Article

Beryl Reference Materials for In Situ Oxygen Isotope Determination

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Abstract: The mineral beryl (Be3Al2(SiO3)6) has the most abundant phase with industrial value for extracting a critical metal—beryllium. Due to multi-stage, fluid-induced growth, individual beryl grains may yield complex geochemical records, revealing variations in the oxygen isotopes of the fluids from which they crystallize. Secondary ion mass spectrometry (SIMS) with high sensitivity and high spatial resolution represents a good tool for in situ isotopic analysis. SIMS oxygen analyses require matrix-matched reference materials to calibrate instrumental mass fractionations during measurement. In this work, the oxygen isotope homogeneities of six beryl samples with different compositions (BS1, BS2, BS3, BS4, BS5, and BS6) were documented by SIMS. These samples’ recommended oxygen isotope compositions were characterized by laser fluorination isotope ratio mass spectrometry (IRMS). This study suggests that there is no matrix effect related to compositional variation in beryl SIMS oxygen isotope analysis. The recommended δ18O values of the four reference materials, BS1, BS2, BS4, and BS5, were 15.01 ± 0.34‰ (2 standard deviations, 2 SD), 7.53 ± 0.16‰ (2 SD), 2.38 ± 0.14‰ (2 SD), and 10.72 ± 0.44‰ (2 SD), respectively. Therefore, BS1, BS2, BS4, and BS5 are recommended as suitable reference materials for in situ mineral beryl oxygen isotope microanalysis.

Keywords: beryl; oxygen isotope; SIMS; matrix effect; reference materials

1. Introduction

One of the most significant current discussions regarding critical metals is that of beryllium (Be) [1,2]. Beryl (Be3Al2(SiO3)6) is definitely the most common manifestation of Be enrichment, as well as the most plentiful of the phases that contain Be [3,4]. In recent years, researchers have shown an increasing interest in beryl’s composition, genesis, and geochemical characteristics [5–7]. Oxygen isotopes, which play a critical role in addressing geochemical evolution processes, have attracted considerable interest [8–10]. Beryl’s mineral oxygen isotopes could be influenced by the composition and temperature of fluids and/or rocks. According to previous studies, the oxygen isotopic compositions of emerald (a variety of beryl) from different occurrences and deposits are variable. They may provide a good fingerprint of the origin of this kind of beryl [11]. In addition, due to multi-stage fluid-induced growth, an individual beryl grain may yield complex isotopic composition, revealing variations in the oxygen isotopes of the fluids from which beryl crystallized [12].
Secondary ion mass spectrometry (SIMS) with high sensitivity and high spatial resolution represents a good tool for in situ beryl analysis. However, the SIMS matrix effect generated by a mismatch between the matrix of the samples being analyzed and that of the standards used to calibrate instrumental mass fractionation (IMF) may cause incorrect results [13]. The matrix effects associated with Fe–Mg-exchangeable minerals (such as olivine, dolomite, and garnet) have been reported [14–16]. Because of matrix effects, matrix-matched reference materials or a suitable fractionation law to calibrate IMF is required during SIMS oxygen isotope measurement [17,18]. As for beryl, the iron content could vary from 0.1 to 3 wt.% [19]. The shortage of in situ reference materials (RMs) for beryl causes an ambiguous matrix effect, hindering in situ oxygen isotope research.

In this study, six SIMS beryl samples with different chemical compositions (BS1, BS2, BS3, BS4, BS5, and BS6) were examined by Raman spectroscopy and an electron microprobe. Their oxygen isotopic homogeneities were demonstrated by SIMS analyses. These samples’ recommended oxygen isotope compositions were characterized by laser fluorination isotope ratio mass spectrometry (IRMS). Our work indicated that there is no observable composition-related matrix effect in SIMS beryl oxygen isotope analyses. Four natural beryl mineral samples are recommended as suitable reference materials for in situ oxygen isotopic composition microanalysis.

### 2. Samples

Six potential beryl RMs, including BS1, BS2, BS3, BS4, BS4, and BS6, as listed in Table 1, were investigated in this study.

