Article

Beryl Reference Materials for In Situ Oxygen Isotope Determination

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Abstract: The mineral beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$) 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 composition variation in beryl SIMS oxygen isotope analysis. The recommended $\delta^{18}\text{O}$ values of the four reference materials, BS1, BS2, BS4, and BS5, were $15.01 \pm 0.34\text{‰}$ (2 standard deviations, 2 SD), $7.53 \pm 0.16\text{‰}$ (2 SD), $2.38 \pm 0.14\text{‰}$ (2 SD), and $10.72 \pm 0.44\text{‰}$ (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

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1. Introduction

One of the most significant current discussions regarding critical metals is that of beryllium (Be) [1,2]. Beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$) 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, BS5, 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).

Figure 2. Representative BSE images of the beryl samples used in this study: (a) BS1, (b) BS2, (c) BS3, (d) BS4, (e) BS5, and (f) BS6. Brl, Beryl; Qtz, quartz.

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 μm ,

and a slit width set to 100 μm . A charge-coupled device detector and a long working-distance objective with a $50\times$ magnification were used. The instrumental spectral resolution was $\sim 1\text{ cm}^{-1}$.

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 TiO_2 for Ti; orthoclase for K; synthetic Al_2O_3 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 (^{27}Al) 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 ($>0.005\text{ }\mu\text{g/g}$), the accuracy was better than $\pm 10\%$ with an analytical precision (1 RSD) of $\pm 10\%$.

After re-polishing, the mounts were cleaned, dried, and coated with $\sim 20\text{ nm}$ of pure gold. The level of surface resistance was $<20\text{ }\Omega$ [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 ^{16}O and ^{18}O 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 $^{18}\text{O}/^{16}\text{O}$ ratios were normalized using Vienna Standard Mean Ocean Water compositions (VSMOW; $^{18}\text{O}/^{16}\text{O} = 0.0020052$) as follows: Measured $\delta^{18}\text{O}_{\text{VSMOW}} = ((^{18}\text{O}/^{16}\text{O})_{\text{Measured}}/0.0020052 - 1) \times 1000$. Then, the IMF was corrected using BS1 as a reference material ($\text{IMF} = \text{Measured } \delta^{18}\text{O}_{\text{VSMOW}}^{(\text{BS1})} - \text{IRMS } \delta^{18}\text{O}_{\text{VSMOW}}^{(\text{BS1})}$). The $\delta^{18}\text{O}$ of the other beryl samples was calculated as $\text{SIMS } \delta^{18}\text{O}_{\text{VSMOW}(\text{sample})} = \text{Measured } \delta^{18}\text{O}_{\text{VSMOW}(\text{sample})} - \text{IMF}$. 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 $\sim 2\text{ mg}$. The beryl minerals were reacted with a purified BrF_5 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 $\delta^{18}\text{O}$ 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} .

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} .

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].

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_2O_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_2O , Na_2O , and Cs_2O , 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 $\mu\text{g/g}$. 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 $\mu\text{g/g}$, ~ 339 $\mu\text{g/g}$, and $\sim 21,900$ $\mu\text{g/g}$, 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.

