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Abstract

In this study, data from thirteen laboratories from around the world are presented for a successful certification of uranium isotope ratios in uranium ore concentrate certified reference materials from the National Research Council Canada. Different mass spectrometric measurement principles (including SF-ICP-MS, quadrupole ICP-MS, TIMS, MC-ICP-MS, SIMS and AMS) and measurement procedures were employed. In general, data from all sources exhibit good consistency with TIMS and MC-ICP-MS showing superior performance. The three candidate uranium ore concentrate CRMs (UCLO-1, UCHI-1 and UPER-1) have natural uranium isotope ratios with certified values of 0.5304(7) × 10^{-4}, 0.5475(2) × 10^{-4} and 0.5361(4) × 10^{-4} for $n(^{234}\text{U})/n(^{238}\text{U})$ and 0.007 2563(13), 0.007 2563(10) and 0.007 2542(11) for $n(^{235}\text{U})/n(^{238}\text{U})$, respectively, with expanded uncertainty (k = 2) applicable to the last digit of the value given in the parentheses. Information values for $n(^{236}\text{U})/n(^{238}\text{U})$ in these three CRMs, measured by AMS, are also provided: 10 × 10^{-12}, 200 × 10^{-12} and 22 × 10^{-12}. The uncertainties of the proposed certified values of uranium isotope ratios in uranium ore concentrate CRMs are superior to available reference materials, and the values of $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ show significant variation among the three CRMs.

Keywords: MC-ICP-MS, TIMS, U isotope ratio, certified reference materials, uranium ore concentrate.

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Uranium ore concentrate (UOC), commonly referred as yellowcake and usually presented as U_3O_8, is an intermediate product in the preparation of fuel for use in nuclear power reactors (El Haddad *et al.* 2018, Robertson *et al.* 2019). Nuclear power is the third most significant source of energy worldwide after fossil fuels and hydroelectric energy, providing estimated one tenth of global electricity in 2016 (Association 2016, 2017). There is significant interest within the nuclear security and forensics communities in the chemical and physical characteristics of uranium ores and UOC for the purpose of attribution and provenance determination (Oliveira Junior and Sarkis 2002, Keegan *et al.* 2008, Švedkauskaitė-LeGore *et al.* 2008, Mercadier *et al.* 2011, Bürger *et al.* 2014, Keegan *et al.* 2014, Balboni *et al.* 2016, Spano *et al.* 2017, Boulyga *et al.* 2017, El Haddad *et al.* 2018, Khumalo and Mathuthu 2018). Most commonly considered characteristics include uranium content, elemental impurities and isotopic compositions of certain elements of these materials. The absence of appropriate matrix reference materials with certified mass fractions of all tested trace elements, uranium content and uranium isotopic composition hinders forensic and provenance applications.

Canada has the world's second largest uranium reserves and is the largest producer/refiner of uranium materials in the world (Association 2017). To underpin international nuclear forensics capabilities, the National Research Council Canada (NRC) has developed a suite of three UOC certified reference materials (UCLO-1 (Nadeau *et al.* 2020a), UCHI-1 (Nadeau *et al.* 2020b) and

UPER-1 (Nadeau *et al.* 2020c), that have different trace element/uranium contents and uranium isotopic composition. The certification of trace elements and uranium mass fractions in these CRMs is detailed elsewhere (LeBlanc *et al.* 2021), with this study focusing on the natural isotope ratios of uranium. Natural uranium primarily consists of three isotopes ^{234}U, ^{235}U and ^{238}U. Whereas extremely small amounts of ^{236}U are formed by neutron capture of ^{235}U in natural uranium ores with ^{236}U/^{238}U values well below 10^{-7}, significantly larger amounts of ^{236}U occur in uranium samples of anthropogenic origin (Diez-Fernández *et al.* 2020) reaching as high as 10^{-3} for ^{236}U/^{238}U. Recent studies have shown that the abundance of uranium isotopes varies significantly in natural uranium ore deposits (Richter *et al.* 1999, Brennecka *et al.* 2010). For example, ^{238}U/^{235}U ratio varies between 137.70 and 137.96 in a wide variety of terrestrial materials (Hiess *et al.* 2012), and variations in ^{238}U/^{235}U of up to ~ 1.0‰ and ^{234}U/^{238}U of > 50‰ have been identified in uranium ore deposits (Keatley *et al.* 2021). These measurable variations raise the possibility that uranium isotope ratios can be used to fingerprint a particular ore deposit or uranium ore concentrate.

