ISOTOPIC COMPOSITION ($^{238}U/^{235}U$) OF SOME COMMONLY USED URANIUM REFERENCE MATERIALS

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ABSTRACT

We have determined $^{238}U/^{235}U$ ratios for a suite of commonly used natural (CRM 112a, SRM 950a, and HU-1) and synthetic (IRMM 184 and CRM U500) uranium reference materials by thermal ionisation mass-spectrometry (TIMS) using the IRMM 3636 ^{233}U-^{236}U double spike to accurately correct for mass fractionation. Total uncertainty on the $^{238}U/^{235}U$ determinations is estimated to be < 0.02% (2σ). These natural $^{238}U/^{235}U$ values are different from the widely used 'consensus' value (137.88), with each standard having lower $^{238}U/^{235}U$ values by up to 0.08%. The $^{238}U/^{235}U$ ratio determined for CRM U500 and IRMM 184 are within error of their certified values; however, the total uncertainty for CRM U500 is substantially reduced (from 0.1% to 0.02%). These reference materials are commonly used to assess mass spectrometer performance and accuracy, calibrate isotope tracers employed in U, U-Th and U-Pb isotopic studies, and as a reference for terrestrial and meteoritic $^{238}U/^{235}U$ variations. These new $^{238}U/^{235}U$ values will thus provide greater accuracy and reduced uncertainty for a wide variety of isotopic determinations.

1. INTRODUCTION

Uranium has three naturally occurring isotopes: ^{238}U ($t_{1/2} \approx 4.5 \times 10^9$ a) (JAFFEY et al., 1971), ^{235}U ($t_{1/2} \approx 7.0 \times 10^8$ a) (JAFFEY et al., 1971) and the shorter-lived ^{234}U ($t_{1/2} \approx 2.5 \times 10^5$ a) (CHENG et al., 2000). Until recently, the present-day ^{238}U/^{235}U ratio has been considered invariant as mass-dependent thermodynamic isotopic fractionations were not expected to be detectable in U due to its high mass. However, recent studies suggest U isotopic fractionation in terrestrial materials is possible as a result of oxidation-reduction reactions (U^{VI} to/from U^{IV}) and/or nuclear field shift (BIGELEISEN, 1996; BUCHACHENKO, 2001; SCHAUBLE, 2007), and its presence has been confirmed in natural systems (BOPP et al., 2009; STIRLING et al., 2007; WEYER et al., 2008). Thus, it is crucial to re-evaluate the ^{238}U/^{235}U of standards for which the consensus value ^{238}U/^{235}U value (≡ 137.88) has been considered accurate and often used with zero uncertainty.

Natural (processed) and synthetic uranium reference materials are employed in isotope ratio and isotope dilution mass spectrometry to assess performance and accuracy and provide benchmark isotopic compositions for calibration purposes. Examples include monitoring mass fractionation and/or detector bias (CHENG et al., 2000), developing gravimetric reference solutions for isotopic tracer calibration ((^{233}U ± ^{235}U ± ^{236}U)/(Th ± Pb)) (CHENG et al., 2000; CONDON et al., 2007; RODDICK et al., 1987), and use as a reference for studies that document the variability of uranium isotopic composition of natural (terrestrial and meteoritic) materials (AMELIN et al., 2010; BOPP et al., 2009; BRENNECKA et al., 2010; STIRLING et al., 2007; STIRLING et al., 2005; WEYER et al., 2008). The uranium reference materials available for these purposes are either derived from ore deposits or are synthesized by mixing highly enriched isotopes to achieve desired ratios. We use the term ‘natural uranium’ for reference materials derived from uranium ores and/or minerals. However, it is possible pre-existing intra-ore variation has been homogenized, and isotopic fractionation may have occurred during processing, so that the isotopic composition of the processed natural uranium differs from the parent ore. Natural uranium reference materials are typically considered to have an invariant isotopic composition, and their $^{238}U/^{235}U$ is taken to be the 'consensus' $^{238}U/^{235}U$ value equal to 137.88 (STEIGER and JAGER, 1977). The isotopic composition of synthetic isotopic reference materials are determined gravimetrically by weighing high purity isotopes (as oxides) prior to mixing, or through cross-calibration against gravimetric isotopic reference materials (CATANZARO et al., 1968; RICHTER et al., 2008).

In this contribution, we present new $^{238}U/^{235}U$ determinations for a series of commonly used natural and synthetic uranium reference materials. These measurements were made using a ^{233}U-^{236}U double spike (IRMM 3636) to accurately correct for mass fractionation during analysis. The $^{233}U/^{236}U$ ratio of IRMM 3636 was determined gravimetrically with an uncertainty of 160 ppm, coverage factor of $k = 2$ (2σ) (RICHTER et al., 2008). Combined with high-precision, high-accuracy, thermal ionisation mass spectrometry (TIMS) we are able to determine $^{238}U/^{235}U$ ratios of these reference materials with a combined standard uncertainty of <200 ppm (95% confidence limit). Quantifying the $^{238}U/^{235}U$ ratio and associated uncertainty for these reference materials will require adjusting the results of previous instrumental and tracer calibration efforts; if the radiogenic $^{238}U/^{235}U$ of U-daughter (U-Pb and U-series) geochronology samples is different from 137.88, small systematic errors will result.

2. NATURAL URANIUM $^{238}U/^{235}U$ RATIO

A compilation of ninety gas source mass spectrometry $^{238}U/^{235}U$ determinations on uranium hexafluoride (UF_6) was used to indicate a lack of variation in natural $^{238}U/^{235}U$ ratios at the sub per-mil level (COWAN and ADLER, 1976; STEIGER and JAGER, 1977). The measurements were made in five laboratories on a variety of uranium ore bodies (COWAN and ADLER, 1976). Examination of the original data reveals a bimodal distribution (noted by Cowan and Adler, 1976), and a mean value >137.88 (Fig 1). Furthermore, all data in this compilation were normalised to an NBS standard (unnamed, from the Belgian Congo) for which a value of 0.7110 weight percent ^{235}U (equivalent to ^{238}U/^{235}U =137.88) was used. Critically, a personal communication and an unpublished report are the only sources cited in Cowan and Adler (1976) for the isotopic composition of the NBS standard used for normalization. Thus, the accuracy of the ^{238}U/^{235}U value in the Cowan and Alder (1976) compilation cannot be traced back to the SI system of units and its uncertainty cannot be quantified. For the purposes of U-daughter geochronology, the IUGS subcommission proposed the adoption of a 'consensus value' of ^{238}U/^{235}U = 137.88, based largely upon the Cowan and Adler (1976) compilation (STEIGER and JAGER, 1977) and this value has been and is currently widely used in the geochronology community.

For the past three decades, researchers have been measuring the ^{238}U/^{235}U of various sources of natural uranium to assess whether it is truly invariant. In the late 1970's and early 1980's several pioneering studies (CHEN and WASSERBURG, 1980; CHEN and WASSERBURG, 1981b; TATSUMOTO and SHIMAMURA, 1980) focused on determining the uranium isotopic composition of meteorites, using ^{233}U-^{236}U tracers to facilitate accurate correction for mass fractionation during mass spectrometry. The ^{233}U/^{236}U ratio of the double spikes used in these studies were calibrated against CRM U500, and thus given the sample sizes and analytical capability of the time could assess variation at the 0.5% level (CHEN and WASSERBURG, 1981b). A summary of their measurements on two terrestrial standards, NBS 950a and the well-known Columbia River basalt whole-rock geochemistry standard BCR-1, showed that the terrestrial material ^{238}U/^{235}U of 137.85 ± 0.4 (2σ) was indistinguishable from the consensus value 137.88 (CHEN and WASSERBURG, 1981a). They also demonstrated that data from a variety of meteorites - including phosphates, CAI's, bulk meteorite fractions, and leaches - had an average $^{238}U/^{235}U$ of 137.83 ± 0.55 (2σ), leading them to conclude that any variation in the $^{238}U/^{235}U$ of extraterrestrial materials must be at the $\leq$0.4% level.

In contrast to the geological community's consensus $^{238}U/^{235}U$ value, the $^{238}U/^{235}U$ value currently recommended by International Union of Pure and Applied Chemists (IUPAC) is 137.80 (mole fraction ^{235}U = 0.007 204(6)) (DE LAETER et al., 2003). The IUPAC value is based upon UF_6 measurements of six natural uranium ore samples by gas-source mass spectrometry (RICHTER et al., 1999). These data are calibrated against gravimetrically prepared synthetic isotope reference materials that are traceable to a fundamental SI unit. Subsequently, Richter et al. (2008) and Keegan et al. (2008) obtained high precision TIMS data, which support the current IUPAC $^{238}U/^{235}U$ value (Figure 1), using a ^{233}U-^{236}U double spike (IRMM 3636), which is also traceable to SI units and has a smaller uncertainty than previous double spike preparations.

Recent studies employing multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) have been able to resolve variation in $^{238}U/^{235}U$ better than 0.01% (BOPP et al., 2009; BRENNECKA et al., 2010; STIRLING et al., 2005; STIRLING et al., 2007; WEYER et al., 2008). A variety of rock types, and to a much lesser extent U-bearing minerals (STIRLING et al., 2007; WEYER et al., 2008) have been examined, as well as revisiting some of the uranium ore bodies reported in the Cowan and Adler (1976) compilation (BOPP et al., 2009). In the case of the Bopp et al (2009) study, the data are normalized to IRMM REMEIP 18A, which has a certified isotope composition traceable to SI units ($^{238}U/^{235}U$ = 137.85 ± 0.05%, (RICHTER et al., 2007). Importantly, the Bopp et al. (2009) study included a suite of uranium ores from the Cowan and Adler (1976) compilation and obtained $^{238}U/^{235}U$ values that are (systematically) 0.1 to 0.05% lower than 137.88 (Figure 1). Stirling et al (STIRLING et al., 2007; STIRLING et al., 2006) and Weyer et al (WEYER et al., 2008) use a "natural" uranium standard (CRM 112a and SRM 950a, respectively) for normalization and present data as fractional deviations from this standard material. For studies that exploit $^{238}U/^{235}U$ variation as a redox-sensitive proxy, absolute $^{238}U/^{235}U$ values are less important. However, absolute $^{238}U/^{235}U$ values are used in U-daughter geochronology, so the absolute value of the comparative reference material is important.

3. URANIUM REFERENCE MATERIALS

A variety of natural uranium (derived from minerals and devoid of any synthetic uranium isotopes) and synthetic uranium (derived from mixing highly enriched single isotopes) reference materials are available and in widespread use within the isotope community. The synthetic uraniums are isotope reference materials (IRM), whereas the 'natural' uraniums are either metals, oxides and/or solutions derived from the processing of natural uranium that are certified for purity/concentration (such as CRM 112a, SRM 950a) or materials such as HU-1 stated to be in 'secular equilibrium'. We have chosen to study three natural (CRM 112a, SRM 950a, HU-1) and two synthetic (CRM U500 and IRMM 184) reference materials that are commonly employed in U-daughter geochronology for calibration of tracers, as isotopic standards for correcting bias effects during isotope ratio mass spectrometry (see discussion below) and as a reference for $^{238}U/^{235}U$ variation in terrestrial and meteoritic materials.

3. 1 CRM 112a.

CRM 112a is a high-purity metal assay standard formerly known as SRM 960. There is also an assay solution standard (CRM 145) which is derived from CRM 112a and hence it is assumed to have the same isotopic composition. These CRMs were produced by NBS (National Bureau of Standards) and are now distributed by New Brunswick Laboratory (NBL, http://www.nbl.doe.gov/). The isotopic composition is not specified in the CRM certificate. The CRM 112a solution used in this study was prepared at the NERC Isotope Geoscience Laboratory (NIGL) in 2008 by dissolving the metal in a pre-cleaned Teflon FEP bottle using high purity 2 M HNO_3 prepared in a Picotrace Teflon double sub-boiling still.

3. 2 SRM 950a.

This material consists of 'normal' uranium in the form U_3O_8 with uranium oxide mass fraction of 99.94 ± 0.02. SRM 950a was produced by National Institute of Standards and Technology (NIST, http://www.nist.gov/), and the isotopic composition is not specified in the certificate. The SRM 950a solution used in this study was prepared at the British Geological Survey in 1978 using U_3O_8 powder from a previously unopened vial of SRM 950a dissolved in 2 M HNO_3 in a pre-cleaned 1 litre borosilicate glass flask.

3. 3 Harwell Uraninite (HU-1).

