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Short communication

# New average values for the $n(^{238}U)/n(^{235}U)$ isotope ratios of natural uranium standards

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ABSTRACT

Reliable standard materials for the precise and accurate measurements of $n(^{238}U)/n(^{235}U)$ isotope ratios in natural sample materials have gained an increasingly important role in modern geochemistry. Recent findings do not only show variability for the $n(^{238}U)/n(^{235}U)$ isotope ratios in nature of up to 0.13% but also emphasize that accurate $n(^{238}U)/n(^{235}U)$ isotope ratios are needed for reliable and consistent Pb–Pb dating of geological samples. The commonly used 'consensus value' of 137.88 for the $n(^{238}U)/n(^{235}U)$ isotope ratio of the NBS SRM 960 (NBL CRM 112a) standard has been re-measured in a collaborative effort by several geochemistry laboratories and the Institute for Reference Materials and Measurements (IRMM), who produced the isotopic reference materials used for these measurements. The new data have been acquired using a variety of new isotopic reference materials, for example the new gravimetrically calibrated $n(^{233}U)/n(^{236}U)$-double spike IRMM-3636, combined with new measurement methods, resulting in a new average value of 137.837(15) for the $n(^{238}U)/n(^{235}U)$ isotope ratio of NBS SRM 960. This new value is about 0.031% lower than the old consensus value. Moreover, it is traceable to the SI and an uncertainty is provided according to the Guide to the Expression of Uncertainty in Measurements (GUM). Additionally a summary of new measurements of the $n(^{234}U)/n(^{238}U)$ isotope ratios of the NBS SRM 960 is given, which are of interest for geochemical applications. As an alternative to NBS SRM 960, the (close to) natural reference material IRMM-184 has been re-measured by several laboratories using the $n(^{233}U)/n(^{236}U)$-double spike IRMM-3636, resulting in a $n(^{238}U)/n(^{235}U)$ value of 137.683(20), which is in agreement with the certified value of 137.697(41).

## 1. Introduction

The isotope composition of uranium, i.e. the ratio of the two primordial uranium isotopes $n(^{238}U)/n(^{235}U)$, has been assumed to be constant on earth and in the solar system. The commonly excepted value for $n(^{238}U)/n(^{235}U)$, which has been used for Pb–Pb dating for the last ~30 years was 137.88 [1–3]. Within the last few years it turned out that (1) there are considerable uranium isotope variations within terrestrial material which were produced by isotope fractionation during chemical reactions [4–8] and (2) there are even larger isotope variations in meteorites, i.e. calcium–aluminum-rich inclusions (CAIs) [9], which define the currently excepted age of the solar system. The discovery of these natural uranium isotope variations was mainly the result of improved analytical precision, in particular for small sample amounts, such as a few ng of U. These findings are dramatic for geochronology, as a constant and known $n(^{238}U)/n(^{235}U)$ is a prerequisite for Pb–Pb dating, the most precise dating technique for absolute ages, as uranium isotope variations between samples may produce artificial shifts of Pb–Pb ages and affect the interpretation of scenarios in geo- and cosmochemistry. However, the question also arises of "how accurate do we know absolute values for $n(^{238}U)/n(^{235}U)$ of individual samples" and with that "how accurate can absolute Pb–Pb ages be?" Recent results using a gravimetrically calibrated $n(^{233}U)/n(^{236}U)$ double spike IRMM 3636 reference material [10] indicate that the uranium standard NBS SRM 950a, which was commonly used to define the excepted "natural" $n(^{238}U)/n(^{235}U)$ isotope ratio, has a slightly lower $n(^{238}U)/n(^{235}U)$ ratio of 137.84. This value is indistinguishable from the U isotope composition for NBS SRM 960 (NBL CRM 112A), which has now been re-determined by several laboratories, using various old and new isotope reference materials. These findings provide new implications about the average uranium isotope composition of the earth and the solar system.

