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Extreme isotopologue disequilibrium in molecular SIMS species during SHRIMP geochronology

Charles W. Magee, Jr.^{1,2}, Martin Danišík³, Terry Mernagh^{2,4}

¹ Australian Scientific Instruments, 111/113 Gladstone St. Fyshwick ACT 2609
 ² Research School of Earth Sciences, Australian National University, Canberra ACT 2600
 ³ GeoHistory Facility, John de Laeter Centre, TIGeR, Applied Geology, Curtin University, Perth, WA 6845, Australia
 ⁴Geoscience Australia, Symonston ACT 2609

Abstract

- 10 Isotopologue deficits of up to 200‰ below ideal mixing are observed in UO_2^+ species during SIMS gechronological analyses using the SHRIMP IIe instrument. These are identified by bombarding natural U-bearing minerals with an ${}^{18}O_2^-$ primary beam. The large anomalies are associated with repeat analyses down a single SIMS sputtering crater (Compston et al., 1984), analysis of high-uranium, radiation damaged zircon, and analysis of baddeleyite. Analysis of zircon under routine conditions yield UO_2^+ isotopologue anomalies generally within a few percent of equilibrium. The conditions under which the
- 15 isotopologue anomalies are observed are also conditions in which the UO_x -based corrections, or calibration, for relative U vs Pb ionization efficiencies fail. The existence of these isotopologue anomalies suggest that failure of the various UO_x species to equilibrate with each other is the reason that none of them will successfully correct the U/Pb ratio. No simple isotopologue-based correction is apparent. However, isotopologue disequilibrium appears to be a more sensitive tool for detecting hi U calibration breakdowns than Raman spectroscopy, which showed sharper peaks for ~37 Ma high uranium
- 20 zircons than for reference zircons OG1 and Temora. U-Th-Sm/He ages were determined for aliquots of reference zircons OG1 (755±71 Ma) and Temora (323±43 Ma), suggesting that the broader Raman lines for the Temora reference zircons may be due to something other than accumulated radiation damage.

Isotopologue abundances for UO^+ and ThO^+ and their energy spectra are consistent with most or all molecular species being 25 the product of atomic recombination when the primary beam impact energy is greater than 5.7 kV. This, in addition with the large UO_2^+ instrumentally generated isotopologue disequilibria, suggest any attempts to use SIMS to detect naturally occurring isotopologue deviations could be tricky.

Introduction

30 Determining the timing of geologic events is a fundamental constraint for unravelling the history of our planet. In the 120 years since the discovery of radioactivity, the use of radioactive decay has been an increasingly versatile, accurate, and precise way of measuring geologic time. One of the major advances in this field was the invention of the SHRIMP (Sensitive High Resolution Ion MicroProbe), which has been used for U-Pb geochronology of zircon for the last 33 years (Froude et al., 1983).

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The SHRIMP is a large radius, magnetic sector SIMS instrument (Ireland et al., 2008). It features a low impact energy floating primary column optimized for Köhler illumination of a projection aperture onto the surface with a mass-filtered primary beam, a low energy (350V/mm) initial extraction field, A quadrupole triplet for matching the secondary ion emittance to the mass spectrometer acceptance, and a large (1 meter turning radius) CQH mass spectrometer with second





order focal aberration correction (Matsuda, 1974). The instrument used in this experiment is equipped with a single electron multiplier as a detector; all data is ion counting on sequential mass peaks. The SHRIMP has been used to provide the geochronological foundations of thousands of papers, usually using a methodology best described several decades ago (Williams, 1998).

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A key requirement for successful SHRIMP U-Pb geochronology is accounting for the differential and variable secondary ionization yields of U and Pb in the Secondary Ion Mass Spectrometry (SIMS) source. The current method for doing this is the use of a calibration relating the detected ion ratio of Pb⁺/U⁺ to the ratio of an oxidized molecular U-bearing ion to a reduced one. The most widely used calibration is a power law relationship between Pb⁺/U⁺ and UO⁺/U⁺ (Claoue-Long et al., 10 1995), but other calibrations using various combinations of U, UO, and UO₂ have been used (Stern and Amelin, 2003).

10 1995), but other calibrations using various combinations of U, UO, and UO_2 have been used (Stern and Amelin, 200. These calibrations apply to both SHRIMP and other SIMS instruments used for geochronology.

There are some drawbacks to this technique. Firstly, the covariation is not exact, and after calibration there remains a residual error that can be anything from 0.5 to 2%, depending on the analytical conditions of the session. Secondly, it
requires corrections for bulk composition for zircons with more than 2000 ppm U (Williams and Hergt, 2000; White and Ireland, 2012), or for minerals that exhibit complex solid solution, such as monazite (Gregory et al., 2007; Fletcher et al., 2010). Thirdly, some simple oxides, such as baddeleyite and rutile, exhibit orientation-related deviations from the calibration (Wingate and Compston, 2000; Schmitt et al., 2010; Taylor et al., 2012).

- 20 As the relationship between uranium oxide formation and Pb ionization efficiency at the SIMS sputter site is not clearly understood, an ¹⁸O₂⁻ primary beam was used to determine the source of the oxygen in the UO species used for calibration (Magee et al., 2014). Previously, the use of ¹⁸O implants in non-oxide species has been used for two purposes. Oxygen diffusion in either oxide or semiconductor matrices has been observed using an ¹⁸O flood or ion implant (Kilner et al., 1996; Manning et al., 1997). In addition, ¹⁸O implants have been used for quantifying behavior of sputtered oxygen introduced by
- 25 either a natural primary beam (Sobers et al., 2004) or by oxygen flooding (Franzreb et al., 2004). This study reverses the Sobers et al. (2004) method in which the ¹⁸O implant is replaced with the stoichiometric natural oxygen composition (99.8% ¹⁶O) of the natural target material, and the ¹⁶O⁻ primary beam used by Sobers et al. (2004) is replaced by a ¹⁸O₂⁻ primary beam. It is the first labelled oxygen SIMS experiment where an untreated natural mineral target is bombarded with an isotopically labelled primary oxygen beam, and the stoichiometry defines the ¹⁶O content of the sputtered volume.
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A description of the monoxide species formed in these experiments (Magee et al., 2014) showed that for primary energies greater than 5 kV, the relationships between uranium, thorium, and their monoxides were consistent with complete atomization and recombination (in the case of molecular species) during the sputtering process. However, the behavior of more complicated molecular species, such as the actinide dioxides, was not considered there. This paper describes the ion

35 abundances of the actinide dioxide species and discusses the possible meaning of the observed abundances.