HU-1 was originally distributed by the UKAEA Harwell (Hoffmann et al. 2007) and is used as a secular equilibrium standard by the U-series community (CHENG et al., 2000; HOFFMANN et al., 2007; LUDWIG et al., 1992). There is no certification for this material. TIMS and MC-ICP-MS data measured for different aliquots sourced from different laboratories indicate that HU-1 is homogeneous with respect to $^{234}U/^{238}U$ at the ≤ 0.1% level, but may vary in $^{230}Th/^{238}U$ as measured (ANDERSEN et al., 2008; CHENG et al., 2000; HOFFMANN et al., 2007) The HU-1 solution used in this study was prepared at NIGL in 1992 by dissolving material obtained from M. Ivanovich (UKAEA) in a precleaned 1 litre FEP bottle using ~1 litre of 2M HNO_3 prepared by sub-boiling distillation in a Teflon two-bottle still.

3.4 IRMM 184.

IRMM 184 is a standard solution with a near natural uranium isotopic composition $^{235}U/^{238}U = 0.0072623(22)$ ($^{238}U/^{235}U = 137.697 \pm 0.041$) and $^{234}U/^{238}U = 0.000053138(32)$ (RICHTER et al., 2005). This material was produced by, and is available from the Institute for Reference Materials and Measurements (IRMM, http://irmm.jrc.ec.europa.eu). Measurements of the $^{238}U/^{235}U$ ratio were performed on a UF_6 gas mass spectrometer calibrated using synthetic uranium isotope mixtures. The minor isotope ratios were measured by TIMS and normalised to the $^{238}U/^{235}U$ ratio. Calibration of this reference material is independent of the consensus value of $^{238}U/^{235}U = 137.88$ that is commonly assumed for various natural uranium standards. We chose to analyse IRMM 184 as an internal check on the accuracy and reproducibility of our TIMS measurements within the limits of the 0.03% uncertainty on the certified $^{238}U/^{235}U$ ratio.

3.5 CRM U500.

CRM U500 is a synthetic uranium isotopic standard prepared from high-purity single isotopes by the National Bureau of Standards (NBS) and now distributed by NBL (http://www.nbl.doe.gov/) to have $^{234}U/^{235}U/^{236}U/^{238}U \approx 0.01/1/0.0015/1$ (GARNER et al., 1971). The $^{238}U/^{235}U$ ratio was determined gravimetrically and therefore can be traced back to the SI system of units. The CRM U500 $^{238}U/^{235}U$ value of ~1 is certified with a maximum uncertainty of 0.1% (GARNER et al., 1971). This reference material is widely used by both the U-Pb and U-series community in applications where accuracy and uncertainty quantification is a priority, such as in tracer calibrations (CHENG et al., 2000). It is noteworthy that routine analysis of CRM U500 by the MC-ICP-MS community is not as common as by the TIMS community because of the risk of ‘memory effects’, especially when operating in dry plasma mode employing a desolvating nebuliser. However, it is of critical importance to calibrations of double ^{233}U-^{236}U spikes, excluding the IRMM 3636 spike, and therefore currently underpins MC-ICP-MS analyses in several U-series geochronology labs (CHENG et al., 2000).

Two batches of CRM U500 were used in this study. The CRM U500 solution analysed at NIGL was prepared at NIGL in 2004 by dissolving U_3O_8 powder from a previously unopened vial of U500 in a pre-cleaned Teflon FEP bottle using high purity 2 M HNO_3 prepared in a Picotrace Teflon double sub-boiling still. The CRM U500 solution analyzed at MIT was prepared at Washington University in 1988 in a pre-cleaned Teflon bottle and high-purity HNO_3.

4. EXPERIMENTAL (small font section)

4.1 IRMM 3636 double spike.

To correct for mass-dependent fractionation during $^{238}U/^{235}U$ ratio measurement, we have employed the IRMM 3636 ^{233}U-^{236}U double spike with $^{233}U/^{236}U = 1.01906$ (RICHTER et al., 2008). Derived from high-purity isotopes, its $^{233}U/^{236}U$ ratio and uncertainty were determined by gravimetric principles and therefore can be traced to the SI system of units (RICHTER et al., 2008). The abundance of ^{235}U and ^{238}U are low $^{235}U/^{236}U = 0.000\ 045\ 480$; $^{238}U/^{236}U = 0.000234$), but a correction is still required to strip the ^{235}U and ^{238}U contributions from IRMM 3636 and calculate a sample $^{238}U/^{235}U$ ratio (see Appendix 1). The nature and propagation of uncertainties associated with the isotopic composition of IRMM 3636a are discussed in detail in section 4.3. Although ^{236}U has been reported to have been detected in some natural uranium samples (BERKOVITS et al., 2000) levels are extremely low ($^{236}U/U \leq 30e^{-11}$); however, some reference materials have elevated ^{236}U concentrations from contamination during manufacture. Berkovits et al. (2000) analysed different batches of SRM 950 (950, 950a and 950b) and determined $^{236}U/U \approx 8e^{-10}$ for batch 950a. For the sample/tracer ratios used in this study this source of ^{236}U is can be safely ignored.

4.2 Mass spectrometry.

Measurements were performed on a ThermoFinnegan Triton TIMS instrument (Triton 2) at NIGL and GV Isoprobe-T TIMS instrument at MIT. Prior to sample loading, the filaments were outgassed for >40 minutes at between 1.5 and 4.5 amps (>20 minutes at 4.5 amps). Batches of Re used for filaments were first checked in the mass spectrometer on the SEM at typical running temperatures to ensure U emitted directly from the outgassed Re was insignificant. At NIGL, samples were loaded on zone-refined Re filaments in a double filament configuration in dilute HNO_3 and slowly dried down at 0.5 – 1.0 amps. During the run, ionisation filaments were heated to ~1700 - 1750˚C (4.6 to 5.4 amps) with the evaporation filament at 1.8 to 2.4 amps, and the uranium ionized as U+ ions. At MIT, uranium was ionized as UO_2^+ on a single Re filament loaded in a Si Gel emitter (GERSTENBERGER and HAASE, 1997) and real time correction for $^{233}U^{16}O^{18}O$ interference on $^{235}U^{16}O^{16}O$ was possible by measuring oxide species at masses 272 and 269. Details and equations used for mass fractionation correction, oxide correction, and stripping of minor isotope contributions are outlined for both labs in Appendix 1.

At NIGL the abundance sensitivity, following the IUPAC recommended definition (TODD, 1991) as "the ratio of the maximum ion current recorded at a mass m to the ion current arising from the same species recorded at an adjacent mass (m ± 1)", was determined by measuring what are interpreted to be down-mass scattered ions from the ^{238}U peak at m/z = 237 and was ~1 ppm. Considering the range of $^{236}U/^{235}U$ measured for the 'natural' uranium materials, the maximum effect in excess of amplifier-Faraday baseline on ^{235}U by scattered

^{236}U ions was ~8 ppm, small compared to our target total uncertainty and largely accounted for by the interpolated half-mass baseline measurements. At MIT, abundance sensitivity was < 3 ppm and the effects of scattered ^{236}U ions on the ^{235}U peak for the CRM U500 analyses were similarly accounted for. Faraday amplifiers in both labs employed 10^{11} Ω resistors and amplifier electronic gains were measured <24 hours prior to analyses. Amplifier cup rotation was employed at NIGL to minimize biases arising from residual differences in amplifier performance/gain. Baselines were obtained at masses 232.55 and 233.55 as measured on the axial Faraday (on-peak mass was 233.05), with on-peak corrections based on a linear interpolation of the half-mass baselines. Each baseline measurement was integrated over 60 seconds and taken before each data block, employing a delay of at least 10 seconds between exposure of the Faraday amplifiers to an on-peak signal and the baseline measurements. Further details of mass spectrometry performance are listed in Appendix 2.

Our aim was to obtain ^{238}U/^{235}U data with a total uncertainty of < 200 ppm, including the ~160 ppm contribution from the uncertainty of the IRMM 3636 tracer isotopic composition. This necessitates that the external reproducibility contribution from mass spectrometry be ≤ 120 ppm when combined in quadrature. For standards with “natural” isotopic compositions, minimum ^{235}U ion beam intensities for between 0.1-0.35 V (1-3.5 pA) ensured sufficient counting statistics, and the maximum ^{238}U beam size was limited by the need to avoid amplifier saturation, corresponding to ^{238}U >14V (140 pA) and <50V (500 pA) for natural U and IRMM 184.

Measurement of all tracer and sample isotopes required four Faraday cups and thus inter-cup biases were required to be relatively small. Cup matching tests at NIGL using Nd isotopes show that these biases are on the order of ~10-20 ppm and therefore are not a limiting factor (Appendix 2). Furthermore, individual 10^{11} ohm amplifier responses at NIGL (i.e., signal decay) were checked by loading with a constant current source, demonstrating that all amplifiers achieved <10 ppm residual signal after 2 seconds, and verified by loading with large ion beams, as measured on both a single Faraday cup and all required Faraday cup-amplifier pair responses. The ion beam signal decay experiments employed >40 V ^{238}U beams, and determined that residual long term (>3 second magnet settling time) effects of large ion beam exposure were not present.

Sample/spike mixing ratios for the natural uranium materials and IRMM 184 were optimised to give ^{238}U/^{236}U ratios between 25 and 120 in order to minimise potential for tailing of the ^{236}U peak on the ^{235}U peak in the mixture. In the case of CRM U500, the ^{238}U/^{236}U of the spike/CRM mixes ranged from ~0.5 to ~10. It is useful to note that U mass fractionation analysed by TIMS is typically ≤0.1%/u, almost an order of magnitude smaller than that observed for MC-ICP-MS, and the correction is insensitive to the fractionation law used (WASSERBURG et al., 1981).

4.3 Uncertainty estimation.

"There are known knowns. These are things we know that we know. There are known unknowns. That is to say, there are things that we now know we don't know. But there are also unknown unknowns. These are things we do not know we don't know." – D. Rumsfeld (2002)

We have attempted to identify and quantify the major sources of uncertainty in the ^{238}U/^{235}U measurements that arise from both random and systematic effects. The quantifiable uncertainty component due to random effects is largely from data acquisition, and comprises counting statistics on ion beams and baseline noise. Known systematic contributions include uncertainty in the isotopic composition of the IRMM 3636 tracer used for fractionation correction, amplifier gain and collector efficiency differences, and the fractionation law used.

Replicate determinations in a single laboratory do not reveal all potential sources of systematic error. To quantify reproducibility, we performed an inter-laboratory comparison of CRM U500 measurements at both NIGL and MIT. The isotopic composition of CRM U500 is amenable to higher precision determinations and therefore provides a means to assess repeatability within each laboratory, and also resolve inter-laboratory bias at the level of tens of ppm. Reference materials with a natural isotopic composition were measured at NIGL, and the combined CRM U500 data was used to estimate the full uncertainty budget, which was applied to all determinations.

The ^{238}U/^{235}U determinations for the reference material/IRMM 3636 mixtures are presented in Table 2 and summarised in Table 4. The analytical uncertainty reported for each mix is the standard error of the fractionation- and tracer-corrected ^{238}U/^{235}U ratios, multiplied by a coverage factor of $k = 2$, following the approach and terminology of the Joint Committee for Guides in Metrology (JCGM, 2008). This is equivalent to a ~95% confidence interval, or 2σ of a normal distribution, and is justified due to the large number of effective degrees of freedom for each measurement. Each two step (see Table A2.1) measurement cycle's fractionation- and tracer-corrected ^{238}U/^{235}U measurement, represents an independent measurement, with only systematic components of uncertainty from the tracer IC in common.

The uncertainty contribution from the isotopic composition of IRMM 3636 from (RICHTER et al., 2008) was assessed at the weighted mean level for each standard. Because each weighted mean includes mixes with sample/spike ratios that vary by up to an order of magnitude, the tracer subtraction uncertainty contribution is not constant. Instead of adding a single standard uncertainty in quadrature to the measurement uncertainty, we use a more sophisticated algorithm that computes the maximum likelihood of the weighted mean, its standard error, and MSWD by treating the tracer uncertainty contributions to analyses as error correlations between them (LYONS et al., 1988; VALASSI, 2003). The generalized weighted mean statistics computed in this way incorporate the components of uncertainty from systematic and random effects without incorrectly reducing systematic contributions during averaging. The uncertainty contribution from the IRMM 3636 isotopic composition, and in particular the uncertainty in its ^{233}U/^{236}U ratio, contributes >75% of the combined variance of each weighted mean.

Close examination of the precise CRM U500 ^{238}U/^{235}U determinations from both labs indicates that there are (at least) two additional sources of uncertainty. First, both labs report individual measurement uncertainties that are too small to explain the variability between measurements, which is reflected by the relatively high MSWDs (2.3 at MIT and 16.5 at NIGL) of both large datasets. This overdispersion, or "excess scatter," implies an unrecognized or underestimated component of variability in the measurements, yet to be identified but potentially amplifier gain drift or other instrumental parameters. One simple way to estimate the magnitude of this missing component is to calculate the increase in uncertainty required to bring the MSWD of each dataset to 1, and is 41 ppm for NIGL and 42 ppm for MIT (2σ). Second, there is a significant difference (ca. 50 ppm) between the weighted means for each lab outside these expanded measurement uncertainties. There is no a priori reason to believe that one lab's results are more accurate so we must ascribe the difference to unrecognized mass spectrometer or method-dependent effects such as measuring U as a metal (NIGL) vs. as an oxide (MIT). An additional 65 ppm (2σ) standard uncertainty added in quadrature to both labs' weighted means brings the NIGL and MIT CRM U500 weighted means into agreement within uncertainties and a MSWD of 1.

