



Metrology and traceability of U–Pb isotope dilution geochronology (EARTHTIME Tracer Calibration Part I)

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Abstract

Mixed ^{235}U – ^{233}U – ^{205}Pb (^{202}Pb) tracers for U–Pb isotope-dilution isotope ratio mass spectrometry have been prepared under the auspices of the EARTHTIME Initiative. The methods and results for the preparation and calibration of the U/Pb ratio and isotopic abundances are given, and the various sources of uncertainty are discussed and quantified. The accuracy of the EARTHTIME U–Pb tracer isotopic composition can be traced back to SI units via a series of assay and isotopic composition reference materials combined with the experiments described herein. The parameters used in calculating U/Pb ratios (and inferentially U–Pb dates) have correlated uncertainties that result in a total uncertainty contribution to $^{206}\text{Pb}/^{238}\text{U}$ dates of $\pm < 0.03\%$ (95% confidence). For suitable terrestrial materials such as zircon, when other sources of uncertainty have been minimised (e.g., open-system behaviour, $^{238}\text{U}/^{235}\text{U}$ variation, intermediate daughter product disequilibrium, common Pb, etc.) the U–Pb tracer calibration uncertainty is a limiting factor in the accuracy of U–Pb geochronology – but less so than the uncertainty in the ^{238}U and ^{235}U decay constants (± 0.11 and 0.14% 2σ). The calibration approach of the mixed EARTHTIME ^{235}U – ^{233}U – ^{205}Pb (^{202}Pb) tracers, in addition to updated values for reference materials (e.g., mixed gravimetric reference solutions), and parameters (e.g., Pb reference material assay), can be applied to other laboratory-specific U–Pb tracers and will facilitate the generation of accurate and directly inter-comparable U–Pb data.

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1. INTRODUCTION

The U–Pb method is the most widely used long-lived isotope chronometer for age determination of rocks and minerals (see [Mattinson, 2013](#) and [Schoene, 2014](#) for recent reviews). It is applicable to materials from less than 1 million years old (e.g., [Richards et al., 1998](#)) to the age of the solar system (e.g., [Amelin et al., 2002](#)). This is in part a result of the dual decay of ^{238}U and ^{235}U , which aids evaluation of closed-system behaviour, the precision to which

the U decay constants have been determined (± 0.11 and 0.14% 2σ for $\lambda^{238}\text{U}$ and $\lambda^{235}\text{U}$ respectively; [Jaffey et al., 1971](#); [Mattinson, 2010](#)), and the occurrence of minerals that preferentially incorporate U over Pb during crystallisation (e.g., zircon, xenotime etc.).

Calculation of a U–Pb date requires determination of a U/Pb ratio. However, the relative U and Pb concentrations cannot be accurately determined via a direct isotope ratio mass spectrometry (IRMS) measurement. This is due to variability in ionisation of the two elements and the difficulty in quantifying the element/mass bias. Two approaches have been developed to determine U/Pb ratios via IRMS. The first is known as isotope dilution (ID) and employs a

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mixture of isotopically enriched ‘synthetic’ tracer isotopes (Stracke et al., 2014, and references therein). In U–Pb geochronology, these are typically $^{235}\text{U} \pm ^{233}\text{U} \pm ^{236}\text{U}$ and $^{205}\text{Pb} \pm ^{202}\text{Pb}$, which, when added to the sample allow determination of the concentration and isotopic composition of both U and Pb via two separate (Pb and U) IRMS measurements, determining the U/Pb ratio of the sample relative to the U/Pb ratio of the tracer. In this way, the accuracy of the U/Pb ratio of the tracer directly controls the accuracy of the U/Pb ratio of the sample, and inferentially the age. The second approach is termed ‘sample-standard bracketing’ and is used where the U/Pb ratio for a sample is measured interspersed with analyses of a reference material of ‘known’ U/Pb ratio, such that it is possible to approximate the elemental bias for the unknown samples via quantification of elemental bias determined on the interspersed reference materials (e.g., Williams, 1998). For this approach, the composition of the reference materials must be known via ID-IRMS such that the instrumental mass/elemental bias can be quantified and transferred to the ‘unknowns’. For example, microbeam U–Pb methods, such as secondary ionisation mass spectrometry and laser-ablation ICP-MS (Kosler and Sylvester, 2003), rely on a sample-standard bracketing approach to derive the accuracy of the U/Pb determinations. Isotope dilution isotope ratio mass spectrometry (ID-IRMS), with IRMS achieved via either thermal or plasma source mass spectrometry (TIMS and ICP-MS respectively), has been and still remains the most accurate technique for determining U/Pb and Pb/Pb ratios used to calculate dates given suitable materials for analyses (Schoene et al., 2013; Stracke et al., 2014).

Calibration of the U/Pb ratio of a mixed U–Pb tracer is achieved by combining a quantity of the tracer with a mixed U–Pb gravimetric reference solution that has a known U/Pb ratio. Gravimetric reference solutions are prepared by weighing and then dissolving high-purity U and Pb metals, whose isotopic composition is known with a quantified uncertainty, so that the U/Pb ratio of the gravimetric solution is known via weighing. Gravimetric U and Pb reference materials do not contain synthetic isotopes (e.g., ^{205}Pb , ^{233}U) and, therefore, the concentration of such tracer isotopes can be determined relative to the ‘gravimetric’ isotopes (i.e., ^{206}Pb , ^{238}U) via mass spectrometry.

Following the gravimetric calibration scheme outlined above the accuracy of the U–Pb system can be directly traceable to the SI system of units (De Bièvre et al., 2011) (Fig. 1). Traceability is critical for quantifying the accuracy of absolute U/Pb geochronology and comparing U/Pb dates with other isotope dating systems, whose ages are determined using an independent set of experiments (e.g., $^{40}\text{Ar}/^{39}\text{Ar}$) or using numerical models of solar system orbital dynamics (i.e., astrochronology). Decay constants for several other isotopic systems have been calibrated with respect to, or informed by, the U–Pb system through ‘inter-calibration’ experiments as a means to augment first-principles counting or ingrowth experiments (e.g., Rb–Sr, Re–Os K–Ar, Lu–Hf; Nebel et al., 2011; Scherer et al., 2001; Selby et al., 2007; Renne et al., 2010). For these cases, the ability to trace the U–Pb system back to SI units means that these other decay

systems can also be traced back, within limits, through assumptions about the samples used for inter-calibration. For the U–Pb system, the same approach can be taken to inter-calibrate $^{238}\text{U}/^{206}\text{Pb}$ and $^{235}\text{U}/^{207}\text{Pb}$ dates (Mattinson, 2000, 2010; Schoene et al., 2006), for instance by re-determining the ^{235}U decay constant (relative to the ^{238}U decay constant), exploiting the closed-system U–Pb systematics of zircons and assumed equivalence of $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ dates. Similarly, estimates for the ^{234}U and ^{230}Th decay constants have been determined relative to the ^{238}U decay constant using isotope dilution analyses of closed system secular equilibrium materials using gravimetrically calibrated U–Th tracers (Cheng et al., 2013).

Another significant source of uncertainty comes from mass-dependent isotopic fractionation, especially during TIMS mass spectrometric analyses, which is the observation that lighter isotopes evaporate, ionise, and/or are detected preferentially over heavier isotopes to a degree that is roughly inversely proportional to their mass. In modern low-blank U–Pb ID-TIMS geochronology, the uncertainty contribution from the long-term reproducibility of this correction can contribute >50% of the analytical uncertainty in a U–Pb date (Schmitz and Schoene, 2007). A more precise correction for mass fractionation can be made utilising ‘double spike’ (DS) tracers, which are composed of two synthetic or artificially enriched isotopes of the same element (Dodson, 1963; Galer, 1999; Rudge et al., 2009). DS tracers allow for real-time fractionation correction and a significant reduction in the uncertainty in mass bias correction as a source of analytical uncertainty. For DS analyses, the difference between the measured ratio of these artificial isotopes and its known value is attributed to mass fractionation, and this correction is then applied to all other measured isotope ratios. For uranium isotope analyses for the purposes of isotope dilution U–Pb geochronology, ^{233}U – ^{235}U or ^{233}U – ^{236}U tracers (Roddick et al., 1987) are routinely employed, and less commonly ^{202}Pb – ^{205}Pb for lead isotope analyses (Todd et al., 1996), due to the rarity of purified ^{202}Pb and ^{205}Pb .

A variation of DS is to use highly-enriched isotopes that also occur naturally and have variable proportions in the samples. This approach commonly requires two IRMS measurements, one of the pure sample for isotopic composition (IC) and another with sample plus DS for ID and is therefore less ideal compared to DS with synthetic tracer isotopes, especially where sample size is limited (see Galer, 1999; Rudge et al., 2009, and references therein). Determining the absolute magnitude of mass fractionation requires knowledge of the absolute isotopic composition of the DS, which is achieved via calibration against reference materials of known isotopic composition.

The choice of DS ratio for uranium analyses depends on a number of factors (see discussion below). It is important to note the ^{233}U – ^{235}U DS employed in the EARTHTIME tracers described herein requires a priori knowledge of $^{238}\text{U}/^{235}\text{U}_{\text{sample}}$. Though the variance of this ratio has been shown to be relatively limited in high temperature crustal samples most commonly targeted for U–Pb geochronology, Hiess et al. (2012) demonstrated variability of $^{238}\text{U}/^{235}\text{U}_{\text{sample}}$ in early solar system samples (Brennecka