EMPA wt. %	BS1 (<i>n</i> = 25)		BS2 (<i>n</i> = 25)		BS3 (<i>n</i> = 25)		BS4 (<i>n</i> = 25)		BS5 (<i>n</i> = 25)		BS6 (<i>n</i> = 25)	
	Mean	1 SD	Mean	1 SD	Mean	1 SD	Mean	1 SD	Mean	1 SD	Mean	1 SD
SiO ₂	66.15	0.55	66.63	0.87	66.80	0.90	67.05	0.93	66.01	0.76	66.89	0.67
Al ₂ O ₃	17.88	0.19	18.09	0.13	18.06	0.24	18.41	0.15	18.13	0.15	17.86	0.11
FeO	0.17	0.05	0.61	0.02	0.61	0.15	0.21	0.02	0.03	0.03	0.88	0.03
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
CaO	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
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
Li ₂ O _{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
Na ₂ O	1.26	0.29	0.19	0.03	0.20	0.08	0.21	0.29	1.02	0.36	0.27	0.06
K ₂ O	0.03	0.01	-	-	0.01	0.01	-	-	0.04	0.01	-	-
Cs ₂ O	0.40	0.10	0.41	0.02	0.11	0.08	0.04	0.10	0.78	0.67	0.01	0.01
Total	99.33	-	99.72	-	99.75	-	99.82	-	99.35	-	99.88	-
Si	6.00	-	6.00	-	6.00	-	6.00	-	6.00	-	6.00	-
Be _{cal}	2.76	-	2.95	-	2.96	-	2.96	-	2.79	-	2.95	-
Li _{cal}	0.24	-	0.05	-	0.04	-	0.04	-	0.21	-	0.05	-
sum	3.00	-	3.00	-	3.00	-	3.00	-	3.00	-	3.00	-
Al	1.91	-	1.92	-	1.91	-	1.94	-	1.94	-	1.89	-
Fe ²⁺	0.01	-	0.05	-	0.05	-	0.02	-	0.00	-	0.07	-
Mn	0.00	-	0.00	-	0.00	-	0.00	-	0.00	-	0.00	-
Mg	0.01	-	0.00	-	0.02	-	0.00	-	0.00	-	0.02	-
sum	1.94	-	1.97	-	1.98	-	1.96	-	1.94	-	1.97	-
Ca	0.00	-	0.00	-	0.00	-	0.00	-	0.00	-	0.00	-
Na	0.22	-	0.03	-	0.03	-	0.04	-	0.18	-	0.05	-
K	0.00	-	0.00	-	0.00	-	0.00	-	0.00	-	0.00	-
Cs	0.02	-	0.02	-	0.00	-	0.00	-	0.03	-	0.00	-
sum	0.24	-	0.05	-	0.04	-	0.04	-	0.21	-	0.05	-
Cs/Na	0.07	-	0.49	-	0.16	-	0.04	-	0.21	-	0.01	-
Mg/Fe	1.04	-	0.01	-	0.38	-	0.10	-	/	-	0.26	-
LA-ICP-MS µg/g	BS1 (<i>n</i> = 7)		BS2 (<i>n</i> = 7)		BS3 (<i>n</i> = 7)		BS4 (<i>n</i> = 7)		BS5 (<i>n</i> = 7)		BS6 (<i>n</i> = 10)	
	Mean	1 SD	Mean	1 SD	Mean	1 SD	Mean	1 SD	Mean	1 SD	Mean	1 SD
Li	3381	77	408	6	253	18	233	8	5095	68	87	5
Rb	67	5	114	3	46	8	19	0.1	339	5	4	0.1
Cs	3769	576	3653	88	1163	381	154	8	21,913	211	31	1
Fe	1370	245	3983	144	5059	528	1417	34	-	-	5667	69
Mn	72	9	72	2	105	20	84	2	19	1	126	5
Mg	799	61	26	1	354	38	12	1	-	-	614	6
Ti	197	8	219	7	218	3	218	4	193	2	219	3
K	115	15	-	-	61	23	-	-	144	41	-	-
P	94	5	128	10	122	7	121	7	112	7	120	5
Zn	61	11	185	8	441	11	282	4	10	1	174	4
Ga	24	3	31	1	25	1	11	0.1	13	1	19	0.1
V	4	1	0.9	0.1	-	-	1.3	0.1	-	-	1.6	0.1
Sc	2.2	0.7	1.3	0.1	0.5	0.1	0.5	0.1	-	-	0.6	0.1
Sn	2.1	0.6	323.0	30	-	-	-	-	-	-	-	-
Cu	1.4	0.1	-	-	-	-	-	-	-	-	-	-
Ta	-	-	-	-	-	-	-	-	14.2	0.7	-	-
Sr	-	-	-	-	-	-	-	-	-	-	0.5	0.4
Ge	-	-	-	-	-	-	-	-	8.4	0.5	-	-
Be	45,478	282	51,460	531	51,998	315	51,514	508	43,967	543	51,566	355
Na	11,844	294	1400	27	1581	115	1117	30	6901	131	2375	82

