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# Evaluating the robustness of a consensus $^{238}\text{U}/^{235}\text{U}$ value for U-Pb geochronology

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## Abstract

U-Pb geochronology requires knowledge of a precise and accurate value for the  $^{238}\text{U}/^{235}\text{U}$  ratio of any mineral or material being dated by this method. It is now well established that the long-accepted value of 137.88 is not representative of most terrestrial materials and that the ratio is variant both between and within samples. As most samples used for chronology have insufficient amounts of U to determine a precise isotopic composition, the U-Pb geochronology community has informally adopted the recommended value of  $137.818 \pm 0.045$  based on a single data set of 44 zircons by Hiess et al. (2012). To evaluate the robustness of this value and the true range of U isotopic compositions in U-bearing minerals, we have measured the U isotopic composition of 28 bulk zircon samples as well as several co-existing accessory minerals from rocks with a wide range of ages and geographical distributions. The  $^{238}\text{U}/^{235}\text{U}$  ratio of  $137.817 \pm 0.031$  represents the mid-point value of our data with an uncertainty that includes all 28 zircon populations analyzed and their respective uncertainties. This value is indistinguishable from the previously recommended value but with a smaller uncertainty that may reflect the refined analytical methods employed in our study. This result provides confidence to the U-Pb geochronology community that the value recommended by Hiess et al. (2012) is appropriate and that their stated uncertainty appears to be conservative. We find variability in the  $^{238}\text{U}/^{235}\text{U}$  ratio of coexisting phases within single samples of up to 2.9  $\epsilon$ -units (parts per 10,000). In addition, our range of U isotopic compositions for zircon is heavier than that reported for bulk continental crust in general and most granitoid intrusive rocks specifically. We attribute these observations to differences in the coordination environment of U in zircon and other U-bearing phases. With the amount of zircon formed in magmatic systems limited by the abundance of Zr, we estimate that the majority of U in granitoid rocks must reside in other phases with a bulk isotopic composition that represents a lighter complement to that of zircon.

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**Keywords:** Uranium isotopes; Recommended value; Zircon; U-Pb geochronology

## 1. INTRODUCTION

Zircon ( $\text{ZrSiO}_4$ ) is the most widely used mineral for studying the timing and tempo of geological processes throughout Earth's history by exploiting the dual decay of  $^{238}\text{U}$  and  $^{235}\text{U}$  to  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$ , respectively. It is a

robust accessory mineral that is nearly ubiquitous in the felsic crust of Earth making it applicable to a wide range of geological settings and processes. The utility of zircon as a U-Pb chronometer is based on the capacity of zircon to include the large +4 charged U parent at the 100 s of parts per million (ppm) level while effectively excluding the +2 charged Pb daughter. The calculation of U-Pb ages by conventional isotope dilution techniques and Pb-Pb ages by any technique requires knowledge of the  $^{238}\text{U}/^{235}\text{U}$

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ratio, which was previously assumed to be invariant at 137.88 (Steiger and Jäger, 1977). This assumption was based on theoretical arguments (e.g. Bigeleisen and Mayer, 1947) that the relative mass difference between  $^{238}\text{U}$  and  $^{235}\text{U}$  was too small for measurable mass-dependent isotopic fractionation to occur by any natural process. Attempts to find measurable U isotopic variations in naturally occurring materials were unsuccessful (Chen and Wasserburg, 1980; 1981; Stirling et al., 2005; 2006) until improvements in mass spectrometry led to studies that documented U isotopic variation in terrestrial settings (e.g. Stirling et al., 2007; Weyer et al., 2008; Andersen et al., 2014; Dahl et al., 2014; Tissot and Dauphas, 2015). Studies have also found that significant U isotopic variations occur in some meteoritic materials (e.g. Stirling et al., 2006; Amelin et al., 2010; Brennecka et al., 2010; Bouvier et al., 2011; Brennecka and Wadhwa, 2012; Connelly et al., 2012; Andersen et al., 2015; Goldmann et al., 2015; Tissot et al., 2016).

Uranium isotopic variations in natural materials are attributed to fractionation caused by the nuclear field shift effect principally during oxidation-reduction reactions that result in U(IV) and U(VI) states (Schauble, 2007) but also during change in the coordination environment for U without redox changes (Brennecka et al., 2011; Tissot et al., 2017). Although the documentation of variations in the  $^{238}\text{U}/^{235}\text{U}$  ratio make clear that the assumption of a fixed standard value is not fully correct, it is not currently possible to precisely measure the isotopic composition of the U present in the small amounts of zircon typically used for modern U-Pb dating. Measuring U isotopic compositions of bulk zircon samples, Hiess et al. (2012) documented U isotopic variations of up to  $9.9 \epsilon^{238}\text{U}$  (parts per 10,000 variation of the  $^{238}\text{U}/^{235}\text{U}$  ratio) in zircon (excluding one extreme outlier of  $33.7 \epsilon$ ) and up to  $8.2 \epsilon$  in other U-bearing minerals (excluding two extreme samples of  $17.3$  and  $48.0 \epsilon$ ). Their average value for zircon requires adjustment of the calculated  $^{207}\text{Pb}/^{206}\text{Pb}$  age of up to approximately 1 Myr relative to the previously accepted value of 137.88. The value recommended by Hiess et al. (2012) is now widely used by geochronology laboratories worldwide without validation by a second study or any formal acceptance procedure.

The main aim of the present study is to further explore the  $^{238}\text{U}/^{235}\text{U}$  variability in zircons based on refined methods intended to reduce analytical scatter. This will expand the data set of  $^{238}\text{U}/^{235}\text{U}$  ratios for phases employed in U-Pb geochronology (mainly zircon but also apatite, monazite and garnet) to test the practicality of using a single U isotopic composition with an assigned uncertainty for all U-Pb zircon geochronology. A secondary goal is to further test the extent to which  $^{238}\text{U}/^{235}\text{U}$  variations occur in other phases in samples where multiple U-bearing phases are present. We also include tests of whether it is possible to induce  $^{238}\text{U}/^{235}\text{U}$  variability by altering a general procedure used during the dissolution, separation and analytical protocols. Finally, we consider the U isotopic composition of zircons in the context of the values reported for felsic continental crust.

## 1.1. The U-Pb system

The U-Pb system is a high-resolution chronometer that exploits the decay of two isotopes of U to two isotopes of Pb with distinct half-lives. In detail,  $^{235}\text{U}$  decays to  $^{207}\text{Pb}$  with a half-life of 0.703 Gyr whereas  $^{238}\text{U}$  decays to  $^{206}\text{Pb}$  with a half-life of 4.468 Gyr (Steiger and Jäger, 1977). Having two independent decay schemes permits testing whether a sample returns the same age for both schemes, which evaluates whether the sample avoided isotopic disturbances since its formation. U-Pb data for zircon is presented and assessed using a so-called Concordia plot with axes of  $^{207}\text{Pb}_r/^{235}\text{U}$  vs  $^{206}\text{Pb}_r/^{238}\text{U}$  where the subscript “r” refers to radiogenic Pb. For conventional isotope dilution methods using a purified  $^{235}\text{U}$  tracer, both the  $^{238}\text{U}$ - $^{206}\text{Pb}$  and  $^{235}\text{U}$ - $^{207}\text{Pb}$  ages require knowledge of the  $^{238}\text{U}/^{235}\text{U}$  ratio of the sample to calculate the amount of U in the zircon and, thus, the respective U/Pb ratios. For conventional isotope dilution method using a  $^{233}\text{U}$  and/or  $^{236}\text{U}$  tracer, only the  $^{235}\text{U}$ - $^{207}\text{Pb}$  age requires knowledge of the  $^{238}\text{U}/^{235}\text{U}$  ratio. The calculation of a  $^{207}\text{Pb}_r/^{206}\text{Pb}_r$  age by any method requires knowledge of the  $^{238}\text{U}/^{235}\text{U}$  ratio of the zircon to calculate an age from the decay equation:

$$\frac{^{207}\text{Pb}_r}{^{206}\text{Pb}_r} = \frac{^{235}\text{U}}{^{238}\text{U}} \left( \frac{e^{\lambda_1 t} - 1}{e^{\lambda_2 t} - 1} \right)$$

where  $\lambda_1$  and  $\lambda_2$  represent the decay constants of  $^{235}\text{U}$  and  $^{238}\text{U}$ , respectively. Collectively, this means that the  $^{238}\text{U}/^{235}\text{U}$  ratio is required to determine either one or both U-Pb ages and all Pb-Pb ages for high-precision conventional U-Pb geochronology.