One prediction of the atomization and recombination process is that the isotopologues of the molecular dioxide species should occur with abundances that are consistent with the isotopic ratio of the monoxide and elemental sputtered species. For example, if (as is the case in standard zircon geochronology) $U^{16}O$ and $U^{18}O$ are sputtered in equal proportion (Magee et

40 al., 2014), then the predicted ratio of $U^{16}O_2$ to $U^{16}O^{18}O$ to $U^{18}O_2$ is 1:2:1. This study tests this prediction of isotopologuous equilibrium, and tries to explain the observed deviations from it. The conclusions drawn are then applied to practical SIMS geochronology, in an attempt to propose methodologies that will improve analytical performance.





Methods

The experiments were performed on the SHRIMP IIe instrument at Geoscience Australia (Stern et al., 2009). Following the first "blank" experiment (see section A, below), the tank of (isotopically natural) high purity oxygen gas usually used to feed the duoplasmatron was replaced with a tank of 99.9% ¹⁸O₂ gas (Icon Isotope Services, Troy NY). The primary beam Wein

- 5 filter electrostatic voltage was then dropped to transmit mass 36, selecting the ¹⁸O₂⁻ ion for sample bombardment. As the samples were all natural oxides, this instrumental setup yielded a situation where 99.7% of the sputtered oxygen originating from the sample is ¹⁶O, and essentially all the resputtered primary beam oxygen is ¹⁸O. No oxygen flooding was used, yielding a simple two-component system.
- 10 The analytical run table included standard uranium lead geochronology peaks: ⁹⁰Zr₂¹⁶O reference peak, a background position, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, and ²³⁸U. In addition to the standard actinide oxides used for U-Pb calibration (Williams, 1998), the ¹⁸O isotopologues of those masses were also included: ²³²Th¹⁶O (248), ²³²Th¹⁸O (250), ²³⁸U¹⁶O (254), ²³⁸U¹⁸O (256), ²³⁸U¹⁶O₂ (270), ²³⁸U¹⁶O (272), and ²³⁸U¹⁸O₂ (274). For analytical session 130058, the ThO₂ isotopologues were also counted, so additional peaks of ²³²Th¹⁶O₂ (264), ²³²Th¹⁶O¹⁸O (266), and ²³²Th¹⁸O₂ (268) were collected.

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Aside from the additional mass stations, and the isotopically labeled primary beam, analyses were run automatically using standard Geoscience Australia procedures. A primary impact energy of 10680 Volts was used, with secondary ions initially extracted at 680 volts before acceleration to 10 kV for mass spectrometric analysis. The SHRIMP was set up with a 110 micron source slit and a 100 micron collector slit, yielding a 1% mass resolution ($M/\Delta M$) of 5000 or greater for all peaks.

- 20 Data were collected in six scans through the run table on a single electron multiplier. Data were reduced using SQUID 2.5 (Ludwig, 2010). Analytical and data reduction procedures are described in detail elsewhere (Magee et al., 2012). The mounts analyzed were a mix of standard 25mm mounts and 35mm "megamounts" (Ickert et al., 2008). Baddeleyite analyses were performed using the same instrumental setup and analytical run table.
- 25 The following experiments were performed.

Analytical "blank".

Before the ¹⁸O bottle was connected to the duoplasmatron, the run table with the ¹⁸O species was run using standard, isotopically undisturbed oxygen with both zircon and baddeleyite targets (zircon: session 110056; baddeleyite: session 110057). The primary beam Wein filter was used to select mass 32, so that the primary beam in this experiment (as is usually the case in standard SHRIMP II and SHRIMP RG analyses) was ¹⁶O₂⁻. The purpose of this was to see if any unexpected mass interferences existed that would complicate interpretations of the ¹⁸O-bearing species. In session 110056, 25 grains of Temora-2 (Black et al., 2004) zircon were analyzed, along with 22 grains of R-33 (Black et al., 2004) and 8 grains of OG1 (Stern et al., 2009). In 110057, an oriented Phalabowra baddeleyite mount from the original orientation work (Wingate and Compston, 2000) was analyzed, with a dozen analyses on each of the four oriented

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Standard zircon

megacrysts.

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Four analytical sessions (110061, 110066, 110088, 110106) were run with standard zircon using the ¹⁸O₂⁻ primary beam. Two of these contained zircons of unknown age, the geochronological results of which will be published elsewhere. The reference materials in those runs consisted of:





Session 110061: 24 Temora-2 and 21 R-33. Session 110066: 28 Temora-2 and 26 R-33. Session 110088: 79 Temora-2 and 49 R-33 Session 110106: 12 Temora, 6 R-33, 4 OG1

Session 130056: 14 Temora Session 130058: 9 Temora

High uranium zircon

The zircon mount used in a recent study of the high-U effect (White and Ireland, 2012) was repolished and reanalyzed using the ${}^{18}O_2^{-}$ beam. These sessions were:

Session 110067: Ten Temora and 16 Red Hill (Williams and Hergt, 2000; White and Ireland, 2012) zircons. Session 130028: 9 Temora, 10 OG1, and 18 Raumid (Kostitsyn et al., 2007) zircons

Session 130056: 37 Bishop Tuff (Ickert et al., 2015) zircons.

Session 130058: 8 100 Raumid and 10 119 Raumid zircons.

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Baddeleyite.

Baddeleyite was analyzed in session 110060 and 110065. 12 spots on each of four oriented sections of Phalabowra were analysed in session 110060. In 110065, twenty randomly oriented Phalabowra and 20 randomly oriented Kurinelli dolerite (Claoué-Long et al., 2008) grains were analyzed.

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Impact energy effect.

Five sessions were run using primary beam impact energies between 3.7 and 15.7 kV. The effect of impact energy on Pb ionization and the U-Pb calibration is discussed previously (Magee et al., 2014)..However the UO_2 species are not discussed there. The sessions, primary energy (add ~680V for impact energy) and analyzed grains were:

- 25 110098: 15 kV, 13 Temora, 6 R-33, 3 OG1.
 - 110099: 12.5 kV, 12 Temora, 6 R-33, 4 OG1
 - 110101: 5 kV, 12 Temora, 6 R-33, 4 OG1
 - 110103: 3 kV, 10 Temora, 5 R-33, 3 OG-1
 - 110105: 7.5 kV, 12 Temora, 6 R-33, 4 OG1

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Repetitive down-hole analysis test.

