰ (2 s) and for JAY02-4 is 18.29 ± 0.28‰ (2 s). The precision of SIMS oxygen isotope measurements is 0.57‰ (2 s) for JAY03-3 and 0.70‰ (2 s) for JAY02-4. These two minerals have the potential to be used as standard materials for calibrating the oxygen isotope value of end-member forsterite during in situ analysis of SIMS oxygen isotope.

Keywords: olivine; SIMS; standard materials; oxygen isotope

1. Introduction

Olivine, the simplest silicate mineral, is a major constituent mineral in mafic–ultramafic rocks and metamorphic rocks [1–3]. The olivine mineral group is a common solid-solution mineral group, including complete isomorphous series of forsterite (Mg₂SiO₄)-fayalite (Fe₂SiO₄). In recent years, researchers have shown an increasing interest in olivine’s composition, genesis, and geochemical characteristics [4–8]. The oxygen isotope analysis of olivine can provide detailed information on mantle processes, magma assimilation, or contamination and trace the origin of fluids in metamorphic or igneous systems [9–12]. The precise determination of oxygen isotopes in olivine is the key to tracing geochemical processes successfully. Secondary ion mass spectrometry (SIMS) is an effective and cutting-edge analytical method for in situ oxygen isotope analysis for olivine. Compared to conventional laser fluorination (LF) techniques, SIMS offers improved precision and spatial resolution in oxygen isotope analyses [13,14]. However, large instrumental mass fractionation and matrix bias are present in the SIMS oxygen isotope analyses of solid solution mineral groups such as olivine, garnet, and pyroxene [14–18]. Accurate ion microprobe analysis requires appropriate reference materials that are chemically similar to the target sample [13,14,19–21].

Significant efforts have been made to develop standard materials or correct matrix effects during SIMS oxygen isotope analyses of olivine [16,17,22]. Eiler et al. [13] measured 40 silicate and phosphate minerals and glasses to characterize instrumental fractionation...
(so-called ‘matrix effects’) and proposed two mechanisms for producing matrix effect. Isa et al. [22] investigated the correlation between matrix effects and Cs concentrations in the sample’s surface and developed a calibration curve for SIMS oxygen isotope analyses of olivine crystals with intermediate chemical compositions. Tang et al. [16] investigated the homogeneity of oxygen isotopes for five olivine, three clinopyroxene, and three orthopyroxene minerals using the secondary ion mass spectrometry and laser fluorination method and discussed the matrix effect caused by variable Mg numbers of olivine. Zhang et al. [23] investigated the homogeneity of an oxygen isotope for a suite of olivine (Fo 0–100) and found that instrumental bias values in olivine reference materials are a function of Fo mol%. Scicchitano et al. [17] demonstrated that the matrix bias of SIMS oxygen isotope analyses of olivine is correlated with Mg/Fe content variations and is more pronounced when the composition of olivine is close to end-member constituents. The matrix bias is negligible for SIMS oxygen isotope analyses of olivine with an Fo (100 × Mg/[Mg + Fe], mol%) value of 88–92, while a matrix bias of up to ~2.0‰ is observed in olivine with forsterite content above 92 mol% and up to ~11.0‰ in olivine with fayalite content near 100 mol% [17]. In addition, olivine typically used as a standard for oxygen isotope analysis has an Fo content of around 90–91, such as San Carlos olivine. The shortage of in situ reference material (RMs) for olivine with different contents hinders the development of oxygen isotope research. To obtain the accurate SIMS oxygen isotope analysis of olivine, a suite of standard materials that spans the composition range of olivine is required.