In this study, we describe the development of a suite of uranium ore concentrate reference materials certified for U isotope ratios. An international team was assembled to provide data for this certification campaign. The participating laboratories were allowed to choose their own methods for determining isotope amount ratios, $n(^{A}\mathrm{U})/n(^{238}\mathrm{U})$, hereafter referred to as $R_{A/238}$. This study utilised a variety of instrumentation, including thermal ionisation mass spectrometry (TIMS), multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS), sector field ICP-MS (SF-ICP-MS), quadrupole ICP-MS, secondary ion mass spectrometry (SIMS) and accelerator mass spectrometry (AMS). High-precision bulk uranium isotope ratio measurements are typically performed using multi-collector TIMS (Pereira de Oliveira Jr *et al.* 2010, Kraiem *et al.* 2011, Richter *et al.* 2011, Raptis *et al.* 2013, Quemet *et al.* 2019) or MC-ICP-MS (Andersen *et al.* 2004, Fietzke *et al.* 2005, Boulyga *et al.* 2006, Buchholz *et al.* 2007, Martinelli *et al.* 2009, Brennecka *et al.* 2010, Pereira de Oliveira Jr *et al.* 2010, Uvarova *et al.* 2014, Spano *et al.* 2017). With these techniques, correction of instrumental isotopic fractionation (IIF) is necessary and this study included a variety of common methods (Yang *et al.* 2018). The standard-sample bracketing (SSB) IIF correction method (Andersen *et al.* 2004, Buchholz *et al.* 2007, Spano *et al.* 2017, Nadeau *et al.* 2020b) and double spike method (Fietzke *et al.* 2005, Uvarova *et al.* 2014) are often employed for the determination of uranium isotope ratios, and both rely on isotopic standards of uranium. The primary method for absolute isotope ratio measurements is based on the full gravimetric isotope mixture model (FGIM) (Yang *et al.* 2018), which requires suitable amounts of all near-pure isotopes of an element in a pure chemical form. Note that the FGIM is not the same as the commonly used double spike (DS) method (Yang *et al.* 2018, Klaver and Coath 2018). The DS method relies on isotopic measurement of the sample and its mixture with the double spike, and requires the isotopic composition of the double spike to be known. In addition, DS method only corrects mass dependent fractionation (MDF) of the instrument because the exponential fractionation model (Russell's law) is built into the mathematical framework of the DS method. FGIM also employs isotopically enriched materials (spikes) but, unlike the DS method, it does not require that true isotope ratios of the enriched spikes are known beforehand. Instead, for an element with *N* stable isotopes the FGIM relies on measurements of all isotope ratios in *N* enriched spikes and all unique pairwise mixtures of these spikes to derive the instrumental isotope ratio correction factors. These requirements are not easily attainable for uranium. Alternatively, the total evaporation (TE) TIMS procedure is used where isotope intensities are collected during the entire evaporation process, which minimises the isotopic fractionation. More recently, a modified total evaporation (MTE) TIMS was developed, wherein the total evaporation process is interrupted on a regular basis to allow for correction for background from peak tailing, internal calibration of a secondary electron multiplier detector versus the Faraday cups, peak-centring and ion source re-focusing, thus allowing improved accuracy, in particular on the minor isotope ratio measurement, i.e., $n(^{234}\text{U})/n(^{238}\text{U})$ (Richter *et al.* 2011).