Two MSWDs are reported for each solution. The first incorporates both the measurement uncertainty, represented by the standard error of the fractionation-corrected ratios, and the variability caused by predictable systematic effects. For example, the $^{238}U/^{236}U$ ratio of the tracer may be slightly higher than, but within uncertainty of, it's certified value. In this case, relatively large sample/tracer ratios would yield corrected $^{238}U/^{235}U$ values that are too high, and relatively small sample/tracer ratios would yield even higher $^{238}U/^{235}U$ values. This would subtly increase the scatter between analyses with different sample/tracer ratios, but the trend would not be resolvable at our level of precision. Since the certified value is not perfectly accurate, this source of variability must be included when determining whether the data are consistent with a single weighted mean. The second MSWD is calculated after the adding the intra-laboratory reproducibility (41 to 42 ppm) uncertainty term in quadrature to each measurement to account for the overdispersion of the CRM U500 dataset.

Including data from two independent laboratories using two different methods increases our confidence in the measurements' accuracy and ensures its uncertainty estimate is realistic. For the other solutions analysed in a single laboratory, the combined standard uncertainty must include these two effects, as well as the measurement and tracer uncertainties. We consider this the best estimate of the true external reproducibility of our experiment.

5. RESULTS

The results of the determinations are outlined below and listed in Tables 2 and 3. The final values and associated uncertainties are summarised in Table 4. Uncertainties of the $^{238}U/^{235}U$ ratio means are presented as ±X/Y. The X uncertainty is our best estimate of the external reproducibility, twice the standard error of the weighted mean measurement uncertainty combined in quadrature with the intra- and inter-laboratory components (see section 4.3). The Y uncertainty includes these combined with the propagated systematic uncertainty in the $^{233}U/^{236}U$ ratio and minor isotope composition of the IRMM 3636 double spike. In the case of

U500 and IRMM 184, Y also includes the uncertainty in the $^{236}U/^{235}U$ ratio of the standard solution, all added in quadrature (JCGM, 2008). The MSWDs are reported as A/B, where A incorporates only measurement (without intra- and inter-laboratory components included) and tracer variability and B incorporates the extra sources of variability inferred and estimated from the CRM U500 data. The observation that the re-calculated MSWDs for reference materials with natural composition are between 0.5 and 1.9, values that are acceptable for the given sample sizes (WENDT and CARL, 1991), supports applying the CRM U500-based external reproducibility to the reference materials with natural $^{238}U/^{235}U$ compositions.

5.1 CRM 112a.

Seven CRM 112a/IRMM 3636 mixes were analysed with a weighted mean $^{238}U/^{235}U$ value of 137.844 ± 0.011/0.024, MSWD = 2.0/0.6 (2σ absolute).

5.2 SRM 950a

Six SRM 950a/IRMM 3636 mixes were analysed with a weighted mean $^{238}U/^{235}U$ value of 137.847 ± 0.011/0.024, MSWD = 1.0/0.5 (2σ absolute). These data show that CRM 112a has a $^{238}U/^{235}U$ indistinguishable from SRM 950a; however, the two materials do have significantly different $^{234}U/^{238}U$ ratios (CHEN et al., 1986).

5.3 Harwell Uraninite (HU-1).

Six HU-1/IRMM 3636 mixes were analysed with a weighted mean $^{238}U/^{235}U$ value of 137.769 ± 0.011/0.024, MSWD = 3.1/1.2 (2σ absolute). Our results for HU-1 relative to CRM 112a ($\varepsilon^{235}U_{CRM\ 112a}$ = 5.5 ± 1.1, 2σ) where $\varepsilon^{235}U = 10^4 \times$

[($^{235}U/^{238}U_{sample}/^{235}U/^{238}U_{standard}$) − 1], are in good agreement with those of (STIRLING et al., 2007) who documented $\varepsilon^{235}U_{CRM\ 112a}$ of 5.6 ± 0.9 for the HU-1 standard.

5.4 IRMM 184.

Five IRMM 184/IRMM 3636 mixes were analysed with a weighted mean $^{238}U/^{235}U$ value of 137.682 ± 0.011/0.024, MSWD = 4.3/1.9 (2σ absolute). This result is 109 ppm lower than certified value $^{238}U/^{235}U$ = 137.697 but within the certified 300 ppm uncertainty which is based upon UF_6 gas source mass spectrometry calibrated against synthetic uranium isotope mixtures (RICHTER et al., 2005).

5.5 CRM U500.

$^{238}U/^{235}U$. A total of 38 CRM U500/IRMM 3636 mixes were run at both NIGL and MIT. NIGL determined a weighted mean $^{238}U/^{235}U$ ratio of 0.999758 ± 0.000077/0.00017, MSWD = 16.5/1.0 and MIT a weighted mean $^{238}U/^{235}U$ of 0.999805 ± 0.000078/0.00017, MSWD = 2.3/1.0 (2σ absolute) (Tables 1 and 2). A weighted mean of the combined NIGL and MIT dataset, including intra- and inter-laboratory uncertainties (see section 4.3) results in $^{238}U/^{235}U$ = 0.99978 ± 0.00016 (2σ absolute). This $^{238}U/^{235}U$ value is ~520 ppm lower than the certified value of 1.0003 but well within the stated 1000 ppm uncertainty (GARNER et al., 1971).

$^{234}U/^{235}U$ and $^{236}U/^{235}U$. Six non-spiked aliquots of CRM U500 were analysed as metal (with ^{236}U intensity >10mV) using our new $^{235}U/^{238}U$ value (see above) for internal mass bias correction in order to determine the ^{234}U and ^{236}U abundances (see Table 3). $^{234}U/^{235}U$ and $^{236}U/^{235}U$ of 0.010 418 10 ± 0.000 000 30/0.000 000 62, MSWD = 19.5/1.0 and 0.001 5190 54 ± 0.000 000 22/0.000 000 23, MSWD = 15.6/1.0 (2σ absolute), respectively, were obtained. These ratios are 0.02% and 0.22% lower than $^{234}U/^{235}U$ and $^{236}U/^{235}U$ determined by NBL-modified total evaporation and normalized to $^{235}U/^{238}U = 0.999698$ (RICHTER and GOLDBERG, 2003). These differences increase to 0.095% and 0.26% if the NBL data are normalized to the NIGL $^{235}U/^{238}U$ value. In contrast, the NIGL data are nearly identical to the original NBS certificate values (0.010422 ± 0.18% and 0.0015195 ± 0.41%).

6. DISCUSSION

New values for the $^{238}U/^{235}U$ ratios of these reference materials have implications for U-series, U-Pb and Pb-Pb geochronology, tracer calibrations, and nuclear forensics. These include the magnitude of routine instrumental mass bias corrections using internal normalization or double spiking, as well as the precision and accuracy of both isotopic tracer calibrations and the ^{234}U and ^{235}U decay constants. For U-Pb geochronology, if the parent U isotopes show the same spread in modern $^{238}U/^{235}U$ ratios, then using the consensus value of 137.88 will result in small systematic errors in age calculations. For U-Th geochronology the impact of uncertainty in the $^{238}U/^{235}U$ value of reference materials used for both tracer calibration, and correction of instrumental mass fractionation effects, is explored by Stirling et al (2007).

6.1 Mass bias correction.

The term mass bias is taken here to be the sum of all mass-dependent isotopic effects related to mass spectrometry, including both the source and detector. Uranium isotopic standards are used to make mass bias corrections during mass spectrometry in three ways: (1) Internal normalization (TIMS and ICP-MS) employs a “known” isotope ratio (e.g. $^{238}U/^{235}U$) to determine mass bias during the run and to correct the isotope ratio of interest (e.g. $^{234}U/^{235}U$). (2) Sample-standard bracketing (ICP-MS) is based on analyzing a standard or reference with a "known" isotope ratio to determine the mass bias drift during an analytical session and alternated with unknowns. The mass bias in the unknown samples is calculated by interpolation from the standard measurements. (3) "Double-spiking" (TIMS and ICP-MS) involves adding two synthetic and/or enriched isotopes (e.g., ^{233}U, ^{235}U, ^{236}U) of known relative abundance to the sample, allowing mass bias to be corrected during the measurement ratio by ratio. "Double-spike" tracers require calibration against standard reference materials, which limits the accuracy of this approach. Our new ^{238}U/^{235}U values for a number of commonly used standards allow us to assess the impact of this assumption on the accuracy of the resultant determinations.

For ^{238}U/^{235}U studies, e.g. forensic studies of nuclear materials, the absolute error in the measured ^{238}U/^{235}U ratio should include and be no less than that of the reference material ^{238}U/^{235}U ratio, regardless of the approach taken to constrain mass bias. In U-series geochronology by ICP-MS, the ^{234}U/^{238}U ratio is often determined using either natural uranium reference materials (CRM 112a, SRM 950a, HU-1) for sample-standard external bracketing, or by internally measuring the ^{238}U/^{235}U in the sample material, provided the ^{233}U or ^{236}U tracer is relatively pure. In both cases, a value of 137.88 has been used for normalization. In U-series, many U-Th laboratory tracers are calibrated using the assumed secular equilibrium value of HU-1, and using 137.88 for ^{238}U/^{235}U to correct for mass bias. Using HU-1 for mass bias correction of the ^{238}U/^{234}U ratio ($\Delta u \approx 4$) by standard-sample bracketing using an assumed ^{238}U/^{235}U value of 137.88 will result in an inaccuracy of ~ 0.027 %/u, which results in an error of ~ 0.1% for the corrected ^{238}U/^{234}U ratio. HU-1 is often used as a check on Faraday/ion-counting calibrations as well, using the assumed ^{238}U/^{235}U value to correct for mass bias. This may not be a critical issue when dating material to routine precision or when open system behaviour controls data quality, but inaccuracies arising from consensus value normalization will impact high precision chronologies. Stirling et al. (2007) further discuss the impact of deviation from the consensus ^{238}U/^{235}U value for mass bias corrections.

The ^{238}U/^{235}U ratio of CRM U500 determined here is within the stated 0.1% uncertainty of the certified value (GARNER et al., 1971). Our new value, however, is 0.05% lower and the combined standard uncertainty is reduced to 0.02%. Because the ^{238}U/^{235}U ratio of CRM U500 is determined gravimetrically, it has been used for high-accuracy calibration of ^{233}U-^{235}U (CONDON et al., 2007) and ^{233}U-^{236}U tracers (CHENG et al., 2000) for U-daughter geochronology. In the calibration of ^{233}U-^{235}U and ^{233}U-^{236}U double spikes, the systematic 0.1% uncertainty in the ^{238}U/^{235}U ratio of CRM U500 results in systematic uncertainties of 0.07% and 0.1% for the derived the ^{233}U/^{235}U ($\Delta u \approx 2$) and ^{233}U/^{236}U ($\Delta u \approx 3$) double spike ratios respectively (0.033%/u) and therefore a 0.1% uncertainty in resultant ^{238}U/^{235}U determinations and 0.13% uncertainty in ^{234}U/^{238}U determinations. Reducing the CRM U500 ^{238}U/^{235}U ratio uncertainty from 0.1% to 0.02% will reduce the uncertainty of ^{233}U/^{235}U and ^{233}U/^{236}U double spikes calibrated against CRM U500 significantly and thus reduce the combined standard uncertainty of sample determinations.

6.2 U-daughter tracer calibration.

Uranium reference materials are relied upon for the calibration of the synthetic isotopic tracer (^{236}U ± ^{235}U ± ^{233}U ± ^{229}Th ± ^{205}Pb ± ^{202}Pb) that is used for isotope dilution measurements. The impact of inaccuracies in the ^{238}U/^{235}U ratio of various references materials on calibration of a (mixed) U-daughter solution is dependent in on the detailed experimental approach.

Accurate calibration of a tracer to be used for isotope dilution purposes requires mixing the tracer with a gravimetric reference solution of known concentration and isotopic composition. For most uranium-based tracers, a gravimetric solution of a reference metal (e.g., CRM 112a) with known purity is used. When the tracer and reference solution are mixed, a common approach is to use the (assumed) isotopic composition of the reference material to correct for fractionation of the tracer/gravimetric solution mixture in order to accurately determine the concentration of the tracer isotope relative to the reference isotope. In such an approach the uncertainty in the isotopic composition of the reference material will result in inaccurate fractionation correction as described above (section 6.1); resulting is an inaccurate tracer concentration estimate. For instance, calibrating a ^{233}U tracer using a ^{238}U/^{235}U ratio of 137.88 for CRM 112a to correct the ^{238}U/^{233}U of the mixture results in a ^{233}U concentration too low by 0.05% if isotopic fractionation is 1%/u, and if HU-1 was used this inaccuracy would increase to 0.15%.