Tem53.1 (4); 110105 Tem-65 (2).

Several of the sessions listed above had one or two spots with repeated analyses down a single sputtering crater, under a variety of conditions. For Monazite there were: 1409-4 (3 down hole analyses), 44069-1.1 (3 down hole analyses), 8153-1 (3 down hole analyses), all is session 110064. Baddeleyite (110065) Phalabowra 1.1 (three). Zircon: 110066: Temora34.1 (3), R-36 (2), R-47.1 (3); 110098 Tem-1.1 (4); 110099 Tem-14.1 (4); 110101 R33-18.1 (4); 110103





Monazite.

Session 110064 included multiple analyses of three popular monazite reference materials: 1409 (Stern and Berman, 2001), 8153 (Carson et al., 2008), and 44069 (Aleinikoff et al., 2006) were each analyzed in 11 separate spots (one of each had the multiple down-hole analyses described above).

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ThO₂ disequilibria

In session 130058, the run table was further expanded to include all three major ThO_2 isotopologues, with the intention of comparing UO_2 and ThO_2 isotopologic deviations. The run table containing these additional peaks was used to analyze the high-U Raumid zircons. The purpose of this experiment is to see if the more variable charge state of U causes different deviations to that of Th.

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Raman

Laser Raman spectra were recorded on a Dilor® SuperLabram spectrometer equipped with a holographic notch filter, 600 and 1800 g/mm gratings, and a liquid N_2 cooled, 2000 × 450 pixel CCD detector. The samples were illuminated with 514.5 nm laser excitation from a Melles Griot 543 Series argon ion laser, using 5 mW power at the sample surface, and a single 30

15 second accumulation. A 100X Olympus microscope objective was used to focus the laser beam and collect the scattered light. The focused laser spot on the samples was approximately 1 μ m in diameter. Wavenumbers are accurate to \pm 1 cm⁻¹ as determined by plasma and neon emission lines.

Helium dating

- In order to more fully understand the Raman result of the reference zircons Temora 2 and OG1, conventional (U-Th-Sm)/He dating was performed on several whole OG1 and Temora 2 zircons using methodology described in Danišík et al. (2012). Euhedral to subhedral single crystals were degassed at ~1250°C under ultra-high vacuum using a diode laser, and ⁴He was measured by isotope dilution on a Pfeiffer Prisma QMS-200 mass spectrometer. Then the crystals were spiked with ²³⁵U and ²³⁰Th, dissolved and analyzed by isotope dilution for U and Th on solution ICP-MS. (U-Th-Sm)/He ages were corrected for alpha recoil following the procedure of Farley et al. (1996) assuming a homogeneous U-Th distribution.
- 25 The (U-Th-Sm)/He dating was performed because, although the paleoarchean OG1 has a crystallization age more than eight times older than the Silurian Temora 2, it is possible that for much of that time the OG1 was at an elevated temperature, where radiation damage could anneal out. Assuming this temperature threshold is similar to the He retention temperature of ~150-220°C (Guenthner et al., 2013), this experiment was performed to see if a (U-Th-Sm)/He age much younger than the crystallization age could explain the Raman results.

30 Results

The relation between total UO/U and the $U^{18}O/U^{16}O$ for different minerals is shown in **figure 1**. The relation between total UO/U and the $U^{18}O/U^{16}O$ based on impact energy was shown (Magee et al., 2014).

The predicted ratios of $U^{18}O_2$ and $U^{16}O^{18}O$ relative to $U^{16}O_2$ were calculated from the observed $U^{18}O^+/U^{16}O^+$ ratio, and compared to the observed ratios. For any observed $U^{18}O^+/U^{16}O^+$ ratio, R, the equilibrium fractions of the dioxide species

are:

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 $\begin{array}{l} U^{16}O_2{:}\left(1/(R{+}1)\right)^2;\\ U^{18}O_2{:}\left(R/(R{+}1)\right)^2; \end{array}$





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U¹⁶O ¹⁸O: 2 x 1/(R+1) x R/(R+1)

The observed $U^{18}O_2$ and $U^{16}O^{18}O$ and $U^{16}O_2$ were then used to calculate delta values: $\Delta 272 = (Observed U^{16}O^{18}O / U^{16}O_2 - Predicted U^{16}O^{18}O / U^{16}O_2) / (Predicted U^{16}O / U^{16}O_2)$ $\Delta 274 = (Observed U^{18}O_2 / U^{16}O_2 - Predicted U^{18}O_2 / U^{16}O_2) / (Predicted U^{18}O_2 / U^{16}O_2)$

Ratios are then typically multiplied by 100 and expressed as percent (%), as the deviations here are large and the precision does not reach the permil level.

10 A summary of results is listed in **Table 1**, while the full analysis-by-analysis results are listed in **Table 2** (electronic dataset).

Experiment A: Analytical blank:

110056: For the Temora zircons, the total UO/U was about 6.2. U¹⁸O⁺/U¹⁶O⁺ ratio averaged about 9.3E-4, about half the

- 15 natural ¹⁸O/¹⁶O ratio (figure 1). This is consistent with about half the oxygen coming from the natural abundance sample, and half from the pure ¹⁶O₂ beam (Magee et al., 2014). The weighted mean $\Delta 272$ is positive, 9.0% \pm 3.2% (1 σ). This indicates an interference on U¹⁶O¹⁸O⁺ which increases its intensity by about 10%. However, U¹⁶O¹⁸O⁺ is very low intensity peak (generally less than 10 cps), so this interference is, on average, less than 1 cps. It is not known what the interfering species is, but U(¹⁶OH)₂⁺ is a possibility.
- 20 As count rates on U¹⁶O¹⁸O⁺ using the ¹⁸O beam were 1000 times higher, this minor excess was ignored when processing the ¹⁸O primary beam data, where it will contribute less than 1‰ excess.

The expected $U^{18}O_2^+$ counts are less than one millionth of the $U^{16}O_2^+$ counts, and only 100,000 $U^{16}O_2^+$ counts were collected. Therefore we expect a fraction of a $U^{18}O_2^+$ count, and the $\Delta 274$ is dominated by counting noise on the background. Any interfering peak present is negligible.

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110057: Although the total UO/U ratio for Baddeleyite was much lower (a mean of 3.46, but scattered from just under 3 to almost 4), the same experiment performed on Baddeleyite yielded broadly similar results; the $U^{18}O^+/U^{16}O^+$ ratio averaged about 9.4E-4, and the weighted mean $\Delta 272$ is positive but somewhat smaller than for zircon, 4.4% \pm 4.9%. This puts it within error of both zero and the zircon value. Once again, $\Delta 274$ is dominated by counting noise on the background, as the expected value is a fraction of a count.