Materials, instrumentation and methods

UCLO-1 and UCHI-1 CRMs are uranium ore concentrates and UPER-1 is a uranium peroxide material. These industrial grade materials were homogenised and aliquoted into 60 ml amber glass bottles. A unit of UCLO-1, UCHI-1 and UPER-1 consists of approximately 25 g of uranium ore concentrate. The radiation levels of these CRMs are in the range of 570–620 kBq per bottle, and a licence is required to handle these materials in the laboratory. The three UOC CRMs can be purchased at http://nrc-cnrc.gc.ca/crm.

Each participating laboratory (Table 1) was given a bottle each of UCLO-1, UCHI-1 and UPER-1. In this certification campaign, participating laboratories chose their own method of analysis to perform uranium isotope ratio measurements. Each participating laboratory provided results with a complete description of sample preparation, instrumentation, mass bias correction model and calibrator employed, as summarised in Table 2.

< Table 1 here >
< Table 2 here >

Results and discussion

Homogenity assessment

Homogeneity of UCLO-1, UCHI-1 and UPER-1 was assessed by analysing twelve units of each CRM, randomly sampled across the entire CRM production series by L1. From each unit, 0.25 g sample was digested in 7 ml HNO_3 + 3 ml HCl + 1 ml HF in a hot block at 85 °C for 24 h. The solution was evaporated down to about 1 ml and then diluted to 25 g with de-ionised water. Subsequently, a 1 ml digest was diluted to 10 ml in 3 mol l^{-1} HNO_3, and 1 ml of that diluted solution was used to chromatographically separate uranium from other elements using UTEVA resin (0.5 ml in Eichrom Technologies Inc. columns, part No: AC-141-AL with a resin bed length of 1.6 cm, column internal diameter of 0.64 cm). The column separation procedure is presented in Table 3, a modified procedure of a previous study (Wang and You 2013). The collected uranium fraction was further diluted ten-fold with de-ionised water prior to MC-ICP-MS isotope ratio measurements using a static analysis routine and a Faraday cup configuration: C (^{234}U), H1

(^{235}U) and H3 (^{238}U) at low mass resolution. Mass bias correction was done using the SSB method with IRMM-184 U standard (Richter *et al.* 2005) as a calibrator.

< Table 3 here >

The method developed by laboratory L1 was further validated with matrix doping experiments. The three steps of column separation from load to the second rinse (Table 3) were collected from UPER-1 (which contains the highest matrix elements), containing matrix elements except uranium. This uranium-free solution of matrix elements was then doped with the IRMM-184 uranium reference material to replace uranium sample with the same mass of uranium that would have been in the original processed sample aliquot. It was then evaporated to dryness and processed through the entire column separation before isotopic measurement. The UPER-1 matrix doped with IRMM-184 should yield isotope delta values $\delta(^{234/238}\text{U}) = \delta(^{235/238}\text{U}) = 0$ ‰ when measured against the IRMM-184 itself. Values of $\delta(^{234/238}\text{U}) = -0.02 \pm 0.10$ ‰ and $\delta(^{235/238}\text{U}) = -0.02 \pm 0.04$ ‰ ($n = 3$, 1s) were obtained, confirming the unbiased results obtained by the proposed method.

The method, which was tested by the doping experiment, was applied to evaluate the unit-to-unit homogeneity of uranium isotope ratios in the three CRMs (UCLO-1, UCHI-1 and UPER-1) measured by laboratory L1. Each purified solution was measured against IRMM-184, and mass fractions of U in the sample and IRMM-184 were matched at 1 µg g^{-1}. Relative isotope ratios (isotope deltas) to the IRMM-184 from twelve CRM units of each CRM are presented in Figure 1 and Appendix A1.