Recently, a rare end-member forsterite from Jian forsterite jade has been reported. Olivine has extremely high Mg contents, which is chemically close to end-member forsterite. End-member olivine is very rare in terrestrial rocks and its origin is complex and diverse. End-member forsterite has drawn widespread attention around the world, especially the end-member forsterite in Jian forsterite jade from China. Several studies have been conducted on the end-member forsterite from Jian forsterite jade, including major and trace element chemical composition [24], Raman and infrared spectra [25,26], and crystal structure [26] studies. In this study, we investigated the oxygen isotope homogeneity of two natural olivine materials (Fo = 99.3 and Fo = 99.6, respectively) using a secondary ion mass spectrometer. The two natural olivine sources were collected from the Jian forsterite jade, which is a metamorphic magnesian skarn. We presented electron probe microanalysis, the backscattered electron (BSE) images, and Raman spectrum analysis for the purpose of confirming the homogeneity of the chemical composition. Precise oxygen isotope compositions of olivine were determined via the laser fluorination (LF) method. The purpose of this study was to find suitable standard materials for calibrating the SIMS oxygen isotope analysis of high-Mg olivine (near end-member forsterite). Our work demonstrates that the two olivine samples have the potential to be used as reference materials to calibrate the oxygen isotope value of end-member forsterite during in situ SIMS analysis.

2. Materials and Methods

The olivine samples used in the study were collected from the Jian forsterite jade in Jian province, northeast China. The main mineral composition of Jian forsterite jade is forsterite and serpentine. Detailed petrographic descriptions and investigations can be found in Wang et al. [25] and Peng et al. [24]. Two types of crystals, JAY03-3 and JAY02-4, were handpicked from the Jian forsterite jade with different colors under a binocular microscope. Sample JAY03-3 was handpicked from dark-green Jian forsterite jade, and sample JAY02-4 was handpicked from yellowish-green Jian forsterite jade. The olivine grains were separated from Jian forsterite jade via the heavy liquid method, which is a common method used in single-mineral separation in the geological field. All grains were colorless and transparent with a crystal size of 0.3–1 mm (Figure 1a). Fragments of olivine crystals JAY02-4 and JAY03-3 were randomly selected and mounted in random orientations on the 25 mm epoxy mount (Figure 1b). The stability of the SIMS instrument was monitored using reference materials (Nist610). All samples were located in the central 10 mm of the 25 mm epoxy mount to avoid possible sample location effects [27]. The epoxy mounts were...
polished with 6, 3, and 1 μm diamond paste to obtain flat analytical surfaces and were coated with gold before SIMS analysis.

Figure 1. The olivine samples used in this work. (a) The representative olivine grains handpicked from Jian forsterite jade under binocular microscope. All grains are colorless and without inclusions. The photo was taken under a gemstone microscope with a magnification of 40 at the National Mineral Rock and Fossil Specimens Resource Center, China University of Geosciences (Beijing). (b) The two 25 mm epoxy mounts mounted with all selected olivine grains and reference materials.

Mineral Raman spectra were acquired at the School of Gemmology, China University of Geosciences (Beijing). The Horiba HR-Evolution Raman microspectrometer coupled with an Ar-ion laser (532 nm) was used to collect data. The entrance slit was 100 µm, and the grating was 1200 grooves per mm. The scanning ranges were 4000–100 cm⁻¹, the resolution was 1 cm⁻¹, and the scan time was 10 s. All original spectral data were processed using Origin software, and all spectra were offset vertically for clarity. The RRUFF spectral database was used to identify the phases and was used for comparisons.

Electron probe microanalysis (EPMA) was carried out at the Electron Probe Laboratory, China University of Geosciences (Beijing), using an EPMA-1720 electron microprobe. Chemical composition analyses were conducted using an acceleration voltage of 15 kV, a beam current of 10 nA, and a beam size of 5 µm. The following standards were used: diopside (Si), rutile (Ti), chlorite (Al), chromite (Fe), chromite (Cr), rhodonite (Mn), diopside (Ca), olivine (Mg), pentlandite (Ni), willemite (Zn), albite (Na), and sanidine (K).

The backscattered electron (BSE) images of the two olivine samples were captured with a scanning electron microscope (SEM), using a Phenom XL G2 instrument at the National Mineral Rock and Fossil Specimens Resource Center, China University of Geosciences (Beijing). The accelerating voltage was 15 kV, the beam current was 10 nA, and the working distance was 10 mm.