The two isotopes of uranium decay to their respective stable Pb daughters through a series of  $\alpha$ - and  $\beta$ -decays. The emitted  $\alpha$ -particles damage the surrounding crystal structure, creating radiation damaged zones where Pb may be lost via diffusion. To minimize the effects of Pb loss through diffusion in radiation damaged zones, Mattinson (2005) presented a method of heat-treating zircons to thermally anneal less damaged zones coupled with the subsequent selective dissolution of those zones too damaged to be annealed by the heat treatment. This so-called “chemical abrasion” method has become a standard procedure in zircon geochronology. This method was used in the U isotopic measurement of zircons by Hiess et al. (2012) without directly comparing annealed and unannealed zircon fractions to evaluate whether there is any impact of this procedure on U isotopes.

## 2. PREVIOUS WORK

The evaluation of the variability of the  $^{238}\text{U}/^{235}\text{U}$  ratio of U-bearing phases used in U-Pb dating must be based on a wide range of samples with varying ages, petrogeneses and geological settings. Tissot and Dauphas (2015) presented a comprehensive study combined with data from literature to show the  $^{238}\text{U}/^{235}\text{U}$  variability for a wide range of terrestrial samples. This highlighted a variation of  $6.7 \epsilon^{238}\text{U}$  with discernible differences between the different sample types among the continental crustal samples.

Importantly, they reported identical average  $^{238}\text{U}/^{235}\text{U}$  values for continental crust, oceanic crust and the mantle of  $137.789 \pm 0.022$  with the exception of the top 500 m of oceanic crust that yields a value of  $137.806 \pm 0.022$ . These absolute estimates are adjusted relative to the standard CRM-145 with a reported ratio of  $137.829 \pm 0.022$  (Hiess et al., 2012) and the errors have been adjusted to include the uncertainty on the standard.

Hiess et al. (2012) performed the only study of zircon with additional analyses of apatite, titanite, uraninite, xenotime, baddeleyite and monazite to determine the variability of  $^{238}\text{U}/^{235}\text{U}$  ratios in these U-bearing phases. They recommended a  $^{238}\text{U}/^{235}\text{U}$  ratio of  $137.818 \pm 0.045$  to be used for all future U-Pb analyses, a ratio and uncertainty based on their main cluster of 44 of 45 analyses. The study also included the analyses of fractions of different mineral types from the same sample, showing resolvable  $^{238}\text{U}/^{235}\text{U}$  variations between different phases from the same sample.

### 3. METHODS

#### 3.1. General procedure

##### 3.1.1. Pre-processing

Most of the samples used in this study were originally processed U-Pb geochronology studies at The University of Texas at Austin, USA with several additional samples obtained from the Jack Satterly Laboratory at the University of Toronto, Canada (see Table S1 in Supplementary Information for sample descriptions). For zircon ages available but not previously published, the U-Pb methods are outlined in Appendix A. The mineral separates used for this study were obtained in the course of U-Pb geochronology studies using standard processing procedures. In all cases, the rocks were first crushed in a jaw crusher and then pulverised using a disc mill equipped with steel grinding plates. High-density minerals were isolated using a Wilfley™ Table, followed by the first density separation using the heavy liquid bromoform. Minerals denser than bromoform were separated according to their different magnetic properties using a Frantz™ Isodynamic Magnetic Separator. To isolate zircon and apatite, the least magnetic fraction from this step was then subjected to a second density separation using methylene iodide (MEI). The minerals denser than MEI were further separated according to their magnetic properties using a Frantz™ Isodynamic Magnetic Separator. This procedure produced relatively pure separates of zircon but included varying amounts of apatite (up to 50%) and lesser amounts of pyrite. Pyrite was dissolved from this fraction using warm (60 °C) 4 M  $\text{HNO}_3$  for approximately 20 min.

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.gca.2018.06.014>.

Zircon separates containing significant amounts of apatite were subjected to a small-scale heavy-liquid separation procedure using fresh MEI. The zircon and apatite fractions produced in this separation procedure, were inspected visually using a binocular microscope, and any other phases manually removed from the samples. Garnet and monazite were separated from other phases manually using a

binocular microscope from fractions that were already concentrated by a Frantz™ Isodynamic Magnetic Separator.

##### 3.1.2. Zircon annealing

The zircons were exposed to the chemical abrasion procedure (Mattinson, 2005), where they were heated in ceramic crucibles in a furnace at 900 °C for 3 days. The zircons were subsequently cleaned using distilled Milli-Q™ water and ultrasonification in an attempt to remove surficial contaminants, including organics from the heavy liquids. Following the annealing procedure, 130  $\mu\text{l}$  of 28 M HF were added to each sample and heated to 180 °C in a Parr™ pressure bomb for 12 h. The residual zircon was then cleaned in 0.6 ml double-distilled 6 M HCl (at 120 °C for 30 min.), rinsed with distilled Milli-Q™ water and cleaned with 0.6 ml double-distilled 7 M  $\text{HNO}_3$  (at 120 °C for 2 h). For larger samples, the material dissolved during the annealing and subsequent cleaning procedure (leachate) was saved for later analysis. The samples were evaporated to dryness on a hotplate and weighed to determine the weight of both the sample and, by subtraction, the dissolved fraction. After the samples were cleaned with distilled Milli-Q™ water again, they were spiked with the mixed IRRM3636 tracer (Richter et al., 2008) and dissolved.

##### 3.1.3. Spiking and dissolution

Using either published U concentration data or analyses of a separate representative aliquot (+100 grains) of the sample (using the Thermo-Fisher Scientific X-Series 2™ Quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the Centre for Star and Planet Formation), the samples were spiked prior to dissolution with approximately 0.210 ng of  $^{233}\text{U}$  and  $^{236}\text{U}$  from the IRMM-3636 spike per ng of natural U in the sample. To get the required sub-epsilon precision on the U isotopic composition, the aim was to have at least 500 ng of natural U from each sample, so they could be measured multiple times by a Thermo-Fisher Neptune Plus™ multi-collector inductively-coupled-plasma mass spectrometer (MC-ICP-MS; see below) with a  $^{235}\text{U}$  signal intensity in excess of 125 mV.

For zircon dissolution, a 3:1 mixture of 28 M HF and 7 M  $\text{HNO}_3$  was added to each sample in 3 ml Savillex™ vials that were placed inside Parr™ pressure bombs in an oven at 210 °C for 5 days. After removal from the oven, the samples were evaporated to dryness on a hotplate at 115 °C before 6 M HCl was added and the closed beakers were left to flux on the hotplate at 125 °C for 24 h. All samples were inspected at this point with a binocular microscope to evaluate whether the zircons were fully dissolved. If not, the last step was repeated using 7 M  $\text{HNO}_3$  instead of 6 M HCl. This was repeated until the sample was fully dissolved, alternating between HCl and  $\text{HNO}_3$ . If still not completely dissolved after several cycles of this routine, a 3:1 mixture of 28 M HF and 7 M  $\text{HNO}_3$  was added, and they were placed inside a Parr™ pressure bomb again and the entire procedure was repeated until dissolved.

For apatite, monazite and garnet dissolution, the samples were pre-cleaned with distilled Milli-Q™ water before they were spiked with the  $^{233}\text{U}$ - $^{236}\text{U}$  IRMM-3636 tracer

and dissolved. Apatite and monazite were dissolved using 6 M HCl, on a hotplate at 120 °C. Garnet was dissolved by adding 0.5 ml 28 M HF and 7 M HNO<sub>3</sub> to the sample in a 3:1 mixture and left on a hotplate at 135 °C for 24 h. After drying down this solution, the sample was placed on a hotplate at 125 °C in 6 M HCl for a few hours or until complete dissolution as verified by inspection using a binocular microscope.

#### 3.1.4. Ion-exchange chromatography

Purification of U using ion-exchange chromatography was performed in the clean laboratories at the Centre for Star and Planet Formation at the Natural History Museum of Denmark, University of Copenhagen following a four-step method described in [Connelly et al. \(2012\)](#). The first two steps are identical and use Eichrom Technologies™ UTEVA resin in 2 ml BioRad™ columns. Pre-cleaned resin was transferred into the columns and further cleaned using 10 ml 7 M HNO<sub>3</sub>, 6 M HCl and 0.05 M HCl, repeated three times and subsequently conditioned with 5 ml of 7 M HNO<sub>3</sub>. The samples, dissolved in 7 M HNO<sub>3</sub>, were loaded onto the columns and settled onto the resin using 100 µl of 7 M HNO<sub>3</sub>, repeated three times. Three 10 ml aliquots of 3 M HNO<sub>3</sub> were added to wash most of the matrix elements off the column. By adding 3 ml 8 M HCl followed by 2 × 5 ml 5 M HCl, the Th was eluted from the resin into the same vials used to collect the matrix elements. U was eluted into a clean 23 ml Savillex™ PFA capsule using first 3 × 1 ml followed by 2 × 9 ml of 0.05 M HCl. The samples were dried down over night on a hotplate at 100 °C and subsequently brought up again in 1.5 ml 7 M HNO<sub>3</sub> and the whole procedure repeated using the same columns and resin. Following the second UTEVA™ step, the samples were dried down, dissolved in 7 M HNO<sub>3</sub> and left on the hotplate at 115 °C for ~10 h. To prepare for the next chemical separation step, the samples were dried down on a hotplate at 115 °C and dissolved in 1.5 ml of 8 M HCl.