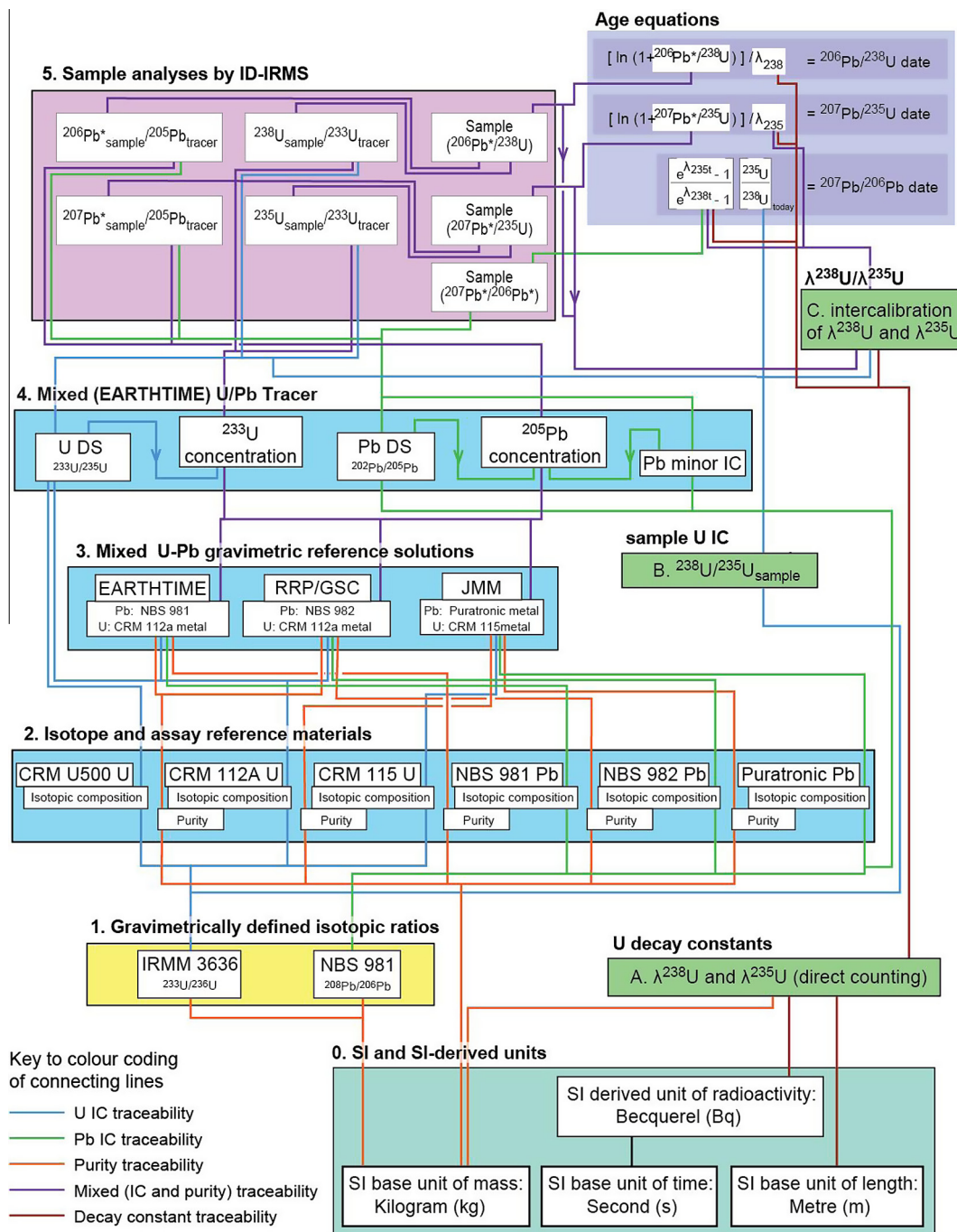


Fig. 1. Schematic showing the metrologic traceability of U–Pb ($^{238}\text{U}/^{206}\text{Pb}^*$, $^{235}\text{U}/^{207}\text{Pb}^*$ and $^{207}\text{Pb}^*/^{206}\text{Pb}^*$, *Denotes radiogenic Pb) dates to standard units via a series of linked experiments. The coloured boxes represent groups of similar experiments with white boxes contained within representing individual experiments (e.g. ^{233}U – ^{235}U double spike calibration). The individual experiments are linked (see text for discussion) and this is represented by the lines connecting the different boxes. The traceability of U–Pb dates goes from the top right (age equations) of the schematic to the bottom (standard units), such that information moves from the bottom to the top (except where indicated by arrows) along the traceability lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

et al., 2010) and low temperature systems (Stirling et al., 2007; Weyer et al., 2008; Murphy et al., 2014) require information from a ^{233}U – ^{235}U DS derived analyses for accurate high-precision U–Pb dating of such materials (see Section 4.2 for further discussion).

From the ~1980s, ID-TIMS U–Pb dating improved through increased availability of ^{205}Pb for use in mixed tracers (Parrish and Krogh, 1987), but no single mixed U–Pb tracer using this ^{205}Pb was widely available for use in many laboratories. As a result, most U–Pb ID-TIMS

laboratories utilised a U–Pb tracer that was/is limited in quantity and specific to a single laboratory. Therefore, comparison of U–Pb dates generated in different laboratories with different tracers required incorporation of the systematic errors related to the calibration of each tracer. Historically, few studies have incorporated this additional uncertainty into final published ages, and details of the tracer calibrations are infrequently documented. Where addressed in publications, most laboratories estimated that the U/Pb ratio of their tracer was known to about 0.1–0.3%, with uncertainty budgets likely dominated by parameters such as the purity of the Pb reference material (e.g., the purity of the NBS 981 and 982 Pb reference materials is certified to be >99.9%) and a lack of consideration of the covariance in the uncertainty model (McLean et al., 2015).

Through continued advances in high-precision U–Pb ID-TIMS geochronology, such as lower analytical blank (Mattinson, 1972; Krogh, 1973; Bowring et al., 2006), pre-treatment of accessory phases to minimise Pb loss (Krogh, 1982; Mattinson, 2005) and developments in mass spectrometry (e.g., improved ion counters and low-noise signal amplifiers), it is now routine for $^{206}\text{Pb}/^{238}\text{U}$ dates to have analytical uncertainties of <0.1% (e.g., Schoene et al., 2006; Mattinson, 2010). Therefore a 0.1–0.3% uncertainty in the U/Pb ratio of the tracer is a major component of the total U–Pb age uncertainty and an impediment to comparing and combining data from different laboratories at the level of precision typically reported. An inter-laboratory experiment carried out under the auspices of the EARTHTIME Initiative (Condon, 2005) confirmed the presence of >0.1% variation between laboratories that used different tracers, highlighting the importance of this issue and implying that a common well-calibrated mixed tracer could herald significant further improvement in inter-comparability of U–Pb dates.

To facilitate better inter-calibration within the U–Pb community and improve the accuracy and precision of U–Pb geochronology, we prepared and calibrated two mixed U–Pb tracers that are now being used widely, a $^{205}\text{Pb}\text{--}^{233}\text{U}\text{--}^{235}\text{U}$ tracer (ET535) and another that also contains ^{202}Pb (ET2535). In addition to the mixed U–Pb tracer, a new mixed U–Pb gravimetric solution has been prepared (ET) to complement two mixed U–Pb gravimetric solutions (JMM and RP) that have been available prior to this study and can be distributed freely in the future. In this paper, we attempt to emulate the effort made by Wasserburg et al. (1981) in their preparation and well-documented calibration of a Sm/Nd reference solution. We present the data and assumptions that go into this U/Pb tracer calibration and conclude that the U/Pb ratio of the tracer is known to <0.05% accuracy and is fully traceable to the SI base unit for mass (kg). Comparison of data generated in different laboratories using this tracer will not require propagation of uncertainty in the U/Pb ratio of the tracer, therefore effectively eliminating a major source of inter-laboratory bias. The traceability of this calibration is shown graphically in Fig. 1, as a series of connected experiments that permit tracing U–Pb dates produced by ID-IRMS back to SI units. In this figure, each element of the U–Pb calibration

system is represented by a box and within these boxes details of the materials and/or compositional elements are listed. An enhanced version of this figure with explanatory notes and compositional data is included as an online supplement.

In addition to providing details that relate to the calibration of the EARTHTIME tracers, much of the information in this paper relates to commonly used reference materials (e.g., purity of NBS 981, isotopic composition of CRM 115) that have been, and will continue to be used by laboratories to calibrate their own U–Pb tracers, extending the impact of this effort beyond dates generated using the EARTHTIME tracers. In a companion paper (McLean et al., 2015), we outline the algorithm(s) required for the transformation of the tracer calibration inputs and their associated uncertainties (e.g., metal purity, U and Pb isotopic composition) into the tracer parameters required for U–Pb ID-TIMS data reduction (Schmitz and Schoene, 2007; McLean et al., 2011).

2. EXPERIMENTAL

2.1. Preparation of the U/Pb tracers

High-purity U (^{235}U and ^{233}U) and Pb (^{205}Pb and ^{202}Pb) tracers were acquired from various sources within the isotope geoscience community in 2004 and 2005. Before opening any vials, all labware was thoroughly cleaned and Pb and U contributions from the labware were determined to be indistinguishable from the loading blank (<0.1 pg of each) prior to use. Several litres of double quartz distilled 1 M HNO_3 were prepared and checked for common Pb (Pb_c) levels, which were <0.1 pg/mL. The isotopes ^{205}Pb and ^{202}Pb were acquired in several aliquots, the isotopic compositions of which were checked prior to their combination into two separate ^{205}Pb and ^{202}Pb solutions. Both ^{202}Pb and ^{205}Pb were determined to be >99.8% isotopic purity. The mixed U–Pb tracers use ^{235}U and ^{233}U for the uranium double spike, for which high-purity ^{233}U and ^{235}U were obtained from The New Brunswick Laboratory (NBL) as CRM 135 (99.8% ^{235}U) and CRM 111-A (99.49% ^{233}U), in the form of high purity nitrate solutions.

The ^{235}U and ^{233}U were mixed with a ratio close to unity and subsequently cleaned of impurities (Pb and other interfering species) by loading onto a 1 mL column filled with UTEVA[®] resin in 4 M HNO_3 , then washed with several column volumes of 4 M HNO_3 prior to elution in 14 mL of 0.05 M HNO_3 . After this initial clean-up there was still a significant Pb blank of ca. 3 pg Pb_c per 1 μg U, therefore a second column clean-up was performed by retention of Pb on Eichrom anion exchange resin AG[®] 1-X8 in 1 M HBr. This resulted in a final Pb_c content of <0.1 pg per 1 μg U. Once the chemical purity of all Pb and U isotopes were verified, they were combined with a $^{235}\text{U}/^{205}\text{Pb}$ ratio of ca. 100. This ratio is approximately the same as the $^{238}\text{U}/^{206}\text{Pb}$ for Mesozoic age samples, but is also well suited to younger (Cenozoic) and older (Precambrian) samples (Schoene et al., 2006; Mattinson, 2010).

