SIMS Zircon Hydrogen Isotope and H₂O Content Analyses and Reference Material Development

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ABSTRACT: Water is perhaps the most important molecule in the solar system, and determining its origin and distribution in planetary interiors has significant implications for understanding the formation and evolution of planetary bodies. Zircon (present in both extraterrestrial and terrestrial samples) is a resistant and versatile accessory mineral, and its water content has the potential to characterize the hydrous status of zircon-crystallizing magma. However, the hydrous status can be altered by magma fractionation, mixing, or degassing. Although hydrogen isotopes of zircon can help to trace these processes, the lack of relevant microanalytical technology and reference materials has hindered significant breakthroughs in this area. In this study, we employed an analytical technique of secondary ion mass spectrometry (SIMS) to simultaneously measure the hydrogen isotopes of zircon and their H₂O content. The homogeneity test of hydrogen isotope and the H₂O content of the potential reference materials (D15395, D15814, and Temora 2) were conducted by measuring the ¹⁶OD and ¹⁶O¹H signals (using SIMS) in a conventional peak-hopping mono-collector mode with electron-multiplier (EM) detectors. SIMS results show that the apparent external precision (1SD) of hydrogen isotope of large grains D15395 and D15814 are 16‰ and 22‰, which is comparable with their internal error and theoretical precision according to counting statistics, indicating that they are sufficiently homogenous at the micrometer sampling level in terms of hydrogen isotopes. However, zircon Temora 2 shows a much worse external precision (83‰, 1SD) and an obvious negative correlation between hydrogen isotope and H₂O content, hence it is not suitable to be used as reference material for hydrogen isotope. Both hydrogen isotope and H₂O content of three samples were also measured using a continuous-flow thermal conversion elemental analyzer operating online with a mass spectrometer (TC/EA-MS). The homogeneous samples zircon D15395 and D15814 yielded recommended δD values of $-87 \pm 9\text{‰}$ and $-68 \pm 2\text{‰}$ (1SD) and H₂O content of ~ 478 ppm and ~ 332 ppm, respectively. Additionally, H₂O contents acquired by TC/EA-MS and SIMS (calibrated by FTIR determined standards) were consistent within a 10% error range, demonstrating the reliability of the SIMS H₂O content calibration curve for zircon and the FTIR absorption coefficient used before.

INTRODUCTION

Hydrogen is the lightest element and is omnipresent in both

extraterrestrial and terrestrial environments. It exists in different forms (H₂O, H₃O⁺, OH⁻, H₂, and CH₄).¹ Hydrogen has the largest relative mass difference between its two stable isotopes, ¹H and ²D,

with natural abundances of ~99.9885% and ~0.0115%, respectively. The hydrogen isotope compositions of terrestrial rocks have been used to trace geological processes such as water cycling in subduction zones,^{2,3} volatile degassing in lavas,^{4–6} fluid-rock interactions,^{7,8} and were furthermore used to study chemical heterogeneity of the mantle.^{9–11} The hydrogen isotope compositions of extraterrestrial rocks have been used to study the abundance and origin of water on planetary and asteroidal bodies.^{12–16} Different fluid sources or processes have distinct D/H ratios, which are expressed as $\delta D \left[\left(\frac{D/H_{\text{sample}}}{D/H_{\text{VSMOW}}} - 1 \right) \times 1000 \right]$, where VSMOW (Vienna Standard Mean Ocean Water) has $D/H = 0.00015576$.¹⁷

Nominally anhydrous minerals (NAMs), which do not contain hydrogen in their chemical formulas, usually contain trace amounts of water in the form of structural bonds (H^+ , NH_4^+ , OH^- groups).^{18–20} Over the past decades, there has been an increased focus on NAMs because they may represent an important water reservoir in the Earth's interior.^{21–23} They could potentially play a major role in the distribution, cycling, and inventory of water between and within the mantle, crust, and exosphere.^{21,24–27} Although NAMs contain only trace amounts of water, their hydrogen isotopic compositions can be determined with precision to trace the hydrogen heterogeneity of the planet's interior.²⁸ Additionally, they have been used to constrain fluid transport during metamorphism in the Earth.^{8,29–31}