For accurate mass spectrometric measurements of geological samples suitable isotope reference materials are needed to validate measurement procedures and to calibrate multi-collector and

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**Table 1**
$n(^{238}\text{U})/n(^{235}\text{U})$ ratios for NBS SRM 960 (NBL112a) and IRMM-184 measured by all contributing laboratories.

| Laboratory | Instrumentation | Reference material | NBS SRM 960 (NBL CRM 112a) $n(^{238}\text{U})/n(^{235}\text{U})$ (U with $k = 2$) | IRMM-184 $n(^{238}\text{U})/n(^{235}\text{U})$ (U with $k = 2$) |
|---|---|---|---|---|
| Institute for Reference Materials and Measurements, IRMM | Triton TIMS | $n(^{233}\text{U})/n(^{236}\text{U})$ double spike IRMM-3636, $n(^{233}\text{U})/n(^{236}\text{U}) = 1.01906(16)$ | 137.836(23) | 137.689(22) |
| NIGL Isotope Geoscience Laboratory | Triton TIMS | $n(^{233}\text{U})/n(^{236}\text{U})$ double spike IRMM-3636, $n(^{233}\text{U})/n(^{236}\text{U}) = 1.01906(16)$ | 137.844(25) | 137.685(22) |
| University of Frankfurt | Neptune MC-ICPMS | $n(^{233}\text{U})/n(^{236}\text{U})$ double spike IRMM-3636, $n(^{233}\text{U})/n(^{236}\text{U}) = 1.01906(16)$ | 137.833(28) | 137.671(25) |
| Thermo Fisher Scientific | Neptune-PLUS MC-ICPMS | $n(^{233}\text{U})/n(^{236}\text{U})$ double spike IRMM-3636, $n(^{233}\text{U})/n(^{236}\text{U}) = 1.01906(16)$ | 137.836(23) | 137.681(23) |
| National Taiwan University, NTU | Neptune MC-ICPMS | $n(^{233}\text{U})/n(^{236}\text{U})$ double spike made by UMN, calibrated using IRMM-074/10, $n(^{238}\text{U})/n(^{235}\text{U}) = 0.99974(15)$ | 137.834(21) | Not measured |
| University of Minnesota, UMN | Neptune MC-ICPMS | $n(^{233}\text{U})/n(^{236}\text{U})$ double spike made by UMN, calibrated using IRMM-074/10, $n(^{238}\text{U})/n(^{235}\text{U}) = 0.99974(15)$ | 137.830(25) | Not measured |
| Lawrence Livermore National Laboratory, LLNL | Triton TIMS | $n(^{233}\text{U})/n(^{236}\text{U})$ double spike made by LLNL, calibrated using IRMM-184, $n(^{238}\text{U})/n(^{235}\text{U}) = 137.697(41)$ | 137.823(42) | N/A, used to calibrate own double spike |
| Seibersdorf Analytical Laboratory (SAL/IAEA) | Triton TIMS | Modified total evaporation measurement, external calibration using IRMM-072/15, $n(^{238}\text{U})/n(^{235}\text{U}) = 1.00684(20)$ | 137.862(31) | 137.693(31) |

ion counting detector systems. The National Institute of Standards and Technology (NIST) and, since the late 1970s in particular for the nuclear elements uranium and plutonium, also the New Brunswick Laboratory (NBL, US-DOE) have provided various isotope reference materials for this purpose. From the European Union, the Institute for Reference Materials and Measurements (IRMM) is a recognized provider for nuclear isotope reference materials to the nuclear industry and nuclear safeguards authorities, which are also being utilized widely for geochemical applications. One example is the gravimetrically prepared double spike IRMM-3636 with a $n(^{233}\text{U})/n(^{236}\text{U})$ ratio of 1/1, which allows internal mass fractionation correction for high precision $n(^{238}\text{U})/n(^{235}\text{U})$ ratio measurements [10]. At several other laboratories double spikes with $n(^{233}\text{U})/n(^{236}\text{U})$ ratios of about 1/1 have also been prepared, some of which are calibrated against other reference materials, e.g. using NBL CRM U500 or IRMM-074/10 with $n(^{238}\text{U})/n(^{235}\text{U})$ ratios close to 1/1 or even using close to natural materials such as IRMM-184, NBS SRM 950a or NBS SRM 960.

In this paper results from several geochemistry laboratories and the Institute for Reference Materials and Measurements (IRMM) are combined to provide new values for the mostly used natural standards NBS SRM 960 (NBL CRM 112a) and IRMM-184. For each participating laboratory the instrumentation and the used reference materials will be described briefly. Besides the IRMM the following laboratories have contributed: NIGL Isotope Geoscience Laboratory (British Geological Survey, UK), University of Frankfurt (Germany), Thermo Fisher Scientific (Bremen, Germany), National Taiwan University (NTU, Taiwan), University of Minnesota (UMN, USA), Lawrence Livermore National Laboratory (LLNL, US-DOE) and the Seibersdorf Analytical Laboratory of the International Atomic Energy Agency (SAL/IAEA).