< Figure 1 here >

The uncertainty due to homogeneity was evaluated using the DerSimonian-Laird random effects model (DerSimonian and Laird 1986), a commonly used approach for evaluating homogeneity of reference materials (ISO Guide 35). In this statistical model, the effect of the between-unit homogeneity is the spread of the isotope ratio values that cannot be explained by the measurement uncertainty alone (also known as the over dispersion). No substantial inhomogeneity was detected for either ^{234}U/^{235}U or ^{235}U/^{238}U ratio. Hence, the inhomogeneity in uranium isotope ratios is shown to be below 1 part per thousand (^{234}U/^{238}U) or 0.1 part per thousand (^{235}U/^{238}U) neither of which contribute to any significant manner to the overall uncertainties assigned to the consensus values.

Uranium isotope ratio characterisation for the UOC CRMs

Results reported by the participating laboratories are presented in Table 4. Note that the test samples of UCLO-1, UCHI-1, UPER-1 contain high levels of total uranium, at 750–840 mg g^{-1} (LeBlanc *et al.* 2021), thus sample solutions needed to be further diluted prior to isotope ratio measurements. The procedural blank is insignificant, for example, intensities of 0.000002 to 0.00016 V were obtained for ^{234}U, ^{235}U and ^{238}U in the procedural blank compared with intensities of 0.00248 to 46.7 V in the samples by L1. Despite insignificant blank, blank intensities were still subtracted from all samples to avoid any adverse effect on the isotope ratio. The combined standard uncertainty of reported U isotope ratios by the participating laboratories was requested to follow the JCGM Guides (Evaluation of measurement data: Guide to the expression of uncertainty in measurement, JCGM 100:2008), which included the contributions from the primary calibrators used. Note that L3 used a calibrator without uncertainty, and thus its data were not included for the final calculation of certified values in the three UOC CRMs. The majority of the laboratories used either TIMS or MC-ICP-MS for the uranium isotope ratio measurements (see Table 2), involving the separation of uranium from other elements prior to sample analysis, a variety of correction methods for the instrumental isotopic fractionation, and a variety of uranium isotope standards.

As an example, L5 used a ^{233}U-^{236}U double spike (IRMM-3636a) (Richter *et al.* 2008) for the determination of $R_{235/238}$ in all three uranium CRMs whereas a number of other laboratories

(L2, L6 and L12) employed the total evaporation (TE) method using TIMS, which is an established method for accurate isotope ratio measurements without the need to correct for instrumental isotopic fractionation, as isotopic signals are collected during the entire evaporation process (Fiedler 1995, Fujii *et al.* 2006, Mialle *et al.* 2011, Richter *et al.* 2011, Jakopič *et al.* 2013, Kraiem *et al.* 2013, Wegener *et al.* 2013, Mialle *et al.* 2015, Mathew and Haoszbek 2016, Fukami *et al.* 2017, Quemet *et al.* 2018, 2019, Wakaki and Ishikawa 2018, Wang *et al.* 2018, 2019, Song *et al.* 2019). However, both L2 and L6 employed isotopic standard-sample bracketing (SSB) for an additional correction of mass bias, resulting in a slightly better measurement precision in results, compared with that of L12 using TE-TIMS.

The most common measurement method, however, was to apply SSB. This approach relies on the alternating measurements of the sample and the isotopic calibrator, and requries matching analyte and matrix in the sample and the calibrator for the determination of isotope ratios with small uncertainties (Yang *et al.* 2018). Therefore, column separation of matrix prior to measurements is generally required. Overall, this interlaboratory comparison study involved a variety of commercially available uranium reference materials, which included IRMM-184, IRMM-3636a, NBL U125A, NBL 112A, NBL 129A and NBL U010. Although different instrumental isotopic fractionation correction models and different uranium calibrators were employed, the uranium isotope ratios obtained by TIMS or MC-ICP-MS are in excellent agreement with much smaller uncertainties compared with other techniques (e.g., SIMS and SF-ICP-MS) used, with the exception of laboratory L2 using TIMS for $R_{234/238}$. Among the laboratories that used either TE-TIMS or MC-ICP-MS, neither L2 nor L6 performed the separation of matrix elements prior to measurements. L6 used SSB for mass bias correction, which produced bias-free results. Although L2 also used SSB (but with a different calibrator), biases in L2 results could be attributed to some matrix effect or the NBL 129A reference material.