Zircon is a ubiquitous accessory mineral found in most mafic and felsic rocks, as well as in some mantle-derived rocks such as carbonatites and kimberlites.^{32,33} It has also been identified in some meteorites and lunar rocks.^{34,35} Owing to its resistance to heating ($> 1000^\circ C$), mechanical wear, and chemical corrosion^{36–38} and its low chemical diffusion coefficient,^{39–41} zircon is widely used in several analytical studies and procedures. This includes U–Pb dating,^{42,43} Ti geothermometry,^{44,45} trace element (for provenance studies)^{46,47} and isotope (*e.g.*, Hf,⁴⁸ O,⁴⁹ and Li⁵⁰) analyses (for magma source tracing). Recently, Xia *et al.*⁵¹ developed a new reference material suite and an analytical procedure for the simultaneous measurement of H_2O content and oxygen isotopes in zircon by secondary ion mass spectroscopy (SIMS). Subsequently, Xia *et al.*⁵² and Meng *et al.*⁵³ suggested that zircon, similar to other NAMs, has the potential to characterize the hydrous status of its parental magma. Combined with chronological information,³⁴ zircon can provide more reliable evolutionary information for both extraterrestrial and terrestrial samples. However, the hydrous status can be altered by magma fractionation, mixing, or degassing. The hydrogen isotopes of zircon can help trace the origin of water and its degassing or mixing processes, but such studies are hampered by the lack of suitable microanalytical technology and reference materials.

In this study, we developed the first suite of zircon reference materials for hydrogen isotope analyses and presented a modified

analytical procedure for SIMS to simultaneously determine the H_2O content and hydrogen isotope composition of zircon.

EXPERIMENTAL

Samples information and preparation. Zircon D15395, an alluvial sample (likely from high-Al basalt), was sourced from the Rocky River in Uralla, New South Wales (NSW), Australia. The sample, which was composed of many big crystals, 1–4 mm in size, was dark-brown and translucent in appearance. Two D15395 grains (D15395-3 and D15395-4) were previously used as reference materials for zircon H_2O content measurement,⁵¹ and one $3 \times 3 \times 2$ mm grain (weight: ~80 mg) was used in this study. Another alluvial sample, Zircon D15814, was obtained from Horse Gully (high-Al basalt) in northern Inverell, NSW. The grains were mostly coarse (1–15 mm), and one $5 \times 5 \times 4$ mm grain (weight: ~460 mg) was used in this study. Zircon Temora 2 is a widely used standard for microbeam U–Pb and Hf–O isotope analyses in many laboratories that utilize SIMS or laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS).^{54,55} Temora 2 was procured from the Middledale Gabbroic Diorite, a shallow intrusive stock in the Paleozoic Lachlan Orogen of Eastern Australia.

In this study, zircon samples D15395 and D15814 were crushed into 100–150 μm fragments, and those without inclusions or cracks were hand-picked for subsequent analyses. Fifty fragments for all three samples were embedded in random orientations to form a Sn-based alloy SIMS mount, following the method described by Zhang *et al.*⁵⁶ They were first checked for their hydrogen homogeneity by SIMS, and then their hydrogen isotopes and H_2O contents were determined by SIMS and thermal conversion elemental analyzer operating online with a mass spectrometer (TC/EA-MS) using the remaining fragments/grains.

TC/EA-MS analysis. The hydrogen isotope composition and the total H_2O content of all samples were analyzed by the online continuous-flow method, using a thermal conversion elemental analyzer (TC/EA) with isotope ratio mass spectrometry (IRMS) at the University of Science and Technology of China (Hefei). Detailed descriptions of this method were provided by Gong *et al.*⁵⁷ Mineral samples were wrapped in silver foil capsules and dropped into a reduction furnace using an auto-sampler and then preheated at $90^\circ C$ for 12 h to eliminate the adsorbed water on their surface. Water liberation and carbon reduction were carried out in a furnace at $1450^\circ C$. The products generated in this step, namely, hydrogen and carbon monoxide gases, were transferred by the helium carrier gas, separated in a gas chromatograph (GC), and then analyzed by IRMS in the continuous-flow mode. During the analysis of hydrogen, the GC was operated at $90^\circ C$ to minimize the retention time and peak broadening. At other times, it was heated to $300^\circ C$ under a low-flow helium stream for cleaning. The

time-integrated intensity of the sample peak was used to determine both the D/H ratio and H₂O content.