The choice of $^{233}\text{U}\text{--}^{235}\text{U}$ over $^{233}\text{U}\text{--}^{236}\text{U}$ for the U DS for use in the EARTHTIME tracers was made in 2005,

prior to publication of a number of studies that demonstrated measurable variation in $^{238}\text{U}/^{235}\text{U}$ in terrestrial materials (Stirling et al., 2007; Weyer et al., 2008; Hiess et al., 2012). Use of a ^{233}U – ^{235}U DS, like the tracers described here, requires a priori knowledge or assumption about the $^{238}\text{U}/^{235}\text{U}_{\text{sample}}$. A ^{233}U – ^{236}U DS would be preferable when a concurrent precise $^{238}\text{U}/^{235}\text{U}_{\text{sample}}$ determination is both possible and important to the precision and accuracy of the U–Pb study (see Section 4.2). However, the practical implications depend upon the type and amount of materials being analysed as well as the analytical methods employed. One such consideration is the accurate correction for isobaric interferences for U measured via TIMS as UO_2^+ ions (common in U–Pb dating of terrestrial materials due to higher ionization efficiency for low U loads) where the $\text{U}(^{18}\text{O}^{16}\text{O})$ and $\text{U}(^{16}\text{O}^{18}\text{O})$ molecules interfere with the U^{16}O_2 for an isotope of uranium that is two mass units higher (i.e., ^{233}U on ^{235}U and/or ^{236}U on ^{238}U). The impact of uncertainty in $^{18}\text{O}/^{16}\text{O}$ is variable between ^{233}U – ^{235}U or ^{233}U – ^{236}U double spikes (see Appendix A) with trade-offs existing for each DS depending on the $\text{U}_{\text{tracer}}/\text{U}_{\text{sample}}$ ratio and on the types of samples analysed (size, U/Pb ratio, expected $^{238}\text{U}/^{235}\text{U}$ variation). As the EARTHTIME tracers were developed predominantly for zircon U–Pb geochronology, where there is a trend towards decreasing sample size, a ^{233}U – ^{235}U DS was chosen due to the advantages over a ^{233}U – ^{236}U DS related to the uranium oxide correction uncertainty at lower $^{238}\text{U}_{\text{sample}}/^{233}\text{U}_{\text{tracer}}$ ratios (Fig. A1). Disadvantages related to the need for a priori information about $^{238}\text{U}/^{235}\text{U}_{\text{sample}}$ are discussed in Section 4.2.

Due to the limited amount of ^{202}Pb available, it was not possible to make a single ^{202}Pb – ^{205}Pb – ^{233}U – ^{235}U tracer, and therefore two separate tracers were prepared, one ^{205}Pb – ^{233}U – ^{235}U (ET535) and another ^{202}Pb – ^{205}Pb – ^{233}U – ^{235}U (ET2535). The latter is more restricted in supply and reserved for studies that benefit

from higher-accuracy Pb isotopic measurements (i.e., those where uncertainty in Pb mass fractionation is a dominating source of uncertainty). So that both the ET535 and ET2535 tracers have the same $\text{U}/^{205}\text{Pb}$ ratios and uranium isotopic compositions, the ET2535 tracer was prepared as a derivative of ET535 by addition of ^{202}Pb to an aliquot of ET535 to create a $^{202}\text{Pb}/^{205}\text{Pb}$ ratio close to unity.

2.2. Preparation of gravimetric reference solutions

Three mixed U–Pb gravimetric reference solutions were used for the calibration of the ET535 and ET2535 tracers. Details of each solution are given below and outlined in Table 1 and is shown in Fig. 1 Box 3. Two of these solutions (RP and JMM) were made prior to this experiment. The isotopic composition of each reference material has been (inter-)calibrated relative to key ratios from U and Pb isotopic reference materials, the $^{233}\text{U}/^{236}\text{U}$ of IRMM 3636 (Richter et al., 2008; Verbruggen et al., 2008) and the $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of NBS 981 (Catanzaro et al., 1968) that have been precisely determined by gravimetric calibration (Fig. 1, Boxes 1 and 2). Details of the isotopic (inter-)calibration are outlined in (McLean et al., 2015). Primary isotopic composition data are available for all certified reference materials employed in this study except for CRM 115. We have determined new $^{238}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ values for CRM 115 using the $^{233}\text{U}/^{236}\text{U}$ of IRMM 3636 to correct for mass fractionation using the approach outlined in Condon et al. (2010). Analyses of CRM 115 involved the use of virgin Teflon beakers for the mixing of CRM 115 and IRMM 3636 prior to analysis by TIMS on new zone refined Re filaments. Analysis by TIMS also ensured that contamination from enriched ^{235}U tracers or other sources in ICP-MS sample introduction systems was not an issue.

JMM – This solution was prepared by J. Mattinson in 2000 at the University of California, Santa Barbara, from

Table 1

Summary of the parameters associated with each of the gravimetric reference solutions. For a discussion concerning the magnitude of uncertainties and their covariance see text and McLean et al. (2015) for full details.

	JMM	RP/GSC	ET
Pb source metal	Puratronic	NBS 982	NBS 981
U source metal	CRM 115	CRM 112a	CRM 112a
Pb metal weight (g) ¹	0.89463	0.05175	0.31973
U metal weight (g) ¹	5.15157	0.25564	5.34448
Pb metal purity ²	0.9999890	0.9999767	0.9999986
U metal purity ³	0.99977	0.99975	0.99975
$^{204}\text{Pb}/^{206}\text{Pb}$ ⁴	0.0548861	0.0272058	0.0590074
$^{207}\text{Pb}/^{206}\text{Pb}$ ⁴	0.856720	0.466967	0.914683
$^{208}\text{Pb}/^{206}\text{Pb}$ ⁴	2.10227	1.000249	2.1681
$^{238}\text{U}/^{235}\text{U}$ ⁵	491.548	137.841	137.841
$^{238}\text{U}/^{206}\text{Pb}$ ⁶	20.0741 ± 0.0048	10.6337 ± 0.0021	59.820 ± 0.014

¹ Corrected for mass of air displaced by Pb or U metal during mass determination.

² Determined by glow discharge mass spectrometry (this study).

³ Certificate values (NBL, 2010, 2012).

⁴ Pb reference material ICs determined using data from Amelin and Davis (2006) calibrated relative to the $^{208}\text{Pb}/^{206}\text{Pb}$ of NBS 981 is 2.1681 (Catanzaro et al., 1968).

⁵ Value for CRM 112a from Condon et al. (2010), CRM 115 data (this study), all measured against IRMM 3636 (Verbruggen et al., 2008).

⁶ Total U/Pb uncertainty reflects uncertainty in estimates of mass, purity, and isotopic composition.

a high-purity (99.9989 wt%, see Section 2.3) Pb metal wire (Puratronic Pb obtained from Alfa Aesar) and high-purity (99.9770 wt%) depleted U metal (CRM 115 obtained from NBL).

RP – This solution was prepared by R. Parrish in 1996 at the Geological Survey of Canada from a high-purity (99.99767 wt%, see Section 2.3) Pb metal wire (NBS 982 obtained from National Institute of Standards and Technology, NIST) and high-purity (99.99975 wt%) natural U metal (CRM 112a obtained from NBL). It also contains gravimetric ^{232}Th , though it is not utilised in the present study.

ET – This solution was prepared by R. Parrish, D. Condon and B. Schoene in 2005 at the Massachusetts Institute of Technology, from a high-purity (99.99986 wt%, see Section 2.3) Pb metal wire (NBS 981 obtained from NIST) and high-purity (99.99975 wt%) natural U metal (CRM 112a obtained from NBL).

The three gravimetric solutions were each prepared in a similar fashion. Pieces of metal weighing 0.052 to 5.1 g (see Table 1) were etched (in order to remove any surface oxide or other contaminant) in $\text{HNO}_3 \pm \text{HCl}$, followed by rinsing in high-purity water and acetone. Metal pieces were dried then weighed (with care to limit time for re-oxidation) on high-precision balances calibrated against certified and/or reference weights before and after.

We undertook to provide a semi-quantitative estimate for the uncertainty contribution to the metal weight gain from surface oxidation in the seconds between leaching and weighing. To do this, we used both theoretical calculations of the mass that a piece of U metal would gain given its surface area and known reaction (oxidation) rates, and time-resolved measurements using high-precision microgram balances during the creation of new gravimetric solutions for the U-series community.

Theoretically, a 5 g bar of the uranium reference material CRM112a should, with roughness, have a surface area near 4.5 cm^2 , and at an oxidation rate of ca. $1 \times 10^{-3} \text{ mg U/cm}^2/\text{h}$ (Abrefah et al., 2002) only $\sim 1 \mu\text{g}$ of U should react in 10 min, a negligible component of the 5 g mass of the bar itself. Experimentally, we found that a more important consideration derived from the fact that we thoroughly removed any previous oxidation in nitric acid, and then rinsed the oxide-free metal bar in acetone. The acetone evaporated from the surface of the uranium metal over the course of 8–10 min, decreasing the measured mass of the 5 g uranium bar by 0.018 g (<4 ppm). This 4 ppm, if propagated as an uncertainty, would be negligible next to the 200–250 ppm uncertainties in the U/Pb ratio of the tracer, and would not affect the significant digits reported here for the tracer IC or its uncertainty. However, there is no reason to believe that, during the RP and JMM gravimetric solution preparation, the practitioners did not wait until all acetone was evaporated before making the final balance reading, therefore we do not adjust the U masses reported here.

Observed weights were, however, corrected for consideration of buoyancy effects resulting from the differential density of the Pb and U metals. Pb and U metal pieces were then transferred to pre-cleaned Teflon bottles, submerged

in concentrated HNO_3 , and left on a hotplate until fully dissolved. Subsequent to dissolution, solutions were diluted with ca. 1 M HNO_3 to achieve a working concentration and keep both elements in solution and therefore ensure the Pb/U is stable for extended intervals of time (years). The advantage of mixed multi-element gravimetric (and tracer) solutions is that the elemental ratio will be stable if held in the correct strength acid and any change in the concentration of the solution (e.g., due to evaporation) will not impact the elemental ratio, the critical parameter for radio-isotopic dating systems. Table 1 summarises the weights of each metal used, the certified and/or determined purities, and the isotopic compositions used to determine the relative abundances of ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{235}U and ^{238}U , and the gravimetric U/Pb ratio. The accuracy of the gravimetric U/Pb ratio is controlled by the uncertainty in both the weight of the metals and their certified/determined purity. Uncertainty in the gravimetric U/Pb ratio of the different reference solutions is discussed below (Section 4.1).

These solutions are considered ‘somewhat independent’ of each other, in that they are derived from different source metals (though the ET and RP solutions have a shared U metal) and prepared in different laboratories using balances calibrated against different sets of certified weights (see Table 1). However, as outlined in McLean et al. (2015) uncertainties in the isotopic composition of each of the reference materials are highly correlated, as each are calibrated against the same underpinning isotope reference materials (Fig. 1).

The masses of the Pb and U reference materials were determined before the metals were dissolved to create the gravimetric solutions. Although care was taken to remove oxidation and surface contamination before weighing on high-precision balances, each mass measurement has finite uncertainty. Because the ultimate parameter of interest is the U/Pb ratio of the solutions, any scale bias that is linearly proportional to the measured mass will divide out. For each weighing experiment, a series of bracketing certified weights was used to verify the linear response of the balances, and we propagate the uncertainty determined from the reproducibility of successive measurements of calibration weights and the Pb and U metals.