Among all eight data sets obtained by using either TIMS or MC-ICP-MS, results from L5 (TIMS) show the best measurement precision, and are in excellent agreement with results from L1 (MC-ICP-MS, the second best), despite different instrumentation (TIMS versus MC-ICP-MS), column separation (UTEVA versus AG1-x4 resin), and mass bias correction models (SSB versus DS for $R_{235/238}$ and SSB for $R_{234/238}$) having been employed. These observations confirm that both techniques (TIMS and MC-ICP-MS) are capable of providing uranium isotope ratio measurements with very small uncertainties, providing care is taken during the matrix separation, as well as instrumental isotopic fractionation correction and measurement processes.

< Table 4 here >

Consensus values of uranium isotope ratios in three UOC CRMs

Since the calibrators used by laboratories L3, L7 and L9 were not SI-traceable isotopic calibrators, the data provided by these laboraries were not considered in the calculation of consensus values for the three candidate UOC CRMs. Additionally, although laboratory L8 employed an SI-traceable isotopic calibrator, the SF-ICP-MS platform provided significantly higher uncertainties. Consequently, data from this laboratory were not taken into account in the calculation of consensus values. The remaining results from the participating laboratories, as shown in Figures 2–4, were combined using the random laboratory effects model which recognises the uncertainties of the individual results as well as overdispersion between the laboratory results that cannot be explained by the reported uncertainties alone (DerSimonian and Laird 1986). We employed the following statistical model:

$$R_i \sim \text{normal}[\lambda_i, u(R_i)] \text{ and } \lambda_i \sim \text{normal}[\mu, \tau] \qquad (1)$$

where the parameter μ represents the consensus isotope ratios and τ represents the overdispersion (random laboratory effect), also known as the dark uncertainty (Thompson and Ellison 2011). The above statistical model was fitted to the data using the method-of-moments procedure, as described by DerSimonian and Laird (1986). Overall, we observed small overdispersion suggesting that all admissible results were in agreement to within their stated uncertainties. In addition, this being the uncertainty-weighted estimator, observations provided by the laboratories with the smallest uncertainties (L1, L5 and L6) largely determine the consensus values. Thus, although the consensus values are traceable to all certified reference materials employed in this study, it is an appropriate simplification that the consensus values are traceable to two reference materials, IRMM-184 and IRMM-3636a. From these two calibrators, the IRMM-3636a double spike has the smallest relative uncertainty associated with any of the isotope ratios, and the consensus values assigned to our three uranium CRMs effectively transfer this precision from a synthetic uranium solution standard to a suite of uranium matrix materials with natural isotopic composition.

< Figure 2 here >

< Figure 3 here >

< Figure 4 here >

< Table 5 here >

Consensus values of uranium isotope ratios in three UOC CRMs are presented in Table 5. In addition, L13 reported isotope ratios $R_{236/238} = 9.9 \times 10^{-12}$, 200×10^{-12} and 22×10^{-12} in UCLO-1, UCHI-1 and UPER-1, respectively, using accelerator mass spectrometry (AMS) (Zhao *et al.* 2019). These values are rather low for natural samples yet not uncommon (Richter *et al.* 1999, Steier *et al.* 2008).

High-quality data contribued from expert laboratories have produced a set of uranium isotope reference materials (solid matrix samples as uranium ore concentrates) with low uncertainties compared with those reported in common CRMs (in pure standard solution form) (see Figure 5). In addition, the achieved uncertainties of the uranium consensus values in the three UOC CRMs are three to seven times lower than those UOC CRMs currently recognised as best measurement of uranium isotopic composition by the IUPAC (Richter *et al.* 1999, IUPAC *best measurements of isotopic composition*), largely because of our ability to harness the low uncertainties afforded by the reference materials IRMM-184 and IRMM-3636a.