Biotite NBS-30 standard ($\delta D = -65.7\text{‰}$, H₂O = 36963 ppm) was used to control the precision and accuracy in both hydrogen isotope and H₂O content analyses.^{57,58} Depending on the mineral H₂O content, the absolute reproducibility for the mineral δD value is generally about ± 1 to $\pm 2\text{‰}$ (1SD), and the relative uncertainty for H₂O content is approximately ± 1 to $\pm 3\%$ (1SD). In practice, analytical errors for the δD value and H₂O content can be as low as $\pm 0.5\text{‰}$ and $\pm 0.3\%$, respectively, for hydrous minerals, but up to $\pm 3\text{‰}$ and $\pm 5\%$, respectively, for NAMs.

SIMS. Analyses were performed using a CAMECA IMS 1280-HR at the SIMS Laboratory of the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). The vacuum in the sample chamber was enhanced by placing the sample mount in the high-vacuum storage chamber overnight, and then further pumped down (for 1 to 2 h) in the analysis chamber to $\sim 1.7 \times 10^{-9}$ mbar. A primary Cs⁺ beam (3.9–4.3 nA) was accelerated at 10 kV and focused in the Gaussian mode to sputter the samples. A 15 μm raster was used to ensure a more uniform flat-bottom sputter crater. A normal-incidence electron gun ensured charge compensation and maintained voltage stability. Negative secondary ions were extracted and accelerated (10 kV) with a 400 μm contrast aperture, 20 μm entrance slit, 80 μm exit slit, and 100 $\times$ transfer optics magnification. The energy slit was closed to a bandwidth of 50 eV and shifted 5 eV below the maximum transmission. To minimize the water background signal, a 2000 μm field aperture (FA) was used. The pre-sputtering process lasted for 60 s with a $25 \times 25 \mu\text{m}$ raster area, which was larger than the analysis area, to minimize the water background signal. Appropriate pre-sputtering in an ultra-high vacuum can reduce the water background to < 10 ppm, or even to 1.2 ppm.⁵⁹

A single EM of the mono-collector system was used to measure secondary ion beam intensities of the ¹⁶O¹H, ¹⁷O¹H, and ¹⁶OD ions by a peak-hopping mode. The value of mass resolving power (MRP) used to separate ¹⁶OD from ¹⁷O¹H was set at 15000. The main purpose of measuring ¹⁷O¹H was to check whether ¹⁶OD was measured correctly, and whether ¹⁷O¹H and ¹⁶OD were completely separated. The counting time and waiting time for ¹⁶O¹H, ¹⁷O¹H, and ¹⁶OD ions were 4.96, 2, 12 s and 3.04, 1.52, 1.52 s, respectively. Each measurement consisted of 16 cycles, with a total analysis time of approximately 12 min, including pre-analysis sputtering and peak centering. The H₂O content of zircon was determined from the measured ¹⁶O¹H/PI (primary beam intensity) ratio (Table S1), and a calibration curve was constructed by the analysis of nine previously-characterized zircon reference materials (ZG7, GJ-1, SA01-A, SA01-B, ZG3, D16314-2, D15395-3, D15395-4, and 91500).⁵¹ The calibration curve ($[\text{H}_2\text{O}] = 0.0279 \times [^{16}\text{O}^1\text{H}/\text{PI}]$; $R_2 = 0.998$, Fig. 1) was used here to invert the measured ¹⁶O¹H/PI ratio into H₂O content.

Fig. 1 H₂O content calibration curve for zircon analyses by SIMS. Independent measurements of the H₂O content of the zircon standards were obtained by FTIR analyses.⁵¹ The error bar represents 1SD. Note that the error bars of SA01-A and SA01-B are smaller than the symbol size.

Fig. 2 Reproducibility of the measured δD in this study. Error bars denote ± 1 SE (standard error). Solid lines and shadow bands denote mean values and external reproducibility (1SD), respectively.

Fig. 3 Theoretical uncertainty and measured within-spot uncertainties versus ¹⁶OD signal intensity. The grey field denotes a 95% confidence limit on the theoretical error.