When a double uranium tracer is used (i.e., ^{233}U-^{236}U) the ratio of enriched isotopes can be calibrated independently of the concentration calibration. This ratio can then be used to correct for mass fractionation of the tracer/gravimetric solution mixture. Both the concentration and composition of different certified reference materials are thus exploited, as in the recent calibration of the EARTHTIME U-Pb tracer (CONDON et al., 2007). In this example, CRM U500 was used to determine the ^{233}U/^{235}U ratio of the tracer, which in turn was used for mass bias correction of the tracer/gravimetric solution mixture measurements used to determine the concentration of the tracer isotopes. The 0.1% uncertainty in the ^{238}U/^{235}U ratio of CRM U500 propagated into a 0.066% uncertainty in the ^{233}U/^{235}U double spike ratio which in turn resulted in a 0.1% uncertainty in the moles of ^{235}U in the tracer relative to the gravimetric isotope of ^{238}U; this uncertainty contributes ca. 50% of the total uncertainty in the U/Pb ratio of the tracer (CONDON et al., 2007). The new CRM U500 ^{238}U/^{235}U data presented herein results in a significant (ca. 50%) reduction in the U/Pb ratio uncertainty of the EARTHTIME U/Pb tracer which translates to a ca. 50% reduction in sample U/Pb ratio uncertainty.

Another common approach used by some U-series workers is to calibrate mixed U-Th tracers against natural materials considered to be in secular equilibrium. For example, HU-1 is considered to be in secular equilibrium, an assumption supported for, in part, U isotopes by direct measurement (CHENG et al., 2000), and is used to calibrate the U/Th ratio of mixed ^{229}Th-^{236}U or ^{229}Th-^{233}U-^{236}U tracers when gravimetric calibration solutions for both U and Th are not used (e.g. HENDERSON and SLOWEY, 2000; LUDWIG et al., 1992). The inaccuracy of the consensus ^{238}U/^{235}U value relative to our determined ^{238}U/^{235}U value (0.027%/u) will impart an inaccuracy in the tracer (^{236}U) concentration if the ^{238}U/^{235}U ratio of HU-1 is used to correct for mass fractionation during the calibration. The magnitude of this bias will depend upon the nature of the tracer calibration experiment, which will vary between laboratories but is on the order of 0.03% to 0.05%.

6.3 Impact on inter-calibration of U decay constants.

Several key studies have demonstrated the potential for inter-calibrating the uranium (and uranium-series) decay constants by analyzing "closed-system" minerals (CHENG et al., 2000; MATTINSON, 2000; SCHOENE et al., 2006; MATTINSON, 2010). The current λ^{234}U value (CHENG et al., 2000) was determined by measuring secular equilibrium ^{234}U/^{238}U ratios using a ^{233}U-^{236}U double spike calibrated against the certified ^{238}U/^{235}U value for CRM U500. The calculation assumes the consensus ^{238}U/^{235}U ratio for U in secular equilibrium in zircons, calcite and HU-1 where the ^{238}U/^{234}U was calculated from a ^{234}U/^{235}U measurement and assumed ^{238}U/^{235}U =137.88. The original data of Cheng et al. (2000) could be used in conjunction with the new data presented here to determine more accurate and precise decay constant values. The most important change would be a reduction in the propagated uncertainty on the ^{234}U decay constant arising from the newly determined reduced uncertainty for CRM U500 ^{235}U/^{238}U. Cheng et al. (2000) also made ^{230}Th/^{238}U determinations on these closed system materials and used these to solve for λ^{230}Th. The ^{230}Th/^{238}U ratio determination is underpinned by the gravimetric calibration of ^{229}Th and ^{233}U-^{236}U tracers and therefore the reference materials against which the concentration and isotopic composition of the tracers are calibrated will directly affect the tracer Th/U ratio and derived ^{230}Th/^{238}U ratio of the closed system materials. As such the new ^{238}U/^{235}U determinations for CRM 112a and CRM U500 will impact the λ^{230}Th determination however without detailed information for the tracer calibration exercise it is not possible to quantify the affect these new reference values will have.

High-precision analyses of demonstrably closed-system materials (zircon) have also been exploited to derive a more accurate and precise λ^{235}U (MATTINSON, 2000; SCHOENE et al., 2006; MATTINSON, 2010). In this approach, the systematic disagreement between ^{206}Pb-^{238}U dates and ^{207}Pb-^{235}U dates is minimized by solving for a new value of λ^{235}U relative to the more precisely determined λ^{238}U of Jaffey et al (1971). Many of the potential uncertainties outlined above for tracer calibrations and fractionation corrections arising from assumed ^{238}U/^{235}U = 137.88 for natural uranium reference materials were not fully explored in these studies. Furthermore, nearly all U-Pb determinations rely in part upon the assumption of the ^{238}U/^{235}U ratio in zircons is equal to 137.88 (usually with zero uncertainty). The impact of this assumption in light of our new data is explored below.

6.4 Impact on U-Pb geochronology

The new ^{238}U/^{235}U determinations reported here allow us to calculate absolute ^{238}U/^{235}U ratios for materials that have been previously determined relative to reference materials (BRENNECKA et al., 2010; STIRLING et al., 2007; STIRLING et al., 2006). For materials that are also used for U-Pb and Pb-Pb geochronology, we can use these absolute values to explore the potential effect on age determinations and associated uncertainties. For example, Stirling et al., (2007) obtained $^{238}U/^{235}U$ data on HNO_3 leaching experiment of zircon from a 900 Ma pegmatite and obtained $\varepsilon^{235}U_{CRM\ 112a}$ values similar to those obtained on HU-1 indicating a $^{238}U/^{235}U$ value for that zircon that is less than 137.88.

In general the U-Pb geochronology community uses the ‘consensus value’ of $^{238}U/^{235}U$ = 137.88 (STEIGER and JAGER, 1977) for both U data reduction and direct calculation of ^{207}Pb-^{206}Pb dates from $^{207}Pb^{*}/^{206}Pb^{*}$ ratios. Because ^{235}U is much less abundant than ^{238}U, the moles of ^{235}U used to calculate the $^{207}Pb/^{235}U$ date is commonly determined by dividing the moles of ^{238}U by the assumed $^{238}U/^{235}U$ = 137.88. This assumption is required when a ^{235}U tracer is employed or when the $^{238}U/^{235}U$ ratio cannot be determined with the required precision. In contrast, calculation of a $^{207}Pb/^{206}Pb$ date is explicitly related to a single assumed present day $^{238}U/^{235}U$ ratio and the determined $^{207}Pb^{*}/^{206}Pb^{*}$ ratio of a sample. Thus both U-Pb and ^{207}Pb-^{206}Pb dates rely in part on the $^{238}U/^{235}U$ ratio used or assumed, but in different ways.

Figure 5 depicts the bias that an incorrectly assumed $^{238}U/^{235}U$ ratio imparts on $^{207}Pb/^{235}U$ and $^{207}Pb/^{206}Pb$ dates. Each graph considers three test cases where the true $^{238}U/^{235}U$ differs from a value of 137.88. The difference (percentage and absolute) between the dates calculated using the test $^{238}U/^{235}U$ values and 137.88 are plotted. Figure 5A illustrates the relative and absolute bias of the $^{207}Pb/^{235}U$ dates when the moles of ^{235}U were determined by dividing the measured moles of ^{238}U by the $^{238}U/^{235}U$ of the sample, as is the case when mass spectrometry protocol does not permit precise measurement of the sample ^{235}U concentration (e.g., when a ^{235}U ($\pm^{233}U$) tracer is employed). The plots show that the percent change in the $^{207}Pb/^{235}U$ date decreases for older dates, but the absolute magnitude of that change increases approximately logarithmically. At ca. 4.567 Ga a 0.1% shift in $^{238}U/^{235}U$ results in a 0.022% difference in the ^{207}Pb-^{235}U date. For Cenozoic dates, that difference increases to 0.1% per

0.1% shift in $^{238}U/^{235}U$. Figures 5B shows that both the percent and absolute change in the $^{207}Pb/^{206}Pb$ date decrease as a function of date. Assuming the $^{238}U/^{235}U$ is 137.88 when it is actually lower, as indicated by this study and others, biases both the calculated $^{207}Pb/^{235}U$ and $^{207}Pb/^{206}Pb$ dates toward older values, and the change in the $^{207}Pb/^{206}Pb$ date is always larger. Although the relative change in the $^{207}Pb/^{206}Pb$ date increases dramatically for younger dates, these young dates cannot be precisely resolved using the $^{207}Pb/^{206}Pb$ system; the more precise $^{206}Pb/^{238}U$ date is usually used instead.

The magnitude of these biases has limited impact on most published U-Pb dates given other sources of uncertainty but is significant for efforts to inter-calibrate $\lambda^{235}U$ and $\lambda^{238}U$ using very high-quality, high-precision, data generated specifically for this purpose (see above). Given the dearth of absolute $^{238}U/^{235}U$ determinations on U-bearing accessory minerals such a zircon, we believe it prudent at this point to refrain from proposing a $^{238}U/^{235}U$ value for use in geochronology until such a dataset exists. However, this study indicates that the assumption that all uranium in geochronologically relevant minerals has a $^{238}U/^{235}U = 137.88$ is unlikely. The question remains, what is the range of $^{238}U/^{235}U$ in commonly dated U-bearing accessory minerals, and how much variation should be expected (and accounted for in uncertainty estimation)?

Of particular interest are the oldest objects in the solar system. No absolute $^{238}U/^{235}U$ data have been reported for any meteorites, their components (e.g., CAIs), or other extraterrestrial materials so far. Brennecka et al (2010) demonstrate that there are variations in $^{238}U/^{235}U$ for CAIs within single meteorites, notably the Allende CV3 carbonaceous chondrite, whose CAI U-Pb dates are thought to record some of the earliest materials to condense in the solar system (AMELIN et al., 2009; BRENNECKA et al., 2010). This previously unappreciated variation in CAI uranium isotope compositions indicates that further inroads in high precision

Pb-Pb geochronology will depend upon determining $^{238}U/^{235}U$ for each dated CAI. Based upon the variation in $^{238}U/^{235}U$ documented by Brennecka et al (2010) these variations could result in a ≤5 Myr change for individual CAIs, although the effect on most CAIs will be much less, on the order of ~1 Myr (BRENNECKA et al., 2010). Published $^{238}U/^{235}U$ determinations on CAIs have been made by MC-ICP-MS using ^{233}U-^{236}U double spikes calibrated against CRM 145 (AMELIN et al., 2010) and SRM 950a (BRENNECKA et al., 2010) and therefore only provided values relative to the given reference material even though absolute values are often presented (calculated relative to an assumed $^{238}U/^{235}U \equiv 137.88$ for a given reference material). Absolute $^{238}U/^{235}U$ values have now been determined for these reference materials (this study) and therefore provide a means to calculate $^{238}U/^{235}U$ values of the CAIs that are traceable to SI units, from both previous and future analyses. Such absolute values can be used for accurate age determinations where coupled ^{207}Pb-^{206}Pb-^{238}U-^{235}U datasets have been generated from the exact same material (i.e., AMELIN et al., 2010).

7. CONCLUSIONS

We have determined new $^{238}U/^{235}U$ values of several commonly used natural uranium standards that lacked high precision isotopic compositions. All of the determinations made in this study are relative to a certified value of $^{233}U/^{236}U = 1.01906 \pm 0.016\%$ for the IRMM 3636 double spike (RICHTER et al., 2008). We estimate that the uncertainty from our mass spectrometry is <0.01% for the $^{238}U/^{235}U$ ratios including inter-laboratory agreement experiments. When the certified uncertainty in the IRMM 3636 $^{233}U/^{236}U$ ratio is considered we estimate the total uncertainty on the $^{238}U/^{235}U$ ratios determined for the various reference materials is < 0.02%.

The low (0.016%) uncertainty of the gravimetrically calibrated ^{233}U-^{236}U double spike (IRMM 3636) has permitted re-evaluation of some commonly used synthetic uranium international reference materials (CRM U500 and IRMM 184) resulting in new values with total uncertainties reduced compared to the certified values. The uncertainty on the $^{238}U/^{235}U$ ratio of CRM U500 has been reduced by a factor of five, from 0.1% to 0.02%. This reference material has been used to calibrate double spikes employed in high-accuracy U-Th and U-Pb geochronology and this reduced uncertainty will impact upon these determinations and estimates of $\lambda^{235}U$, $\lambda^{234}U$ and $\lambda^{230}Th$.