Analyses using EMPA 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		2021			2019-12-20			2021-7-20	
Sample	Mean	2 SD	<i>n</i>	Mean	2 SD	<i>n</i>	Mean	2 SD	<i>n</i>
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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ values of the six beryl samples: (a,c,e,g,i,k) are the SIMS-measured apparent values of $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $15.01 \pm 0.34\text{‰}$ ($n = 14$; Figure 5A1), $7.53 \pm 0.16\text{‰}$ ($n = 3$; Figure 5B1), $10.71 \pm 0.22\text{‰}$ ($n = 3$; Figure 5C1), $2.38 \pm 0.14\text{‰}$ ($n = 3$; Figure 5D1), $10.72 \pm 0.44\text{‰}$ ($n = 3$; Figure 5E1), and $6.35 \pm 0.56\text{‰}$ ($n = 3$; 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 $\delta^{18}\text{O}$ value of 15.01‰ . There is an excellent linear relationship between the SIMS $\delta^{18}\text{O}$ values and the IRMS $\delta^{18}\text{O}$ values ($R^2 = 0.99$) (Figure 6). This means that the SIMS $\delta^{18}\text{O}$ values corrected by one reference material are consistent with the IRMS $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ (‰) values of these samples, which were normalized to the IRMS value of BS1: (A1–F1) are the IRMS $\delta^{18}\text{O}$ mean values of BS1, BS2, BS3, BS4, BS5, and BS6, respectively; (A2–F2) are the SIMS $\delta^{18}\text{O}$ mean values of BS1, BS2, BS3, BS4, BS5, and BS6, respectively; (A3–F3) are the frequency distributions of SIMS $\delta^{18}\text{O}$ values of BS1, BS2, BS3, BS4, BS5, and BS6, respectively.

Figure 6. $\delta^{18}\text{O}$ (SIMS) vs. $\delta^{18}\text{O}$ (IRMS) of the six samples.

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 $\delta^{18}\text{O}$ values of the four reference materials, BS1, BS2, BS4, and BS5, are $15.01 \pm 0.34\text{‰}$ (2 SD), $7.53 \pm 0.16\text{‰}$ (2 SD), $2.38 \pm 0.14\text{‰}$ (2 SD), and $10.72 \pm 0.44\text{‰}$ (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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References