< Figure 5 here >

Conclusions

Joint efforts from thirteen expert laboratories around the world have enabled the successful certification of uranium isotope ratios $R_{234/238}$ and $R_{235/238}$ in three uranium ore concentrate certified reference materials – UCLO-1, UCHI-1 and UPER-1. Most notably, the $R_{234/238}$ ratios show significant variations between the three CRMs, which is useful in identifying the origin of natural uranium samples. These three CRMs are suitable not only to validate measurement procedures for the determination of uranium isotope ratios in uranium ore concentrates and other similar matrix samples, but also provide matrix reference materials to enable further improvement of measurement procedures of uranium isotope measurements.

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Conflict of interest

The authors declare no competing financial interests to influence the work reported in this paper.

Data availability statement

Data available on request due to privacy/ethical restrictions.

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Appendix A1

Uranium isotope ratio relative to IRMM-184 (‰) in twelve units of UCLO-1, UCHI-1 and UPER-1 for homogeneity study

< Appendix A1 here >

Figure captions

Figure 1. Between-unit homogeneity of uranium isotope ratios in UCLO-1, UCHI-1 and UPER-1, measured against IRMM-184 by laboratory L1 from twelve CRM units. The vertical bars represent standard deviation of triplicate measurement results.

Figure 2. Uranium isotope ratios (mol mol^{-1}) in NRC UCLO-1. The bars represent expanded uncertainty (k = 2). Results with black circles employed TIMS and white circle for MC-ICP-MS. The number in the circle refers to calibrator used, 1: IRMM-184, 2: IRMM-3636a, 3: NBL U125A, 4: NBL U020 and NBL 112A and 5: NBL 129A. The icon on the right refers to column separation of uranium. The vertical line represents the consensus value and its expanded uncertainty.

Figure 3. Uranium isotope ratios (mol mol^{-1}) in NRC UCHI-1. The bars represent expanded uncertainty (k = 2). Results with black circles employed TIMS and white circle for MC-ICP-MS. The number in the circle refers to calibrator used, 1: IRMM-184, 2: IRMM-3636a, 3: NBL U125A, 4: NBL U020 and NBL 112A, 5: NBL 129A and 6: NBL U010. The icon on the right refers to column separation of uranium. The vertical line represents the consensus value and its expanded uncertainty.

Figure 4. Uranium isotope ratios (mol mol^{-1}) in NRC UPER-1. The bars represent expanded uncertainty (k = 2). Results with black circles employed TIMS and white circle for MC-ICP-MS. The number in the circle refers to calibrator used, 1: IRMM-184, 2: IRMM-3636a, 3: NBL U125A, 4: NBL U020 and NBL 112A, 5: NBL 129A and 6: NBL U010. The icon on the right refers to column separation of uranium. The vertical line represents the consensus value and its expanded uncertainty.

Figure 5. Comparison of isotopic reference materials of natural uranium. The bars represent expanded uncertainty (with k = 10 for the $^{234}U/^{235}U$ ratio for visual effect). Please note that the relative uncertainties assigned to isotope ratios in all NRC materials are limited by the best reference material used in this study, the IRMM-3636a double spike (see Table 4).