The consensus value of $^{238}U/^{235}U = 137.88$ (STEIGER and JAGER, 1977) has been used for the past three decades. However, improvements in mass spectrometry, combined with the development of the gravimetric reference IRMM ^{233}U-^{236}U double spike (RICHTER et al., 2008) provides us with an opportunity to reassess the consensus value. All the natural uranium standards analysed in this study have yielded $^{238}U/^{235}U$ ratios lower than the widely used ‘consensus’ value by up to 0.08%. These results, combined with the results of previous studies (STIRLING et al., 2007; WEYER et al., 2008), indicate that assuming $^{238}U/^{235}U$ is invariant at the <0.1% level is incorrect and must be considered in all high-precision studies that rely upon this value. The new $^{238}U/^{235}U$ determinations presented in this study provide values for use in tracer calibration and calibration of mass and/or detector bias during mass spectrometry and provide a reference for studies attempting to quantify absolute $^{238}U/^{235}U$ ratios for geochronologic determinations.

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Figure Captions

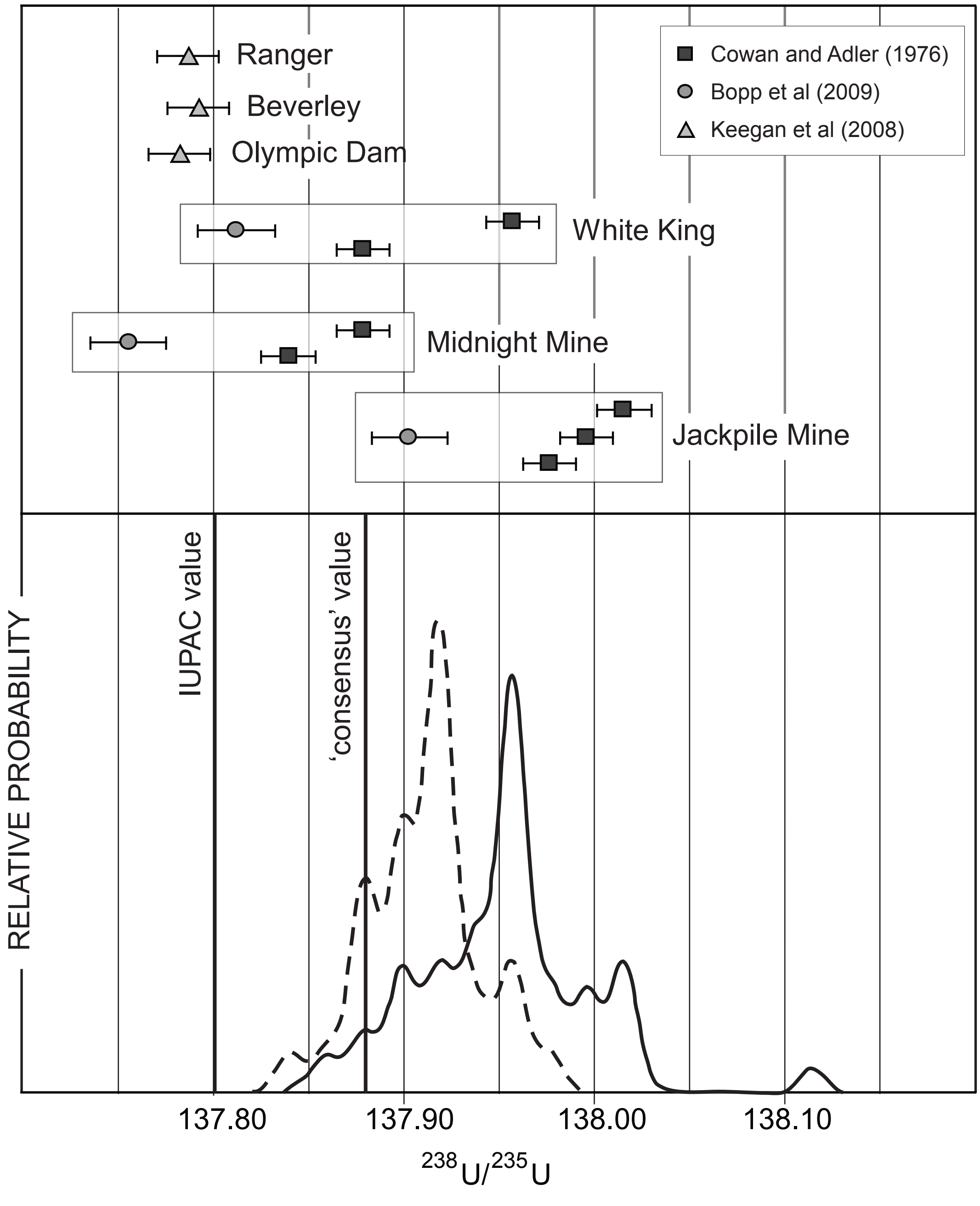
Figure 1. Summary of published data for uranium ore $^{238}U/^{235}U$ determinations. **A**. Plot of $^{238}U/^{235}U$ determinations for several ore uranium bodies. Note the 0.05 to 0.1% offset between the data of Bopp et al (2009) and Cowan and Adler (1976) for data from the same U-ore bodies, which indicates either an error in the normalisation of one of the datasets or isotopic heterogeneity. **B**. Relative probability plot of the Cowan and Adler (1976) compilation. Note, all the data presented in Cowan and Adler (1976) has been normalised to a reference material that has an assigned $^{238}U/^{235}U = 137.88$ although this value itself cannot be verified.

Figure 2. Plot of data showing reproducibility of the $^{238}U/^{235}U$ ratio determinations for CRM 112a, SRM 950a, HU-1 and IRMM-184 in this study. Black bars represent analyses of single reference material-IRMM 3636 mixes, the dark grey band reflects the external reproducibility and the lighter grey bar represent the total uncertainty (see text for discussion). All ranges are plotted with a coverage factor of $k = 2$ (2σ).

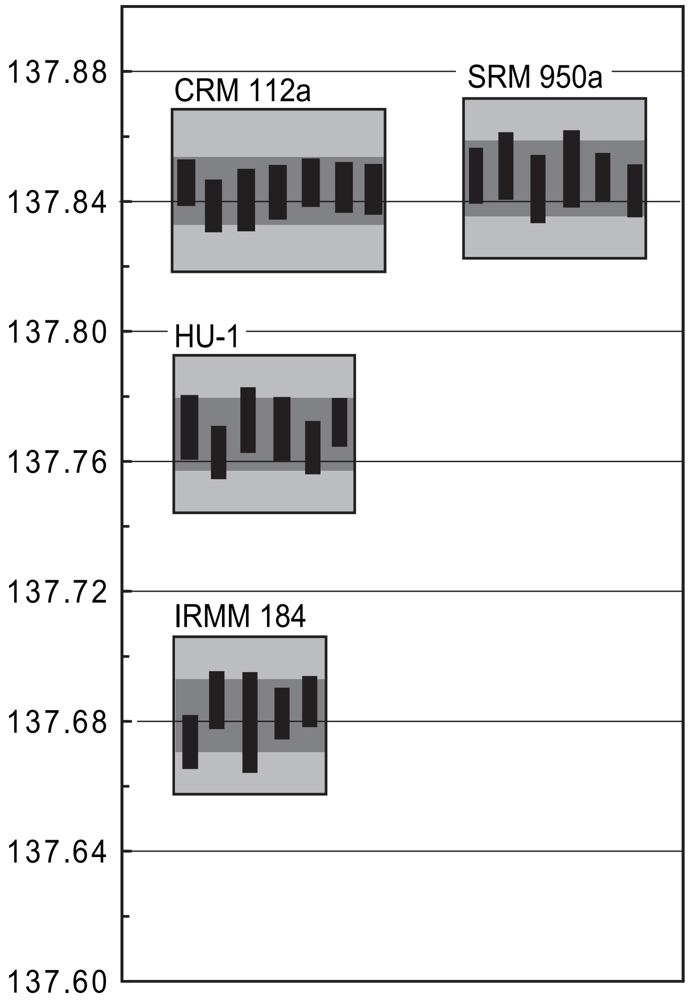
Figure 3. Plot of data showing repeatability and reproducibility of the $^{238}U/^{235}U$ ratio determinations for CRM U500. Smaller black bars represent analyses of single reference material-IRMM 3636 mixes, the dark grey band reflects the external reproducibility and the lighter grey bar represents the total uncertainty (see text for discussion). The larger black bars at right represent the weighted means and combined standard uncertainties from this study and the CRM U500 certificate. All ranges are plotted with a coverage factor of $k = 2$ (2σ).

Figure 4. Summary plot of natural and synthetic U standard values (absolute and epsilon scale relative to 137.88). The dark grey band reflects the external reproducibility and the lighter grey bar represents the combined standard uncertainty (see text for discussion). The black bar represents the certified value and combined standard uncertainty of IRMM 184. All ranges are plotted with a coverage factor of $k = 2$ (2σ).

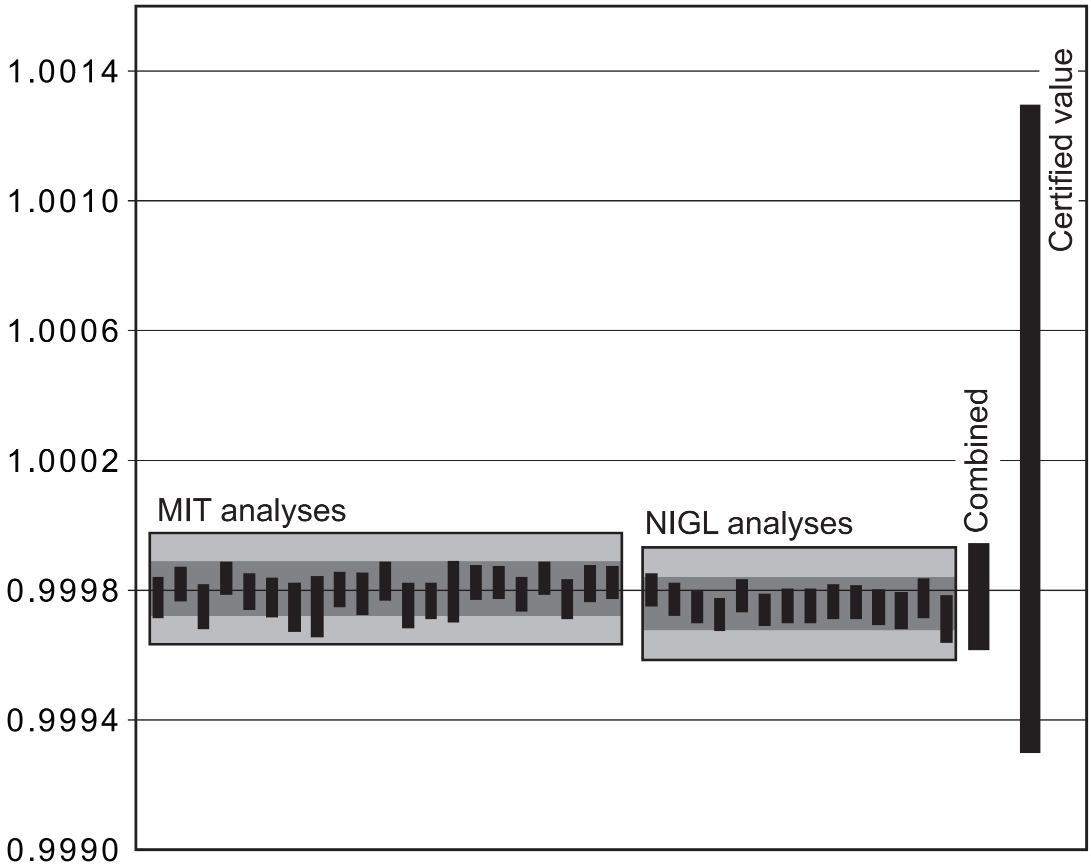
Figure 5. **A.** Plot of the percent and absolute (Ma) difference between the ^{207}Pb/^{235}U date calculated using ^{238}U/^{235}U = 137.88 and that using several alternate ^{238}U/^{235}U values and calculation of the ^{207}Pb/^{235}U ratio from the ^{238}U/^{235}U and ^{206}Pb/^{238}U ratios. See text for details. **B.** Same as in A, illustrating the effect of inaccuracy of ^{238}U/^{235}U ratio on ^{207}Pb/^{206}Pb dates. See text for details.