The third step used Eichrom Technologies™ anion resin AG1-X8 in 200 µl heat-shrink Teflon™ columns. Pre-cleaned resin was transferred to columns and further cleaned three times using 4 ml 7 M HNO<sub>3</sub>, 8 M HCl and 0.05 M HCl. They were conditioned in 2 ml 8 M HCl and the samples loaded in the same acid. For washing out matrix elements, a series of washing steps were performed using 100 µl, 2 × 500 µl 8 M HCl; 3 × 50 µl, 2 × 300 µl 7 M HNO<sub>3</sub>; 3 × 50 µl, 1000 µl 6 M HCl; 600 µl 3 M HCl. U was eluted into a clean 15 ml Savillex™ PFA capsule using first 3 × 50 µl and then 2 × 4 ml 0.05 M HCl. The sample was dried down over night at 100 °C, 7 M HNO<sub>3</sub> was added and the sample left on hotplate for 10 hrs. Finally, it was dried down and 360 µl 6 M HCl added.

The last step in the procedure used Eichrom Technologies™ anion resin AG1-X8 in 120 µl heat-shrink Teflon™ columns with the intention to remove organic material inherited from previous chemistry steps. Pre-cleaned resin was transferred into the columns and further cleaned three times using 3 ml 7 M HNO<sub>3</sub>, 6 M HCl, 0.05 M HCl and H<sub>2</sub>O, conditioned, loaded, and washed (3 × 50 µl, 200 µl and 250 µl) using 6 M HCl. U was eluted into a clean

7 ml Savillex™ PFA capsule with 0.05 M HCl in volumes of 3 × 50 µl followed by 12 ml.

To ensure low levels of organics in the final U concentrate after the last chemistry step, the sample was first evaporated to dryness on a hotplate at 100 °C, 250 µl of concentrated HNO<sub>3</sub> added and left to flux for 48 h at 125 °C. 750 µl concentrated HCl was added to form Aqua Regia and the samples were left again at 125 °C for 48 h. The samples were then dried fully again before 75 µl of concentrated HNO<sub>3</sub> was added to convert to the nitric form. The samples were again evaporated to dryness at which point they were ready for analysis. The total procedural blank for our method is less than 10 pg, an amount that is inconsequential relative to the amounts of U analyzed in each sample.

#### 3.2. Mass spectrometry

Uranium isotopic measurements were performed on a Thermo-Fisher Neptune™ MC-ICP-MS at the Centre for Star and Planet Formation, Natural History Museum of Denmark, University of Copenhagen following the procedure of [Connelly et al. \(2012\)](#). For analyses, the samples were dissolved in a 2% HNO<sub>3</sub> solution that was introduced into the ionising plasma source using an Aridus II™ desolvating nebuliser at an approximate aspiration rate of 100 µl/min. The U isotopic measurements were acquired using four Faraday collectors: <sup>233</sup>U in the low-1 collector, <sup>235</sup>U in the axial collector, <sup>236</sup>U in high-1 collector and <sup>238</sup>U in the high-3 collector. All four Faraday collectors were connected to amplifiers with 10<sup>11</sup> Ω feedback resistors. Samples were analyzed with a minimum signal intensity of 125 mV of <sup>235</sup>U corresponding to 100–300 mV of <sup>233</sup>U and <sup>236</sup>U, depending on the sample to spike ratio. The MC-ICP-MS provided a sensitivity of approximately 0.8–1.0 V/ppb and samples were typically diluted to a concentration of 35–40 ppb. A single analysis consisted of a total of 834 s of data acquisition on both the baseline and the sample measurements. All analyses we performed on-peak using the normal sampler cone and H-skimmer cone configuration.

Full analyses were conducted by standard bracketing, where each sample measurement was bracketed by two measurements of the CRM-145 standard with the mixed <sup>233</sup>U-<sup>236</sup>U tracer IRMM3636 added so that the intensities of both the standard and tracer isotopes were matched to within 5% of the samples. Backgrounds were measured before every analysis of both standards and samples where the backgrounds were determined as a full analysis while aspirating the 2% HNO<sub>3</sub> solution used for the dilution of the standard and samples during that session. For the majority of samples, there was sufficient U in the sample for each standard-sample-standard set to be analyzed 5 times. For those samples with insufficient U for this full procedure, the samples were diluted to a concentration where the <sup>235</sup>U ion beam was approximately 125 mv and the sample was run as many times as the volume permitted by the uptake rate (see Table S2).

All data reduction was performed utilising the open source Iolite data reduction software ([Paton et al., 2011](#))

that is run within the Igor Pro™ software. Background intensities were interpolated using a smoothed cubic spline function, as were changes in mass bias over the course of the run. Iolite's smooth spline auto choice was used in all cases, which determines a theoretically optimal degree of smoothing based on variability in the reference standard throughout an analytical session, which typically corresponds to 24 h of continuous measurement without adjusting the instrument's tuning parameters. For each analysis, the mean and standard error of the measured ratios were calculated using a 2SD threshold to reject outliers.

### 3.3. Variations to the general procedure

Whereas natural variations in the U compositions demonstrably exist in nature (e.g. Stirling et al., 2007; Weyer et al., 2008; Amelin et al., 2010; Brennecke et al., 2010; Brennecke et al., 2011; Connelly et al., 2012; Hiess et al., 2012; Andersen et al., 2017; Tissot et al., 2017 for review), it is important to test whether analytical artefacts can be created by sample processing and/or during mass spectrometry. In this study, several different steps identified as potentially creating analytical artefacts are tested systematically with the measured U isotopic ratios of the modified routines compared to those of the full procedure described above.

#### 3.3.1. A reduced ion-exchange chromatography procedure

Given the possibility that small amounts of residual matrix elements or organics from the chemical purification may induce artificial  $^{238}\text{U}/^{235}\text{U}$  variability, a test was designed to determine whether multi-stage chemistries shown to be necessary in previous studies of more complex matrixes (Connelly et al., 2012; Bollard et al., 2017) is necessary to avoid interferences when analyzing U from zircon (Hiess et al., 2012 following Krogh, 1973). For this test, the protocols described in Connelly et al. (2012) and Hiess et al. (2012) are compared as they differ greatly in complexity. Hiess et al. (2012) used a single-step U-purification procedure using Eichrom Technologies™ anion resin AG1-X8. Their columns had resin beds 2 cm long by 0.5 cm wide with a volume of 0.4 ml. Pre-cleaned resin was transferred to the columns, cleaned further in 2 ml 6.2 M HCl and 2 ml H<sub>2</sub>O, and conditioned in 1 ml 3.1 M HCl. The samples were loaded and Zr and Pb were removed with 1 ml 3.1 M HCl and 1 ml 6.2 M HCl respectively. U was eluted in 1 ml H<sub>2</sub>O. The samples were dried down and organics removed using the same procedure as described above. All steps prior to and after the chemical separation procedure are identical to those described above for the general procedure.

#### 3.3.2. Late addition of the $^{233}\text{U}$ - $^{236}\text{U}$ tracer

A mixed, equal-atom  $^{233}\text{U}$ - $^{236}\text{U}$  tracer is added to samples and standards to track instrumental mass fractionation. Given the theoretical possibility of fractionating  $^{238}\text{U}$  from  $^{235}\text{U}$  during the digestion and purification procedure if there is less than 100% sample recovery, the tracer is normally added to the sample at the start of the dissolution procedure. Indeed, it has been

shown that  $^{238}\text{U}/^{235}\text{U}$  variability may be induced if the tracer is added to rock standards after the first HF-HNO<sub>3</sub> dissolution step (Stirling et al., 2005). We investigate the effects of the timing of tracer addition in zircon analyses, by comparing the  $^{238}\text{U}/^{235}\text{U}$  ratio produced by the general procedure where the tracer was added before dissolution with that of an aliquot of the same sample where the tracer was added after complete dissolution but before the U separation procedure.