Experiment B: Standard zircons:

The mean results for typical reference material and unknown zircons are shown in Table 1. These zircons showed a small but consistent negative D272 deviation, with a mean value of $-1.4\% \pm 0.5\%$. There was also a small but consistent positive D274 deviation of $1.8\% \pm 1.0\%$. The range and uncertainty of 79 Temora analyses is shown in **figure 2**. No statistically

35 significant isotopologue disequilibrium trends related to age are observed, but only one session (130058) had OG1 grains analyzed, and the extreme age of this reference material (Stern et al., 2009) dominates any age-related statistics. The geochronologic results from unknowns M750 and M736 analyzed in session 110088 are given in Laurie et al. (In Review) alongside ID-TIMS results for the same samples. The agreement between the SHRIMP ages and the ID-TIMS ages for these samples suggests that the ¹⁸O₂⁻ primary beam introduces no detectable geochronological bias.





Experiment C: High Uranium zircon

Two of three high uranium samples, the Triassic Red Hill and the Eocene Raumid, exhibited a Δ 274 excess of up to 10% (**Figure 3- A,B**). The Pleistocene Bishop Tuff showed no such deviation (**figure 3-C**). The Red Hill and Raumid also showed apparent excess radiogenic Pb (the "High U effect"; (Williams and Hergt, 2000), but this effect was not evident in

5 the Bishop Tuff samples (Ickert et al., 2015). There is not a strong correlation between degree of $\Delta 274$ anomaly and degree of excess apparent radiogenic ²⁰⁶Pb (**Figure 3,D-F**).

Experiment D: Baddeleyite

The results of the Baddeleyite experiments are shown in **Figure 4**. There are moderate to extreme negative $\Delta 272$ anomalies present. In addition, although the mean $\Delta 274$ is close to zero (**Table 1**), this belies substantial variation, between -7% and

10 +11%. There is a strong correspondence between the degree of negative $\Delta 272$ and sign of $\Delta 274$, and the overall $U^{18}O^+/U^{16}O^+$ ratio. In the analyses of the oriented crystal fragments (**Figure 4-A**), there is good overall agreement between most analyses of each segment, but large differences between them. These orthogonally mounted sections (Wingate and Compston, 2000) do not show the low $U^{18}O^+/U^{16}O^+$, and high $\Delta 272$, $\Delta 274$ results that were revealed from analyzing randomly oriented crystals (**Figure 4-B**).

15 Experiment E: Impact energy:

The results of the impact energy experiments are shown in **Figure 5**. The 3 kV results have poor counting stats due to the low sputter yield and primary beam current. Ignoring these, for the rest of the analyses there was a slight trend to more negative $\Delta 272$ and $\Delta 274$ with increasing impact energy (**Figure 5**).

Experiment F: Downhole analyses.

20 Additional analyses in a single spot were performed at a variety of primary ion energies (**Table 2**). For energies below 10 kV, the additional measurements downhole resulted in a slight increase in Δ272 and a larger increase in Δ274 (**Figure 6-A**), although the poor counting stats on the 3 kV experiment reduces the statistical significance for those results. For a primary energy of 10kV and up, the repeated downhole analyses resulted in a slight decrease in Δ272, and a slight increase in Δ274. So the repeated downhole analyses in both instances moved away from the origin, and the location of standard, well-behaved analyses, but in different directions.

Figure 6-B shows that a scan-by-scan breakdown of multiple down-hole analyses can detect when the analyses "fall off" the calibration, an effect known since the early days of SHRIMP (Compston et al., 1984). This fall-off corresponds with a minimum in the $U^{18}O^+/U^{16}O^+$ ratio. It is these off-calibration analyses which have the slightly lower $\Delta 272$ and slightly higher $\Delta 274$ values, compared to the on-calibration scans.

30 Experiment G: Monazite.

All monazite analyses showed extreme $\Delta 274$ anomalies, which were different between monazites of different composition. As no unlabeled monazite analyses were performed, a composition-related interference cannot be ruled out, so no further interpretation will be done with this data.

Experiment H: ThO₂ isotopologue disequilibrium

35 ThO₂ isotopologue deviations were calculated in the same way as the UO₂ isotopologue deviations.





The predicted ratios of $Th^{18}O_2$ and $Th^{16}O^{18}O$ relative to $Th^{16}O_2$ were calculated from the observed $Th^{18}O^+/Th^{16}O^+$ ratio, and compared to the observed ratios. For any observed $Th^{18}O^+/Th^{16}O^+$ ratio, R, the equilibrium fractions of the dioxide species are:

 $Th^{16}O_2: (1/(R+1))^2;$

5 $Th^{18}O_2$: $(R/(R+1))^2$; $Th^{16}O^{18}O$: 2 x 1/(R+1) x R/(R+1)

The observed Th¹⁸O₂ and Th¹⁶O¹⁸O and Th¹⁶O₂ were then used to calculate delta values:

 $\Delta 266 = (Observed Th^{16}O^{18}O / Th^{16}O_2 - Predicted Th^{16}O^{18}O / Th^{16}O_2) / (Predicted Th^{16}O^{18}O / Th^{16}O_2)$

10 $\Delta 268 = (\text{Observed Th}^{18}\text{O}_2 / \text{Th}^{16}\text{O}_2 - \text{Predicted Th}^{18}\text{O}_2 / \text{Th}^{16}\text{O}_2) / (\text{Predicted Th}^{18}\text{O}_2 / \text{Th}^{16}\text{O}_2)$

As with UO₂, ratios are then typically multiplied by 100 and expressed as percent (%).

Raman

Raman measurements were made on the high-U Raumid zircons, to determine if they high actinide contents had produced enough damage to broaden the Raman peaks. Measurements were also made on the OG1 and Temora grains in the same grainmount, so that the Raumid results could be compared to U-Pb reference material. The results are given in **Table 3** and **Figure 7.**

Helium

(U-Th-Sm)/He dating was performed on several Temora 2 and OG1 grains, in order to better constrain the radiation history of these reference materials, and to estimate their relative radiation damage histories. Single grain (U-Th-Sm)/He ages for OG1 range from 677.5±36.3 to 815.5±44.6 Ma (n=6; average: 755±71 Ma) and are by ~400 Myrs older than (U-Th-Sm)/He ages of Temora 2, which range from 287.9±15.3 to 370.6±19.8 Ma (n=5; average: 323±43 Ma) (Table 4). There results indicate that OG1 accumulated radiation damage for significantly longer time than Temora 2.