The recommended oxygen isotope of olivine was analyzed via CO₂ laser fluorination technology in two sessions (the Institute of Geophysics and Geology, Chinese Academy Sciences (IGGCAS) and the University of Science and Technology of China in Hefei (USTC)). Each analysis consumed 2–3 mg of the sample. The sample reacted with purified BrF₅ reagent in the laser chamber to release oxygen first. The resulting gas was subsequently purified using a series of cryogenic traps that maintained the temperature of the liquid nitrogen. The oxygen gas was eventually analyzed on MAT252 with the reference materials of Penglai zircon (δ¹⁸O = 5.3‰) [28] and 04BXL07 garnet (δ¹⁸O = 3.7‰) [29] and the Delta XP mass spectrometer using the reference materials of 04BXL07 garnet (δ¹⁸O = 3.7‰) and San Carlos olivine (δ¹⁸O = 5.25‰) [30]. All oxygen isotope data are reported in the δ-notations for Vienna Standard Mean Ocean Water (V-SMOW).

SIMS oxygen isotope analysis for olivine was conducted at the Beijing Research Institute of Uranium Geology (BRIUG) on a CAMECA IMS-1280HR SIMS. Here, 20 kV Cs⁺ ions were used as primary ions to liberate 16O⁻ and 18O⁻ from the samples with 4–4.1 nA current. This resulted in a typical spot size of 20 µm. Entrance slit widths of
152 μm and exit slit widths of 405 μm were used. An energy window of 50 eV width was used, and the mass resolution was set to 3003. A normal incident electron flood gun was used to compensate for surface charge. The signals of $^{16}$O and $^{18}$O were measured simultaneously on two Faraday cups. The secondary ion intensity for $^{18}$O ranged from ~2 to $3.5 \times 10^9$ cps (counts per second). Three to five points were randomly selected on each grain to ensure the validity of the data, and the samples of the standard material were analyzed every 10–20 analyses to monitor the stability of the instrument. Instrumental uncertainty from counting statistics was generally better than 0.2–0.3‰ (2SE). The measured $^{18}$O/$^{16}$O ratios were expressed in delta notation ($\delta$ in ‰ ) and normalized to the value for Vienna Standard Mean Ocean Water (0.00200520) [31].

3. Results

3.1. Chemical Composition

The detailed major elements’ chemical compositions of olivine are listed in Table 1. EPMA analyses showed that the main chemical compositions of the two olivine samples were SiO$_2$, MgO, and FeO, with minor Al$_2$O$_3$ and Cr$_2$O$_3$. The contents of SiO$_2$ ranged from 41.04 to 43.34 wt.%. The contents of MgO ranged from 56.01 to 57.68 wt.%. The contents of FeO ranged from 0.35 to 0.77 wt.%. The Fo ($100 \times$ Mg/[Mg + Fe], mol%) contents of the two olivine samples were 99.3 and 99.6. The chemical composition analysis of olivine was consistent with previous studies. In addition, all olivine grains were checked via backscattered electron (BSE) analysis before the oxygen isotope determinations. BSE images showed that all the tested olivine samples were homogeneous in chemical composition and free of inclusions. The representative BSE images are shown in Figure 2.