Material	$\boldsymbol{\delta^{234/238}U}$	***s* (*n* = 3)**	$\boldsymbol{\delta^{235/238}U}$	***s* (*n* = 3)**
UCLO-1	-2.65	0.89	-0.76	0.06
	-2.71	1.17	-0.78	0.08
	-2.70	0.43	-0.77	0.004
	-2.96	0.25	-0.79	0.04
	-2.77	1.24	-0.84	0.05
	-2.44	0.14	-0.81	0.05
	-2.94	0.74	-0.76	0.01
	-2.50	0.84	-0.75	0.03
	-2.81	0.64	-0.83	0.03
	-2.63	0.88	-0.82	0.03
	-2.89	1.32	-0.84	0.04
	-2.53	0.14	-0.80	0.09
Mean	**-2.71**		**-0.80**	
s	**0.17**		**0.03**	
UCHI-1	28.61	0.88	-0.78	0.04
	30.18	1.51	-0.84	0.06
	29.27	0.65	-0.75	0.09
	29.39	0.44	-0.81	0.08
	29.03	0.71	-0.83	0.01
	29.50	0.07	-0.76	0.06
	28.85	1.23	-0.81	0.02
	30.07	0.60	-0.84	0.05
	30.22	0.58	-0.85	0.03
	29.55	0.70	-0.83	0.08
	30.14	0.88	-0.77	0.10
	30.02	0.95	-0.81	0.02
Mean	**29.57**		**-0.81**	

s	**0.56**		**0.03**	
UPER-1	8.70	0.34	-1.09	0.05
	7.60	0.80	-1.13	0.002
	8.18	0.46	-1.11	0.02
	8.52	0.38	-1.09	0.04
	8.62	0.16	-1.09	0.02
	8.68	0.21	-1.10	0.03
	7.87	0.44	-1.07	0.03
	8.69	0.40	-1.10	0.00
	8.45	1.05	-1.14	0.04
	8.60	0.85	-1.13	0.06
	8.01	1.18	-1.07	0.07
	8.10	0.57	-1.10	0.03
Mean	**8.30**		**-1.10**	
s	**0.37**		**0.02**	

Table 1.

List of participants and uranium isotope ratios reported

ID	Institute	$R_{234/238}$	$R_{235/238}$	$R_{236/238}$
L1	NRC (Canada)	•	•	
L2	CNEA (Argentina)	•	•	
L3	IFIN-HH (Romania)	•	•	
L4	JAEA (Japan)	•	•	
L5	JRC-GEEL (EC, Belgium)	•	•	
L6	JRC-KRU (EC, Germany)	•	•	
L7	KINAC (South Korea)		•	
L8	EK (Hungary)	•	•	
L9	UM (Canada)	•	•	
L10	LLNL (USA)	•	•	
L11	CNL (Canada)	•	•	
L12	LANL (USA)	•	•	
L13	AEL-AMS (Canada)			•

Table 2.

Summary of methods for U isotope ratio measurements

ID	Sample digestion	Column separation	Instrumentation	Mass bias correction	Calibrator
L1	0.25 g of sample was digested with 7 ml of HNO_3, 3 ml of HCl and 1 ml of HF in a	UTEVA	MC-ICP-MS	SSB	IRMM-184[a]
L2	0.8 g of sample was digested with 5ml HNO_3, evaporated to dryness and	none	TE-TIMS	SSB	NBL 129A[b]
L3	0.05 g of sample, 1 ml digestion matrix or spike (2% *v/v* HNO_3, 0.5% *v/v* HCl), 2 ml of 60% *v/v* HNO_3, 1 ml of 30% *v/v* HCl in a Milestone Ultrawave microwave digestor	none	q-ICP-MS	SSB	Merck 8471[h]
L4	0.03 g of sample was digested with 3 ml of HNO_3 in a hot block.	UTEVA	TIMS	SSBRL	NBL U125A[c]
L5	0.5 g of sample was digested with 15-20 ml of 8 M HNO_3 in a hot block.	AG1-x4	TIMS	DS ($^{235/238}U$) and SSB ($^{234/238}U$)	IRMM-3636a[g], IRMM-184[a]
L6	0.8 g of sample was digested with 30 ml of 8 mol l^{-1} HNO_3/0.02 mol l^{-1} HF in a hot	none	MTE TIMS	SSB	IRMM-184[a]
L7	0.01 ~ 0.06 g of sample was digested with 1 ml of 60% *v/v* ultra-pure HNO_3 in	UTEVA	Alpha spectrometry	SSB	Eckert and Ziegler 94370[i]
L8	0.2 g of sample was digested with 5 ml of 1 mol l^{-1} HNO_3 in a hot block.	none	HR-ICP-MS	SSB	IRMM-184[a]
L9	100 mg with 20 mg boric acid pressed to pellet	none	SIMS	SSB	Scotty mine U ore using