Discussion

- 25 In general, the UO₂ isotopologue disequilibrium data show that in most known situations where the SIMS UO_x/U based calibration breaks down, the UO_2 isotopologue disequilibrium also increases. This is consistent with the long-known observation that Pb ionization is closely related to oxygen availability at the sputter site (Schuhmacher et al., 1993; Schmitt et al., 2010), and that the uranium oxide ratios are an accurate monitor of oxygen availability (Schmitt and Zack, 2012). The UO_2 isotopologue deviations show that in the calibration breakdown scenarios previously discovered (Compston et al., 1984;
- 30 Williams and Hergt, 2000; Wingate and Compston, 2000), the various combinations of uranium and oxygen are, by definition, not in equilibrium with each other. Therefore it is no surprise if they fail to predict the Pb⁺ ionization efficiency.

Similar calibration problems have been reported from smaller radius magnetic sector ion probes (Schmitt et al., 2010; Schmitt and Zack, 2012; Schaltegger et al., 2015). The use of oxygen flooding to enhance Pb sensitivity in those experiments

- 35 complicates the repeat of this study in such SIMS instruments, as it adds a third oxygen source (the flood), in addition to the silicate/oxide matrix and the primary beam. However, the reduction of calibration problems in the baddeleyite matrix under flooding conditions (Schmitt et al., 2010) is consistent with the UO₂ isotopologue results presented here, which show that the oxygen from the matrix and the primary beam have vastly different behavior from grain to grain (as evidenced by Δ 272 and Δ 274 deviations in the tens of percent). Sadly, no simple Δ 272 or Δ 274-based correction puts the baddeleyite data collected
- 40 here back on the calibration line to a useful precision, as the spot-to-spot scatter can only be reduced from ~10% to ~5% by





applying such a correction. The physical explanation for the observed UO_2 isotopologue disequilibrium is still unclear, but a potential candidate is discussed below.

Molecular ion escape model

- If intact $U^{16}O^+$ ions from the sample are escaping the sputtering site to the mass spectrometer without reacting with 5 other species, the $U^{18}O^+/U^{16}O^+$ measured by the mass spectrometer will be lower than that of the sputtering site. As a result, the equilibrium mixture of UO₂ species in equilibrium with the (unknown) $U^{18}O^+/U^{16}O^+$ of the sputtering site will have positive $\Delta 272$ and $\Delta 274$ values relative to the observed $U^{18}O^+/U^{16}O^+$.
- Should $U^{16}O_2^+$ molecules escape from the sputtering surface intact and be counted, then the $U^{18}O_2^+/U^{16}O_2^+$ and 10 $U^{16}O^{-18}O^+/U^{16}O_2^+$ ratios measured by the mass spectrometer would be lower than the equilibrium ratios in the sputtering area, and lower than predictions from the $U^{18}O^+/U^{16}O^+$ ratio, leading to negative $\Delta 272$ and $\Delta 274$ values like thus:

Δ272 = 1/(1-B) - (1+C) / (1+C) Δ274= (1/(1-B)^2 / (1+C)) +1

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Where B is the fraction of $U^{16}O^+$ which escapes without reaction, and C is the fraction of $U^{16}O_2^+$ which escapes without reacting. As the $U^{16}O^+$ escape curve has a steeper slope than the $U^{16}O_2^+$ escape line, combinations of these two mechanisms can produce $\Delta 272$ and $\Delta 274$ values that lie above the $U^{16}O_2^+$ escape line in the southwest quadrant of $\Delta 272$ by $\Delta 274$ space, to the left of the $U^{16}O^+$ escape curve in the northeast quadrant of $\Delta 272$ by $\Delta 274$ space, or anywhere in the northwest quadrant. The southeast quadrant is inaccessible via either of these mechanisms in any combination. The prediction of an inaccessible area (positive $\Delta 272$, negative $\Delta 274$) is consistent with the observation that not a single analysis

lies in this quadrant.

This $U^{16}O^+$ escape curve, the $U^{16}O_2^+$ escape line, and the measured $\Delta 272$ and $\Delta 274$ values for baddeleyite analyses are plotted in **figure 8**. These results suggest that if the intact molecular ion escape for matrix UO and UO₂ is responsible for

25 the $\Delta 272$ and $\Delta 274$ deviations, the escaped unreactive ions must be present at the 5 to 20% level. However, unreactive UO_x species should result in a UO_x production that is high relative to the Pb⁺ production, not low, and baddeleyite miscalibrations can be either high or low relative to the ²⁰⁷Pb/²⁰⁶Pb age. So even at a qualitative level, this hypothesis is somewhat lacking.

The trend towards slightly positive $\Delta 274$ in the UO₂⁺ ions is not understood, although for the low energy ions it may be consistent with a few % ejection of intact U¹⁶O⁺ ions from the surface. The negative $\Delta 272$ of UO₂⁺ ions produced by the 30 12.5 and 15 kV primary ions is consistent with UO₂⁺ and UO⁺ ions being ejected in a 2:1 ratio.

All UO_2^+ isotopologues exhibit gas phase (ion energy less than the extraction potential) tails not present in UO^+ , U^+ , or Pb⁺ ion energy spectra. This suggests that inferring percent level or better U/Pb ratios using a calibration based on UO_2^+ may be fraught with unforeseen complications compared with the traditional UO^+ -based calibration. An additional complication may occur for UO_2^+ -based calibrations at impact energies greater than 10 KeV, if intact matrix UO_2^+ ejection is occurring and masking the oxygen availability for Pb ionization enhancement.

High uranium effect

The ~36 Ma Raumid and ~180 Ma Red Hill (Williams and Hergt, 2000; White and Ireland, 2012) zircons show a Δ 274 excess up to about 10%. However, the 0.8 Ma Bishop Tuff zircons, which do not seem to exhibit this high uranium effect (Chamberlain et al., 2014; Ickert et al., 2015), have only one analytical spot with a Δ 274 above 2.5%, and none above 5%. A





comparison of $\Delta 274$ and $\Delta 268$ in the Raumid zircons show that both the uranium and the thorium isotopologues agree (**figure 9**). Thus the effect is probably unrelated to the higher potential valence states of uranium.