Table 1. The major element composition (wt.%) of the olivine samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Cr$_2$O$_3$</th>
<th>FeO</th>
<th>MnO</th>
<th>NiO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>Total</th>
<th>Fo</th>
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<tbody>
<tr>
<td>JAY03-3-1 *</td>
<td>42.32</td>
<td>0.00</td>
<td>0.02</td>
<td>0.08</td>
<td>0.76</td>
<td>0.06</td>
<td>0.00</td>
<td>57.12</td>
<td>0.01</td>
<td>0.01</td>
<td>100.37</td>
<td>99.26</td>
</tr>
<tr>
<td>JAY03-3-2 *</td>
<td>41.98</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
<td>0.70</td>
<td>0.02</td>
<td>0.05</td>
<td>57.68</td>
<td>0.01</td>
<td>0.00</td>
<td>100.50</td>
<td>99.32</td>
</tr>
<tr>
<td>JAY03-3-3 *</td>
<td>42.01</td>
<td>0.04</td>
<td>0.02</td>
<td>0.09</td>
<td>0.76</td>
<td>0.00</td>
<td>0.00</td>
<td>57.53</td>
<td>0.01</td>
<td>0.00</td>
<td>100.43</td>
<td>99.27</td>
</tr>
<tr>
<td>JAY03-3-4 *</td>
<td>41.41</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.77</td>
<td>0.03</td>
<td>0.02</td>
<td>57.01</td>
<td>0.02</td>
<td>0.00</td>
<td>99.26</td>
<td>99.25</td>
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<tr>
<td>mean</td>
<td>41.93</td>
<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.75</td>
<td>0.03</td>
<td>0.02</td>
<td>57.33</td>
<td>0.01</td>
<td>0.00</td>
<td>100.14</td>
<td>99.28</td>
</tr>
<tr>
<td>JAY02-4-1</td>
<td>43.34</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.35</td>
<td>0.03</td>
<td>0.03</td>
<td>56.01</td>
<td>0.02</td>
<td>0.04</td>
<td>99.82</td>
<td>99.65</td>
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<td>JAY02-4-2</td>
<td>42.61</td>
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<td>0.02</td>
<td>0.00</td>
<td>0.38</td>
<td>0.08</td>
<td>0.02</td>
<td>56.20</td>
<td>0.01</td>
<td>0.04</td>
<td>99.41</td>
<td>99.62</td>
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<td>JAY02-4-3</td>
<td>41.99</td>
<td>0.04</td>
<td>0.02</td>
<td>0.00</td>
<td>0.35</td>
<td>0.05</td>
<td>0.06</td>
<td>56.69</td>
<td>0.00</td>
<td>0.01</td>
<td>99.21</td>
<td>99.66</td>
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<td>0.00</td>
<td>0.40</td>
<td>0.06</td>
<td>0.02</td>
<td>56.73</td>
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<td>0.03</td>
<td>99.43</td>
<td>99.61</td>
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<tr>
<td>JAY02-4-5</td>
<td>42.31</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.35</td>
<td>0.01</td>
<td>0.06</td>
<td>56.90</td>
<td>0.02</td>
<td>0.03</td>
<td>99.74</td>
<td>99.65</td>
</tr>
<tr>
<td>JAY02-4-6</td>
<td>42.26</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.35</td>
<td>0.00</td>
<td>0.06</td>
<td>56.96</td>
<td>0.02</td>
<td>0.00</td>
<td>99.65</td>
<td>99.66</td>
</tr>
<tr>
<td>JAY02-4-7</td>
<td>41.91</td>
<td>0.00</td>
<td>0.03</td>
<td>0.00</td>
<td>0.35</td>
<td>0.05</td>
<td>0.05</td>
<td>57.08</td>
<td>0.01</td>
<td>0.01</td>
<td>99.48</td>
<td>99.66</td>
</tr>
<tr>
<td>JAY02-4-8</td>
<td>41.04</td>
<td>0.00</td>
<td>0.03</td>
<td>0.01</td>
<td>0.42</td>
<td>0.02</td>
<td>0.00</td>
<td>57.13</td>
<td>0.01</td>
<td>0.01</td>
<td>98.65</td>
<td>99.59</td>
</tr>
<tr>
<td>JAY02-4-9</td>
<td>41.78</td>
<td>0.00</td>
<td>0.00</td>
<td>0.03</td>
<td>0.41</td>
<td>0.00</td>
<td>0.00</td>
<td>57.38</td>
<td>0.00</td>
<td>0.02</td>
<td>99.60</td>
<td>99.60</td>
</tr>
<tr>
<td>JAY02-4-10</td>
<td>42.16</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.36</td>
<td>0.00</td>
<td>0.06</td>
<td>56.88</td>
<td>0.02</td>
<td>0.00</td>
<td>99.48</td>
<td>99.64</td>
</tr>
<tr>
<td>mean</td>
<td>42.16</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.37</td>
<td>0.03</td>
<td>0.04</td>
<td>56.80</td>
<td>0.01</td>
<td>0.02</td>
<td>99.45</td>
<td>99.63</td>
</tr>
</tbody>
</table>

* Data from Peng et al. [24].