RESULTS

Hydrogen isotopes. The SIMS analyzed δD values (uncorrected) of the zircon samples are listed in Table S2 and shown in Fig. 2. The mean uncertainty of a single analysis for each sample is 14–42‰ (1SE; Fig. 3), which depends on the H₂O content of the

Table 1. Preferred compositional values of glass standards

Sample No.	Weight (mg)	H ₂ voltage (mV)	δD (‰)	H ₂ O (ppm)
D15395@01	17.3	361	-81	517
D15395@02	17.64	287	-94	439
Average	-	-	-87 ± 9	478 ± 55
Temora 2@01	18.02	500	-90	728
Temora 2@02	18.12	453	-92	622
Average	-	-	-91 ± 1	675 ± 75
D15814@01	18.28	248	-70	367
D15814@02	17.75	194	-67	297
Average	-	-	-68 ± 2	332 ± 49
NBS-30@01	0.83	1521	-65	38880
NBS-30@02	0.88	1611	-63	39674
NBS-30@03	0.93	1482	-65	38679
NBS-30@04	0.81	1434	-64	39323
NBS-30@05	0.79	1371	-67	35242
NBS-30@06	0.81	1332	-65	33271
Average	-	-	-65 ± 1	37512 ± 2620

Fig. 4 H₂O content versus corrected δD values of zircon Temora 2 (measured by SIMS). Uncertainty bars are ± 1 SE (standard error).

sample. No time drifting or “X-Y effects” were observed during the analyses.^{60,61} Samples D15395 and D15814 showed homogeneous hydrogen isotope compositions, with the uncorrected average of 174 and 197‰ and apparent external precision (1SD) of 16 and 22‰ (Fig. 2A and 2B), respectively, while the hydrogen isotope analysis of zircon Temora 2 yielded -1 to + 320‰ (average 142‰) and an apparent external precision of 83‰, much higher than those of D15395 and D15814 (Fig. 2C). Two TC/EA-MS measurements of each sample were conducted, yielding absolute δD = -81 and -94‰ (D15395), -70 and -67‰ (D15814), and -90 and -92‰ (Temora 2), with external analytical uncertainties (1SD) of 9, 2, and 1‰, respectively (Table 1).

H₂O content. The simultaneously acquired ¹⁶O¹H/PI ratios (with SIMS) and corrected H₂O contents are presented in Table S2. The range of the H₂O content for every zircon sample measured by SIMS (e.g., D15395: 296–717 ppm) was found to be much wider than that measured by TC/EA-MS (e.g., D15395: 517 and 439 ppm). The H₂O content measured by SIMS of the zircon Temora 2 was in the range of 110–941 ppm.

DISCUSSION

Precision of hydrogen isotope measurement. The analytical precision discussed here includes both the internal (within a single spot analysis, SE) and external precision of spot-to-spot repeatability analysis (reproducibility, SD). The internal precision is calculated by the standard error of the analytical results of the different cycles during a single spot analysis. This is strongly correlated with counting statistics, which are directly related to the H (or H₂O) content, total counting time, and the primary beam intensity. Considering that the ¹⁶OD signal intensity was much lower than that of ¹⁶O¹H, the ¹⁶OD/¹⁶O¹H uncertainty was mainly determined from the counting statistics of the ¹⁶OD signal intensity (Poisson error). In this study, the δD internal precision for all analyzed samples decreased from ca. 42 to 14‰ with increasing ¹⁶OD intensity. Although the internal error for most analysis spots was consistent with the theoretical Poisson error (within the 95% confidence interval; Fig. 3), some Temora 2 data points deviated slightly from the theoretical line and exhibited a higher internal error. We interpret this to be the result of heterogeneous compositions of the hydrogen isotopes and/or micro-inclusions/-cracks encountered during the ion sputtering. However, the latter is unlikely, as sputtering on micro-inclusions/-cracks would also induce high uncertainty for H₂O content, which is not observed (Fig. 4). In addition to that, zircon Temora 2 is a good oxygen isotope reference material, indicating that micro-inclusions or micro-cracks can be avoided.^{54,55} Meanwhile, the uncertainty of samples D15395 and D15814 agree well with the theoretical prediction. External precision depends on many factors, including material homogeneity and instrumental stability, which are influenced by environmental variation and the time drift of the electron gun and EM. SIMS analysis of all the samples was conducted for 22 h, with almost no instrument drift. The external precision of ≥ 20 measurements performed on random fragments was 16‰ (D15395) and 22‰ (D15814) that is comparable with their internal error (Fig. 3), indicating that samples D15395 and D15814 are sufficiently homogenous at the micrometer sampling level in terms of hydrogen isotopes. We suggest that the heterogeneous hydrogen isotope compositions of the Temora 2 sample are the main cause of its poor external precision, as supported by the clear negative H₂O vs. δD correlation (Fig. 4). This may imply modification by a geological event (e.g., magma mixing or degassing); thus, Temora 2 cannot be utilized as a suitable hydrogen isotope reference material.