- 5 Raman measurements were made on the Raumid grains in order to determine whether any lattice damage parameters could be identified that may relate to the production of a $\Delta 274$ excess (**Figure 7**). White and Ireland (2012) have shown that Jurassic high U zircons which show an apparent U-concentration effect are metamict, according to the spectral featured described in Nasdala et. al (1995).
- 10 Depending of the degree of radiation damage, Raman spectroscopy can be used to measure the degree of metamictization in zircons (Nasdala et al., 1995). Well-ordered zircons show narrow internal and external vibrational bands in the spectral range below 1100 cm⁻¹ (for band assignments see Dawson et al., 1971). With increasing metamictization, all main Raman bands decrease in intensity, become increasingly broader, and shift towards lower wavenumbers. These changes are due to decreasing short-range order in the radiation-damaged zircon (Nasdala et al., 2004). In the case of natural zircons, decreased
- 15 short-range order is mainly caused by radiation damage. However, the presence of several wt.% U and Th may also decrease the short-range order and cause detectable effects on the Raman band width. This has been demonstrated by Podor (1995) for synthetic rare-earth monazites.

The Raman results show slight 1007 cm⁻¹ peak broadening in the high U Raumid samples relative to the low U samples. However, The highest U grains are barely broader than the OG-1 analysis, and none of the Raumid Raman results show band

- widths as wide as the Temora zircon (**Figure 10**). The (U-Th-Sm)/He data show that the Paleoarchean OG-1 standard zircons have a Neoproterozoic He age, making their cooling age about twice as old as the Temora grains, instead of 8 times older. The He content of the OG-1 zircons is, on average, about 3 times that of Temora (**Table 4**). So it is unlikely that radiation dose alone explains the broader Raman peak in Temora relative to OG-1 or Raumid. Despite the "hi-U" effect of
- 25 excess apparent ²⁰⁶Pb being present in the Raumid sample, there is no evidence of metamictization. The absence of a "high-U effect" in the Pleistocene Bishop Tuff, combined with the presence of a "high-U effect" and the Δ 274 and Δ 268 anomalies in the Eocene Raumid zircons with relatively low levels of Raman broadening, suggests that the Δ 274 anomaly is a more sensitive indicator of a high-U effect than the 1005 cm⁻¹ Raman peak width, and that the radiation dose in the zircon required to trigger the "hi-U effect" is relatively small.
- 30

20

There is some debate as to whether or not the zircon self-annealing temperature is at the ~200°C He closure temperature (Weber et al., 1997), or up in the Greenschist facies around the biotite closure temperature (Pidgeon, 2014). However, for the Temora and OG1 results described here, this is irrelevant. The Biotite Ar closure time of the Middledale Gabbro (host of the Temora zircons) cannot be older than the crystallization age of 417 Ma (Black et al. 2004). The Ar-in-biotite closure

- 35 temperature for the Owen's Gully Diorite (OG1) cannot be younger than the He age presented here. So just like the He age, the biotite Ar age of OG1 must be significantly older than that of Temora. Further investigation of the Raman behaviour of Temora zircons would be a good idea, to ascertain if this particular grain was an outlier, or if there is a non-radiation component of peak broadening.
- 40 In terms of radiation damage, A Bishop Tuff zircon would have one decay chain per 1700 nm³, while a Raumid zircon of the same U concentration would have one per 3700 nm³. This is a similar dosage to a 200 ppm zircon of 1 Ga age, and such zircons show no trace of the high uranium effect.





Conclusions

When using an isotopically labelled oxygen primary beam, the ratio of beam/sample oxygen in oxide species can be used to predict the ratio of dioxide species. For UO and UO_2 in minerals of geochronological interest, these predictions are close in systems where SIMS geochronology works well, but show large deviations in systems such as baddeleyite dating, high

- 5 uranium zircon, and repetitive downhole measurements, where U-Pb geochronology has poor accuracy. This is consistent with the UO_x term in the U-Pb calibration being a monitor of oxygen availability for Pb⁺ ion production, as if various UO species can be shown to be out of disequilibrium with each other, then it is unlikely that any particular one will be useful for predicting the oxygen-based enhancement of Pb ion formation.
- 10 The excess in $\Delta 274$ appears to correlate with the high uranium effect better than crystal lattice damage, as determined by the broadening of the 1005cm⁻¹ Raman band. The cost of the ¹⁸O₂ gas (~US\$ 750/liter) might prevent routine use for analyzing zircons where the SIMS high-U effect might be present, but as the duoplasmatron uses only a few tens of milliliters per day, it is not inconceivable that this technique could be used on zircons with ages intermediate between the ~37 Ma Raumid and the 0.8 Ma Bishop Tuff, to ascertain when the high-U effect is initiated, and what other crystallographic features can be 15 associated with it.
- 15 associated with it.

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Tables

Table	1. Summary	of isotopc	logue	deviations	for anal	vtical	sessions
1 abie	1. Summary	of isotope	nogue	ueviations	101 anai	yucai	2022210112

	Sessio				UO/		U18O+/U16		$\Delta 272$		$\Delta 274$	
Experiment	n	sample	mineral	feature	U	±	0+	±	(%)	±%	%	± %
A: 16O	11005							1.00E-			-	
beam	6	Temora	zircon	reference	6.2	0.11	9.32E-04	04	8.6	15.2	1159	1732
A [.] 16O	11005							8 25E-			-	
beam	6	R33	zircon	reference	6.08	0.19	8.84E-04	05	14.2	14.8	1645	3219
A [.] 16O	11005							5 08E-			-	
beam	6	OG1	zircon	reference	6.08	0.14	9.14E-04	0.002	19	12	1052	1792
A: 16O	11005	Phalabow	baddelevi					1 28E-				
beam	7	ra	te	reference	3.49	0.24	9.35E-04	04	5.9	12.7	48.6	2396
	11006											
B: Std	1	Temora	zircon	reference	5.38	0.06	1.00	0.01	-1.9	0.7	1.2	1.5
	11006											
B: Std	1	R33	zircon	reference	5.37	0.05	1.00	0.02	-1.8	1.7	0.9	1.5
	11006											-
B: Std	6	Temora	zircon	reference	5.4	0.07	1.00	0.02	-1.1	1.0	2.2	1.4
	11006											
B: Std	6	R33	zircon	reference	5.39	0.06	1.00	0.01	-1.6	0.9	1.5	1.4
2.010	11009		2.10011	1010101100	0.00	0.00		0.01		0.0		
B [.] Std	8	Temora	zircon	reference	5 33	0 11	1 02	0.01	-1 1	0.8	15	10
2.010	11000	romora	2.10011	1010101100	0.00	0		0.01		0.0		
B. Std	8	R33	zircon	reference	5 35	0.12	1 02	0.02	-14	07	15	11
D. 010	11000	1100	20000	1010101100	0.00	0.12	1.02	0.02	1.4	0.7	1.0	
B. Std	8	Can	zircon	unknown	5 46	0.18	1 02	0.03	-15	04	15	07
2.00	11000	cun	2.10011		0.40	0.10	1.02	0.00	1.0	0.1	1.5	0.7
B: Std	80011 8	M735	zircon	unknown	5.4	0.11	1.02	0.02	-0.9	0.7	1.6	1.3