3.2. Raman Spectrum

Representative Raman spectra of the two olivine samples are shown in Figure 3. The Raman spectra of olivine had typical bands at approximately 227, 305, 434, 544, 591, 824, 857, 919, and 966 cm$^{-1}$. The characteristic bands, at approximately 824 and 857 cm$^{-1}$, were attributed to the internal symmetric and asymmetric stretching vibrational modes of the SiO$_4$ ionic group. Low intense bands, at 434, 544, and 591 cm$^{-1}$, were attributed to the internal bending vibrational modes of the SiO$_4$ ionic groups. Two bands at around 227 and 305 cm$^{-1}$ were attributed to the lattice vibration modes.
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Figure 2. The representative BSE images of two types of olivine samples. (a) Representative olivine grains for sample JAY03-3. (b) Representative olivine grains for sample JAY02-4. All olivine grains were homogeneous in chemical composition. Olivine grains with fractures were eliminated before secondary ion mass spectrometry (SIMS) oxygen isotope analysis.

Figure 3. Representative Raman spectra of olivine samples used in this work. The Raman spectra of the two types of olivine (JAY02-4 on the top and JAY03-3 below) have typical bands at approximately 227, 305, 434, 544, 591, 824, 857, 919, and 966 cm⁻¹, which are consistent with end-member forsterite. All spectra were offset vertically for clarity.

The spectral regions of 815–825 and 838–857 cm⁻¹ are the most characteristic bands of olivine-group minerals. With the increase in magnesium content in olivine, the band will shift from a low wave number to the higher wave number [32,33]. In our study, the Raman spectra of the two olivine samples showed two bands at 824 and 857 cm⁻¹, with the characteristics of end-member forsterite, which are consistent with the EPMA chemical composition analyses.

In addition, Raman spectra were used to study the fluid inclusion in olivine. The Raman spectra analysis showed that there was very little inclusion in the olivine, which
only existed in the healing fissure. Before our oxygen isotope determinations, we already excluded the olivine with healing fissures using the microscope and backscattered electron (BSE) images.

3.3. Oxygen Isotope

The oxygen isotope compositions of JAY02-4 and JAY03-3 were obtained via laser fluorination (LF). Each sample was analyzed two times, with the average value as the recommended value and 1 s as the analytical uncertainty. A summary of the laser fluorination data is given in Table 2.

Table 2. Recommended oxygen isotope composition determined via CO$_2$ laser fluorination analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ$^{18}$O VSMOW * (‰)</th>
<th>1σ</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>JAY02-4</td>
<td>IGCAS 18.29 0.14</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>USTC 18.28</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mean 18.29</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>JAY03-3</td>
<td>IGCAS 16.57 0.11</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>USTC 16.17</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mean 16.37</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

* Data from Peng et al. [24].

The homogeneity was checked via in situ measurements using SIMS between different grains. The analysis data of SIMS are shown in Figure 4, and the raw data are given in Table S1. In addition, the Nist 610 was analyzed to monitor the analysis conditions. The analytical accuracy levels (two standard deviations (SD)) of standard Nist 610 were 0.38 and 0.44 in two analysis sessions, which represented the stability of the instrument during the analysis process.

Figure 4. (a) SIMS δ$^{18}$O mean values of JAY03-3. A total of 88 points were measured. (b) The frequency distributions of SIMS δ$^{18}$O values of JAY03-3. (c) SIMS δ$^{18}$O mean values of JAY02-4. A total of 143 points were measured. (d) The frequency distributions of SIMS δ$^{18}$O values of JAY02-4 (The area of each bar on a histogram represents the frequency of data, the line represents the frequency of data consistent with normal distribution).
The homogeneity of sample JAY03-3 was tested on sixteen olivine grains, for a total of 88 points measured over one analysis session. The mean measure $\delta^{18}O$ values were $26.12 \pm 0.36$‰ (2 s) (Figure 4a). The precision of sample JAY03-3 during the sessions was $0.57$ (2 s) (Figure 4b). The recommended oxygen isotope value of JAY03-3 (Fo = 99.3) determined via laser fluorination analysis was $16.37 \pm 0.11$‰ (1 s, n = 3).