**Table 1.** The beryl samples used in this work.

| Sample | Location      | Color             | Transparency   | Weight/Gram |
|--------|---------------|-------------------|----------------|-------------|
| BS1    | Sichuan, China| Colorless to pale blue | Transparent    | 15          |
| BS2    | Norway        | Light greenish-blue | Transparent    | 15          |
| BS3    | Hunan, China  | Greenish-white    | Semitransparent| 12          |
| BS4    | Nigeria       | Colorless         | Transparent    | 15          |
| BS5    | Myanmar       | Light pink        | Transparent    | 10          |
| BS6    | Brazil        | Light blue        | Transparent    | 10          |

The BS1 beryl sample, including two beryl crystals (BS1-1 and BS1-2), was isolated from one specimen, previously investigated by Liu et al. [20]. They were collected from a hydrothermal W–Sn–Be deposit in Xuebaoding, Sichuan Province, western China. These crystals were colorless transparent to pale blue, with a well-crystallized tabular habit (Figure 1a). The two crystals weighed approximately 15 g. The BS2 beryl was a megacrystal collected from Norway, which was light greenish-blue, transparent, and weighed 15 g (Figure 1b). The BS3 beryl was separated from a pegmatite rock from Hunan, China (Figure 1c). This sample was semitransparent greenish-white and had lots of cracks. The BS4, BS5, and BS6 crystals were purchased from mineral dealers, collected from Nigeria, Myanmar, and Brazil, respectively. Their exact provenances and petrological characteristics are unknown. The BS4 megacrystals were colorless and transparent, with a total weight of ~15 g. The crystals were approximately 1–2 cm in their most extended dimensions and contained a few sub-parallel fractures but no visible inclusions (Figure 1d). The BS5 crystals, weighing approximately 10 g, were light pink and transparent (Figure 1e). The BS6 crystals, weighing around 10 g, were light blue and clean (Figure 1f).
Figure 1. Hand specimens of beryl crystals were used in this study: (a) BS1 (including two crystals, BS1-1 and BS1-2) from Sichuan, China; (b) BS2 from Norway; (c) BS3 from Hunan, China; (d) BS4 from Nigeria; (e) BS5 from Myanmar; (f) BS6 from Brazil.

All of the megacrystals were crushed into tiny shards of around 0.1–1 mm. The small fragments were colorless and transparent. Backscattered electron (BSE) images revealed that these shards were homogeneous (Figure 2), except for some cracks in BS3 and BS5 and quartz inclusions in BS3 (Figure 2c,f).

3. Methods

All analyses were conducted at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing, China.

For each sample, approximately 80 fragments, together with NIST SRM 610 glass, were selected and embedded in random orientations to form an epoxy resin mount for analysis. The mount was polished to obtain a flat surface and expose the interiors of the crystals.

The Raman spectra of the samples were performed using a LabRam micro-Raman spectrometer (Horiba Jobin Yvon, Paris, France), which was equipped with a Peltier cooled multichannel CCD detector and coupled with an Olympus BX41 petrographic microscope. A frequency-doubled Nd:YAG laser was used for excitation ($\lambda = 532$ nm, output laser power on the sample is 15 mW) with a grating of 600 lines/mm, a confocal hole set to 400 $\mu$m, and a slit width set to 100 $\mu$m. A charge-coupled device detector and a long pass filter were used.
and a slit width set to 100 µm. A charge-coupled device detector and a long-working-distance objective with a 50× magnification were used. The instrumental spectral resolution was ~1 cm⁻¹.

Electron probe microanalysis (EPMA) and backscattered electron (BSE) images were collected using a CAMECA SXFive FE electron microprobe (CAMECA, Paris, France), which was equipped with four wavelength dispersive spectrometers (WDS) after the mounts were cleaned and coated with carbon. Qualitative analyses were conducted using an acceleration voltage of 15 kV, a beam current of 20 nA, and a beam size of 5 µm. The elements were obtained using three crystals as follows: One TAP for Na, Mg, Al, and Si; one LLIF for Fe; and one LPET for K, Ca, Ti, and Cs. The standards used were albite for Na; diopside for Si, Ca, and Mg; hematite for Fe; synthetic TiO₂ for Ti; orthoclase for K; synthetic Al₂O₃ for Al; and synthetic Cs-bearing glass for Cs. The peak counting time was 30 s for all elements, and the background counting time was 15 s on the high- and low-energy background positions. Matrix compositional effects were corrected using the CAMECA software X-PHI correction method. Detection limits were in the range of 0.008–0.02 wt.% (3σ). The precision and accuracy for major and minor elements were better than 2% based on analyses of the internal laboratory standards. The analytical spots were located close to the SIMS pits to accurately document the compositional matrix effect.