#### 3.3.3. Comparing annealed vs. unannealed zircons

Mattinson (2005) showed that heating ancient zircons to ~900 °C causes zones with low radiation damage to recrystallize, whereas the volumes with extensive damage do not recrystallize and can be preferentially dissolved by HF acid. This “chemical abrasion” method has become the standard procedure for determining the U-Pb ages of zircons, with the result of returning more concordant U-Pb analyses by preferentially analyzing the most crystalline, and, therefore concordant, parts of the zircon. Hiess et al. (2012) followed that same chemical abrasion pre-treatment where the residue after a step of HF leaching is used to determine the U isotopic composition. Whereas our general procedure included this annealing step, we analyzed seven duplicates without the heat-treating procedure with the aim of assessing whether chemical abrasion has any impact on the U isotopic measurement. After heat-treating the samples, the U from both the annealed (residue) and unannealed (leachate) components were analyzed where there were sufficient amounts of U in the leachate.

## 4. RESULTS

### 4.1. External reproducibility

The external reproducibility of the analyses in this study is based on six analyses of the zircon reference material 91500 dissolved as a single bulk sample with the U purified using separate full chemistry procedures, as described above. We obtain an offset from CRM-145 of  $-0.22 \pm 0.24 \text{ } \epsilon^{238}\text{U}$  (2SD uncertainty), which corresponds to an absolute value of  $137.8259 \pm 0.0034$  ( $\pm 0.22 \text{ } \epsilon^{238}\text{U}$ ) using the U isotopic composition of CRM-145 recommended by Hiess et al. (2012) and adding their 2SD uncertainty in quadrature to the uncertainty for our six analyses (Table S3 and Fig. 1). For comparison, Hiess et al. (2012) presented an external reproducibility for their MC-ICMPS analyses of  $0.68 \text{ } \epsilon^{238}\text{U}$  (2SD) for repeated analyses of the pure U standard CRM112a ( $n = 29$ ) and  $0.78 \text{ } \epsilon^{238}\text{U}$  (2SD) for U separated from the uraninite reference material HU-1 ( $n = 18$ ). As such, the external reproducibility for our study based on repeat analyses of the zircon reference material 91500 is approximately 2.8 times better than the study by Hiess et al. (2012) where their reproducibility is based on either a pure U standard or an uraninite reference material. This difference mainly reflects the longer data acquisition times in our study, longer on-peak baselines and that each zircon reference material was analyzed five times for each reported ratio, as described in Section 3.2.

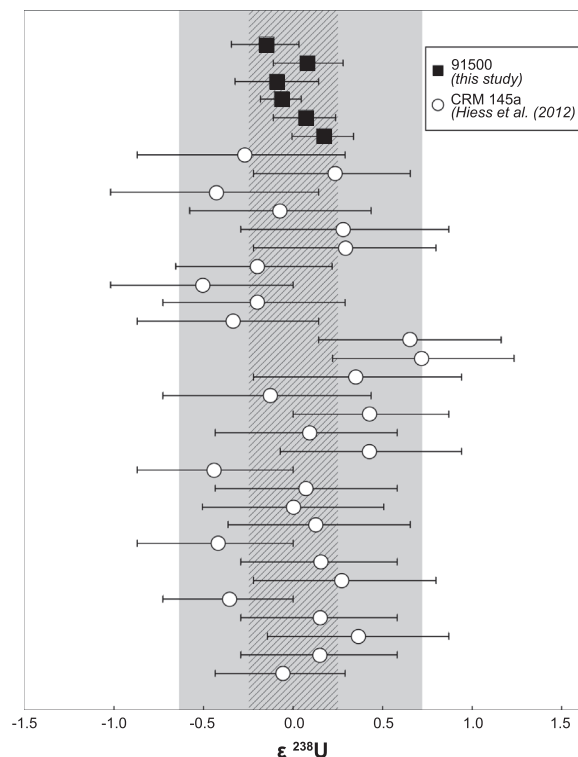


Fig. 1. Twenty-nine analyses of standard material CRM-145 presented by Hiess et al. (2012) and six analyses of the zircon reference material 91500 reported in this study. The data is illustrated as the  $\epsilon^{238}\text{U}$  deviation around the average value of the analyzed standard/reference material (CRM-145 or 91500). The error bars on individual analyzes reflect the 2SE error on each individual analysis. The gray band represents the 2SD variation of the analyses presented by Hiess et al. (2012) and the hatched band represents the 2SD variation of the measurements presented in this study.

#### 4.2. $^{238}\text{U}/^{235}\text{U}$ ratio of zircon

A set of 28 zircon samples was analyzed using the general procedure described in Section 3.1. The reported error for each individual analysis represents either the internal error (2SE) for an individual measurement or the external reproducibility of  $0.24 \epsilon^{238}\text{U}$  (2SD), whichever is larger. These uncertainties do not include the  $1.6 \epsilon^{238}\text{U}$  uncertainties on the IRMM 3636 tracer calibration or the standards that were used to calibrate this tracer. It is unnecessary to incorporate this uncertainty into our reported uncertainties because all laboratories reporting high precision  $^{238}\text{U}/^{235}\text{U}$  isotope ratios use this tracer solution. The results of the zircon analyses are reported in Fig. 2 and Table S2 and yield a mid-point value of  $-0.87 \pm 1.60 \epsilon^{238}\text{U}$  offset from the standard CRM-145 where the uncertainty reflects the full range of analyses including their respective uncertainties rather than 2SD. This ratio and uncertainty is based solely on all samples in this study produced by the general procedure.

To obtain an absolute U isotopic ratio for the zircons, we use the absolute value and uncertainty of the standard CRM-145 that was determined by Hiess et al. (2012) to be  $137.829 \pm 0.022 (\pm 1.6 \epsilon^{238}\text{U} \text{ units})$ . Using this frame

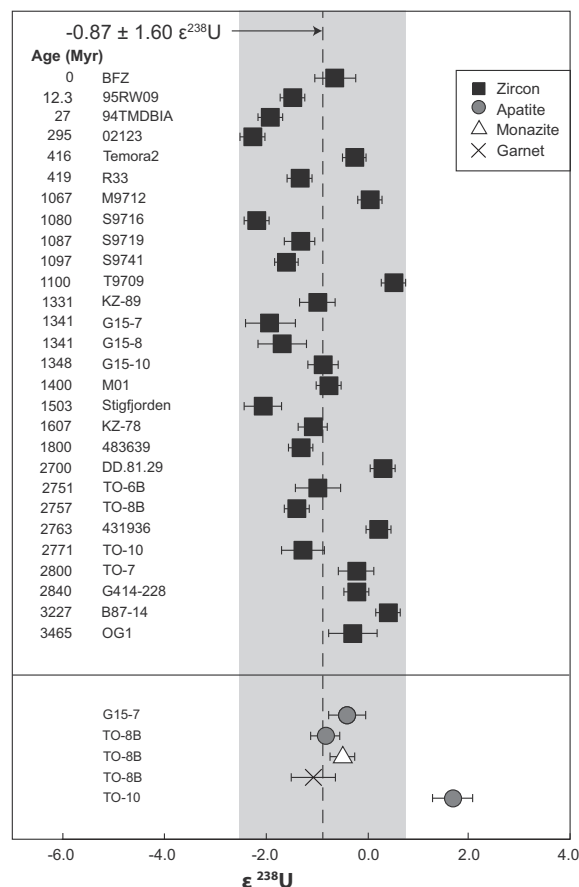


Fig. 2. Summary of all U-bearing minerals analyzed for their  $^{238}\text{U}/^{235}\text{U}$  ratios based on the general method, where the x-axis represents the offset in  $\epsilon$ -units from CRM-145. The dotted line represents the equally weighted mid-point value, the gray area represents the range of values and their respective uncertainties.

of reference, we obtain a mid-point value of  $137.817 \pm 0.031 (\pm 2.2 \epsilon^{238}\text{U} \text{ units})$  for the 28 zircon fractions, where the uncertainty of the standard has been added in quadrature with the full range of values around the mid-point value to derive a total absolute uncertainty.

#### 4.3. Testing for analytical bias

In our tests of whether the U purification methods of Connelly et al. (2012) and Hiess et al. (2012) return equivalent results, seven duplicate zircon fractions were processed by both methods. In all seven samples, the zircon fractions processed by the two different methods consistently return  $^{238}\text{U}/^{235}\text{U}$  ratios that are indistinguishable from each other (Fig. 3). Our standard procedure added the IRMM-3636 spike to the sample with the first dissolution step using HF and  $\text{HNO}_3$ . For seven replicate samples, we also added the  $^{233}\text{U}$ - $^{236}\text{U}$  IRMM-3636 isotopic double spike after the sample was dissolved but before the chemical purification of U. We find resolvable differences in the measured  $^{238}\text{U}/^{235}\text{U}$  ratios in two out of seven analyzed samples, with one late spiked fraction heavier than the early spiked fraction and one in the opposite direction (Fig. 4).