Each measured mass is adjusted for the mass of air that is above the scale during taring and then displaced by the metal when it is weighed. Since the displaced air mass is present during the taring but not during metal measurement, the true mass of the metal is somewhat greater than the measured mass. The air density was assumed to range between 1.195 and 1.205 kg/m^3 , calculated using an ideal gas law and estimates for ambient barometric pressure, humidity, and lab temperature based on normal operating conditions in each laboratory. Importantly, both U and Pb metals were weighed sequentially using the same balance with less than one hour between weighing of Pb and U, under the same environmental conditions. The densities of metallic U and Pb were calculated using their measured isotopic compositions and standard unit cell parameters. After buoyancy correction, each mass of Pb metal is heavier by 106 ppm and each U metal by 63 ppm, increasing the calculated U/Pb ratio of the solution by $43 \pm 1 \text{ ppm}$ (2σ).

2.3. Sample preparation, instrument setup and running conditions

Isotopic composition measurements were made on three thermal ionization mass spectrometers, a Thermo-Fisher Triton at the NERC Isotope Geosciences Laboratory (NIGL), a GV Isoprobe-T at the Massachusetts Institute of Technology (MIT) and a Thermo-Fisher Triton at the University of Geneva (UNIGE). All measurements were made in static mode using Faraday collectors, except for determination of the Pb isotopic composition of the tracer, which involved a mixed ion counting and Faraday detection protocol (see Section 3.2).

In order to calibrate the tracer U and Pb elemental and isotopic composition, mixtures of tracer and/or reference solutions were weighed or volumetrically measured and then combined in a pre-cleaned 7 mL Savillex beaker. This mixture was dried down prior to the addition of ca. 0.3 mL ultra-clean ($Pb_c < 0.1$ pg/ml) 6 N HCl. Beakers were then capped and fluxed overnight at ca. 120 °C. Following this, ca. 20 μ l of 0.015 N H_3PO_4 was added and the solutions were dried. Pb and U were loaded together with a silica gel – phosphoric acid emitter solution (Gerstenberger and Haase, 1997) on single out-gassed zone-refined Re filaments. Pb and U isotopic compositions were measured sequentially as Pb^+ ions (emitted at approximately 1300–1400 °C) and UO_2^+ ions (emitted at approximately 1450–1650 °C).

2.4. Correction for mass fractionation during TIMS analyses

Typical mass fractionation for TIMS Pb and U measurements using the silica gel and phosphoric acid emitter were ca. 0.1% per atomic mass unit based upon analyses of reference materials. Measured ratios were corrected for mass fractionation using an exponential fractionation law (Russell et al., 1978) for U and a modified exponential law for Pb that includes separate terms for mass independent fractionation of the odd-numbered masses of Pb isotopes ^{205}Pb and ^{207}Pb (Thirlwall, 2000; Amelin et al., 2005; McLean, 2014). Because the magnitude of isotopic fractionation is small, the errors relating to the choice of fractionation law are vanishingly small (Wasserburg et al., 1981). For example, if mass fractionation was 0.1%/u, then the variation in predicted isotopic composition between linear, exponential, and power laws is <7 ppm.

2.5. Oxide correction for UO_2^+

Uranium was loaded (with Pb) in a silica gel (Gerstenberger and Haase, 1997) and phosphoric acid mixture and ionised as UO_2^+ ions. This approach has several advantages: improved ion yields over analysis as a U^+ ion by TIMS by orders of magnitude for the sample load amounts in this experiment, based upon our prior experience of U^+ analyses (Condon et al., 2010), the lack of need for chemical separation of Pb from U, and lower ionization temperature, which reduces blank contribution from the filament, as well as reducing the possibility of introducing any extraneous interfering elements. When measuring both $^{233}UO_2$ and $^{235}UO_2$, this approach requires a correction

to account for the interference of $^{233}U^{18}O^{16}O$ and $^{233}U^{16}O^{18}O$ on the target peak $^{235}U^{16}O_2$ at mass 267; therefore, the isotopic composition ($^{18}O/^{16}O$) of the oxygen must be known or measured.

Nier (1950) determined the following percent abundances: ^{16}O , 99.759; ^{17}O , 0.0374; ^{18}O , 0.2039 corresponding to $R_{17} = ^{17}O/^{16}O = 0.0003749$ and $R_{18} = ^{18}O/^{16}O = 0.0020439$ based upon measurements of atmospheric oxygen. These data has been used for the basis of the atomic mass of oxygen by the International Union of Pure and Applied Chemistry (IUPAC) since 1961. For the purposes of this experiment it is uncertain whether the atmospheric oxygen IC is representative of the composition of the oxygen that forms the UO_2 molecule, which may be derived from a number of sources (e.g., silica gel emitter, reagents). The issue of variable oxygen isotopic composition within the thermal ionisation source environment where isotopic fractionation could occur has been encountered in other high-precision isotopic determinations where the isotopes were measured as oxide. Notable studies include Wasserburg et al. (1981) and Harvey and Baxter (2009) with TIMS NdO^+ measurements and associated with negative-ion TIMS Os analyses (Luguet et al., 2008). These studies documented intra-laboratory variation in R_{18} , as well as within-run variation.

In order to assess the accuracy of our uranium oxide isobaric interference correction, we have also made an effort to directly determine R_{18} for each of the systems used in this study. We have adapted the approach of Wasserburg et al. (1981) using CRM 112a, measuring masses 270 ($^{238}U^{16}O^{16}O$) and 272 ($^{238}U^{18}O^{16}O$, $^{238}U^{16}O^{18}O$) so that $R_{18} = (^{238}U^{18}O^{16}O + ^{238}U^{16}O^{18}O)/(^{238}U^{16}O^{16}O) = (272/270)/2$. Each laboratory observed that R_{18} increases during the first portion (ca. 0–20 min) of the analysis and then remains relatively constant until the UO_2^+ signal is exhausted. On the basis of this observed pattern and our previous experience running uranium produced as UO_2^+ on ^{233}U – ^{235}U spiked uranium from accessory minerals, we reject the initial blocks of uranium oxide data where there is an obvious trend indicating changing R_{18} . At NIGL, the R_{18} for UO_2^+ determination was made on routine analyses of accessory phases and matrix-free U solutions in order to mimic the pre-conditioning of the load that would occur during the tracer calibration Pb analyses. Measurements were made in peak-hopping mode on the SEM with mass 270 at ca. 0.8 M to 1 M cps and mass 272 at 3000 to 4000 cps. Run average R_{18} values ($n = 83$) ranged from 0.00200 to 0.00214 with an average value in good agreement with the IUPAC (Nier, 1950; de Laeter et al., 2003) value of $R_{18} = 0.002055$ (Fig. 2). Similar determinations were made at MIT and UNIGE, with a grand mean of $R_{18} = 0.00207 \pm 0.00002$ (2σ), within uncertainty but slightly more depleted than the IUPAC/Nier (1950) atmospheric value. This uncertainty was propagated into the uncertainty of each oxide-corrected mean $^{233}U/^{235}U$ and $^{238}U/^{235}U$.

3. RESULTS AND DATA INTERPRETATION

In this section we report the composition (isotopic and elemental) of the EARTHTIME tracers based upon the

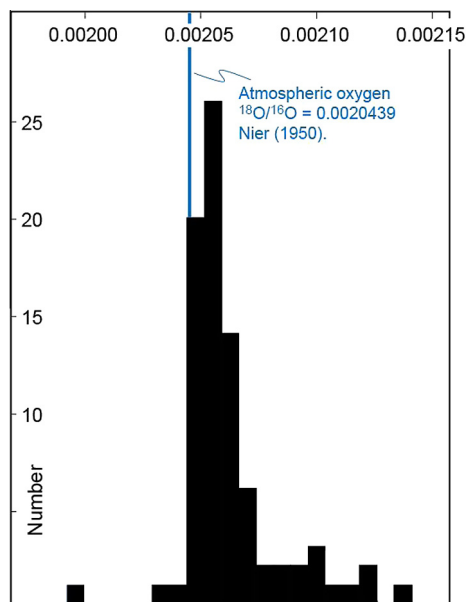


Fig. 2. Histogram of $^{18}\text{O}/^{16}\text{O}$ determinations made with the approach outlined in Section 2.5. Note the strong peak with $^{18}\text{O}/^{16}\text{O}$ at values greater than 0.00205. For reference the Nier (1950) $^{18}\text{O}/^{16}\text{O}$ 0.0020439 value determined on atmospheric oxygen is shown. This histogram includes the data used to derive the R_{18} value used in this study and additional concurrent data obtained on other samples that yield smaller signals.

results of the experiments outlined above. All of the data used for this tracer calibration experiment are included as supporting auxiliary material. These data have been combined using the algorithms outlined in the McLean et al. (2015) companion paper and readers are directed to this paper for further details of the algorithm and uncertainty model.

3.1. Inter-calibration of Pb and U reference materials

Six isotopic reference materials are used to determine the tracer U/Pb ratio (Fig. 1, Box 2), and their uncertainties all contribute to the final uncertainty budget of the tracer IC. Any correlation between the uncertainties in their ICs must therefore be considered when combining the results from the three gravimetric solutions. This uncertainty correlation derives from relating the ICs of the reference materials to SI units, accomplished for both U and Pb by measuring the isotope ratios of the reference materials against an independent gravimetrically calibrated isotope ratio.

A single gravimetrically determined isotope ratio was chosen to calibrate the Pb and U reference materials. For the Pb, we chose the $^{208}\text{Pb}/^{206}\text{Pb}$ of NBS 981 measured by Catanzaro et al. (1968) (Fig. 1, Box 1). While NBS 981 is not itself directly gravimetrically formulated, it is calibrated by sample-standard bracketing against a solution created by weighing nearly pure ^{208}Pb and ^{206}Pb . We herein use the stated value and uncertainty from this publication, of $^{208}\text{Pb}/^{206}\text{Pb} = 2.1681 \pm 0.0008$ (2σ). Although the Pb isotopic reference material NBS 982 also has a certified isotopic composition against the same gravimetric ^{208}Pb – ^{206}Pb

mixture, we prefer to use NBS 981 because it requires a negligible correction for laboratory blank Pb, which has approximately the same IC.