Trace elements of the beryl samples were conducted by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). An Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a 193 nm ArF excimer laser system (Geolas HD, Lambda Physik, Goettingen, Germany) was used. The analytical method was as described by Wu et al. [21]. A spot size of 60 µm and a laser frequency of 5 Hz were used. External calibration was performed relative to NIST SRM 610 glass. USGS BCR-2G and ARM-1 glass were used for quality control monitoring [22]. Aluminum (27Al) was used as an internal standard, which was independently determined using EMPA. The resulting data were reduced based on the GLITTER program [23]. For most trace elements (>0.005 µg/g), the accuracy was better than ±10% with an analytical precision (1 RSD) of ±10%.

After re-polishing, the mounts were cleaned, dried, and coated with ~20 nm of pure gold. The level of surface resistance was <20 Ω [24]. Beryl oxygen isotopes were measured using a CAMECA IMS-1280 SIMS (CAMECA, Paris, France). A detailed description of the instrumentation and the analytical procedures can be found in the work of Tang et al. [25]. The primary beam Cs⁺ ions were accelerated at 10 kV and focused in a Gaussian mode with an intensity of 1.0–2.0 nA. The analytical spot size was approximately 20 µm squared (10 µm beam size + 10 µm raster). The signals of 16O and 18O were simultaneously collected by two Faraday cups using a multi-collection mode. A normal electron gun was used to compensate for the charge effect. The measured 18O/16O ratios were normalized using Vienna Standard Mean Ocean Water compositions (VSMOW; 18O/16O = 0.0020052) as follows: Measured δ¹⁸O_VSMOW = ((18O/16O)_Measured / 0.0020052 − 1) × 1000. Then, the IMF was corrected using BS1 as a reference material (IMF = Measured δ¹⁸O_VSMOW(BS1) − IRMS δ¹⁸O_VSMOW(BS1)). The δ¹⁸O of the other beryl samples was calculated as SIMS δ¹⁸O_VSMOW(sample) = Measured δ¹⁸O_VSMOW(sample) − IMF). The Isoplot 3.75 software package was used for data processing and calculations [26].

The oxygen isotopes of the BS1–BS6 beryl crystals were acquired using the laser-based fluorination oxygen extraction line at the Stable Isotope Laboratory. A New Wave Research MIR10-30 laser was coupled to a vacuum extraction system [27]. Each analysis consumed ~2 mg. The beryl minerals were reacted with a purified BrF₅ reagent in a chamber to generate oxygen. The gases were purified through a series of cryogenic traps held at the temperature of liquid nitrogen. The oxygen gas was then analyzed on a Finnigan MAT 252 isotopic ratio mass spectrometer. The results are reported in the conventional δ¹⁸O notation regarding VSMOW per mil. The Chinese national reference material GBW04409 (Penglai) was measured during this study as a quality monitor [28].
4. Results and Discussion

4.1. Structural Study by Raman Spectroscopy

Representative Raman spectra obtained from the analyzed samples are shown in Figure 3, which are very typical for beryl. All of the samples exhibited characteristic peaks near ~322, ~395, ~527, ~684, ~1019, and ~1068 cm\(^{-1}\).

The peaks below 1400 cm\(^{-1}\) are associated with beryl lattice phonon modes [29]. The strong peaks at 684 cm\(^{-1}\) and 1068 cm\(^{-1}\) are due to Si–O vibrations. The modes at 322 cm\(^{-1}\) and 395 cm\(^{-1}\) are from Al–O bands. The two bands at 527 cm\(^{-1}\) and 1019 cm\(^{-1}\) represent Be–O vibrations [30,31].

Figure 3. Raman spectra of the beryl samples. The main beryl Raman bands were found at ~322, ~395, ~527, ~684, ~1019, and ~1068 cm\(^{-1}\).