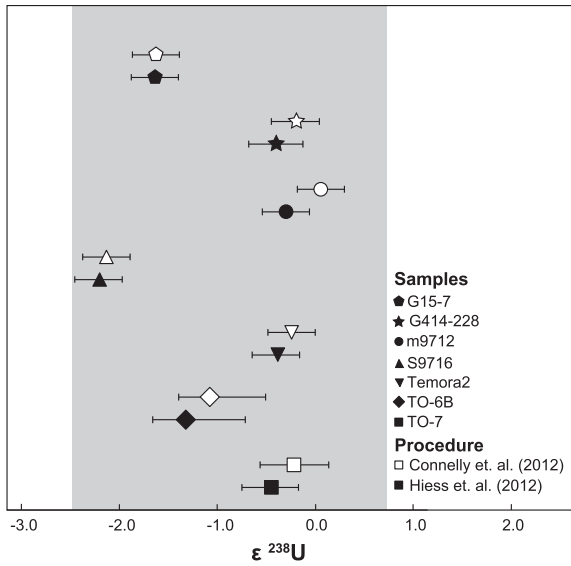


Fig. 3. The offset in  $\epsilon$ -units from CRM-145 for samples following two different ion-exchange procedures for separating U (Connolly et al., 2012; Hiess et al., 2012). The gray area represents the full range of zircon analyses and their respective uncertainties in this study that were prepared using the general method.

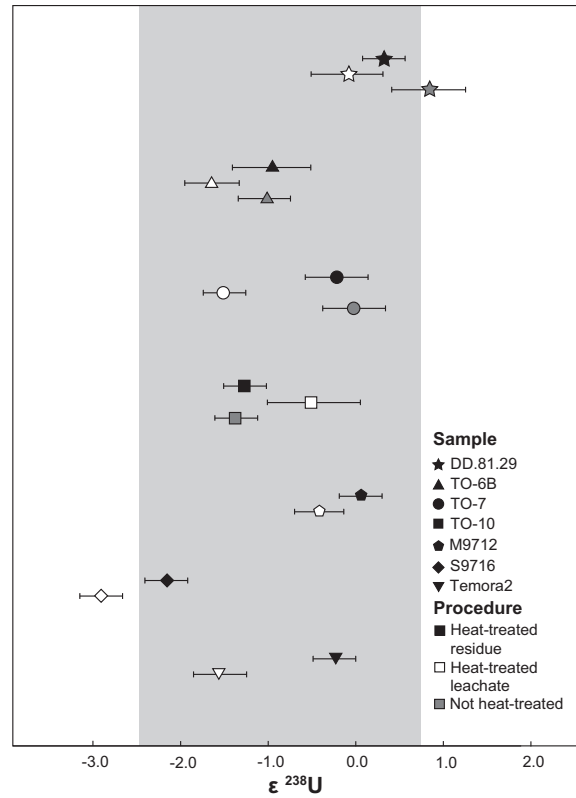


Fig. 5. The offset in  $\epsilon$ -units from CRM-145 for zircon fractions that have been heat-treated (both annealed residue and unannealed leachate) and replicate samples that were not heat-treated. The gray area represents the full range of zircon analyses and their respective uncertainties in this study that were prepared using the general method.

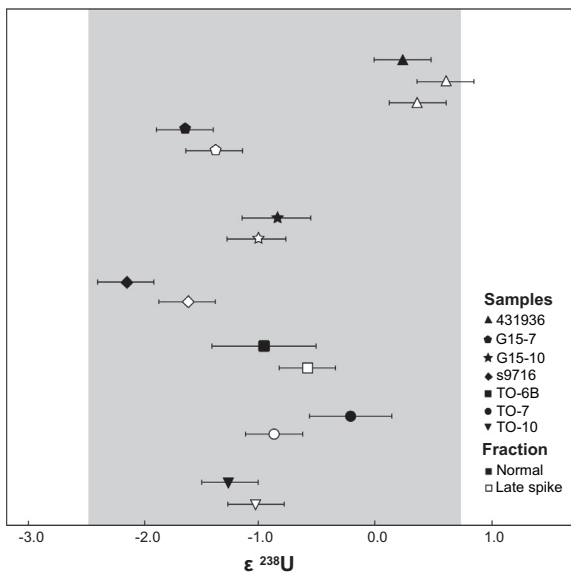


Fig. 4. The offset in  $\epsilon$ -units from CRM-145 for samples with tracer added before (Normal) and after (Late Spiking = LS) the first dissolution step. The gray area represents the full range of zircon analyses and their respective uncertainties in this study that were prepared using the general method.

Another part of the study exposed replicate fractions of zircons from four samples to two different procedures – one heat-treated with the thermal annealing method and one that was not thermally treated (NA) – thereby testing whether analyzing the residual component of annealed zircons returns a different U isotopic composition than an

unannealed duplicate. The leachates of these four heat-treated zircon fractions and an additional three fractions were also analyzed for comparison. The results (Fig. 5) show no difference between the fractions that were not heat-treated and the residues of the heat-treated fractions outside of the analytical uncertainty for the four samples tested. In comparing the leachates and residues from seven heat-treated samples, three overlap within their uncertainties, three leachates are isotopically lighter than the residues and one leachate is isotopically heavier than the residue.

#### 4.4. Multiple phases in same host rock

Three of the rocks used to obtain the zircon samples also yielded sufficient high-quality mineral separates to allow for the analyses of U isotopes in pure aliquots of apatite (3), monazite (1) and garnet (1) (Fig. 2). Of the three analyses of apatite, TO-10 shows the greatest deviation from its corresponding zircon with apatite being 2.95  $\epsilon$ -units heavier. The apatite from sample G15-7 is 1.26  $\epsilon$ -units heavier than the zircon from this sample. The U isotopic composition of apatite from TO-8B is marginally overlapping zircon from this sample, with apatite being on the heavier side. The U isotopic composition of monazite from TO-8B is heavier



than the corresponding zircon but overlaps that of apatite from this sample. Finally, the U isotopic composition of garnet from TO-8B overlaps all other phases from this sample (Fig. 2).

## 5. DISCUSSION

The U isotopic analyses of the residues of 28 annealed zircon separates that were spiked before the first dissolution step, processed using the full chemistry and analyzed by MC-ICP-MS yields a mid-point value that is offset from the CRM-145 bracketing standard by  $-0.87 \pm 1.60 \epsilon^{238}\text{U}$  where the uncertainty reflects the full range of values and their respective errors. Accepting  $137.829 \pm 0.022$  as the value for the  $^{238}\text{U}/^{235}\text{U}$  ratio of the standard (Hiess et al., 2012), we determine an absolute value and uncertainty of  $137.817 \pm 0.031 (\pm 2.2 \epsilon^{238}\text{U} \text{ units})$  where the uncertainty of this value incorporates the uncertainty of the standard

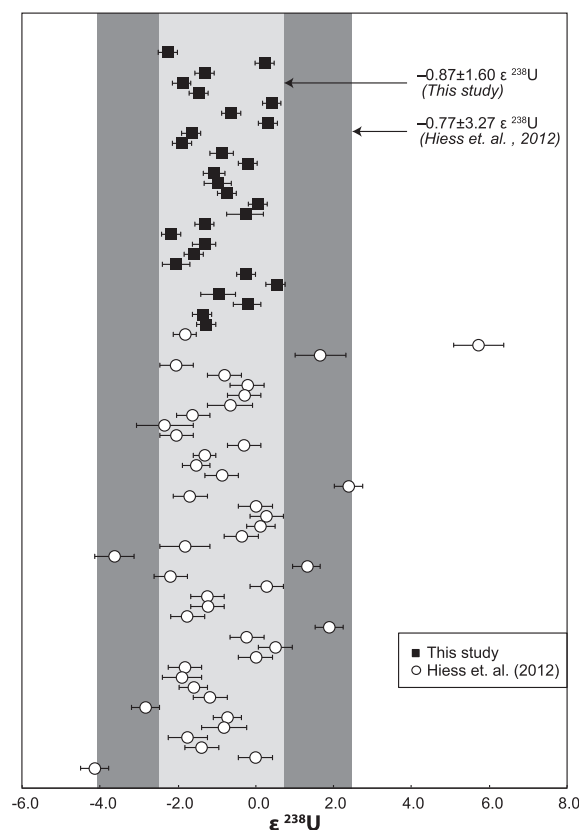


Fig. 6. Compilation of samples presented by Hiess et al. (2012) and this study where the x-axis represents the offset in  $\epsilon$ -units from CRM-145. The light gray band represents the mid-point value and full range of zircons analyzed in this project, namely  $-0.87 \pm 1.60 \epsilon^{238}\text{U}$  units. The dark shading shows the recommended average by Hiess et al. (2012) of  $-0.80 \pm 3.26 \epsilon^{238}\text{U}$  units. The uncertainties for each individual sample are the 2SE measured uncertainties or 2SD external reproducibility, whichever is larger. Converted into absolute  $^{238}\text{U}/^{235}\text{U}$  ratios based on the CRM-145 value from Hiess et al. (2012), the value presented in this study corresponds to a mid-point value of  $137.817 \pm 0.031$ , and the value presented by Hiess et al. (2012) to  $137.818 \pm 0.045$ , where the uncertainties on CRM-145 are added in quadrature to both values.