The dataset used to inter-calibrate isotopic compositions of the Pb reference materials in the gravimetric solutions is that of Amelin and Davis (2006), who measured NBS 981 and 982 as well as Puratronic Pb against their own ^{202}Pb – ^{205}Pb tracer. Assuming that the $^{202}\text{Pb}/^{205}\text{Pb}$ ratio is the same for each analysis, we can use the $^{208}\text{Pb}/^{206}\text{Pb}$ of NBS 981 to determine the $^{202}\text{Pb}/^{205}\text{Pb}$ of their tracer, and then use this ratio to determine internally consistent isotopic compositions for the other Pb reference materials. Using this large high-precision published dataset, we avoid both data duplication and consumption of valuable ^{202}Pb . The approach, statistical model, and results for inter-calibrating the Pb reference materials are presented in McLean et al. (2015) and data are presented in the Electronic Supplement.

To inter-calibrate the U isotopic reference materials, we used the same approach with IRMM 3636, a gravimetric mixture of ^{233}U and ^{236}U (Verbruggen et al., 2008) (Fig. 1, Box 1). We use the certified $^{233}\text{U}/^{236}\text{U}$, with a small correction for radioactive decay of ^{236}U between the time of certification and analysis. The ICs of CRM 112a and CRM U500 are reported in Condon et al. (2010), calculated against this reference material, and we add new data for CRM 115 (results in Table 1, data in Electronic Supplement).

The uncertainty in the inter-calibrated isotope ratios cannot be smaller than the assumed uncertainty in the primary isotopic reference material as this is used to fractionation correct all other ratios. For tracer and gravimetric solution measurements, the amount of sample, and therefore the size of an ion beam, is essentially unlimited, so the uncertainty in a measured isotope ratio almost completely derives from the fractionation correction. Thus, the propagated uncertainty in an isotope ratio depends on the difference in mass between the isotopes in its numerator and denominator. For Pb, the ± 360 ppm uncertainty in the $^{208}\text{Pb}/^{206}\text{Pb}$ of NBS 981 results in an uncertainty of 180 ppm/u (2σ), and for U the ± 170 ppm uncertainty in the $^{233}\text{U}/^{236}\text{U}$ ratio of IRMM 3636 yields an uncertainty of about 60 ppm/u (2σ). Fractionation-corrected ratios of the same element therefore have highly correlated uncertainties, reflecting the fact that isotope ratio measurements can be made to much higher precision before fractionation correction.

3.2. Determining the ‘minor’ Pb IC of the tracer

In addition to the enriched synthetic isotopes ^{205}Pb and ^{202}Pb , both tracers contain trace amounts of the naturally occurring ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb , though not in their natural relative proportions. The contribution from the tracer to the amount of each of these geochronologically important isotopes must be subtracted from the total amount measured to determine how much is in the sample. Unfortunately, it is impossible to measure the isotopic composition of the tracer without contaminating it with a small amount of natural Pb, or ‘laboratory blank’, whose isotopic

composition and mass (usually 0.2–0.5 pg) varies measurably and unpredictably from analysis to analysis. To determine the abundances of these isotopes relative to ^{205}Pb , we measured several mixtures of tracer and Pb blank, varying the mass of tracer loaded to provide additional spread in the tracer/blank ratio.

Interpretation of this data is explored in [McLean et al. \(2015\)](#), and is based on the multi-dimensional linear regression method of ([McLean, 2014](#)). The end result is not only the ‘minor’ Pb IC of the tracer, but also the IC and variability of the Pb blank, and the uncertainty correlation between the two.

3.3. Determining the U IC of the tracer with critical mixtures

The biggest barrier to making accurate measurements of the IC of a single element, such as the U and Pb of the tracer, is the unknown and variable magnitude of isotopic fractionation. As the tracer contains both ^{233}U and ^{235}U , it cannot be internally corrected for fractionation after mixing with a double spike that contains either ^{233}U or ^{235}U ; this is in contrast to the ^{202}Pb – ^{205}Pb double spike that is calibrated against an isotope reference material containing no amount of either synthetic Pb isotope. In theory we consider two uranium solutions, A and B, which contain three total U isotopes of interest, have distinct isotopic compositions and one common isotope between the two solutions. In our experiment reference ‘solution A’ has known $^{238}\text{U}/^{235}\text{U}$ and little or no ^{233}U (similar to uranium reference solutions such as CRM U500 and CRM 112a), and unknown ‘solution B’ has unknown $^{233}\text{U}/^{235}\text{U}$ and little or no ^{238}U (similar to the uranium ^{233}U – ^{235}U DS). For mixtures of solution A and solution B, there is a composition where the fractionation trend of the mixture parallels the mixing line between the true IC of both solutions, this is known as the critical mixture ([Krogh and Hurley, 1968](#); [Hofmann, 1971](#)) ([Fig. 3A](#)). As such, if the IC of solution A is known (i.e., it has an IC that can be traced to a certified isotopic reference material), the IC of the other (unknown) solution B must lie on the line that is defined by the reference solution IC and the measured IC of the critical mixture ([Fig. 3A](#)). Measuring the pure unknown solution (B) provides an additional constraint: its true IC must lie on a fractionation line that goes through the measured pure IC ([Fig. 3D](#)) and the line defined by the reference solution defined IC and the critical mixture measured IC.

Mixtures of the U isotopic reference materials CRM U500 and CRM 112a, whose $^{238}\text{U}/^{235}\text{U}$ were determined against the certified $^{233}\text{U}/^{236}\text{U}$ in ([Condon et al., 2010](#)), and the ^{233}U – ^{235}U tracer solution used to make ET(2)535 were made with target measured compositions that were within 0.1% of the expected measured critical mixture composition (based upon an assumed fraction factor of 0.1%/u). These mixtures were analysed repetitively with low analytical uncertainties such that, when considered in combination with the isotopic composition of CRM U500 and CRM 112a, they precisely constrain the critical mixture lines. Measurement of the tracer solution provides an additional constraint: they must lie on a fractionation line that goes through the true tracer U IC ([Fig. 3](#)).

3.4. U/Pb ratios of the gravimetric reference solutions

We weighed pieces of metal (ca. 0.05–5.3 g each) with a balance capable of reporting mass to 0.00001 g. The precisely measured masses were corrected for the air they displaced using ambient temperature, humidity, and air pressure during the weighing (see [Section 2.2](#)). Determinations of the contaminating elements in the Pb standards used were made by glow discharge mass spectrometry as part of this study, and then summed to calculate the total impurity concentration in the standard (see [Section 3.5](#)). We also used the recently re-certified purities determined by NBL for the U certified reference materials (CRM 112a certification September 2010; CRM 115 certification April 2012 ([NBL, 2010, 2012](#))). The uranium content for CRM 112a was determined using a constant-current coulometric reduction method whereas the assay of CRM 115 was determined by titrimetric methods ([NBL, 2010, 2012](#)).

3.5. Quantification of Pb metal purity

The certified purity of NBS 981 and NBS 982 is >99.9% (NIST Reference) indicating that the actual purity could range from 99.9% to 100% indicating a substantial source of uncertainty for this tracer calibration experiment. In contrast the purity of the Puratronic Pb utilised in the JMM gravimetric reference solution is quoted as >99.993% indicating that the uncertainty in purity is <35 ppm. In order to reduce the uncertainty contribution from the purity estimates of NBS 981 and NBS 982 we solicited Glow Discharge Mass Spectrometric (GD-MS) elemental analyses of the NBS 981, 982, and 983 series metals as well as the same purity level Puratronic Pb used in the JMM gravimetric reference solution. GD-MS analyses were carried out in 2010 under the supervision of Ralph Sturgeon using a high resolution VG 9000 GD-MS system at the National Research Council (NRC) of Canada GD-MS facility (<http://www.nrc-cnrc.gc.ca/eng/services/inms/glow-discharge.html>).

Analysis by GD-MS entails sputtering a solid sample that forms the cathode of a steady-state electrical discharge in an enclosure filled with Ar gas, where the sputtered atoms are ionised by an Ar plasma. Ionised elements from Li to U are accelerated into a magnetic sector mass spectrometer, where they are separated and their relative abundances are measured, with a detection limit well below 1 ppb ([King et al., 1995](#)). Traceability to SI units within stated uncertainties was established at the NRC by analysis of international reference standards ([Gusarova et al., 2011](#)). Sixty elements (results summarised in [Table 2](#), data in Electronic Supplement) were analysed at the ppb level.

3.6. Tracer-gravimetric solution mixes and the $^{235}\text{U}/^{205}\text{Pb}$ and $^{202}\text{Pb}/^{205}\text{Pb}$ of the tracer

The isotopic composition of the Pb and U standards in the gravimetric reference solutions, the uranium IC and ‘minor’ Pb IC of the tracer, and the Pb/U ratios of the gravimetric solutions calculated from the metal weights