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B: Std	11008 8	M750	zircon	unknown	5.35	0.09	1.02	0.01	-1.1	0.7	1.9	0.8
B: Std	11008 8	M736	zircon	unknown	5.36	0.11	1.02	0.02	-1.2	0.6	1.3	0.7
B: Std	11010 6	Temora	zircon	reference	6.3	0.14	1.01	0.01	-0.4	1.4	1.5	1.4
B: Std	13005 6	Temora	zircon	reference	6.16	0.46	1.09	0.03	-0.9	0.04	0.4	0.7
B: Std	13005 8	Temora	zircon	reference	6.46	0.09	1.03	0.02	-2.3	0.8	4.2	1.4
B: Std	13005 8	OG1	zircon	reference	6.67	0.21	1.02	0.03	-1.7	1.2	3.5	1.5
C: High U	11006 7	Temora	zircon	reference	5.76	0.02	0.98	0.02	-1.4	0.9	1.4	1.2
C: High U	11006 7	rh	zircon	all: average=48 68 ppm	5.83	0.21	0.96	0.02	-1.4	0.7	3.8	2.3
	11006			>2500ppm: average=56	5.00	0.00	0.00	0.00	4.5		4.0	.
	13002	rn 	zircon	60	5.82	0.23	0.96	0.02	-1.5	8.0	4.2	2.4
C: High U	8 13002	Temora	zircon	reference	6.46	0.09	1.03	0.02	-2.3	0.8	4.2	1.4
C: High U	8 13002	OG1	zircon	reference all: average=38	6.45	0.21	1.02	0.03	-1.7	1.2	3.5	1.5
C: High U	8	100	zircon	28 ppm >2500ppm:	6.40	0.27	1.00	0.05	-1.7	1.2	5.6	1.0
C: High U	13002 8	100	zircon	average=46 00	6.38	0.30	0.99	0.05	-1.3	0.7	5.6	1.2
C: High U	13002 8	119	zircon	all: average=63 76	6.63	0.19	1.03	0.03	-1.5	0.8	6.4	1.8
C: High U	13002 8	119	zircon	>2500ppm: 6968	6.57	0.25	1.01	0.03	-1.4	0.7	6.8	1.9
C: High U	13005 6	Temora	zircon	reference	6.24	0.46	1.09	0.03	-0.9	0.4	0.4	0.7
C: High U	13005 6	BT	zircon	all: average=25 11	6.37	0.29	1.07	0.03	-0.6	0.4	0.9	0.7
C: High U	13005 6	BT	zircon	>2500 ppm; average=29 52	6.37	0.31	1.07	0.03	-0.5	0.3	0.8	0.3
D: Baddeleyite	11006 0	Phalabow ra	baddeleyi te	reference	3.55	0.23	1.14	0.08	-13	2.3	0.5	2.8
D: Baddeleyite	11006 5	Phalabow ra	baddeleyi te	reference	3.43	0.24	1.11	0.15	- 11.3	3.8	1.0	3.9
D: Baddeleyite	11006 5	Kur	baddeleyi te	unknown	3.59	0.26	1.10	0.11	-12	2.7	-0.5	3.4
E: Impact energy	11009 8	Temora	zircon	15kV	5.15	0.12	0.99	0.01	-0.3	1.3	0.9	1.1
E: Impact energy	11009 9	Temora	zircon	12.5kV	5.16	0.05	1.00	0.01	-0.9	0.8	1.1	0.9
E: Impact energy	11010 1	Temora	zircon	5kV	7.19	0.14	1.16	0.90	0.9	0.8	2.5	1.2
E: Impact energy	11010 3	Temora	zircon	3kV	11.6 9	0.39	1.38	0.02	-0.4	3.1	0.2	8.0
E: Impact energy	11010 5	Temora	zircon	7.5kV	6.68	0.10	1.05	0.01	0.1	1.0	2.3	1.3
G: Monazite	11006 4	1409	monazite	reference	10.4 1	0.25	0.73	0.01	1.4	0.3	27	2.9
G: Monazite	11006 4	44069	monazite	reference	11.4 5	0.27	0.74	0.10	1.4	0.3	21	3.4





 11006
 11.1

 G: Monazite
 4
 8153 monazite
 reference
 2
 0.20
 0.74
 0.01
 2.0
 0.3
 25
 2.1

 Table 2: Complete list of isotopologue analyses: See electronic supplement





Table 3: Raman peak positions and widths at half height

				936		968 cm-		1001		Correcte	1050		1085		1110		114
Sample No.	Δ274	906 cm-1	FWHM	cm-1	FWHM	1	FWHM	cm-1	FWHM	d FWHM	cm-1	FWHM	cm-1	FWHM	cm-1	FWHM	cm
										_							
119C-02	9.3%	906.09	20.097	936.61	49.1277	968.449	12.4205	1001.1	14.4285	14.15	1050.09	32.3049	1085.85	17.4895	1109.83	30.1047	1143
119C-101	9.0%			929.68	46.3347	970.975	9.28378	1003.97	10.2128	9.81	1052.85	14.553	1086.68	14.9993	1111.5	27.1343	1145
119C-102	4.9%	919.579	43.139			974.486	5.87495	1007.79	11.186	10.82	1055.13	8.55725	1088.42	11.7994	1111.82	11.7222	1147
10012-01	7.5%			924.19	50	970.034	11.79	1003.53	17.05	16.81	1052.6	16.5492	1086.34	16.6387	1109.75	30.1011	1144
10012-02	6.0%					974.683	4.12456	1008.12	5.99615	5.29	1055.29	6.30735	1088.53	10.3381	1112.17	10.8124	1147
10012-03	5.3%					973.637	4.83455	1006.71	7.5837	7.04	1054.35	11.0909	1089.48	9.46699	1111.7	13.3114	114
10012-04	5.8%			926.78	47.6052	967.643	17.5074	1001.54	17.3563	17.12	1050.28	27.2656	1084.6	17.5387	1108.67	40.9032	1144
11912-03	9.2%	918.372	44.852			971.864	8.07466	1005.23	8.94675	8.49	1053.61	12.2088	1087.61	13.0064	1111.28	19.0282	1145
11913-01	6.4%	917.402	50			971.96	9.29099	1005.52	9.10216	8.65	1052.8	15.414	1086.54	15.2361	1111.15	27.2963	1144
11913-02	9.3%			937.38	50	968.95	10.1773	1001.81	15.1778	14.91	1050.9	29.7652	1086	17.1007	1109.92	30.418	1143
OG1C-01	4.7%	907.656	20.437			973.62	6.49937	1007.02	10.6665	10.28	1054.64	9.90155	1087.73	12.1064	1112.03	16.2253	1146
TEMC-01	1.1%					968.464	9.15696	1000.74	14.5862	14.31	1052.65	6.30873	1086.59	11.8758	1109.86	24.4392	1144
TEMC-01A	1.1%			937.38	50			998.923	32.8284	32.71							