The homogeneity of sample JAY02-4 was tested on twenty-six olivine grains, for a total of 143 points measured over one analysis session. The mean measured $\delta^{18}O$ values were $27.91 \pm 0.70$‰ (2 s) (Figure 4c,d). The precision of sample JAY02-4 during the sessions was $0.70$ (2 s). The recommended oxygen isotope value of JAY02-4 (Fo = 99.6) determined via laser fluorination analysis was $18.29 \pm 0.14$‰ (1 s, n = 3).

4. Discussion

4.1. Homogeneity

In the in situ SIMS oxygen isotope analysis, olivine typically used as standards for oxygen isotope analysis had Fo contents around 90–91, such as San Carlos olivine. However, a large instrumental mass fraction existed (the difference relative to San Carlos Olivine), the magnitude of which depended on the chemical composition of the sample (Mg molar fractions). In the past few years, several studies have been conducted on the instrument bias of oxygen isotope in secondary ion mass spectrometry (SIMS). Guo et al. [34] reported that the Mg number typically affects instrument bias in SIMS oxygen isotope measurements. Instrument bias was apparent among magnesian olivine (Fo < 65), while no significant instrument bias was confirmed when Mg numbers >68. Isa et al. [22] confirmed no significant instrument bias among magnesian olivine (Fo > 75). Zhang et al. [23] investigated sixteen olivine reference materials covering the entire Fe-Mg compositional range and found that the instrument bias was up to ~10‰ among fayalite (Fo 0) and within 0 ± 0.5‰ among magnesian olivine (Fo ≥ 60). Scicchitano et al. [12] indicated that there is a large error (up to ~2.0‰) in the calibration of oxygen isotope of end-member forsterite with the traditional San Carlos standard sample (Fo = 91). In order to improve the accuracy of the in situ oxygen isotope analysis of high-magnesium olivine, new standard olivine with high magnesium content is needed.

The homogeneity of oxygen isotope data is an important factor in determining whether a sample can be developed into a specimen reference material [15,35,36]. The homogeneity is accessed by the standard deviation of the measured $\delta^{18}O$ values. In the previous study, the standard deviation (1 s) for standard materials (e.g., zircon, olivine, or apatite) was routinely 0.15–0.25‰ [16,28,37,38].

In the present study, 1~5 points per grain were randomly selected to check the homogeneity of the oxygen isotope composition via in situ SIMS measurements. The measured $\delta^{18}O$ values for two samples followed a normal distribution (Figure 4b,d). The 2SD of the measured oxygen isotope values was 0.57 for sample JAY03-3 and 0.70 for sample JAY02-4. Previous studies indicated that the homogeneity of SIMS oxygen isotope data can be affected by various factors, including instrument stability [16], experimental conditions [22], X-Y axis effect [37], crystal orientation [14,21], and mineral inclusions [35]. However, for olivine crystals, the effect of crystal orientation on homogeneity is negligible (less than 0.5‰). The X-Y axis effect could have been excluded for all samples that were located in the central 10 mm of the 25 mm epoxy mount to avoid possible sample location effects. In both experiments, the standard NIST 610 had relatively large analytical accuracy (two standard deviations (SD)) (0.38 and 0.44, respectively). Thus, the relatively large standard deviation for two olivine samples could be attributed to the instrument stability. In general, the two olivine samples have homogeneous oxygen isotope compositions and have the potential to be used as reference materials to analyze the SIMS oxygen isotope of end-member forsterite.