4.2. Chemical Composition

The average values of the chemical composition data are summarized in Table 2, and the full results are presented in Supplementary Table S1. The studied samples did not show any regular zoning (Figure 2), with only small variations in the composition. The EPMA results show that the main contents of the six beryl samples are SiO\(_2\), Al\(_2\)O\(_3\), and BeO, which ranged from 66.0 to 67.0 wt.%, 17.9 to 18.4 wt.%, and 12.6 to 13.8 wt.%, respectively. The total of the three main contents of the BS4 is more than 99 wt.%. The main substitute elements in the beryl samples are FeO, Li\(_2\)O, Na\(_2\)O, and Cs\(_2\)O, which ranged from <0.1 to 0.9 wt.%, 0.1 to 0.7 wt.%, 0.2 to 1.3 wt.%, and <0.1 to 0.8 wt.%, respectively.

The BS5 beryl is extremely poor in Fe, which was under the detection limit. BS1 and BS4 are very limited in Fe, Mg, and Mn (≤0.02 apfu). BS2, BS3, and BS6 contain slightly increased iron content, ranging from ~4000 to ~5600 \(\mu\)g/g. The LA-ICP-MS analyses show that the contents of Li, Rb, and Cs are the most enriched in BS5, which was up to ~5095 \(\mu\)g/g, ~339 \(\mu\)g/g, and ~21,900 \(\mu\)g/g, respectively. The results indicate that the major compositions and trace elements of these six samples are homogeneous, but the chemical compositions of each sample are different from those of other samples.
Table 2. Quantitative element contents using EMPA and LA-ICP-MS for the beryl crystals used in this study.

| Element | EMPA BS1 (n = 25) Mean 1 SD | EMPA BS2 (n = 25) Mean 1 SD | EMPA BS3 (n = 25) Mean 1 SD | EMPA BS4 (n = 25) Mean 1 SD | EMPA BS5 (n = 25) Mean 1 SD | EMPA BS6 (n = 25) Mean 1 SD | LA-ICP-MS BS1 (n = 7) Mean 1 SD | BS2 (n = 7) Mean 1 SD | BS3 (n = 7) Mean 1 SD | BS4 (n = 7) Mean 1 SD | BS5 (n = 7) Mean 1 SD | BS6 (n = 10) Mean 1 SD |
|---------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| SiO₂    | 66.15 ± 0.55                | 66.63 ± 0.87                | 66.80 ± 0.90                | 67.05 ± 0.93                | 66.01 ± 0.76                | 66.89 ± 0.67                | Li 3381 ± 77                | 408 ± 6                    | 114 ± 3                    | 365 ± 8                    | 1163 ± 8                    | 528 ± 14                    |
| Al₂O₃   | 17.88 ± 0.19                | 18.09 ± 0.13                | 18.06 ± 0.24                | 18.41 ± 0.15                | 18.13 ± 0.15                | 17.86 ± 0.11                | Rb 67 ± 5                   | 11 ± 4                     | 8 ± 1                      | 36 ± 4                     | 52 ± 1                      | 28 ± 1                      |
| MgO     | 0.11 ± 0.06                 | 0.00 ± 0.01                 | 0.14 ± 0.12                 | 0.01 ± 0.03                 | 0.00 ± 0.01                 | 0.13 ± 0.02                 | Cs 3769 ± 576               | 365 ± 8                    | 114 ± 3                    | 365 ± 8                    | 1163 ± 8                    | 528 ± 14                    |
| CaO     | 0.01 ± 0.01                 | 0.00 ± 0.00                 | 0.00 ± 0.00                 | 0.00 ± 0.00                 | 0.00 ± 0.00                 | 0.00 ± 0.00                 | Fe 1370 ± 245               | 3983 ± 144                 | 1441 ± 11                  | 251 ± 1                    | 1227 ± 12                   | 721 ± 39                    |
| BeO cal | 12.65 ± 0.23                | 13.63 ± 0.18                | 13.72 ± 0.21                | 13.77 ± 0.35                | 12.75 ± 0.30                | 13.69 ± 0.15                | Mn 799 ± 61                 | 26 ± 1                     | 1 ± 0                      | 354 ± 38                   | 121 ± 7                     | 172 ± 4                     |
| Li₂O cal| 0.66 ± 0.14                 | 0.14 ± 0.01                 | 0.11 ± 0.04                 | 0.11 ± 0.15                 | 0.59 ± 0.15                 | 0.13 ± 0.03                 | Mg 799 ± 61                 | 26 ± 1                     | 1 ± 0                      | 354 ± 38                   | 121 ± 7                     | 172 ± 4                     |
| Na₂O    | 1.26 ± 0.29                 | 0.19 ± 0.03                 | 0.20 ± 0.08                 | 0.21 ± 0.29                 | 1.02 ± 0.36                 | 0.27 ± 0.06                 | Ti 197 ± 8                  | 219 ± 7                    | 218 ± 4                    | 193 ± 2                    | 219 ± 3                     | 219 ± 3                     |
| K₂O     | 0.03 ± 0.01                 | -                            | 0.01 ± 0.01                 | -                            | 0.04 ± 0.01                 | -                            | K 115 ± 15                  | -                          | -                          | -                          | -                          | -                          |
| Cs₂O    | 0.40 ± 0.10                 | 0.41 ± 0.02                 | 0.11 ± 0.08                 | 0.04 ± 0.10                 | 0.78 ± 0.67                 | 0.01 ± 0.01                 | Mg 115 ± 15                 | -                          | -                          | -                          | -                          | -                          |
| Total   | 99.33 ± 0.55                | 99.72 ± 1.01                | 99.75 ± 1.01                | 99.82 ± 0.98                | 99.35 ± 0.98                | 99.88 ± 1.01                | Sr -                        | -                          | -                          | -                          | -                          | -                          |