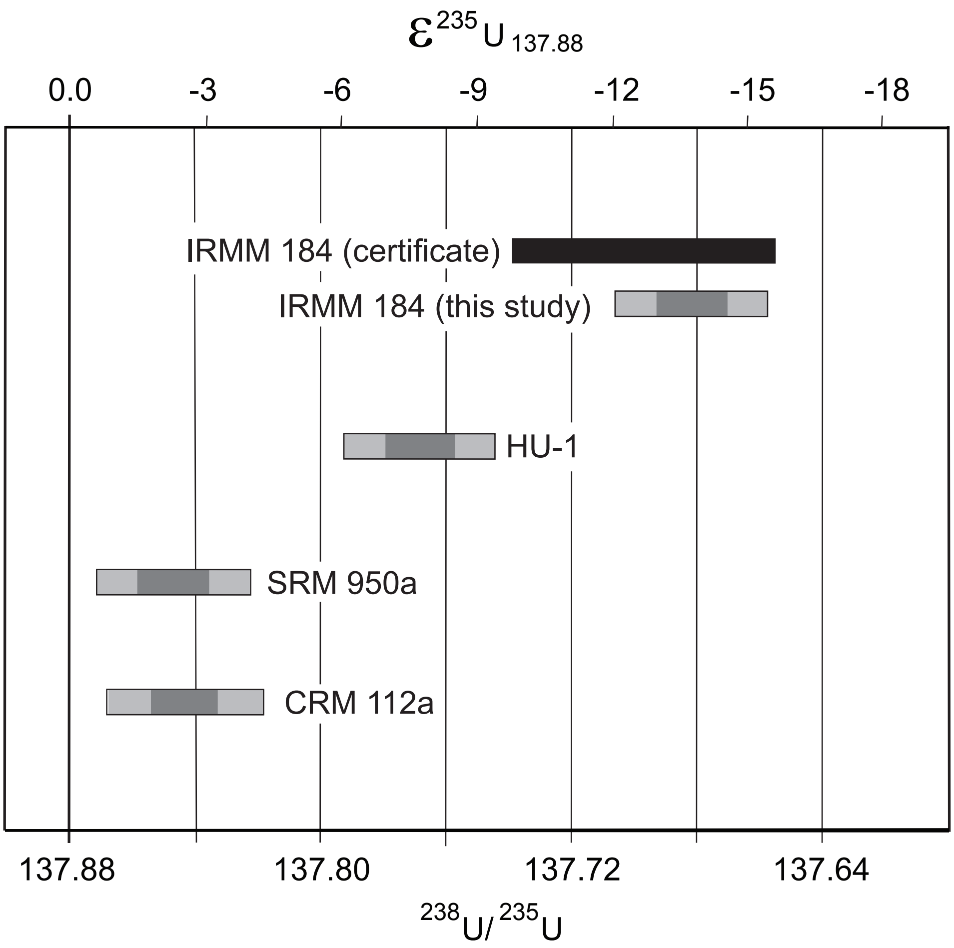
Condon et al (2010) Figure-1



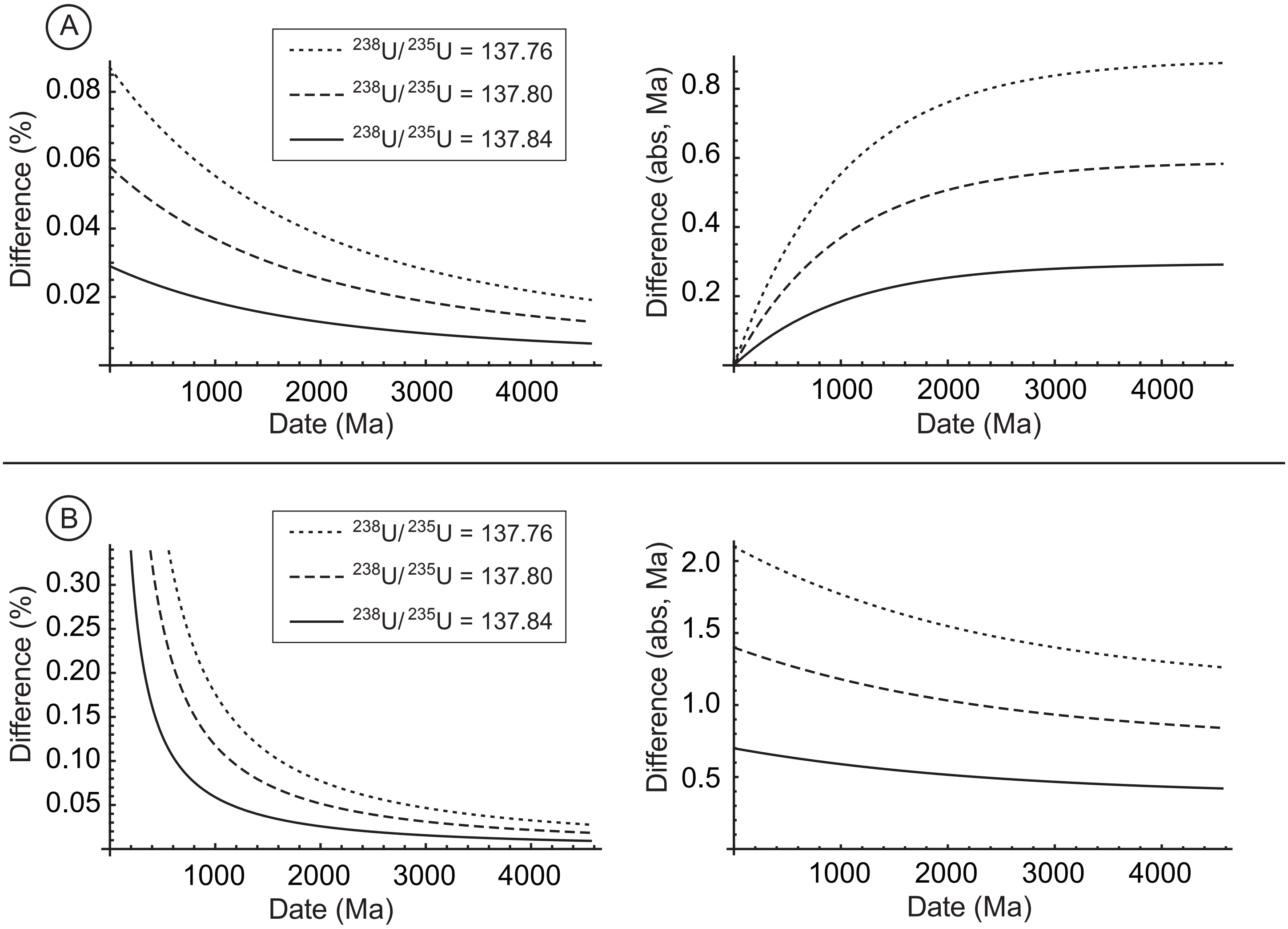
Condon et al (2010) Figure-2



Condon et al (2010) Figure-3



Condon et al (2010) Figure-4



Condon et al (2010) Figure-5

Table 1. Measured ^{233}U/^{235}U, ^{236}U/^{235}U and ^{238}U/^{235}U ratios for analyses of reference materials run as metal at NIGL and derived ^{238}U/^{235}U ratio corrected for mass bias using the IRMM 3636 ^{233}U-^{236}U double spike.

	^{235}U (V) (1)	^{233}U/^{235}U (2)	^{236}U/^{235}U (2)	^{238}U/^{235}U (2)	^{238}U/^{235}U (3)	± 2SE (ppm) (4)
CRM 112a, 11	0.34	2.58742	2.53835	137.795	137.846	16
CRM 112a, 14	0.31	1.31391	1.29004	137.907	137.839	27
CRM 112a, 17	0.13	5.44803	5.34897	137.882	137.841	45
CRM 112a, 18	0.23	7.93882	7.79769	137.926	137.843	31
CRM 112a, 19	0.32	1.62682	1.59697	137.864	137.846	19
CRM 112a, 20	0.34	1.38140	1.35442	137.714	137.845	25
CRM 112a, 21	0.30	2.24836	2.20613	137.818	137.844	23
CRM 112a Average: 137.844 ± 0.011/0.024 (2σ absolute), MSWD = 2.0/0.6						
SRM 950a, A	0.21	1.19303	1.17115	137.891	137.848	39
SRM 950a, B	0.20	1.39246	1.36732	137.937	137.851	56
SRM 950a, C	0.13	1.57875	1.55016	137.918	137.844	58
SRM 950a, E	0.20	1.93255	1.89761	137.927	137.851	69
SRM 950a, G	0.26	1.48146	1.45442	137.903	137.848	27
SRM 950a, H	0.27	1.92750	1.89283	137.933	137.844	32
SRM 950a Average: 137.847 ± 0.011/0.024 (2σ absolute), MSWD = 1.0/0.5						
HU-1, A	0.34	1.33552	1.31123	137.835	137.771	52
HU-1, B	0.19	1.80072	1.76779	137.810	137.763	34
HU-1, C	0.19	1.83035	1.79667	137.804	137.773	53
HU-1, D	0.17	2.84043	2.78855	137.815	137.770	50
HU-1, E	0.29	2.31863	2.27615	137.778	137.764	34
HU-1, F	0.29	2.93357	2.87969	137.801	137.772	26
HU-1 Average: 137.769 ± 0.011/0.024 (2σ absolute), MSWD = 3.1/1.2						
IRMM 184, 2	0.15	2.54410	2.49823	137.752	137.674	37
IRMM 184, 6	0.25	4.89897	4.80888	137.701	137.687	41
IRMM 184, 7	0.06	6.36985	6.24973	137.620	137.680	98
IRMM 184, 8	0.15	6.27835	6.15927	137.608	137.682	31
IRMM 184, C	0.29	7.75110	7.61172	137.741	137.686	32
IRMM 184 Average: 137.682 ± 0.011/0.024 (2σ absolute), MSWD = 4.3/1.9						
NIGL 2	32.78	0.104373	0.103966	1.00008	0.999802	7.5
NIGL 3a	3.02	0.520348	0.512087	0.999779	0.999773	12
NIGL 3b	9.33	0.104432	0.103935	0.999158	0.999747	8.6
NIGL 4	7.93	0.206635	0.204271	0.999674	0.999726	12
NIGL 5a	3.03	0.491417	0.482909	0.998146	0.999784	11

NIGL 5b	2.32	0.520488	0.511995	0.999296	0.999740	10
NIGL 6	0.62	0.488341	0.480275	0.998904	0.999752	20
NIGL 7	0.84	0.491004	0.483113	0.999373	0.999752	19
NIGL 8	0.84	0.489913	0.481939	0.999171	0.999765	20
NIGL 9	1.31	0.486251	0.478604	0.999704	0.999763	17
NIGL 16	1.66	2.075554	2.03702	0.999529	0.999748	23
NIGL 17	1.42	1.023839	1.00721	1.00093	0.999738	29
NIGL 18	0.93	1.984517	1.94959	1.00049	0.999774	34
NIGL 19	0.38	0.955375	0.939194	1.00007	0.999712	50
CRM U500 (NIGL) Weighted Mean: 0.999758 ± 0.000077/0.00017 (2σ absolute), MSWD = 16.5/1.0						

1. Run average ^{235}U signal intensity.

2. Measured ratios, corrected for baselines and Faraday detector amplifier gain only.

3. Ratios corrected for isotopic fractionation determined with the ^{233}U/^{236}U using a linear fractionation law on a cycle-by-cycle basis.

4. Twice the standard error of the mean of fractionation- and tracer-corrected ratios. This value does not include uncertainty terms determined from intra- and inter-laboratory comparison.

Table 2. Measured $^{238}U/^{233}U$ ratio and derived $^{17}O/^{16}O$ and $^{18}O/^{16}O$ for analyses of CRM U500 run at MIT as UO_2^+ and derived $^{238}U/^{235}U$ ratio corrected for mass bias and uranium oxide isobaric interferences using the IRMM 3636 ^{233}U-^{236}U double spike.