Accuracy of hydrogen isotope and H₂O content measurement. In this study, the accuracy of SIMS analysis was quantified using Instrumental Mass Fractionation (IMF) ((δD)_{measured} – (δD)_{recommended}). The IMFs of D15395 and D15814 (with homogeneous hydrogen isotope compositions and different H₂O contents) are consistent within the error range (Fig. 5A). Although Temora 2 is relatively heterogeneous, the average corrected δD value is also consistent with that of the TC/EA-MS analysis (within error) (Fig. 5A).

Fig. 5 Comparison of mean δD (A) and H_2O contents (B) measured by TC/EA-MS with the calculated SIMS values. The SIMS-measured δD values are corrected for IMF based on the sample D15395. Solid black lines in (A) and (B) indicate that the ratio of the two measurements is 1:1, while the shaded area represents an uncertainty range of 10% and 10%, respectively.

The H_2O contents in minerals or melt inclusions were measured by SIMS, using the relative signal intensity of 1H or $^{16}O^1H$ (to ^{16}O , ^{18}O , or ^{30}Si) with a calibration curve.^{51,59,62–71} In this study, the H_2O content calibration curves were established by comparing the Fourier transform infrared spectroscopy (FTIR) results with the SIMS $^{16}O^1H/PI$ ratios obtained for a series of newly introduced zircon H_2O content reference materials (Fig. 1).⁵¹ Previous analysis using FTIR and SIMS yielded different H_2O contents in zircon (calibrated using a rhyolite water standard). The difference (with a factor of 2) was attributed to the uncertainty of the FTIR absorption coefficient of zircon.⁷² Here, the H_2O content of zircon measured by TC/EA-MS can be used to check the reliability of FTIR-determined reference materials and FTIR absorption coefficients. The mean H_2O content of samples D15395 and D15814 calibrated by FTIR-determined reference materials is consistent with that obtained by the absolute method (TC/EA-MS) (within a 10% error range, Fig. 5B), indicating that our calibration line is reliable with an uncertainty of less than 10%. This further demonstrates the accuracy of the FTIR absorption coefficient. The Temora 2 sample deviated from the error field, which we interpret to be mainly due to its highly uneven H_2O content (110–941 ppm).

CONCLUSIONS

We described a new analytical procedure based on secondary ion mass spectrometry, which permits the simultaneous measurement of hydrogen isotopes and H_2O content in zircon. In addition, we characterized the hydrogen isotope ratios of two zircon reference materials (RMs, gem-quality zircon D15395 and D15814) by TC/EA-MS and SIMS. SIMS analysis of samples D15395 and D15814 indicated that they had homogenous hydrogen isotope compositions. Bulk extraction technology using TC/EA-MS yielded $\delta D = -87 \pm 9\%$ (D15395) and $-68 \pm 2\%$ (D15814) (1SD), which we propose as the recommended values. Additionally, the H_2O content simultaneously acquired by TC/EA-MS and SIMS was consistent (within a 10% error range), demonstrating the reliability of the SIMS H_2O content calibration curve and the FTIR

absorption coefficient. Fragments of both the D15395 and D15814 zircon megacrystals presented in this study could be obtained from the corresponding authors upon request.

ASSOCIATED CONTENT

The supporting information (Tables S1–S2) is available at www.at-spectrosc.com/as/home

AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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