*Analyses using EPMA are reported in wt.%, and analyses using LA-ICP-MS are reported in µg/g. BeO cal and Li₂O cal were calculated assuming 3.00 atoms per formula unit (apfu). Be cal = 3—Li cal. *- indicates values below the limit of detection.*
4.3. Oxygen Isotopes Using SIMS and IRMS

Oxygen isotopic determinations were carried out in two sessions to evaluate their micron-level homogeneity. In each session, NIST SRM 610 was analyzed to monitor the instrumental conditions. The analytical precision (2 standard deviations (SD)) of NIST SRM 610 were 0.28‰ and 0.42‰ in two sessions, respectively, representing the instrument’s stability in both sessions. The first session was carried out to identify the inter-grain variation in oxygen isotopes, performed as individual measurements on 35 BS1, 34 BS2, 18 BS3, 32 BS4, 32 BS5, and 35 BS6 shards, respectively. The second session was designed to examine intra-grain variability. Two to four spots were performed on each shard. The second session consisted of 39 BS1, 40 BS2, 32 BS3, 40 BS4, 34 BS5, and 40 BS6 measurements on 15 grains of each beryl sample. The raw data of the two sessions are attached as Supplementary Table S2, and the summarized SIMS data are presented in Table 3.

Table 3. The oxygen isotopes obtained by IRMS and SIMS.

| Methods | IRMS | SIMS/Standard: BS1 |
|---------|------|-------------------|
|         | Time |                   |                   |
| Sample  | Mean | 2 SD   | n   | Mean | 2 SD   | n   | Mean | 2 SD   | n   |
| BS1     | 15.01| 0.34   | 14  | 15.01| 0.39   | 35  | 15.01| 0.38   | 39  |
| BS2     | 7.53 | 0.16   | 3   | 7.31 | 0.26   | 34  | 7.30 | 0.24   | 40  |
| BS3     | 10.71| 0.22   | 3   | 10.75| 0.34   | 18  | 10.80| 0.44   | 32  |
| BS4     | 2.38 | 0.14   | 3   | 2.36 | 0.22   | 32  | 2.58 | 0.20   | 40  |
| BS5     | 10.72| 0.44   | 3   | 10.98| 0.36   | 32  | 10.94| 0.34   | 34  |
| BS6     | 6.35 | 0.56   | 3   | 6.23 | 0.32   | 35  | 6.52 | 0.20   | 40  |

The measured values of δ18O of the six samples during each session formed a Gaussian distribution (Figure 4). The 2 SD of the results got from the beryl minerals ranged from 0.22‰ to 0.40‰. It is noted that the measured apparent values of δ18O of the six samples in the first session are quite different from those in the second session (Figure 4a–l), which demonstrates the importance of matrix-matched reference materials.