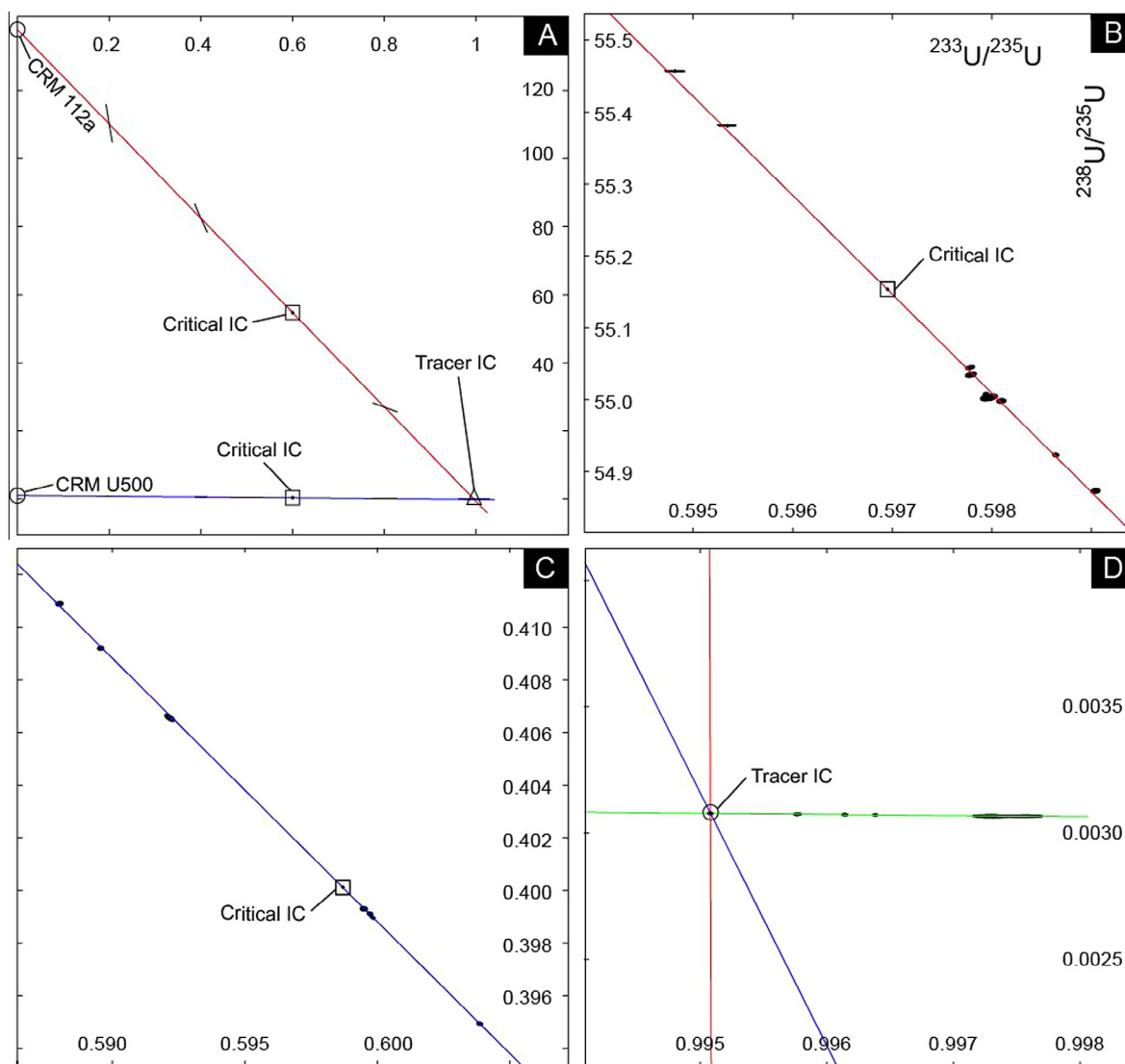


Fig. 3. Critical mixture calibration of the ^{233}U - ^{235}U double spike with two $^{238}\text{U}/^{235}\text{U}$ isotopic reference materials, CRM 112a ($^{238}\text{U}/^{235}\text{U} = 137.841$) and CRM U500 ($^{238}\text{U}/^{235}\text{U} = 0.999781$). All plots are $^{238}\text{U}/^{235}\text{U}$ vs. $^{233}\text{U}/^{235}\text{U}$, red line represents the CRM 112a-tracer mixture and the blue line represents the CRM U500-tracer mixture. (A) Plot showing the mixing lines for both reference materials (circles) and the tracer. Short black lines are fractionation trends for a given reference material-tracer mixture, squares highlight the critical mixture composition for both reference materials. The tracer composition occurs at the intersection of the two mixing lines and is highlighted with a triangle. (B) Plot showing the critical mixture composition for the CRM 112a-tracer mixes and the data points measured in this study. (C) As for B except this plot shows the CRM U500-tracer critical mixture data. (D) Plot showing the intersection of the two critical mixture lines and the analyses of fractionation trend of measurement of the tracer IC (green line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and purities are all used to determine the $^{235}\text{U}/^{205}\text{Pb}$ of the tracer. For these measurements, the gravimetric solution and tracer were mixed and measured together, and the U/Pb ratio of the gravimetric solution was used to determine the U/Pb ratio of the tracer. A total number of 46 tracer-gravimetric mixtures (23, 19 and 18 against RP, ET and JMM gravimetric reference solution respectively) were used to determine the tracer U/Pb ratio, 15 of which used ET2535 and 31 ET535 tracer. Fractionation correction was performed by using the 'known' (see Section 3.1) isotopic composition of the Pb and U reference materials, after correcting for minor contributions to these isotopes from

the tracer and from the UO_2 isobaric interferences. The numerical method used to reduce the large resulting dataset is explained in detail in McLean et al. (2015).

In addition to the U/Pb ratio, mixtures of the ET2535 with the gravimetric solutions, which have known Pb ICs, are also useful for determining the $^{202}\text{Pb}/^{205}\text{Pb}$ of the tracer. The $^{202}\text{Pb}/^{205}\text{Pb}$ is thus measured against the ICs of NBS 981 and 982 as well as the Puratronic Pb, whose IC has also been determined relative to $^{208}\text{Pb}/^{206}\text{Pb} = 2.1681$ (Catanzaro et al., 1968) (see McLean et al., 2015, for further discussion). The Pb measurements here have also been corrected for mass-independent isotopic fractionation, or

Table 2

Summary of elemental concentrations (ppb) for four Pb metal reference materials determined by GD-MS.

Element	Puratronic	NBS 981	NBS 982	NBS 983
Bi	4800	750	18,000	<230
Cu	460	6	4000	7500
Tl	800	425	380	600
Sn	1200	50	57	3200
S	2300	10	64	150
Ni	50	26	44	66
Te	50	<0.3	180	9
Sb	52	8	110	2
Ag	73	10	84	1800
C	50	40	55	47
O	580	40	90	140
Others	541	62	268	136
Total	9560	1427	23,332	13,650
Purity	0.9999904	0.9999986	0.9999767	0.9999863
±(95% CI)	0.0000047	0.0000009	0.0000072	0.0000033

Table 3

Recommended values for the concentration and isotopic composition of the ET535-ET2535 tracers.

ET535 v.3.0		
Composition	Value	±1σ (abs)
²⁰⁴ Pb/ ²⁰⁵ Pb	0.00009	0.000009
²⁰⁶ Pb/ ²⁰⁵ Pb	0.000389	0.00017
²⁰⁷ Pb/ ²⁰⁵ Pb	0.00030	0.00014
²⁰⁸ Pb/ ²⁰⁵ Pb	0.000744	0.00035
²³³ U/ ²³⁵ U	0.995062	0.000054
²³⁸ U/ ²³⁵ U	0.00307993	4.0E−7
Concentration of ²⁰⁵ Pb (mol/g)	1.0312E−11	2.6E−14
Concentration of ²³⁵ U (mol/g)	1.0336E−9	2.6E−12
ET2535 v.3.0		
²⁰² Pb/ ²⁰⁵ Pb	0.99924	0.00027
²⁰⁴ Pb/ ²⁰⁵ Pb	0.000105	0.000009
²⁰⁶ Pb/ ²⁰⁵ Pb	0.00048	0.00017
²⁰⁷ Pb/ ²⁰⁵ Pb	0.00043	0.00014
²⁰⁸ Pb/ ²⁰⁵ Pb	0.00104	0.00033
²³³ U/ ²³⁵ U	0.995062	0.000054
²³⁸ U/ ²³⁵ U	0.00307993	4.0E−7
Concentration of ²⁰⁵ Pb (mol/g)	1.0312E−11	2.6E−14
Concentration of ²³⁵ U (mol/g)	1.0336E−9	2.6E−12

the preferential evaporation, ionisation, and/or detection of odd-numbered Pb isotopes over even ones, to a degree larger than that expected for mass-dependent fractionation (McLean, 2014).

Because the data have been reduced block-by-block in a large statistical optimisation with 3873 measurements and 1759 unknowns, the results are difficult to visualise and plot. However, the conventional reduced chi-square metric (i.e., the MSWD) can still be calculated for all measurements. The resulting value, 1.8, is slightly higher than that expected for an ideal dataset, perhaps reflecting the underestimation of input uncertainties, such as the magnitude of the blank correction, or may reflect several outliers. However, because the measured uncertainty contribution that this MSWD reflects is less than 1% of the total variance

in a ²⁰⁶Pb/²³⁸U date, we consider any uncertainty inflation (for instance, by a factor of $\sqrt{1.8} = 1.3$) negligible.

4. DISCUSSION

4.1. Metrological traceability of EARTHTIME tracer isotopic composition and derived dates

In this paper we describe a series of linked experiments (Fig. 1) that provide the metrological accuracy for the isotopic and elemental composition of the ET535 and ET2535 mixed U–Pb tracers (Table 3). Although this paper focuses on the calibration of the ET(2)535 tracers, it is important to note that other mixed U–Pb tracers can be calibrated to a similar level of accuracy using the appropriate reference materials and methods outlined in this paper and McLean et al. (2015).

Initial estimates for the uncertainty in the ²³⁵U/²⁰⁵Pb ratio of tracers used for ID-TIMS geochronology were approximately 0.1%, or greater, and largely based on estimates of the uncertainties in the purities of isotopic reference materials (e.g., NBS 981 and 982 Pb metals having >99.9% purity) with no real documentation of the calibration experiment and underpinning data. This uncertainty was propagated into U–Pb dates, combined in quadrature with analytical and decay constant uncertainties when determining the total external uncertainty of U–Pb dates, for instance to compare with dates from other isotopic systems like ⁴⁰Ar/³⁹Ar (Schoene et al., 2006) or constraints that are based upon non radio-isotopic dating methods (e.g., astronomical tuning; Sageman et al., 2014). In this study the total uncertainty in our new estimate of the U/Pb ratio of the tracer has been quantified and is less than ±0.05% (95% confidence) due to reduced uncertainty in input parameters (e.g. Pb and U metal purities, U IC), and consideration of the resulting covariance (McLean et al., 2015). Consideration of the correlated uncertainties between the different components of the tracer calibration (e.g., ²³⁵U/²⁰⁵Pb, ²³³U–²³⁵U etc.) means that the effective total tracer calibration uncertainty contribution to a given ²⁰⁶Pb/²³⁸U date is <0.03% (see McLean et al., 2015, for further discussion). As the IRMM ²³³U–²³⁶U DS spike used to

underpin the tracer calibration is also used as the basis for calibration of the U reference materials used in the tracer calibration experiment (this study, Condon et al., 2010) the tracer calibration and $^{238}\text{U}/^{235}\text{U}_{\text{zircon}}$ experiments are linked and covariance of their uncertainties must be considered when using the combined parameters for U–Pb data reduction (McLean et al., 2015).

Calculating a U–Pb date requires more than just a measurement of the tracer isotopic composition—other ingredients include the determinations of the U/Pb ratio and Pb isotopic compositions of the sample, decay constants and corrections for intermediate daughter product disequilibrium (Fig. 1 and see in Schoene, 2014).