## 2. Results

Table 1 shows all contributing laboratories, the instrumentation, the reference materials used and the results for the $n(^{238}\text{U})/n(^{235}\text{U})$ ratios for NBS CRM 960 (NBL CRM 112a) and IRMM-184. All uncertainties are calculated according to the Guide to the Expression of Uncertainty in Measurements [11] using a coverage factor $k = 2$, corresponding to a confidence interval of about 95%. Among the 8 laboratories, 4 have used thermal ionization mass spectrometer (TIMS) instruments and 4 have used multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) instruments (all of type ‘Triton’ or ‘Neptune’, respectively, from Thermo Fisher Scientific). All instruments are state of the art multi-collector mass spectrometers. Thus the relative uncertainties from the Faraday amplifier gains and Faraday detectors themselves are at the level of $10^{-6}$ and can be considered insignificant. In some cases multi-dynamic measurements were performed (IRMM, University of Frankfurt) to cancel them out, e.g. by detecting the $n(^{238}\text{U})/n(^{235}\text{U})$ and $n(^{233}\text{U})/n(^{236}\text{U})$ ratios using the same pair of Faraday cups and amplifiers. At NIGL even additional cup efficiency measurements were performed using high precision Nd isotope measurements in various Faraday cup configurations.

At IRMM, NIGL, University of Frankfurt and Thermo Fisher Scientific the IRMM-3636 double spike with a $n(^{233}\text{U})/n(^{236}\text{U})$ ratio of about 1/1 and a relative uncertainty of 0.016% was used. At the University of Minnesota (UMN) a separate double spike with a $n(^{233}\text{U})/n(^{236}\text{U})$ ratio of about 1/1 has been prepared [12], which was also used at the National Taiwan University (NTU). This double spike was first calibrated at UMN using NBL-U500 with a $n(^{238}\text{U})/n(^{235}\text{U})$ ratio of about 1/1 and an uncertainty of 0.10% [12], and then re-calibrated using IRMM-074/10 [13] with

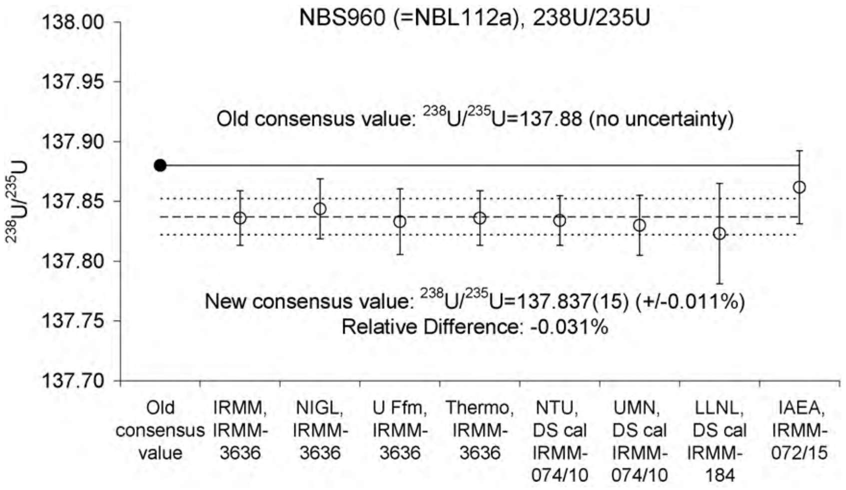

**Fig. 1.** $n(^{238}U)/n(^{235}U)$ ratios for NBS SRM 960 (NBL112a) measured by all contributing laboratories are compared to the old consensus value of 137.88.

a $n(^{238}U)/n(^{235}U)$ ratio of about 1/1 and an uncertainty of 0.015%. IRMM-074/10 also contains $^{233}U$ with a relative abundance of $5 \times 10^{-7}$ with an uncertainty of 0.03%, which can easily be corrected for.

It is worth mentioning that both IRMM-3636 and IRMM-074/10 were prepared recently at IRMM using similar procedures for the chemical purification, oxidation towards $U_3O_8$ and gravimetrical mixing of the highly enriched starting materials of $^{233}U$, $^{236}U$, $^{235}U$ and $^{238}U$. Both reference materials were certified using the calculated ratios from the gravimetrical mixing, which were verified by TIMS measurements using previously certified materials. In case of IRMM-3636, the verification was performed using the reference material IRMM-3050, which is the basic $n(^{235}U)/n(^{238}U)$ mixture of IRMM-074/10, prepared prior to adding the $^{233}U$ (for details see [10,13]). This verification was done by internal correction of the $n(^{233}U)/n(^{236}U)$ ratio of IRMM-3636 using the certified $n(^{235}U)/n(^{238}U)$ ratio of IRMM-3050, mixed on the TIMS filament. The result was a relative difference of 0.0029% [10], which is insignificant due to the combined uncertainty of 0.022%. This good agreement explains why the $n(^{238}U)/n(^{235}U)$ results for NBS SRM 960 obtained from UMN and NTU agree very closely with those obtained by using the $n(^{233}U)/n(^{236}U)$-double spike IRMM-3636, by IRMM, NIGL, etc. However, despite this good agreement, the gravimetrical mixings of IRMM-3636 and IRMM-074/10 were made independently from each other. Therefore the results from UMN and NTU, which used a different double spike, are independent from IRMM, NIGL, etc, which used IRMM 3636. Combining results obtained using various different reference materials provides a broader basis for the proposed new average values.