- Hofstra, A.H.; Kreiner, D.C. *Systems-Deposits-Commodities-Critical Minerals Table for the Earth Mapping Resources Initiative (ver. 1.1, May 2021)*; U.S. Geological Survey Open-File Report 2020-1042; U.S. Geological Survey: Reston, VA, USA, 2020; 26p.
- Wang, R.; Wu, B.; Xie, L.; Che, X.; Xiang, L.; Liu, C. Global tempo-spatial distribution of rare-metal mineralization and continental evolution. *Acta Geol. Sin.* **2021**, *95*, 182–193.
- Ottaway, T.L.; Wicks, F.J.; Bryndzia, L.T.; Kyser, T.K.; Spooner, E.T.C. Formation of the Muzo hydrothermal emerald deposit in Colombia. *Nat. Cell Biol.* **1994**, *369*, 552–554. [[CrossRef](#)]
- Cerný, P. Mineralogy of Beryllium in Granitic Pegmatites. *Rev. Miner. Geochem.* **2002**, *50*, 405–444. [[CrossRef](#)]
- Tao, X.; Xie, L.; Wang, R.; Zhang, R.; Hu, H.; Liu, C. Mineralogical characteristics of beryl: A case study of the beryls from Cuona and Qomolangma district in Himalaya. *J. Nanjing Univ.* **2020**, *56*, 815–829. [[CrossRef](#)]
- Wu, F.-Y.; Liu, X.-C.; Liu, Z.-C.; Wang, R.-C.; Xie, L.; Wang, J.-M.; Ji, W.-Q.; Yang, L.; Liu, C.; Khanal, G.P.; et al. Highly fractionated Himalayan leucogranites and associated rare-metal mineralization. *Lithos* **2020**, *352–353*, 105319. [[CrossRef](#)]
- Zhou, Q.; Qin, K.; Tang, D. Mineralogy of columbite-group minerals from the rare-element pegmatite dykes in the East-Qinling orogen, Central China: Implications for formation times and ore genesis. *J. Asian Earth Sci.* **2021**, *27*, 104879. [[CrossRef](#)]
- Onuma, N.; Clayton, R.N.; Mayeda, T.K. Oxygen Isotope Fractionation between Minerals and an Estimate of the Temperature of Formation. *Science* **1970**, *167*, 536–538. [[CrossRef](#)]
- Taylor, R.P.; Fallick, A.E.; Breaks, F.W. Volatile Evolution in Archean rare-element granitic pegmatites—Evidence from the hydrogen isotopic composition of channel H₂O in beryl. *Can. Mineral.* **1992**, *30*, 877–893.
- Galili, N.; Shemesh, A.; Yam, R.; Brailovsky, I.; Sela-Adler, M.; Schuster, E.M.; Collom, C.; Bekker, A.; Planavsky, N.; Macdonald, F.A.; et al. The geologic history of seawater oxygen isotopes from marine iron oxides. *Science* **2019**, *365*, 469–473. [[CrossRef](#)]
- Giuliani, G.; France-Lanord, C.; Coget, P.; Schwarz, D.; Cheilletz, A.; Branquet, Y.; Giard, D.; Martin-Izard, A.; Alexandrov, P.; Piat, D.H. Oxygen isotope systematics of emerald: Relevance for its origin and geological significance. *Miner. Depos.* **1998**, *33*, 513–519. [[CrossRef](#)]
- Giuliani, G.; Chaussidon, M.; Schubnel, H.-J.; Piat, D.H.; Rollion-Bard, C.; France-Lanord, C.; Giard, D.; de Narvaez, D.; Rondeau, B. Oxygen Isotopes and Emerald Trade Routes Since Antiquity. *Science* **2000**, *287*, 631–633. [[CrossRef](#)]
- Ireland, T.R. Considerations in Zircon Geochronology by SIMS. *Rev. Miner. Geochem.* **2003**, *53*, 215–241. [[CrossRef](#)]
- Isa, J.; Kohl, I.; Liu, M.-C.; Wasson, J.; Young, E.; McKeegan, K. Quantification of oxygen isotope SIMS matrix effects in olivine samples: Correlation with sputter rate. *Chem. Geol.* **2017**, *458*, 14–21. [[CrossRef](#)]
- Scicchitano, M.R.; Rubatto, D.; Hermann, J.; Majumdar, A.S.; Putnis, A. Oxygen isotope analysis of olivine by ion microprobe: Matrix effects and applications to a serpentinised dunite. *Chem. Geol.* **2018**, *499*, 126–137. [[CrossRef](#)]
- Vho, A.; Rubatto, D.; Putlitz, B.; Bouvier, A. New Reference Materials and Assessment of Matrix Effects for SIMS Measurements of Oxygen Isotopes in Garnet. *Geostand. Geoanalytical Res.* **2020**, *44*, 459–471. [[CrossRef](#)]
- Eiler, J.M.; Graham, C.; Valley, J. SIMS analysis of oxygen isotopes: Matrix effects in complex minerals and glasses. *Chem. Geol.* **1997**, *138*, 221–244. [[CrossRef](#)]
- Tang, G.; Su, B.; Li, Q.; Xia, X.; Jing, J.; Feng, L.; Martin, L.; Yang, Q.; Li, X. High-Mg# Olivine, Clinopyroxene and Orthopyroxene Reference Materials for In Situ Oxygen Isotope Determination. *Geostand. Geoanalytical Res.* **2019**, *43*, 585–593. [[CrossRef](#)]
- Lum, J.E.; Viljoen, F.; Cairncross, B.; Frei, D. Mineralogical and geochemical characteristics of Beryl (Aquamarine) from the Erongo Volcanic Complex, Namibia. *J. Afr. Earth Sci.* **2016**, *124*, 104–125. [[CrossRef](#)]
- Liu, Y.; Deng, J.; Shi, G.; Sun, D. Geochemical and morphological characteristics of coarse-grained tabular beryl from the Xuebaoding W–Sn–Be deposit, Sichuan Province, western China. *Int. Geol. Rev.* **2012**, *54*, 1673–1684. [[CrossRef](#)]
- Wu, S.; Karius, V.; Schmidt, B.C.; Simon, K.; Wörner, G. Comparison of Ultrafine Powder Pellet and Flux-free Fusion Glass for Bulk Analysis of Granitoids by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry. *Geostand. Geoanalytical Res.* **2018**, *42*, 575–591. [[CrossRef](#)]
- Wu, S.; Wörner, G.; Jochum, K.P.; Stoll, B.; Simon, K.; Kronz, A. The Preparation and Preliminary Characterisation of Three Synthetic Andesite Reference Glass Materials (ARM-1, ARM-2, ARM-3) for In Situ Microanalysis. *Geostand. Geoanalytical Res.* **2019**, *43*, 567–584. [[CrossRef](#)]
- Griffin, W.; Powell, W.; Pearson, N.J.O.; Reilly, S. GLITTER: Data reduction software for laser ablation ICP-MS. In *Laser Ablation-ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues*; Sylvester, P., Ed.; Mineralogical Association of Canada: Québec, QC, Canada, 2008; pp. 308–311.
- Li, X.H.; Liu, Y.; Li, Q.L.; Guo, C.H.; Chamberlain, K.R. Precise determination of Phanerozoic zircon Pb/Pb age by multi-collector SIMS without external standardization. *Geochem. Geophys. Geosyst.* **2009**, *10*, Q04010. [[CrossRef](#)]
- Tang, G.-Q.; Liu, Y.; Feng, L.-J.; Wei, G.-J.; Su, W.; Li, Y.; Ren, G.-H.; Li, X.-H. New Natural and Fused Quartz Reference Materials for Oxygen Isotope Microanalysis. *At. Spectrosc.* **2020**, *41*, 41. [[CrossRef](#)]