4.2. Comparison with Other Reference Materials

San Carlos olivine ($\delta^{18}O = 5.25$‰; Fo = 91) is widely used as a reference material for SIMS oxygen isotope measurements [11,16,30]. In addition, some new standard olivine
samples for SIMS oxygen isotope analysis have been developed in recent years. Tang et al. [16] examined the homogeneity of oxygen isotope for five olivine samples (Fo = ~90) from mantle peridotite xenoliths and dunite and found them to be suitable to be used as reference materials for in situ oxygen isotope microanalysis. The results showed that the oxygen isotope value of these olivine samples was homogeneous and had no matrix effect. The recommended oxygen isotope value for the five olivine samples ranged from 3.91 ± 0.25‰ to 5.30 ± 0.13‰. Both of these common olivine reference materials were collected from peridotite xenoliths and had Fo values of around 90–91. In addition, Zhang et al. [23] investigated the homogeneity for synthetic end-member crystals (forsterite with an Fo value of 100). This forsterite reference material showed homogeneous oxygen isotope ratios with 2SD typically <0.25‰.

However, the two types of olivine samples investigated in this study are different from the common olivine standard samples in chemical composition, oxygen isotope value, and genesis. They have extremely high magnesium content (Fo = ~99), which is close to end-member forsterite. Furthermore, the two types of olivine samples have higher oxygen isotope values than the common reference materials, such as San Carlos olivine. Comparing with these common olivine reference materials, the two samples (Fo = ~99) are of metamorphic origin and related to the silicification of dolomite during contact metamorphism.

The two types of olivine (JAY03-3 and JAY04-4) were collected from a newly discovered jade deposit. The deposit covers an area of 4455 m² and is located in the contact zone between marble and migmatitic gneiss. The Jian forsterite jade deposit was discovered in around 2000 and is mined via an open pit. Its current production and reserves are unknown. The Jian forsterite jade is mainly yellowish green to dark and has a mesh texture and a massive structure. The main constituent minerals of Jian forsterite jade are forsterite and serpentine, as well as minor brucite, dolomite, calcite, magnesite, spinel, phlogopite, warwickite, and magnetite. These two types of olivine samples (JAY03-3 and JAY04-4) were handpicked from yellow-green and dark-green Jian forsterites jade, respectively. The color of the protolith is a key factor in distinguishing between JAY02-4 and JAY03-3 crystals.

The two types of olivine have extremely high magnesium contents. Various types of research including spectroscopy, mineralogy, and geochemistry have been conducted on this rare end-member forsterite. In this study, we confirmed the homogeneity of the two types of rare olivine and proposed that the two types of olivine have the potential to be used as reference materials of SIMS oxygen isotope analysis for high-magnesium olivine (Fo = ~99). The development of reference materials for high-magnesium olivine can make the analysis of SIMS oxygen isotope experiments more accurate. In general, these reference materials will be available in the future, and further laboratory work needs to be carried out to prove their homogeneity.

5. Conclusions

In this study, the oxygen isotopic homogeneity of two new olivine reference materials, JAY02-4 and JAY03-3, was presented. The main conclusions are as follows:

1) The chemical compositions of the two olivine samples have extremely high Mg contents, with Fo values of 99.3 and 99.6, respectively. The Raman spectra of olivine have typical bands at approximately 227, 305, 434, 544, 591, 824, 857, 919, and 966 cm⁻¹, with the characteristics of end-member forsterite. BSE images and Raman spectra show that olivine is homogeneous in chemical composition and free of inclusions.

2) The precision of SIMS analysis for sample JAY03-3 is 0.57‰ (2 s), and the precision of SIMS analysis for sample JAY02-4 is 0.70‰ (2 s). The SIMS oxygen isotope results suggest that the oxygen isotope compositions of the two olivine samples are homogeneous. These samples are suitable as standard materials for the SIMS oxygen isotope microanalysis of end-member forsterite. The recommended δ¹⁸O values of the two olivine materials are 16.37 ± 0.11‰ for sample JAY03-3 and 18.29 ± 0.14‰ for sample JAY02-4.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst13070987/s1, Table S1: Oxygen isotope compositions determined via SIMS.

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