CRM-145 in quadrature. Hiess et al. (2012) reported an average value of  $137.818 \pm 0.045 (\pm 3.27 \epsilon^{238}\text{U} \text{ units})$  for their main cluster of 44 of 45 zircon, a value that is indistinguishable from the mid-point value obtained in our study but with a larger ( $\sim 30\%$ ) uncertainty (Fig. 6). In addition to reproducing their average value for zircon, our new data also confirm that real variations outside of analytical uncertainties exist between different zircon populations from different rock types.

Despite the overall agreement between the two laboratories for U isotopic composition of zircons from a wide range of rock types, only two of three reference samples analyzed in both studies overlap (Fig. 7). The difference between the results for Temora II is well outside of the uncertainties and may be due to sample inhomogeneity or a measurement bias for this one reference material between the two laboratories.

### 5.1. Testing for bias in the U isotope analysis of zircon

We evaluated the effects of altering the U purification method, adding the tracer late in the digestion process and the chemical abrasion method on the measured isotopic composition of U from zircon.

Recognizing the risk of interference-based  $^{238}\text{U}/^{235}\text{U}$  variability, we elected to use a four-step chemistry adapted from Connelly et al. (2012) for our standard procedure. The seven samples processed using the single step chemistry of Hiess et al. (2012) returned  $^{238}\text{U}/^{235}\text{U}$  ratios that matched those obtained by our standard procedure, indicating that both procedures can be used to purify U from the simple matrix elements of zircon for analyses by MC-ICP-MS.

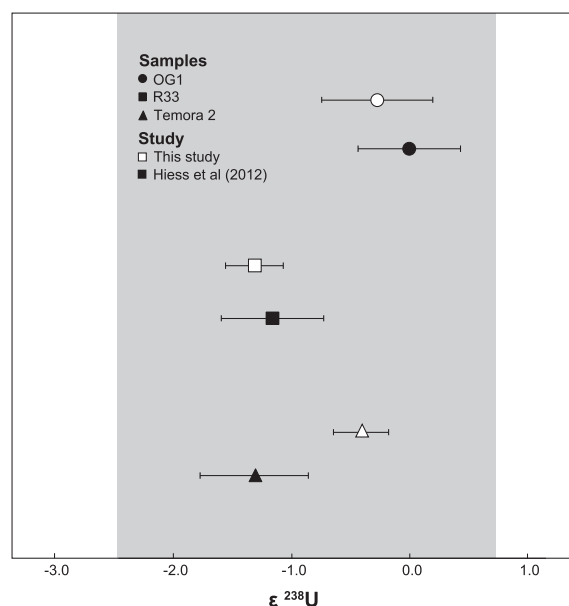


Fig. 7. Comparison of zircon reference samples analyzed in this study and by Hiess et al. (2012) where the x-axis represents the offset in  $\epsilon$ -units from CRM-145. Error bars represent 2SE internal errors or 2SD external reproducibility, whichever is larger.

Following up on previous reports of  $^{238}\text{U}/^{235}\text{U}$  variability caused by adding the tracer late in the dissolution procedure (Stirling et al., 2005), we tested the effect of adding the tracer after the dissolution was complete but before chemical purification of U for seven samples. The effect of adding the  $^{233}\text{U}$ - $^{236}\text{U}$  IRMM-3636 tracer after complete dissolution resulted in different  $^{238}\text{U}/^{235}\text{U}$  ratios for two of seven pairs of zircon fractions, with no consistent direction for the offsets (Fig. 4). Assuming that complete homogenization was accomplished between the sample and tracer by leaving it on a hotplate for several hours, there is no clear explanation for the observed differences in the measured isotopic ratios. However, the results reinforce the conclusion of Stirling et al. (2005) that the tracer used to correct for isotopic fractionation must be added to the sample with the first acids used to dissolve the zircon.

There were no differences outside of uncertainties for the U isotope ratios of zircons that were not heat treated relative to the residues (after leaching) of annealed zircons (Fig. 5). This assures that the process of annealing and partial dissolution of a residue has no measureable effect on the U isotopic ratio and that future studies of zircons could use either method. However, the analyses of the unannealed portions of heat-treated zircon (leachates) resulted in three of seven samples with U isotopic compositions that were isotopically lighter than the residual component, three that were overlapping and one that was heavier. As such, it is possible that three of the seven samples record the preferential entrainment of  $^{235}\text{U}$  in the partially dissolved components without leaving a measurable excess of  $^{238}\text{U}$  in the residual component. A more likely alternative explanation for the offsets may lie in the late spiking that is necessary when removing the leachates from the residues given the documentation here that late spiking (after dissolution but before chemical purification) creates analytical artifacts.

Of the three alterations to our standard method, we find that only the measurement of the leachates of annealed zircons and the late addition of the tracer solution (after dissolution but before chemical purification) have the potential to produce artifacts in the  $^{238}\text{U}/^{235}\text{U}$  ratio for zircons.

## 5.2. The validity of a consensus $^{238}\text{U}/^{235}\text{U}$ value and uncertainty for zircon

The low amount of U in zircon prohibits determining the U isotopic composition of individual zircons in the course of routine single zircon U-Pb geochronology. Instead, a value must be assigned for age calculations requiring this parameter to include an uncertainty that will be incorporated into the error assigned to the final age. With two studies now documenting real variations in the U isotopic composition of zircon outside of analytical uncertainties, the question arises as to the most appropriate method to assign an uncertainty on a parameter that does not have a single value.

In standard statistical treatments of numerical data sets, attempts to define a representative value and uncertainty typically evaluates the standard deviation of analyses

around the mean where the uncertainty incorporates 95% of measured values at the two-sigma level. For the purpose of defining a  $^{238}\text{U}/^{235}\text{U}$  value for zircon, a more appropriate approach would be to report the full range of measured compositions (excluding any clear outliers) so that the resulting uncertainties on calculated ages reflect approximately 100% of the known U isotopic variation. Using this approach, the U isotopic composition for zircon from this study is adequately represented by  $137.817 \pm 0.031$ , a value and uncertainty that covers the full range of measured compositions and their individual uncertainties.

The value of  $137.818 \pm 0.045$  recommended by Hiess et al. (2012) is indistinguishable from our value but with a slightly larger uncertainty. Their value represents a maximum likelihood estimate of 44 of 45 zircon analyses assuming an approximately Gaussian distribution and accounting for overdispersion according to Vermeesch (2010). As such, their recommended value does not include the full range of their main cluster of 44 of 45 analyses and their individual uncertainties so that the assigned error to a zircon age related to the U isotopic composition would underestimate the full possible range predicted by their values.

Whether the greater variation of isotopic composition of zircon in Hiess et al. (2012) is significant may be assessed in three ways. First, we note that eight of 44 analyses used by Hiess et al. (2012) to define their preferred value fall outside the range defined by the present study, a value corresponding to approximately 18% of their analyses. This would predict that approximately five analyses in our study of 28 zircons should exhibit a similar spread of values as Hiess et al. (2012). That such analyses are absent may indicate that this larger spread of values in Hiess et al. (2012) represents greater analytical scatter than is accounted for by their reported uncertainties and external reproducibility assessed by analyzing a pure U standard rather than a zircon reference material multiple times.