Homogeneity can be estimated using the standard deviation of the measured results. In a session, 1 SD for zircon standards was routinely 0.15‰–0.25‰ [32]. SIMS oxygen analysis can achieve excellent repeatability (<0.15‰), as only the measurement condition is perfect [33,34]. These results suggest that the intra- or inter-grain variations in oxygen isotopes are small enough to demonstrate the homogeneity of these beryl samples. Among them, samples BS2 (2 SD = 0.26‰ (Figure 4c) and = 0.24‰ (Figure 4d)) and BS4 (2 SD = 0.22‰ (Figure 4g) and = 0.20‰ (Figure 4h)) show the lowest variation.
Figure 4. Frequency distributions of SIMS-measured apparent $\delta^{18}$O values of the six beryl samples: (a,c,e,g,i,k) are the SIMS-measured apparent values of $\delta^{18}$O of BS1, BS2, BS3, BS4, BS5, and BS6, respectively, in the first session; (b,d,f,h,j,l) are the SIMS-measured apparent values of $\delta^{18}$O of BS1, BS2, BS3, BS4, BS5, and BS6, respectively, in the second session.

The oxygen isotope compositions obtained by the laser fluorination technique are attached as Supplementary Table S3 and are summarized in Table 3. Twenty-nine aliquots of the six beryl samples were analyzed. A total of 14 analyses were performed on BS1, including eight BS-1 shards and six BS-2 shards. Three analyses were carried out for each of the other five samples (BS2–BS6). The recommended values for BS1, BS2, BS3, BS4, BS5, and BS6 are $15.01 \pm 0.34\%$ ($n = 14$; Figure 5A1), $7.53 \pm 0.16\%$ ($n = 3$; Figure 5B1), $10.71 \pm 0.22\%$ ($n = 3$; Figure 5C1), $2.38 \pm 0.14\%$ ($n = 3$; Figure 5D1), $10.72 \pm 0.44\%$ ($n = 3$; Figure 5E1), and $6.35 \pm 0.56\%$ ($n = 3$; Figure 5F1), respectively. The relatively large standard deviation (2 SD = 0.56‰) for BS6 was most likely due to the abundant quartz inclusions.

Then, the SIMS IMF was corrected using BS1 RM as reference material with a $\delta^{18}$O value of $15.01\%$. There is an excellent linear relationship between the SIMS $\delta^{18}$O values and the IRMS $\delta^{18}$O values ($R^2 = 0.99$) (Figure 6). This means that the SIMS $\delta^{18}$O values corrected by one reference material are consistent with the IRMS $\delta^{18}$O value within analytical uncertainty. Thereby, no matrix effect related to composition variation was present in the beryl SIMS oxygen isotope analysis.
Figure 5. The laser fluorination isotope ratio mass spectrometry (IRMS) values of the six beryl samples and the SIMS $\delta^{18}$O (‰) values of these samples, which were normalized to the IRMS value of BS1: (A1–F1) are the IRMS $\delta^{18}$O mean values of BS1, BS2, BS3, BS4, BS5, and BS6, respectively; (A2–F2) are the SIMS $\delta^{18}$O mean values of BS1, BS2, BS3, BS4, BS5, and BS6, respectively; (A3–F3) are the frequency distributions of SIMS $\delta^{18}$O values of BS1, BS2, BS3, BS4, BS5, and BS6, respectively.
5. Conclusions

This study evaluated six natural beryl samples using Raman, EMPA, SIMS, and IRMS. Samples BS1, BS2, BS4, and BS5 were shown to be pure and clean (Figures 1 and 2). The SIMS results of BS1 (2 SD = 0.36‰, $n = 74$), BS2 (2 SD = 0.24‰, $n = 74$), BS4 (2 SD = 0.31‰, $n = 72$), and BS5 (2 SD = 0.35‰, $n = 72$) during the two sessions suggest that the samples are homogeneous in terms of oxygen isotope composition at a micrometer level. They all meet the criteria for use as reference materials for SIMS oxygen isotopic analysis. Compared to the IRMS results, this study showed no matrix effect related to composition variation in the beryl SIMS oxygen isotope analysis. The recommended $\delta^{18}$O values of the four reference materials, BS1, BS2, BS4, and BS5, are 15.01 ± 0.34‰ (2 SD), 7.53 ± 0.16‰ (2 SD), 2.38 ± 0.14‰ (2 SD), and 10.72 ± 0.44‰ (2 SD), respectively. The BS2 and BS4 beryl samples showed the smallest variation and are thus the most suitable reference materials.

All of the beryl materials are available upon request from the corresponding author.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/cryst11111322/s1, Supplementary Table S1: The chemical composition data of the beryl samples; Supplementary Table S2: The oxygen isotopes obtained using SIMS; Supplementary Table S3: The oxygen isotopes obtained using IRMS.

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