4.2. Accurate U–Pb geochronology using a $^{233}\text{U}/^{235}\text{U}$ double spike and natural variation of $^{238}\text{U}/^{235}\text{U}$

The use of ^{235}U paired with ^{233}U for the uranium double spike to correct for mass fractionation requires a priori knowledge of the $^{238}\text{U}/^{235}\text{U}$ ratio of the sample. Until recently, a consensus value of $^{238}\text{U}/^{235}\text{U} = 137.88$ had been used for almost all U–Pb geochronology. However, evidence indicates that the present-day $^{238}\text{U}/^{235}\text{U}$ is not constant in terrestrial geological materials (Stirling et al., 2007; Weyer et al., 2008; Hiess et al., 2012), and now must be a variable in data reduction algorithms. Numerous high-precision U–Pb studies on minerals such as zircon display a consistent relationship between ^{238}U – ^{206}Pb and ^{235}U – ^{207}Pb dates (e.g., Mattinson, 2000, 2010; Schmitz et al., 2003; Stern and Amelin, 2003; Schoene et al., 2006) indicating limited variation in $^{238}\text{U}/^{235}\text{U}$ from high-temperature U-bearing accessory phases (Mattinson, 2010). This has been supported by studies of $^{238}\text{U}/^{235}\text{U}$ in U-bearing accessory minerals (Stirling et al., 2007; Hiess et al., 2012). Specifically $^{238}\text{U}/^{235}\text{U}$ determinations from a suite of U-bearing minerals (Hiess et al., 2012), including a diverse age and compositional range of zircon-bearing samples, confirmed that $^{238}\text{U}/^{235}\text{U}$ is variable in high-temperature U-bearing accessory phases and that the average $^{238}\text{U}/^{235}\text{U}$ value of zircon is 137.818 ± 0.045 ($\pm 2\sigma$ variability based upon 43 out of 45 analyses). This variability reflects the dispersion in the data set but not the systematic uncertainties related to the double spike (IRMM 3636) calibration. One zircon, not included in this data set, gave a distinctly higher $^{238}\text{U}/^{235}\text{U}$ (~ 138.3) as did two titanite samples (~ 138.07 and ~ 138.5). Murphy et al. (2014) obtained $^{238}\text{U}/^{235}\text{U}$ values of ~ 137.23 from a single sample of ‘weakly mineralised sands, $\sim 90\%$ quartz, 5% barite, minor pyrite, rutile, ilmenite and zircon’ (their sample PRC012-22). However, it is not clear if the U composition of this sample reflects that of a high-temperature mineral assemblage normally targeted for U–Pb geochronology, as opposed to phases associated with mineralisation. In high-precision datasets such extreme $^{238}\text{U}/^{235}\text{U}$ ratios result in resolvable discordance between $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ dates (beyond that expected based upon decay constant uncertainties, Schoene et al., 2006; Mattinson, 2010), providing an independent assessment of possible extreme $^{238}\text{U}/^{235}\text{U}$ compositions that would warrant further investigation. For lower precision U–Pb data such as

that obtained on materials with elevated initial Pb levels (e.g., titanite), discordance arising from extreme $^{238}\text{U}/^{235}\text{U}$ values is significant because uncertainty budgets are dominated by uncertainty in the initial Pb composition rather than uncertainty in $^{238}\text{U}/^{235}\text{U}$. To date, terrestrial samples displaying greater variation in $^{238}\text{U}/^{235}\text{U}$ tend to be low-temperature materials such as chemical precipitates (Stirling et al., 2007; Weyer et al., 2008) and minerals that have high initial Pb/U (e.g., titanite; Hiess et al., 2012), none of which are currently amenable to high-precision U–Pb geochronology due to the need to correct for initial Pb and uncertainty inherent in that correction. Analysis of meteorite constituents (Brennecka et al., 2010) has demonstrated significant variation in $^{238}\text{U}/^{235}\text{U}$, indicating that a ^{233}U – ^{236}U DS would be preferable for U–Pb dating of these materials, although this is currently achieved on an aliquot of the sample and not the exact same material which is used for the $^{207}\text{Pb}/^{206}\text{Pb}$ analyses (Amelin et al., 2010; Connelly et al., 2012; Iizuka et al., 2014).

At present it is not practicable to employ a (^{202}Pb)– ^{205}Pb – ^{233}U – ^{236}U tracer to make an accurate determination of $^{238}\text{U}/^{235}\text{U}_{\text{sample}}$ for single zircons, or zircon fragments, (typically <0.5 ng of U) because there is not sufficient U to yield uncertainties smaller than the measured natural variability of the $^{238}\text{U}/^{235}\text{U}_{\text{zircon}}$ ratio (based upon 43 of 45 samples), even with the current high-sensitivity instrumentation (e.g., Connelly et al., 2012). Future improvements in mass spectrometer sensitivity will increase the precision with which $^{238}\text{U}/^{235}\text{U}$ can be determined using a ^{233}U – ^{236}U DS, however at the same time there is a tendency to decrease sample size towards aliquots with improved spatial/chemical context, possibly offsetting improvements in mass spectrometry. Ultimately, whether a ^{233}U – ^{236}U will be advantageous over the ^{233}U – ^{235}U DS in the EARTHTIME tracers will depend on the amount of U available for analysis, the sensitivity of the mass spectrometer available and the degree to which isobaric interferences (both TIMS and ICP-MS) can be accurately corrected for, and these will vary between samples and as protocols develop. For the studies where improved knowledge of $^{238}\text{U}/^{235}\text{U}$ may be advantageous, this can be achieved using a ^{233}U – ^{236}U DS on an aliquot of the sample in conjunction with U–Pb analyses using a mixed ^{202}Pb – ^{205}Pb – ^{233}U – ^{235}U tracer. With respect to the current state of U–Pb geochronology applied to high-temperature terrestrial materials – the intended target for the EARTHTIME tracers – propagating the uncertainty arising from documented $^{238}\text{U}/^{235}\text{U}$ variability in natural zircon into a precise U/Pb analysis typically results in a variance contribution of $<0.01\%$ to a $^{206}\text{Pb}/^{238}\text{U}$ date (see Fig. 2C and S9 of Hiess et al., 2012) and therefore the use of a ^{233}U – ^{235}U double spike and an assumed $^{238}\text{U}/^{235}\text{U}_{\text{sample}}$ ratio and uncertainty is not considered a significant limitation to high-accuracy U–Pb determinations using the ET535 and ET2535 tracers for the majority of studies.

4.3. Comparing ET(2)535 dates to previously published dates

Because the tracer calibration poses a systematic source of uncertainty, it is attractive to consider the bias between

data derived from this tracer calibration and legacy data in the published literature. Our experience during the past ~5 years is that there is no constant offset between old and new dates relative to other calibrated tracers (e.g., Schoene et al., 2006). This is due to the fact that during the time of this tracer calibration exercise a number of changes have been introduced into U–Pb zircon dating by ID-TIMS and by the likelihood that previous inaccuracies are more random than systematic. These include but are not limited to: use of measured R_{18} value for use in uranium oxide interference corrections; advent of new $^{238}\text{U}/^{235}\text{U}$ for reference materials and minerals; introduction of zone refined Re with significantly low blank for Tl; more appropriate consideration of Pb blank isotopic composition. These changes combine such that the relative magnitude of each of these effects depends on the analysis such that the bias between old and new data is not in general predictable; although laboratory specific tracers may show a consistent sense of bias. A major difference with the use of the ET tracer is that tracer calibration uncertainties are dramatically reduced and we have transitioned from poorly defined uncertainty approximations to a metrologically traceable foundation with a suitably nuanced uncertainty model (McLean et al., 2015). For critical experiments, new data should be acquired instead of correcting old data by a constant offset or relative magnitude.

4.4. Decay constant intercalibration

More accurate determination of U/Pb ratios impacts the determination of $\lambda^{235}\text{U}$ relative to $\lambda^{238}\text{U}$. Several studies have demonstrated the utility of coupled high-precision $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ dates on samples of zircon and/or xenotime that have demonstrably remained closed systems (Mattinson, 2000, 2010; Schoene et al., 2006). These experiments rely upon accurate determination of $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ ratios, such that a value for $\lambda^{235}\text{U}$ can be determined with respect to $\lambda^{238}\text{U}$ assuming equivalence of $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ dates, potentially improving the accuracy of $\lambda^{235}\text{U}$ compared to published counting data (Jaffey et al., 1971). Experiments that report improved estimates of $\lambda^{235}\text{U}$ (Mattinson, 2000, 2010; Schoene et al., 2006) utilise mixed U–Pb tracers that are calibrated against high-purity gravimetric reference solutions; therefore the accuracy of an inter-calibrated $\lambda^{235}\text{U}$ is underpinned by U/Pb tracer calibration experiments, which have not been published in detail prior to this study. Improvements in the calibration of the U–Pb system as a result of the EARTHTIME tracer calibration experiment can now be used to retrospectively inform these previous experiments by providing better-constrained input parameters (e.g., isotopic composition of CRM 115). Fully traceable $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ datasets produced with the ET2535 tracer or similarly calibrated U–Pb tracers, combined with $^{238}\text{U}/^{235}\text{U}_{\text{sample}}$ determined relative to IRMM3636, will permit increased confidence in estimates of $\lambda^{235}\text{U}/\lambda^{238}\text{U}$ based upon the analyses of closed system materials (e.g., zircon) where the equivalence of $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ dates can be quantified.

The accuracy of U–Pb data can also be used to inform the accuracy of other radio-isotopic dating systems. Several studies exploit the accuracy of the U–Pb system, derived from its metrological calibration and well-known decay constants, to improve other systems where precise determinations of decay constants from first principles calibration experiments are lacking or imprecise. In this approach, mineral pairs from a single rock are dated by both U–Pb (mineral A, typically zircon) and another system (mineral B) and these pairs are used to transfer accuracy from the U–Pb system to the other system. This approach requires a priori assumption that the radio-isotopic dates for minerals A and B should be equivalent and/or have an established systematic relationship. This approach has contributed to calibrations of the $^{40}\text{Ar}/^{39}\text{Ar}$ (Renne et al., 2010), Re–Os (Selby et al., 2007), Lu–Hf (Söderlund et al., 2004), Rb–Sr (Nebel et al., 2011) radio-isotopic dating systems, and also U–Th, which uses the same principle but involves calibration against secular equilibrium ratios (Cheng et al., 2000, 2013). Improvements in the accuracy of the U–Pb system as a result of the EARTHTIME tracer calibration experiment (e.g., reduced uncertainty in the purity of NBS 981 and 982 Pb metals, isotopic composition of U reference materials) can now be used to inform these previous experiments (excluding the U–Th system) where the input data are fully documented and permit full re-processing of the raw mass spectrometric data using new input parameters and data reduction algorithms. Where legacy U–Pb data are not fully documented the community should seek to develop new data sets using the EARTHTIME tracers (or similarly calibrated) in order to improve the accuracy of these other radio-isotopic decay systems.