To assess this possibility further, the second approach examines the external reproducibility as determined by the dispersion of standard data analyzed in the two studies. Hiess et al. (2012) analyzed the pure U standard CRM-145 in the course of their study and found dispersion corresponding to a 2SD uncertainty of  $\pm 0.68 \epsilon^{238}\text{U}$  for MC-ICPMS analyses ( $n = 29$ ). They also measured the uraninite reference material HU-1 and determined dispersion corresponding to a 2SD uncertainty of  $0.78 \epsilon^{238}\text{U}$  by MC-ICPMS analyses ( $n = 18$ ). In this study, we analyzed six individually chemically-processed aliquots of the zircon reference material 91500 and found a dispersion corresponding to a 2SD of  $\pm 0.24 \epsilon^{238}\text{U}$  (Table S3 and Fig. 1). We recognize that there are fewer analyses of reference materials in our study but we note that the standard deviation about the mean of any random six analyses of CRM-112a with the MC-ICPMS by Hiess et al. (2012) hovers around  $\pm 0.68 \epsilon^{238}\text{U}$ . As such, the ratios of the estimated external reproducibility for the two studies is approximately 2.8, a value very similar to the ratio of the full spread in the zircon analyses in the two studies ( $4.86 \epsilon^{238}\text{U}/1.67 \epsilon^{238}\text{U} = 2.9$ , excluding one point from Hiess et al. (2012) that is effectively ignored in their error analyses). Given this coincidence, we infer that the greater variation in the zircon

analyses reported by [Hiess et al. \(2012\)](#) may be in part related to the lower reproducibility of individual analyses. If this were proven to be correct, it would indicate that the variability for zircons may be lower than that estimated by [Hiess et al. \(2012\)](#).

Thirdly, we note that only two of three zircon reference samples analyzed in both studies have returned overlapping values (R33 and OG1) whereas the offsets from CRM-145 reported for Temora II lie outside of their analytical uncertainties ([Fig. 7](#)). Assuming that this sample is homogeneous on a bulk scale, this requires that the analyses from at least one of the two studies is incorrect or that the uncertainties of at least one laboratory are underestimated.

As discussed above, there are several lines of evidence to suggest there may be greater analytical dispersion in the data presented by [Hiess et al. \(2012\)](#) than in the data set presented in this study. Unfortunately, the true external reproducibility for U in zircon is difficult to assess for [Hiess et al. \(2012\)](#) as they did not produce replicate analyses of a zircon reference material. The tighter cluster of 28 analyses in our study may reflect the longer counting times on peaks, longer on peak background measurements and bracketing every analysis by standards. Despite these differences in methods, our study confirms the average value of [Hiess et al. \(2012\)](#) so that only the uncertainty assigned to this value may need refinement.

Given that many U-Pb laboratories already use the value and uncertainty of  $137.818 \pm 0.045$  from [Hiess et al. \(2012\)](#) and the full range of our data lies within their value, the most conservative approach would be to continue using their value with the added confidence our study provides. Further studies using refined methods may ultimately support our narrower range of U isotopic compositions of zircon so that a smaller uncertainty may be assigned to this value. Finally, accepting as valid the one analysis from [Hiess et al. \(2012\)](#) that is 33  $\epsilon$ -units heavier than their recommended value indicates that there are zircon populations that lie outside this range and that the errors on the ages for these zircons will be incorrect based on a standard value and uncertainty. The fact that only 1 in 72 zircons analyzed to date returned such anomalous U isotopic compositions provides some assurance that such cases may be rare.

### 5.3. Consequences for the uncertainties on U-Pb and Pb-Pb ages

Implementation of a new  $^{238}\text{U}/^{235}\text{U}$  value of  $137.818 \pm 0.045$  has had direct consequences for both the absolute U-Pb and Pb-Pb ages and their uncertainties. The impact of the new value on the absolute age has been reviewed thoroughly by [Hiess et al. \(2012\)](#) and [Tissot and Dauphas \(2015\)](#), so it is not reviewed again here. Instead, we focus on the additional uncertainties on the final age calculation that results from the U isotopic composition of a zircon population. The full uncertainty on the U isotopic composition of  $\pm 0.045$  translates into age uncertainties of 0.77–0.58 Myr for  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of 0–4.56 Ga, respectively, 0–242 kyr for  $^{206}\text{Pb}/^{238}\text{U}$  ages when using a  $^{235}\text{U}$  spike for ages of 0–4.56 Ga, respectively and 0–19.6 kyr for  $^{207}\text{Pb}/^{235}\text{U}$  ages, respectively. These uncertainties are

best added in quadrature to other known contributions to the errors on final ages. If the results from our study are proven to be more representative of the full range of U isotopic compositions for zircon, these uncertainties are reduced by approximately 27%.

### 5.4. Isotopic composition of other U-bearing minerals existing with zircon

The U isotopic compositions of minerals other than zircon were measured in three samples where resolvable differences relative to the paired zircon are reported in all three. Sample TO-10 shows the largest offset, with apatite being  $2.95 \pm 0.59$   $\epsilon$ -units heavier than zircon. In this sample of an Archean orthogneiss from northern Labrador, the zircon returned a concordant age of 2771 Ma that was assumed to reflect the primary igneous crystallization age of this rock ([Connelly, 2001](#)). The apatite is not dated but is presumed to be part of the Archean metamorphic assemblage and, thus, not necessarily a cogenetic phase with the igneous zircon or in isotopic equilibrium with the zircon. The significantly heavier signature of the apatite suggests that the U available during metamorphism may have been different from the original igneous system as recorded by the zircon and that metamorphism occurred as an open system.

Sample TO-8B is also an orthogneiss from northern Labrador but it represents an Archean granitoid rock that was (re)metamorphosed during the Paleoproterozoic. Zircon in this sample first crystallized at 2757 Ma but significant amounts of Pb was lost during metamorphism at 1811 Ma. Monazite and garnet are both dated to be Paleoproterozoic phases and the apatite is also assumed to be a metamorphic phase given the complete recrystallization of this rock save the primary zircon. All three metamorphic phases have indistinguishable U isotopic compositions that are  $0.53 \pm 0.24$  (apatite),  $0.89 \pm 0.24$  (monazite) and  $0.33 \pm 0.24$  (garnet)  $\epsilon$ -units heavier than zircon. Since all are metamorphic phases and not necessarily in equilibrium with zircon, some or all of the U in these phases may have been added during open system metamorphism. As the only major, rock-forming mineral analyzed for U, garnet overlaps zircon and apatite but is slightly lighter than monazite.

Sample G15-7 is a 1341 Ma pristine leucogabbro from the Nain Plutonic Suite of Labrador where all phases are igneous and, therefore, presumed to be co-genetic ([Ryan et al., 2017](#)). The apatite from this sample is  $1.26 \pm 0.53$   $\epsilon$ -units heavier than the zircon, despite the two minerals incorporating U(IV) and having crystallized from a single magma. These results suggest either that the two minerals crystallized at different times as the U isotopic composition was changing in an evolving magma or that the coordination environments for U in these two minerals are different.

The U isotopic variations observed for different phases within a single sample is consistent with [Hiess et al. \(2012\)](#) who reported an offset of  $2.25 \pm 0.62$   $\epsilon$ -units between zircon and apatite from a pristine igneous sample (Mud Tank carbonatite). Collectively, the limited high-precision U isotopic data from different phases in single samples of continental crustal rocks show that there are

significant variations that must reflect fractionation by some mechanism at high temperatures associated with igneous and, perhaps, metamorphic systems.

### 5.5. Uranium isotopic composition of zircon relative to continental crust

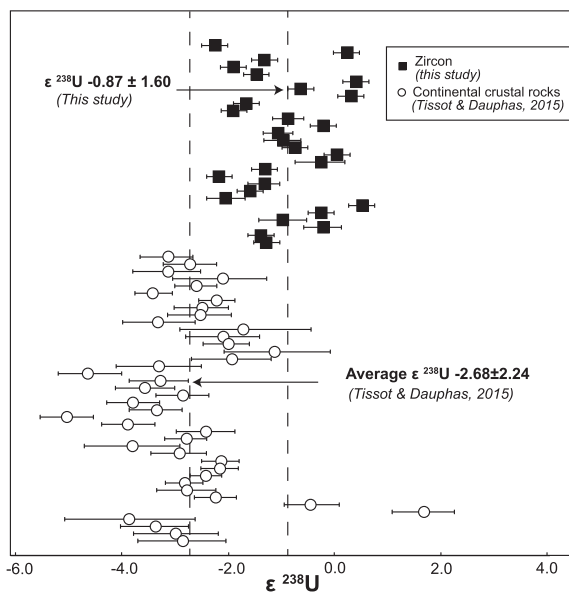
The average U isotopic composition of continental crust has recently been estimated by [Tissot and Dauphas \(2015\)](#) to be  $-2.9 \pm 0.3 \text{ } \epsilon$ -units relative to CRM-145 ([Fig. 8](#)). This estimate is based on a distribution model of continental crustal rock types in combination with weighed means of multiple U isotopic measurements of each rock type (see [Tissot and Dauphas, 2015](#) for compilation of U isotopic data). This value agrees with those proposed by [Kaltenbach \(2012;  \$-3.0 \pm 0.6 \text{ } \epsilon\$   \$^{238}\text{U}\$ \)](#) and [Goldmann et al. \(2015;  \$-3.0 \pm 0.5 \text{ } \epsilon\$   \$^{238}\text{U}\$ \)](#). In addition, [Telus et al. \(2012\)](#) has shown that granitoids including I-type, S-type and A-type granites all cluster between  $-4.0$  and  $-2.0 \text{ } \epsilon$   $^{238}\text{U}$  relative to CRM-145. Given the similarity of the U isotopic composition of most rock types in the model, the average value is not very sensitive to any single assumption in the model or U isotopic measurement of any one rock type. As such, it is a rather robust estimate that is indistinguishable from estimates of the U isotopic composition of the mantle ( $-2.9 \pm 0.2 \text{ } \epsilon$   $^{238}\text{U}$ ) and bulk earth ( $-2.9 \pm 0.2 \text{ } \epsilon$   $^{238}\text{U}$ ) by [Tissot and Dauphas \(2015\)](#).