-
26. Ludwig, K.R. *User's Manual for Isoplot 3.75, A Geochronological Toolkit for Microsoft Excel*; Berkeley Geochronology Center Special Publication: Berkeley, CA, USA, 2012.
 27. Feng, L.; Li, H.; Li, T. Potential Reference Materials for Hematite Oxygen Isotope Analysis. *Minerals* **2020**, *10*, 987. [[CrossRef](#)]
 28. Li, X.-H.; Long, W.-G.; Li, Q.; Liu, Y.; Zheng, Y.-F.; Yang, Y.-H.; Chamberlain, K.R.; Wan, D.-F.; Guo, C.-H.; Wang, X.-C.; et al. Penglai Zircon Megacrysts: A Potential New Working Reference Material for Microbeam Determination of Hf-O Isotopes and U-Pb Age. *Geostand. Geoanalytical Res.* **2010**, *34*, 117–134. [[CrossRef](#)]
 29. Kim, C.C.; Bell, M.; McKeown, D. Vibrational analysis of beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) and its constituent ring (Si_6O_{18}). *Phys. B Condens. Matter* **1995**, *205*, 193–208. [[CrossRef](#)]
 30. Hagemann, H.; Lucken, A.; Bill, H.; Gysler-Sanz, J.; Stalder, H. Polarized Raman spectra of beryl and bazzite. *Phys. Chem. Miner.* **1990**, *17*, 395–401. [[CrossRef](#)]
 31. Wang, P.; Gray, T.P.; Li, Z.; Anderson, E.J.D.; Allaz, J.; Smyth, J.R.; Koenig, A.E.; Qi, L.; Zhou, Y.; Raschke, M.B. Mineralogical classification and crystal water characterisation of beryl from the W–Sn–Be occurrence of Xuebaoding, Sichuan province, western China. *Miner. Mag.* **2021**, *85*, 172–188. [[CrossRef](#)]
 32. Tang, G.-Q.; Li, X.-H.; Li, Q.-L.; Liu, Y.; Ling, X.-X.; Yin, Q.-Z. Deciphering the physical mechanism of the topography effect for oxygen isotope measurements using a Cameca IMS-1280 SIMS. *J. Anal. At. Spectrom.* **2015**, *30*, 950–956. [[CrossRef](#)]
 33. Peres, P.; Kita, N.T.; Valley, J.W.; Fernandes, F.; Schuhmacher, M. New sample holder geometry for high precision isotope analyses. *Surf. Interface Anal.* **2013**, *45*, 553–556. [[CrossRef](#)]
 34. Treble, P.; Schmitt, A.; Edwards, R.; McKeegan, K.; Harrison, T.; Grove, M.; Cheng, H.; Wang, Y. High resolution Secondary Ionisation Mass Spectrometry (SIMS) $\delta^{18}\text{O}$ analyses of Hulu Cave speleothem at the time of Heinrich Event 1. *Chem. Geol.* **2007**, *238*, 197–212. [[CrossRef](#)]