5. CONCLUSIONS

Here we demonstrate the full traceability of U–Pb geochronology back to SI units by documenting calibration of mixed ^{235}U – ^{233}U – ^{205}Pb –(^{202}Pb) tracers for high-accuracy U–Pb isotope-dilution mass spectrometry carried out under the auspices of the EARTHTIME initiative through a series of inter-related experiments that begin with the first-principles measurements and end with the tracer isotopic composition. The connections from first-principles measurements to the tracer IC are illustrated in Fig. 1, and show that the uncertainties in the derived tracer IC ratios all depend on a common set of measurements. Calibration of the U/Pb ratio and isotopic abundances are documented in this paper and the various sources of uncertainty are discussed and quantified (see also McLean et al., 2015) such that U/Pb data produced using these tracers can be considered metrologically traceable. These calibration experiments are applicable to other systems that require accurate determination of multi-element isotope ratios (i.e., radio-isotopic decay schemes) and the traceability documentation has yielded insights into the importance of covariance when the input parameters and experiment measurements are very high-precision (McLean et al., 2015).

The uncertainty of the EARTHTIME U–Pb tracer isotopic composition can be traced back to SI units via a series of assay and isotopic composition reference materials

combined with the experiments described herein and is estimated at <0.05% (95% confidence), and considering the covariance results in effective total uncertainty contribution on the order of 0.03% for $^{206}\text{Pb}/^{238}\text{U}$ dates. This is approximately one third the magnitude of previous estimates for U/Pb calibration which themselves did not consider all sources of uncertainty and is a result of reduced uncertainty in key input parameters (e.g., Pb metal purity) and consideration of how the uncertainty covariance manifests in sample U/Pb determinations (McLean et al., 2015). Combined with the ^{238}U and ^{235}U decay constant determination, the accuracy of U–Pb tracer calibration controls the foundations for accurate U–Pb geochronology and inferentially other radio-isotopic dating system that derive accuracy from U–Pb via inter-calibration experiments.

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Supplemental files have been deposited with the NERC National Geoscience Data Centre (DOI: [10.5285/a483a041-170a-4072-844e-c2c5d070a3e3](https://doi.org/10.5285/a483a041-170a-4072-844e-c2c5d070a3e3)).

APPENDIX A. OXIDE CORRECTION UNCERTAINTY FOR ^{233}U – ^{235}U AND ^{233}U – ^{236}U DOUBLE SPIKES WITH VARIABLE SAMPLE/TRACER RATIOS

U–Pb ID-IRMS is typically performed by TIMS, with U analysed as UO_2 . U O_2 by TIMS using a silica gel emitter

(e.g., Gerstenberger and Haase, 1997) is practical, expedient and precise because: (a) both elements may be loaded onto the same rhenium filament and U–Pb dates determined during the same analytical session; (b) high ionisation efficiencies produce large, stable ion beams suitable for static Faraday analysis when compared to U metal by TIMS using a graphite emitter for equivalent small load sizes (e.g., Condon et al., 2010); (c) the magnitude of isotopic fractionation is roughly an order of magnitude smaller than ICPMS analyses, and (d) many U–Pb laboratories do not have ready access to MC-ICP-MS.

Accurate determination of the uranium isotopic composition of the sample/tracer mix analysed as UO_2 requires correction for the $\text{U}^{18}\text{O}^{16}\text{O}$ isobaric interference that occurs on the U^{16}O_2 peak that is two mass units heavier (i.e., $^{233}\text{U}^{18}\text{O}^{16}\text{O}$ on $^{235}\text{U}^{16}\text{O}^{16}\text{O}$ and $^{236}\text{U}^{18}\text{O}^{16}\text{O}$ on $^{238}\text{U}^{16}\text{O}^{16}\text{O}$). As such, accurate ‘oxide correction’ requires knowledge of the $^{18}\text{O}/^{16}\text{O}$ and associated uncertainty, and studies of the oxygen isotopic composition of oxides of U, Nd or Os within thermal ionisation mass spectrometers record variation at the ~2% level (this study; Wasserburg et al., 1981; Luguet et al., 2008; Harvey and Baxter, 2009).

This oxide isobaric interference occurs on a tracer isotope for a ^{233}U – ^{235}U DS (i.e., ^{233}U interferes on ^{235}U), affecting the estimated fractionation correction, and on the major sample isotope (^{238}U) for a ^{233}U – ^{236}U DS (i.e., ^{236}U interferes on ^{238}U , directly affecting the measured sample/tracer ratio). The magnitude of the correction depends on the relative intensity of the interfering and interfered uranium masses, so it follows that ^{233}U – ^{235}U and ^{233}U – ^{236}U double spike analyses will be variably impacted by the uncertainty associated with this correction. For ^{233}U – ^{235}U DS analyses with $^{233}\text{U}/^{235}\text{U} \sim 1$, the oxide correction only affects the fractionation correction, and the uncertainty in a typical $^{18}\text{O}/^{16}\text{O}$ value of 0.00205 ± 5 (2σ) results in an uncertainty contribution of ~0.025% to the estimated moles of ^{238}U in the sample and is practically

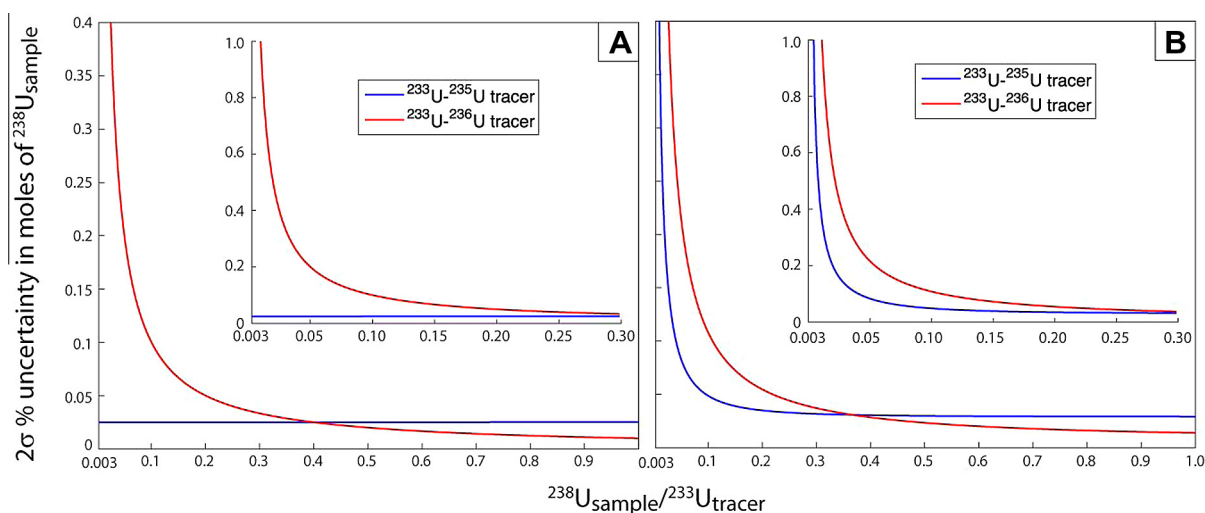


Fig. A1. Plot of the 2σ percent uncertainty in the moles of ^{238}U derived from isotope dilution based upon IRMS of natural uranium mixed with either a ^{233}U – ^{235}U or a ^{233}U – ^{236}U DS for a range of $^{238}\text{U}/^{233}\text{U}$ ratios. (A) Uncertainty contribution arising only from uncertainty in $^{18}\text{O}/^{16}\text{O} = 0.00205 \pm 5$ (2σ). (B) Modelled total uncertainty from both oxide correction and mass spectrometry. This plot assumes a fixed ^{233}U signal intensity of 100 mV, static signal detection using Faraday cups with $10^{11} \Omega$ resistors, and $^{233}\text{U}/^{236}\text{U}_{\text{tracer}}$ and $^{233}\text{U}/^{235}\text{U}_{\text{tracer}} = 1$.

invariant with respect to variation in the sample/tracer ratio (Fig. A1). Alternately, ^{233}U – ^{236}U DS samples are subject to an increasingly significant correction as $^{238}\text{U}/^{233}\text{U}$ decreases and the $^{236}\text{U}^{18}\text{O}^{16}\text{O}$ interference increases relative to the sample ^{238}U . Relative uncertainty contributions to the moles of $^{238}\text{U}_{\text{sample}}$ derived from the oxide correction are 0.05% and 0.10% at $^{238}\text{U}/^{233}\text{U}$ values of 0.2 and 0.1, respectively, for a $^{233}\text{U}/^{236}\text{U} = 1$ (Fig. A1), and increase to 2% for $^{238}\text{U}/^{233}\text{U}$ value of 0.005, not atypical for a small Precambrian zircon crystal/fragment.

For samples with low measured $^{238}\text{U}/^{233}\text{U}$ (<0.4), there are two competing sources of uncertainty: the increased measurement uncertainty due to the smaller ^{238}U signal, and for the ^{233}U – ^{236}U DS, the increased uncertainty due to the constant magnitude oxide interference on a decreasing magnitude ^{238}U beam. If the former was the dominant uncertainty contribution, then the latter could justifiably be ignored. Modelling this scenario by predicting the measurement uncertainty from Johnson noise on commonly used $10^{11} \Omega$ amplifiers and shot noise from typical U beam sizes ($^{233}\text{U} \sim 100$ mV), then estimating the resulting uncertainty in the calculated moles of sample ^{238}U (Fig. A1B) shows that, for a ^{233}U – ^{236}U tracer, the oxide correction uncertainty dominates and that a ^{233}U – ^{235}U DS is advantageous.

However, for samples with higher $^{238}\text{U}/^{233}\text{U}$ (>0.4), the same two sources of uncertainty play different roles. For a ^{233}U – ^{235}U DS, the magnitude of the oxide correction remains nearly constant because the $^{233}\text{U}/^{235}\text{U}$ approximates the constant ratio of the tracer (Fig. A1). Alternately, the oxide correction for a ^{233}U – ^{236}U DS becomes less significant as the sample ^{238}U increases relative to the tracer ^{236}U (Fig. A1), and the higher mass difference between the tracer isotopes for a ^{233}U – ^{236}U DS results in a more precise isotopic fractionation correction, and therefore more precise estimate of the moles of sample ^{238}U (Fig. A1B). However, it should be noted that as the ^{238}U signal increases, it is possible to determine the $^{18}\text{O}/^{16}\text{O}$ of the oxygen forming the UO_2 in real time by measuring the 272/270 ratio (see Section 2.5) with an uncertainty that is less than that associated with the assumed value and its associated variance.

APPENDIX B. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2015.05.026>.

This data set comprises six Microsoft Excel workbooks that contain the isotope ratio data used in the tracer calibration experiment outlined in this manuscript and its companion paper (McLean et al., 2015).

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