The range of U isotopic compositions of zircon from this study is  $-0.87 \pm 1.60 \text{ } \epsilon$   $^{238}\text{U}$ , a value that lies mainly outside the estimate for continental crust estimate above ([Fig. 8](#)) and from all the granitoids rocks measured in [Telus et al. \(2012\)](#). Even though the average value with its uncertainty marginally overlaps the average value for continental crust, the majority of the individual analyses are distinctly heavier than the U isotopic composition of the

continental crust ([Fig. 8](#)). Since conventional equilibrium mass dependent isotopic fractionation based on the difference of zero-point energy between molecules depends on the relative mass difference between the isotopes, it is not expected to be significant for heavy elements such as U ([Schauble, 2004](#)). The nuclear field shift (NFS; [Bigeisen, 1996](#)) effect that influences the minimum point energy of molecules may lead to isotopic fractionation of heavy elements ([Schauble, 2007; Abe et al., 2008; Moynier et al., 2013](#)). Therefore, NFS must be predominantly responsible for the U isotopic offset between zircon formed in a crystallizing magma and zircon-bearing rocks of the continental crust.

Since the oxygen fugacity of magmatic systems is not high enough to form significant amounts of U(VI) ([Halse, 2014](#)), NFS related U(IV)/U(VI) fractionation seems unlikely to account for the U isotopic offset of zircon relative to continental crust. Instead, the U isotopic fractionation must be controlled by the difference in coordination environment of U between zircon and the parental magma. This mechanism has been recently proposed in high temperature magmatic systems to explain the evolution of a progressively crystallizing magma ocean on the angrite parent body ([Tissot et al., 2017](#)). In this case, a total variation of approximately 2  $\epsilon$ -units have been reported, a magnitude comparable to the offset between zircons and continental crust. As such, we suggest that the offset in U isotopic composition between zircon and bulk continental crust reflects a coordination environment in zircon that favors  $^{238}\text{U}$  relative to the parental magma.

The incorporation of isotopically heavy U in zircon predicts that there must be a complementary lighter component to satisfy the mass balance where the magnitude of the offset depends on the amount of U in zircon. To assess the amount of U incorporated in zircon in the granitoid rocks of the continental crust, we use a bulk crustal concentration of  $\sim 200$  ppm for Zr ([Rudnick and Gao, 2003](#)) and assume that all Zr is in zircon. This last assumption will provide a maximum estimate for the amount of zircon in continental crust. With Zr comprising 63% of the mass of zircon, this corresponds to zircon contents of 0.032% in the continental crust. If we assign an average U concentration in zircon of 350 ppm ([Wang et al., 2011](#)), then our estimate of the amount of U contained in zircon corresponds to only 112 ppb of the 1500 ppb U in continental crust. In other words, only 7.5% of continental crust U is stored in zircon. This requires that the remaining  $>90\%$  of U present in rocks comprising granitoid rocks of the continental crust must be harbored in other phases, including major, rock-forming phases. The relatively small amount of U in zircon with a modest offset in isotopic composition from the parental magma, suggests that bulk isotopic composition of U not bound in zircon may not be very different from the bulk rock value. Whether other phases may have U isotopic compositions with larger offsets from the bulk rock than zircon, either lighter or heavier, will depend on the coordination environment of U in these phases relative to the parental magma. Defining the full extent of possible U isotopic compositions in minerals in continental crustal rocks will require a future study and the separation and



**Fig. 8.** Comparison of the continental crustal rocks reported by [Tissot & Dauphas \(2015\)](#) and the zircons analyzed in this study (see [Table S4](#)).

analyses of all U-bearing phases within single samples as well as spectroscopic studies of the coordination of U in these phases.

## 6. CONCLUSIONS

The analyses of 28 zircon fractions from diverse rock types by MC-ICP-MS yields an absolute mid-point  $^{238}\text{U}/^{235}\text{U}$  ratio of  $137.817 \pm 0.031$  ( $\pm 2.2 \text{ } \epsilon$   $^{238}\text{U}$ ) relative to the CRM-145 standard value used in [Hiess et al. \(2012\)](#). Our uncertainty includes the full range of the 28 zircon fractions and their uncertainties. This value is identical to the value of [Hiess et al. \(2012\)](#) for their main cluster of 44 zircons, but with an improved uncertainty that may be related to the improved reproducibility of our refined methods. The confirmation of their value with lower variability provides assurance that their recommended value currently used in many U-Pb laboratories is accurate and that their uncertainty may be conservative. The uncertainty of  $2.3 \text{ } \epsilon$   $^{238}\text{U}$ -units on the  $^{238}\text{U}/^{235}\text{U}$  ratio translates into an uncertainty on  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of 0.57 Myr for 100 Ma zircons and 0.35 Myr for 4500 Ma zircons, which must be added to the other sources of uncertainty in quadrature. The uncertainties on the U-Pb ages are significantly smaller. Unlike uncertainties on decay constants that are only important when comparing to other radiometric systems, the uncertainty on the  $^{238}\text{U}/^{235}\text{U}$  ratio is an intrinsic property of all U-Pb and Pb-Pb ages that depend on this parameter.

We also find that other phases coexisting with zircon have distinct U isotopic compositions, implying that the bulk rock composition is also distinct from zircon. At least one of the coexisting phases with a distinct U isotopic composition formed from the same magma as zircon. These observations collectively imply that the zircon does not simply inherit the U isotopic composition of the parental magma but that high temperature fractionation is an important process. In addition, the average isotopic composition of U in zircon is isotopically heavier than estimates of the average value for bulk continental crust in general and granitic rocks more specifically. We attribute this offset to the different coordination environment in zircon relative to the parental magma, where the heavier  $^{238}\text{U}$  isotope is preferentially accommodated in zircon.

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## APPENDIX A. U-PB METHODS

Rock samples were crushed to mineral size under clean conditions using a jaw crusher and disc pulverizer, and minerals were separated using a Wilfley table, disposable sieves, heavy liquids and a Frantz magnetic separator. Zircons

were characterized using a binocular reflected-light microscope, transmitted light petrographic microscope and a scanning cathodoluminescence imaging system on a JEOL 730 scanning electron microscope.

Multiple or single grains of each population were selected for U-Pb analysis on the basis of optical and magnetic properties to ensure that only the highest quality grains were analyzed. All mineral fractions analyzed were strongly abraded ([Krogh, 1982](#)), subsequently re-evaluated optically and then washed successively in distilled 4 M  $\text{HNO}_3$ , water and acetone. They were loaded dry into Teflon™ capsules with a mixed  $^{205}\text{Pb}/^{235}\text{U}$  isotopic tracer solution and dissolved with HF and  $\text{HNO}_3$ . Chemical separation of U and Pb from zircon using 0.055 ml columns (after [Krogh, 1973](#)) resulted in a total Pb procedural blank of approximately 1 pg over the period of analyses. The U procedural blank is estimated to be 0.25 pg. Pb and U were loaded together with silica gel ([Gerstenberger and Haase, 1997](#)) and phosphoric acid onto an outgassed filament of zone-refined rhenium ribbon and analyzed on a multi-collector MAT 261 thermal ionization mass spectrometer, either operating in static mode (with  $^{204}\text{Pb}$  measured in the axial secondary electron multiplier (SEM) – ion counting system) or dynamic mode with all masses measured sequentially by the SEM – ion counting system. Ages were calculated using decay constants of [Jaffey et al. \(1971\)](#). Errors on isotopic ratios were calculated by propagating uncertainties in measurement of isotopic ratios, fractionation and amount of blank. Results are reported in Table S5 with  $2\sigma$  errors.

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