	^{235}U (V) (1)	$^{238}U/^{233}U$ (2)	$^{17}O/^{16}O$ (3)	$^{18}O/^{16}O$ (3)	alpha (4)	$^{238}U/^{235}U$ (5)	± 2SE (ppm) (6)
MIT AA	1.10	0.877586	0.000380	0.002075	0.047	0.999777	19
MIT AB	1.81	0.891797	0.000383	0.002068	0.035	0.999820	9.2
MIT AC	0.88	0.941793	0.000376	0.002069	0.032	0.999749	23
MIT AD	1.81	0.811309	0.000382	0.002065	0.031	0.999837	7.8
MIT AE	1.29	0.946123	0.000380	0.002073	0.022	0.999797	13
MIT BB	1.74	1.81078	0.000372	0.002074	0.027	0.999777	17
MIT BC	1.24	0.916028	0.000380	0.002075	0.021	0.999749	27
MIT BE	1.10	0.887954	0.000376	0.002063	-0.015	0.999750	39
MIT BF	1.15	0.874353	0.000380	0.002068	0.039	0.999803	12
MIT BG	0.82	0.877542	0.000382	0.002075	-0.047	0.999789	20
MIT BJ	0.84	0.894506	0.000385	0.002068	0.010	0.999829	16
MIT	1.90	1.00740	0.000376	0.002066	0.068	0.999754	24
MIT	1.85	1.00897	0.000378	0.002073	0.065	0.999767	13
MIT	0.66	0.967510	0.000379	0.002076	0.071	0.999795	39
MIT B1	1.40	0.848095	0.000379	0.002074	0.055	0.999825	8.8
MIT B2	1.10	0.857560	0.000378	0.002070	0.072	0.999825	7.6
MIT B3	1.35	0.862788	0.000379	0.002069	0.034	0.999789	10
MIT B4	1.48	0.855084	0.000380	0.002066	0.060	0.999839	6.8
MIT A	3.65	4.42551	0.000371	0.002065	0.061	0.999772	17
MIT I	1.50	0.985840	0.000382	0.002053	0.070	0.999821	14
MIT K	2.48	0.944622	0.000378	0.002065	0.079	0.999824	6.9
Weighted Mean: 0.999805 ± 0.000078/0.00017 (2σ absolute), MSWD = 2.3/1.0							

1. Run average ^{235}U signal intensity.

2. Measured ratio, corrected for baselines and Faraday detector amplifier gain only.

3. Average isotopic composition of oxygen in UO_2 during analysis. An oxygen isotopic composition was determined for each cycle and used to correct for isobaric oxide interferences in that cycle (see Appendix 1.2)

4. Average fractionation during analysis, determined using a linear fractionation law. A fractionation value was determined each cycle and used for correcting that cycle.

5. Ratios corrected for isotopic fractionation and oxygen isobaric interferences on a cycle-by-cycle basis.

6. Twice the standard error of the mean of fractionation- oxide- and tracer-corrected ratios. This value does not include uncertainty terms determined from intra- and inter-laboratory comparison.

Table 3. Minor isotope ratio (^{234}U/^{235}U and ^{236}U/^{235}U) data for CRM U500 based upon analyses of non-spiked aliquots run at NIGL using the newly determined ^{238}U/^{235}U ratio for internal normalisation.

	^{235}U (V) (1)	^{238}U/^{235}U (2)	^{234}U/^{235}U (3)	± 2SE (ppm)	^{236}U/^{235}U (2)	± 2SE (ppm)
1a	14.5	1.000049	0.01042031	44	0.001517657	264
3a	15.7	1.000697	0.01042325	61	0.001519614	311
4a	15.2	1.000017	0.01042240	56	0.001519427	244
5a	11.4	1.000597	0.01042190	124	0.001519947	601
6a	21.4	1.000906	0.01042415	253	0.001520208	835
7a	15.4	1.000085	0.01042691	187	0.001520980	710
^{234}U/^{235}U Average: 0.010421810 ± 0.00000030/0.00000062 (2σ absolute), MSWD = 19.5/1.0						
^{236}U/^{235}U Average: 0.001519054 ± 0.00000022/0.00000023 (2σ absolute), MSWD = 15.6/1.0						

1. Run average ^{235}U signal intensity.

2. Measured ratios, corrected for baselines and faraday amplifier gain only.

3. Ratios corrected for mass fractionation using the measured ^{238}U/^{235}U using a linear fractionation law.

Table 4. Summary of results.

	$^{238}U/^{235}U$ (1)	± (abs) (2)	$\varepsilon^{235}U_{137.88}$ (3)	$^{238}U/^{235}U$ (4)	± (%) (5)
CRM 112a	137.844	0.024	-2.6	-	-
SRM 950a	137.847	0.024	-2.4	-	-
HU-1	137.769	0.024	-8.1	-	-
IRMM 184	137.682	0.024	-14.3	137.697	0.03
CRM U500	0.999781	0.000164	-	1.0003	0.1

1. Ratio determined in this study using IRMM 3636 ^{233}U-^{236}U double spike to correct for mass fractionation.

2. Total uncertainty (see text for discussion).

3. $\varepsilon^{235}U = 10^4 \times [(^{235}U/^{238}U_{sample}/^{235}U/^{238}U_{standard}) - 1]$, with a $^{235}U/^{238}U_{standard}$ value of 137.88 used for $\varepsilon^{235}U_{137.88}$.

4. Certified value.

5. Uncertainty on certified value.

APPENDIX 1. DATA REDUCTION

Each solution was spiked with IRMM 3636, a ^{233}U-^{236}U tracer with minor amounts of ^{235}U and ^{238}U, to determine the solution ^{238}U/^{235}U ratio. Repeated measurements of the ^{233}U/^{236}U ratio were used to monitor instrumental mass fractionation for each cycle; cycles were then corrected for fractionation and ^{238}U and ^{235}U interferences from the tracer. The standards SRM 950a and SRM U500 also contain a significant quantity of ^{236}U, which must be subtracted from the ^{236}U of the tracer for fractionation correction. The same set of equations can be used for solutions with and without ^{236}U, neglecting ^{236}U$_{std}$ terms for the latter.

For this paper, calculations were performed in MATLAB, using its provided trust-region dogleg method to solve the system of equations.

A1.1 Uranium Metal Analyses at NIGL

The molar contributions to each of the measured uranium isotopes are:

$$233_{total} = 233_{3636} \tag{1}$$
$$235_{total} = 235_{std} + 235_{3636} \tag{2}$$
$$236_{total} = 236_{std} + 236_{3636} \tag{3}$$
$$238_{total} = 238_{std} + 238_{3636} \tag{4}$$

By measuring three isotope ratios as a metal

$$\left(\frac{235}{233}\right)_{meas} \quad \left(\frac{236}{233}\right)_{meas} \quad \left(\frac{238}{233}\right)_{meas}$$

and using the certified isotope ratios of IRMM 3636 and, if ^{236}U is present, the standard:

$$\frac{235_{3636}}{233_{3636}} \quad \frac{236_{3636}}{233_{3636}} \quad \frac{238_{3636}}{233_{3636}} \quad \frac{236_{std}}{235_{std}}$$

it is possible to measure the ^{238}U/^{235}U ratio of the standard,

$$\frac{238_{std}}{235_{std}}$$

To determine the fractionation correction coefficient α, divide the expressions for the total moles of ^{235}U and ^{236}U by ^{233}U:

$$\frac{235_{total}}{233_{total}} = \frac{235_{std} + 235_{3636}}{233_{3636}} \qquad (5)$$

$$\frac{236_{total}}{233_{total}} = \frac{236_{std} + 236_{3636}}{233_{3636}} \qquad (6)$$

The right hand sides of equations *5* and *6* can be split into two fractions, one of which is a certified isotope ratio:

$$\frac{235_{total}}{233_{total}} = \frac{235_{std}}{233_{3636}} + \frac{235_{3636}}{233_{3636}} \qquad (7)$$

$$\frac{236_{total}}{233_{total}} = \frac{236_{std}}{233_{3636}} + \frac{236_{3636}}{233_{3636}} \qquad (8)$$

The left hand side of equations *7* and *8* can be expressed in terms of fractionation-corrected measured ratios:

$$\left(\frac{235}{233}\right)_{meas}(1 + 2\alpha) = \frac{235_{std}}{233_{3636}} + \frac{235_{3636}}{233_{3636}} \qquad (9)$$

$$\left(\frac{236}{233}\right)_{meas}(1 + 3\alpha) = \frac{236_{std}}{233_{3636}} + \frac{236_{3636}}{233_{3636}} \qquad (10)$$

Finally, substitute the equivalent expression

$$\frac{235_{std}}{233_{3636}} \cdot \frac{236_{std}}{235_{std}}$$

for

$$\frac{236_{std}}{233_{3636}}$$

into equation *10*, to give a system of two equations

$$\left(\frac{235}{233}\right)_{meas}(1+2\alpha)=\frac{235_{std}}{233_{3636}}+\frac{235_{3636}}{233_{3636}} \tag{11}$$

$$\left(\frac{236}{233}\right)_{meas}(1+3\alpha)=\frac{235_{std}}{233_{3636}}\cdot\frac{236_{std}}{235_{std}}+\frac{236_{3636}}{233_{3636}} \tag{12}$$

with two unknowns,

$$\alpha \text{ and } \frac{235_{std}}{233_{3636}}$$

Solving this system of equations for α gives:

$$\boldsymbol{\alpha}=\frac{\left(\frac{236}{233}\right)_{meas}-\frac{236_{3636}}{233_{3636}}+\frac{236_{std}}{235_{std}}\cdot\left[\frac{235_{3636}}{233_{3636}}-\left(\frac{235}{233}\right)_{meas}\right]}{2\cdot\left(\frac{235}{233}\right)_{meas}\cdot\frac{236_{std}}{235_{std}}-3\cdot\left(\frac{236}{233}\right)_{meas}} \tag{13}$$

To determine the ^{238}U/^{235}U of the standard, subtract the IRMM 3636 contributions from the total moles of each isotope:

$$235_{total}=235_{std}+235_{3636} \tag{14}$$

$$238_{total}=238_{std}+238_{3636} \tag{15}$$

$$\frac{238_{std}}{235_{std}}=\frac{238_{total}-238_{3636}}{235_{total}-235_{3636}} \tag{16}$$

Multiply the numerator and denominator by $1/233_{total}$,

$$\frac{238_{std}}{235_{std}}=\frac{238_{total}-238_{3636a}}{235_{total}-235_{3636a}}\cdot\frac{1/233_{total}}{1/233_{total}} \qquad \text{(17}$$

Expand the resulting fractions, using $233_{total}=233_{3636a}$

$$\frac{238_{std}}{235_{std}}=\frac{\left[\frac{238_{total}}{233_{total}}-\frac{238_{3636}}{233_{3636}}\right]}{\left[\frac{235_{total}}{233_{total}}-\frac{235_{3636}}{233_{3636}}\right]} \tag{18}$$

Finally, the total isotope ratios can be expressed as fraction-corrected measured ratios, using the α calculated above.

$$\frac{\mathbf{238}_{\boldsymbol{std}}}{\mathbf{235}_{\boldsymbol{std}}} = \frac{\left[\left(\frac{238}{233}\right)_{meas}(1+5\alpha) - \frac{238_{3636}}{233_{3636}}\right]}{\left[\left(\frac{235}{233}\right)_{meas}(1+2\alpha) - \frac{235_{3636}}{233_{3636}}\right]} \tag{19}$$

A1.2 Uranium Oxide Analyses at MIT

The mixture of U500 and IRMM 3636a contains ^{233}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U. The certificate of analysis for U500 contains no mention of ^{233}U, an artificial isotope produced by neutron irradiation of ^{232}Th. Thus, the total molar quantity of each U isotope is:

$$233_{total} = 233_{3636} \tag{20}$$
$$234_{total} = 234_{std} + 234_{3636} \tag{21}$$
$$235_{total} = 235_{std} + 235_{3636} \tag{22}$$
$$236_{total} = 236_{std} + 236_{3636} \tag{23}$$
$$238_{total} = 238_{std} + 238_{3636} \tag{24}$$

Ionization efficiency is improved by evaporation, ionization, and measurement of the U species as a uranium oxide (UO_2^+) instead of as a reduced metal. Most of the oxygen in UO_2^+ is ^{16}O, but about 0.2% is ^{18}O and 0.04% is ^{17}O. These slightly heavier polyatomic ions interfere with heavier isotopes of U with two ^{16}O atoms, adding to the signal measured at that U oxide mass. The interference is proportional to the U isotope abundance and the ratio of ^{18}O or ^{17}O to ^{16}O (represented as R_{18} and R_{17}, respectively), and must be multiplied by two to account for both permutations of 16 with 17 or 18 (e.g. $U^{18}O^{16}O^+$ or $U^{16}O^{18}O^+$). The $^{17}O^{18}O$ combination is unlikely enough (<0.2 per million oxide species) to be ignored here.