Table 4: Uranium-Thorium-Samarium/Helium dating results

Samp code	le	²³² Th	±	²³⁸ U	±	¹⁴⁷ Sm	±	He	±	He atoms/µm ³	TAU	Th/U	Raw age	±1σ	Ft	Cor. age	±1σ
		(ng)	(%)	(ng)	(%)	(ng)	(%)	(ncc)	(%)		(%)		(Ma)	(Ma)		(Ma)	(Ma)
OGC	-1																
OGC	а	0.483	1.4	0.778	1.9	0.006	7.6	77.50	0.7	1.3E+06	1.8	0.62	667.8	11.8	0.84	794.4	42.1
OGC	b	0.958	2.0	1.797	2.4	0.007	12.8	181.77	0.7	2.7E+06	2.2	0.53	688.0	15.2	0.84	815.5	44.6
OGC	С	0.565	1.4	1.724	1.9	0.007	10.0	124.64	0.7	6.5E+06	1.9	0.33	523.2	10.1	0.77	677.5	36.3
OGC	d	0.553	1.4	1.030	1.9	0.005	13.4	107.03	0.7	1.5E+06	1.8	0.53	704.7	12.8	0.85	832.9	44.3
OGC	е	0.568	1.4	0.980	1.9	0.006	13.3	93.32	0.7	2.0E+06	1.8	0.58	645.2	11.6	0.83	777.8	41.3
OGC	f	1.745	2.0	3.194	2.4	0.040	1.9	259.06	0.7	6.5E+06	2.2	0.54	558.9	12.4	0.81	688.1	37.6
																766	

Weighted average ± 95% conf. interval

755 ± 71 Ma



Ма



Temora 2

Weigh	Weighted average ± 95% conf. interval														323 ± 4	3	
TEM	f	0.310	1.5	0.804	1.9	0.003	23.4	28.41	0.7	7.2E+05	1.9	0.38	260.1	4.9	0.83	314.5	16.8
TEM	е	0.566	1.4	1.411	1.9	0.006	14.8	59.55	0.7	9.9E+05	1.8	0.40	307.9	5.7	0.83	370.6	19.8
TEM	d	0.807	2.0	1.942	2.4	0.004	17.8	83.60	0.7	9.9E+05	2.3	0.41	313.1	7.2	0.86	362.6	20.0
TEM	С	1.017	1.4	1.733	1.9	0.004	15.7	86.34	0.7	1.4E+06	1.8	0.58	348.5	6.3	0.79	443.7*	23.6
TEM	b	1.092	1.4	2.080	1.9	0.003	13.7	60.94	0.7	2.2E+06	1.8	0.52	210.4	3.8	0.73	287.9	15.3
TEM	а	0.959	1.4	0.972	1.9	0.004	13.7	36.68	0.7	9.3E+05	1.7	0.98	246.5	4.2	0.79	313.8	16.6

Ft - alpha recoil correction factor after Farley et al. (1996) * Outlier identified based on the corresponding U-Pb age





Figures

Figure 1: Plot of $U^{18}O/U^{16}O$ vs. Total UO ($U^{16}O + U^{18}O$) / U for various target minerals. Monazite sample identifications are given in the text. Two Kohler aperture sizes were used in baddeleyite analyses.

Figure 2: $\Delta 272$ vs $\Delta 274$ plots for zircon analyses under standard operating conditions for SHRIMP geochronology.

5 **Figure 3:** A,B,C: $\Delta 272$ vs $\Delta 274$ plots for analyses of high uranium zircons of three different ages. D, E, F: Apparent ²⁰⁶Pb/²³⁸U ratio vs $\Delta 274$, color coded for U content, for high uranium zircons of three different ages.

Figure 4: $\Delta 272$ vs $\Delta 274$ plots for Badelleyite. **A:** four oriented megacrysts with repeated measurements on each. **B:** randomly oriented unknowns.

Figure 5: Δ272 vs Δ274 plots for zircon analyses at 15-3 kV primary energies. Repeated analyses in the same sputter crater are lighter colors. Color coding by impact energy is the same as for previous figures. Add 680V for impact energy.

Figure 6: A: $\Delta 272$ vs $\Delta 274$ plots for multiple zircon analyses down the same hole under a variety of primary acceleration energies. B: U¹⁸O/U¹⁶O vs calibration constant on a scan-by-scan basis for three down hole analyses. Grey ellipses are singe scan data for individual, non-repeated analyses.

15 **Figure 7:** Raman peak position vs peak width at half height for Raumid zircons and reference zircons OG1 and Temora.

Figure 8: A: $\Delta 272$ vs $\Delta 274$ plot for randomly oriented baddeleyite, with predicted trends for unreactive molecule ejection shown. Note the unreacted molecule ejection well in excess of 10% is required to explain isotopologue deviations of this magnitude.

20 **Figure 9:** A: Δ274 vs Δ268 plot for Raumid zircon. This plot shows that the dioxide disequilibrium is the same for

Th and U oxides, so that the metal phase is unlikely to have much of a role in isotopologue formation.

Figure 10: Comparison of $\Delta 274$ vs Raman peak width for selected ~37Ma Raumid zircon grains. Standard reference zircons OG1 and Temora are shown for comparison.

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