In addition, at LLNL another reference material, the IRMM-184, was used to calibrate the in house $n(^{233}U)/n(^{236}U)$-double spike. At SAL/IAEA the $n(^{238}U)/n(^{235}U)$ ratios for NBS SRM 960 and IRMM-184 were measured using the 'modified total evaporation' (MTE) measurement technique [14], applying an external calibration using the IRMM-072/15 reference material with a $n(^{238}U)/n(^{235}U)$ ratio of about 1/1 with an uncertainty of 0.020% [15].

In Fig. 1 the $n(^{238}U)/n(^{235}U)$ results for NBS SRM 960, which was measured by all contributing laboratories, are compared to the old consensus value of 137.88. An average was calculated which is weighted by the individual uncertainties of the results of the participating laboratories. The uncertainties include the contributions from the reference materials used for their determination. This weighted average for the $n(^{238}U)/n(^{235}U)$ ratio of NBS SRM 960 (NBL CRM 112a) is 137.837(15). The relative uncertainty of this new value is about 0.011%, which is lower than the 0.016% uncertainty of the double spike IRMM-3636 used by 4 of the 8 laboratories. This is due to the fact that the new average value is based on four independently prepared reference materials such as IRMM-3636, IRMM-074/10, IRMM-184 and IRMM-072/15.

According to Fig. 1 the $n(^{238}U)/n(^{235}U)$ results from LLNL and SAL/IAEA seem to be slightly different from all others, which is due to the use of different calibration materials such as IRMM-184 and IRMM-072/15. Using measurements of these calibration materials against IRMM-3636 (performed at IRMM, for IRMM-184 given below in this paper), the $n(^{238}U)/n(^{235}U)$ results for NBS SRM 960 from LLNL and SAL/IAEA could be re-normalized to IRMM-3636, which would in fact lead to a better overall agreement. But it was decided to accept the measured data from all participating laboratories without any change, in order to have as many as possible independent standards contributing to the average.

The new value of 137.837(15) is about 0.031% lower than the old consensus value of 137.88, which is outside the uncertainty range of the new average value. In contrast to the previous consensus value, the new value presented here is traceable to the SI and has an uncertainty assigned to it, calculated according to the GUM.

Because NBL-145 is prepared by dissolving the NBS SRM 960 (NBL CRM 112a) uranium metal, the isotopic composition can be expected to be identical. Some of the laboratories, NIGL and the University of Frankfurt also provided $n(^{238}U)/n(^{235}U)$ ratios for NBS SRM 950a which are indistinguishable from those obtained for NBS SRM 960. However, the materials NBS SRM 950a and NBS SRM 960 are not identical, because their $n(^{234}U)/n(^{238}U)$ ratios differ significantly (>2%). But for the $n(^{238}U)/n(^{235}U)$ ratio the new, multi-lab and multi-standard average value, can be assigned to NBS SRM 950a as well within the given uncertainties. It is worth mentioning that the isotopic composition of the widely known NBS950b is also different from both of them for both the $n(^{238}U)/n(^{235}U)$, and the $n(^{234}U)/n(^{238}U)$ ratios, and in addition also due to an abundance of $^{236}U$ at the level of $10^{-6}$.

For the $n(^{234}U)/n(^{238}U)$ ratio of NBS SRM 960 (NBL112a) a widely used value of 0.000052860(25) was published by Cheng et al. [12]. This has been confirmed at IRMM, by Cheng et al. [16], by Shen et al. and by Bürger at SAL/IAEA, leading to a weighted average value of 0.000052853(16).

For IRMM-184 the weighted average for the $n(^{238}U)/n(^{235}U)$ ratio is 137.683(20), which is in agreement with the certified value of 137.697(41). However, for geochronological applications the new value of 137.683(20) with the much smaller uncertainty of 0.015% is more useful, it is (insignificantly) lower by about 0.014, corresponding to a relative difference of 0.01%.