The molar abundance of each uranium oxide mass, with interfering oxide species, is:

$$265 = 233_{total} \tag{25}$$

$$267 = 235_{total} + 2 \cdot R_{17} \cdot 234_{total} + 2 \cdot R_{18} \cdot 233_{total} \tag{26}$$

$$268 = 236_{total} + 2 \cdot R_{17} \cdot 235_{total} + 2 \cdot R_{18} \cdot 234_{total} \tag{27}$$

$$269 = 2 \cdot R_{17} \cdot 236_{total} + 2 \cdot R_{18} \cdot 235_{total} \tag{28}$$

$$270 = 238_{total} + 2 \cdot R_{18} \cdot 236_{total} \tag{29}$$

$$272 = 2 \cdot R_{18} \cdot 238_{total} \tag{30}$$

Exploiting the fact that mass 265 is produced only by $^{233}U^{16}O^{16}O$, the left side of equations 6-11 can be divided by 265 to produce uranium oxide ratios, and the right side can be divided through by 233 to generate uranium atomic ratios. The measured uranium oxide ratios must be corrected for a linear mass-dependent fractionation factor α.

$$\left(\frac{267}{265}\right)_{meas} \cdot (1 + 2\alpha) = \frac{235_{total}}{233_{total}} + 2 \cdot R_{17} \cdot \frac{234_{total}}{233_{total}} + 2 \cdot R_{18} \cdot \frac{233_{total}}{233_{total}} \tag{31}$$

$$\left(\frac{268}{265}\right)_{meas} \cdot (1 + 3\alpha) = \frac{236_{total}}{233_{total}} + 2 \cdot R_{17} \cdot \frac{235_{total}}{233_{total}} + 2 \cdot R_{18} \cdot \frac{234_{total}}{233_{total}} \tag{32}$$

$$\left(\frac{269}{265}\right)_{meas} \cdot (1 + 4\alpha) = 2 \cdot R_{17} \cdot \frac{236_{total}}{233_{total}} + 2 \cdot R_{18} \cdot \frac{235_{total}}{233_{total}} \tag{33}$$

$$\left(\frac{270}{265}\right)_{meas} \cdot (1 + 5\alpha) = \frac{238_{total}}{233_{total}} + 2 \cdot R_{18} \cdot \frac{236_{total}}{233_{total}} \tag{34}$$

$$\left(\frac{272}{265}\right)_{meas} \cdot (1 + 7\alpha) = 2 \cdot R_{18} \cdot \frac{238_{total}}{233_{total}} \tag{35}$$

These five equations have five unknowns: $\frac{235_{total}}{233_{total}}$ and $\frac{238_{total}}{233_{total}}$, (which are controlled by the CRM U500/ IRMM 3636 ratio of the mixture and the $^{238}U/^{235}U$ of the standard), R_{17} and R_{18} (the ratios of ^{17}O and ^{18}O to ^{16}O), and the fractionation, α. The other two U isotope ratios, $\frac{234_{total}}{233_{total}}$ and $\frac{236_{total}}{233_{total}}$, can be re-cast in terms of the first two and the certified minor isotope ratios of each solution.

$$\frac{234_{total}}{233_{total}} = \frac{234_{std}}{233_{3636}} + \frac{234_{3636}}{233_{3636}} \tag{36}$$

Where

$$\frac{234_{std}}{233_{3636}} = \frac{234_{std}}{235_{std}} \cdot \left(\frac{235_{std} + 235_{3636}}{233_{3636}} - \frac{235_{3636}}{233_{3636}}\right) \tag{37}$$

$$\frac{234_{std}}{233_{3636}} = \frac{234_{std}}{235_{std}} \cdot \left(\frac{235_{total}}{233_{3636}} - \frac{235_{3636}}{233_{3636}}\right) \tag{38}$$

Neglecting the term $\frac{234_{std}}{235_{std}} \cdot \frac{235_{3636}}{233_{3636}} = 4.7 \times 10^{-7}$ for CRM U500,

$$\frac{234_{total}}{233_{total}} = \frac{234_{std}}{235_{std}} \cdot \frac{235_{total}}{233_{total}} + \frac{234_{3636}}{233_{3636}} \tag{39}$$

Likewise,

$$\frac{236_{total}}{233_{total}} = \frac{236_{std}}{235_{std}} \cdot \frac{235_{total}}{233_{total}} + \frac{236_{3636}}{233_{3636}} \tag{40}$$

Substituting these expressions into equations *31-35* yields:

$$\left(\frac{267}{265}\right)_{meas}\cdot(1+2\alpha)=\frac{235_{total}}{233_{total}}+2\cdot R_{17}\cdot\left(\frac{234_{std}}{235_{std}}\cdot\frac{235_{total}}{233_{total}}+\frac{234_{3636}}{233_{3636}}\right)+2\cdot R_{18} \tag{41}$$

$$\left(\frac{268}{265}\right)_{meas}\cdot(1+3\alpha)=\frac{236_{std}}{235_{std}}\cdot\frac{235_{total}}{233_{total}}+\frac{236_{3636}}{233_{3636}}+2\cdot R_{17}\cdot\frac{235_{total}}{233_{total}}+2\cdot R_{18}\cdot\left(\frac{234_{std}}{235_{std}}\cdot\frac{235_{total}}{233_{total}}+\frac{234_{3636}}{233_{3636}}\right) \tag{42}$$

$$\left(\frac{269}{265}\right)_{meas}\cdot(1+4\alpha)=2\cdot R_{17}\cdot\left(\frac{236_{std}}{235_{std}}\cdot\frac{235_{total}}{233_{total}}+\frac{236_{3636}}{233_{3636}}\right)+2\cdot R_{18}\cdot\frac{235_{total}}{233_{total}} \tag{43}$$

$$\left(\frac{270}{265}\right)_{meas}\cdot(1+5\alpha)=\frac{238_{total}}{233_{total}}+2\cdot R_{18}\cdot\left(\frac{236_{std}}{235_{std}}\cdot\frac{235_{total}}{233_{total}}+\frac{236_{3636}}{233_{3636}}\right) \tag{44}$$

$$\left(\frac{272}{265}\right)_{meas}\cdot(1+7\alpha)=2\cdot R_{18}\cdot\frac{238_{total}}{233_{total}} \tag{45}$$

The solution to this set of five non-linear equations with five unknowns is most quickly reached with a numerical non-linear equation solver seeded with reasonable values. In order to track changing fractionation and oxide interference ratios with time, each cycle of measured oxide ratios can be substituted into the left side of equations *41-45*, yielding a time-resolved record of fractionation and oxide interferences during the analysis.

After discarding outliers and calculating the mean values for $\frac{235_{total}}{233_{total}}$ and $\frac{238_{total}}{233_{total}}$, the ^{235}U and ^{238}U contributions from 3636 must be subtracted to determine the ^{238}U/^{235}U of the standard:

$$\frac{238_{std}}{235_{std}} = \frac{238_{total} - 238_{3636}}{235_{total} - 235_{3636}} \cdot \left(\frac{1/233_{total}}{1/233_{total}}\right) \tag{46}$$

$$\frac{\mathbf{238}_{\boldsymbol{std}}}{\mathbf{235}_{\boldsymbol{std}}} = \frac{\left(\frac{238_{total}}{233_{total}} - \frac{238_{3636}}{233_{3636}}\right)}{\left(\frac{235_{total}}{233_{total}} - \frac{235_{3636}}{233_{3636}}\right)} \tag{47}$$

Appendix 2 – Independent assessment of mass spectrometry performance.

In order to independently assess the performance of our mass-spectrometry the matching of the Faraday cups on the NIGL Triton 2 was investigated by replicate analyses of the LaJolla Nd standard (LUGMAIR and CARLSON, 1978) using a method and cup configuration that duplicated our U metal data acquisition protocols (Table 2). The purpose of this experiment was neither to determine the absolute accuracy nor ultimate performance of this TIMS instrument, but rather, to establish the typical level of cup matching and external reproducibility at ion beam intensities typical of the ^{233}U-^{235}U-^{236}U ion beams encountered in the U measurements and to ensure the instrument exhibited no gross anomalies relative to other multi-collector TIMS instruments.

Nd was loaded onto outgassed zone-refined Re filaments prepared and tested as for the U measurements and analysed as Nd+ ions using a double filament configuration. Data obtained for ion beams ranging from 0.3-1.0 V ^{142}Nd were used for comparison with the U data. An identical measurement protocol to U measurements was used for baseline and gain measurement, zoom lens use and amplifier rotation. The data were corrected for mass fractionation using an exponential correction (WASSERBURG et al., 1981), using ^{146}Nd/^{144}Nd ≡ 0.7219, the TIMS mass fractionation normalization value for Nd+ ions was defined on the basis of an average of many ^{146}Nd/^{144}Nd determinations (O'NIONS et al., 1977). We have used the ^{142}Nd/^{144}Nd and ^{145}Nd/^{144}Nd ratios for cup matching, partly because there are recent very high precision TIMS measurements available for comparison from the ^{142}Nd –anomaly literature (e.g. (CARO et al., 2006; SHARMA and CHEN, 2004). The experiment results are summarized in Table 3 and show that all of the data as measured in various Faraday cup pairs agree well within error of the best single-collector peak jumping Nd isotope data (LUGMAIR and CARLSON, 1978; WASSERBURG et al., 1981) which are independent of any inaccuracies related to cup efficiencies. Furthermore, the critical axial – high 2 Faraday pair agree with the Caro et al. (CARO et al., 2006) ^{142}Nd/^{144}Nd data at the ~5 ± 25 ppm level (2 SD), and with the (SHARMA and CHEN, 2004) data at the ~16 ± 25 ppm level (2 SD) based on ^{142}Nd/^{144}Nd normalized for mass fractionation using ^{146}Nd/^{144}Nd measured on the same cups. This further supports our inference that there is little or no significant bias to be expected on the ^{235}U/^{238}U measurements normalized to ^{233}U/^{236}U arising from differences in the axial – high 2 Faraday cups. The Nd measurements also show all other pairs of Faraday cups are matched to levels better than ~9 ± 37 ppm. Based upon these experiments we are confident that our analytical uncertainties, on the order of 0.004 to 0.008% for the corrected ^{238}U/^{235}U determinations, are an accurate reflection of our ability to measure that ratio at these experimental conditions.

Table A2.1. Cup configuration for TIMS analyses at NIGL. For natural uranium materials with no significant overlap of isotopes between the unknown natural uranium and the IRMM 3636 double spike a method using cycles 2 and 3 was employed. Nd isotopes in parentheses indicate the masses used in the cup-matching experiment.

Collector:	**Low 1**	**Axial**	**High 1**	**High 2**	**High 3**
Cycle 1		(^{142}Nd)		(^{144}Nd)	
Cycle 2	^{233}U (^{142}Nd)	^{234}U (^{143}Nd)	^{235}U (^{144}Nd)	(^{145}Nd)	^{238}U (^{146}Nd)
Cycle 3	^{234}U (^{143}Nd)	^{235}U (^{144}Nd)	^{236}U (^{145}Nd)	^{238}U (^{146}Nd)	

Table A2.2. Summary of La Jolla standard Nd isotope data used to assess matching of Faraday cups.

	Ax-H2 ^{142}Nd/^{144}Nd	± 2SE (abs)	**L1-H1** ^{142}Nd/^{144}Nd (1)	± 2SE (abs)	**Ax-H1** ^{145}Nd/^{144}Nd (1)	± 2SE (abs)	**H1-H2** ^{145}Nd/^{144}Nd (2)	± 2SE (abs)
^{142}Nd<1V	1.141866	12	1.141842	11	0.348406	4	0.348396	3
	1.141849	15	1.141841	17	0.348401	5	0.348406	4
	1.141858	16	1.141851	16	0.348403	5	0.348396	3
	1.141845	12	1.141832	11	0.348402	3	0.348403	4
	1.141856	12	1.141842	13	0.348406	3	0.348396	3
	1.141841	12	1.141786	12	0.348402	3	0.348403	3
	1.141833	12	1.141836	13	0.348408	4	0.348404	4
	1.141822	13	1.141817	12	0.348401	4	0.348401	4
	1.141829	13	1.141806	14	0.348407	4	0.348404	3
Average ± 2 RSD (ppm)	**1.141844**	**25**	**1.141824**	**37**	**0.348404**	**16**	**0.348401**	**23**
Deviation from Caro et al 2006 (ppm)	**5.3**		**-8.7**		**-1.7**		**-10.8**	
Deviation from Sharma and Chen 2004 (ppm)	**16.0**		**2.0**		**14.4**		**5.3**	

^{142}Nd~2.5V	1.141833	8	1.141827	8	0.348405	3	0.348398	2
	1.141833	9	1.141841	17	0.348407	3	0.348408	2
	1.141837	9	1.141822	19	0.348409	3	0.348402	3
	1.141858	10	1.141847	9	0.348403	3	0.348401	3
	1.141828	10	1.141821	10	0.348410	3	0.348406	3
	1.141832	8	1.141819	10	0.348408	3	0.348400	3
Average ± 2 RSD (ppm)	**1.141837**	**19**	**1.141830**	**20**	**0.348407**	**15**	**0.348403**	**22**
Deviation from Caro et al 2006 (ppm)	**-1.2**		**-7.6**		**6.6**		**-5.7**	
Deviation from Sharma and Chen 2004 (ppm)	**9.5**		**3.1**		**22.6**		**10.4**	

	^{142}Nd/^{144}Nd	± 2SE (abs)	^{145}Nd/^{144}Nd	± 2SE (abs)
Carro et al., 2006 Ames Metal	1.141838	2	0.348405	1
Sharma and Chen 2004 Wasserburg soln nNd-B	1.141826	6	0.348399	1
Wasserburg et al 1981 Wasserburg soln nNd-B	1.141827		0.348417	