## 3. Conclusions

For the widely used natural uranium isotopic reference materials NBS SRM 960 (NBL CRM 112a) and IRMM-184 new average values for their $n(^{238}\mathrm{U})/n(^{235}\mathrm{U})$ ratios are presented. These are based on results from several geochemical laboratories and the IRMM, for which multiple independent gravimetrically prepared isotope reference materials are used. The consensus value of NBS SRM 960 (NBL CRM 112a) and NBS SRM 950a, $n(^{238}\mathrm{U})/n(^{235}\mathrm{U}) = 137.88$, is generally used for geochronology to present the natural isotope composition of uranium. According to our results, both standards have an identical $n(^{238}\mathrm{U})/n(^{235}\mathrm{U})$ ratio of 137.837(15), which is, however, about 0.031% lower than the old consensus value. Using this new 'multi-lab and multi-standard average value' for geochronology results in $^{207}\mathrm{Pb}/^{206}\mathrm{Pb}$ ages which are 0.4–0.8 Ma younger (depending on the age of the sample) than those calculated with the previously used value for $n(^{238}\mathrm{U})/n(^{235}\mathrm{U})$. As a significant advantage, the new 'multi-lab and multi-standard average value' is traceable to the SI and has an uncertainty associated which is calculated according to the GUM, and therefore includes the contributions from all sources of uncertainties, including those from all used reference materials. The new value presented here should not be considered as the officially certified value, the certification is ongoing at NBL.

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## References

[1] W.R. Shields, Comparison of Belgian Congo and Synthetic "Normal" Samples. Tab. 6 in App. A, Report No. 8, U.S. National Bureau of Standards Meeting of the Advisory Committee for Standard Materials and Methods of Measurement, May 17 and 18 (1960), 37 pp. (unpublished).
[2] G.A. Cowan, H.H. Adler, Geochimica Et Cosmochimica Acta 40 (1976) 1487–1490.
[3] R.H. Steiger, E. Jager, Earth And Planetary Science Letters 36 (1977) 359.
[4] C.H. Stirling, M.B. Andersen, E.-K. Potter, A. Halliday, Earth And Planetary Science Letters 264 (2007) 208–225.
[5] S. Weyer, A.D. Anbar, A. Gerdes, G.W. Gordon, T.J. Algeo, E.A. Boyle, Geochimica Et Cosmochimica Acta 72 (2008) 345–359.
[6] C.H. Bopp, C.C. Lundstrom, T.M. Johnsons, J.G. Glessner, Geology 37 (2009) 611–614.
[7] G.A. Brennecka, L.E. Borg, I.D. Hutcheon, M.A. Sharp, A.D. Anbar, Earth and Planetary Science Letters 291 (2010) 228–233.
[8] C. Montoya-Pino, S. Weyer, A.D. Anbar, J. Pross, W. Oschmann, B. van de Schootbrugge, H.W. Arz, Geology 38 (2010) 315–318.
[9] G.A. Brennecka, S. Weyer, Wadhwa, Science 327 (2010) 449.
[10] S. Richter, A. Alonzo-Munoz, R. Eykens, U. Jacobssen, H. Kuehn, A. Verbruggen, Y. Aregbe, R. Wellum, International Journal of Mass Spectrometry 269 (2008) 145–148.
[11] International Organisaton for Standardisation, Guide to the Expression of Uncertainty in Measurements, ©ISO, Geneva, Switzerland, 1993, ISBN 92-67-10188-9.
[12] H. Cheng, R.L. Edwards, J. Hoff, C.D. Gallup, D.A. Richards, Y. Asmeron, The half-lives of uranium-234 and thorium-230, Chemical Geology 169 (2000) 17–33.
[13] S. Richter, A. Alonso, Y. Aregbe, R. Eykens, F. Kehoe, H. Kühn, N. Kivel, A. Verbruggen, R. Wellum, P.D.P. Taylor, International Journal of Mass Spectrometry 281 (2009) 115–125.
[14] S. Richter, S.A. Goldberg, International Journal of Mass Spectrometry 229 (2003) 181–197.
[15] K.J.R. Rosman, W. Lycke, R. Damen, R. Werz, F. Hendrickx, L. Traas, P. De Bìevre, International Journal of Mass Spectrometry 79 (1987) 61–71.
[16] H. Cheng, R.L. Edwards, C.-C. Shen, J. Woodhead, J. Hellstrom, Y. Wang, X. Kong, X. Wang, Yu-Te Hsieh, submitted to Earth and Planetary Science Letters.