L10	0.1 g of sample was digested with 3 ml of 10.5 mol l^{-1} HCl and 0.05 ml HNO_3 in	AG1-X8, UTEVA	MC-ICP-MS	SSB	NBL U010[d]
L11	0.1 g of sample was digested with 6 ml of HNO_3 in a microwave	AG1-x8, UTEVA	TIMS	SSB	NBL U020A[e] NBL 112A[f]
L12	0.2 g of sample was digested with 6 ml of HNO_3 and 1 ml of HF in a hot block or a	UTEVA	TE TIMS	N/A	N/A
L13	0.015 g mixture of sample and PbF_2 (1:10 by vol.) was pressed into a copper target	none	AMS	N/A	none

q-ICP-MS – quadrupole inductively coupled plasma-mass spectrometry; MC-ICP-MS – multi-collector ICP-MS; TIMS – thermal ionisation mass spectrometry; SF-ICP-MS – sector field ICP-MS; TE TIMS – total evaporation TIMS; MTE TIMS – modified total evaporation TIMS; DS TIMS – double spike TIMS; SIMS – secondary ion mass spectrometry; AMS –accelerator mass spectrometry; DS – double spike; SSB – standard-sample bracketing; SSBRL – standard-sample bracketing with Russell's law.

Links or references for calibrators:

[a]: https://crm.jrc.ec.europa.eu/p/40454/40475/By-application-field/Nuclear/IRMM-184-URANIUM-238-NATURAL-ISOTOPIC-NITRATE-SOLUTION/IRMM-184

[b]: https://www.energy.gov/nnsa/downloads/nbl-program-office-certificate-analysis-certified-reference-material-c129a-25guranium

[c]: https://www.energy.gov/nnsa/downloads/nbl-program-office-certificate-analysis-certified-reference-material-c125a-5guranium

[d]: https://www.energy.gov/nnsa/downloads/nbl-program-office-certificate-analysis-certified-reference-material-crm-u010-5mg

[e]: https://www.energy.gov/nnsa/downloads/nbl-program-office-certificate-analysis-certified-reference-material-crm-u020a-10mg

[f]: https://www.energy.gov/nnsa/downloads/nbl-program-office-certificate-analysis-certified-reference-material-c112a-4guranium

[g]: https://crm.jrc.ec.europa.eu/p/40455/By-material-matrix/IRMM-3636a-URANIUM-233-236-NITRATE-SOLUTION-DOUBLE-SPIKE-DILUTED/IRMM-3636a

[h]: https://www.emdmillipore.com/CA/en/product/Uranium-ICP-standard,MDA_CHEM-170360, only a commercial U standard for concentration, and U isotope ratio measured by ICP-MS by L3 without mass bias correction.

[i]: https://www.ezag.com/home/products/isotope_products/isotrak_calibration_sources/general_technical_information/special_isotopes/, only a commercial U isotopic material without reporting uncertainty.

[j]: Sharpe and Fayek (2016).

Table 3.

Column separation procedure

UTEVA column separation	**Step**
5 ml 3 mol l^{-1} HNO_3	Clean
5 ml 3 mol l^{-1} HCl	Clean
5 ml 1 mol l^{-1} HCl	Clean
5 ml de-ionised water	Clean
3 ml 3 mol l^{-1} HNO_3	Condition
Sample in 1 ml of 3 mol l^{-1} HNO_3	Load
2×2 ml 3 mol l^{-1} HNO_3	Rinse
2×2 ml 6 mol l^{-1} HCl	Rinse
4×2 ml 1 mol l^{-1} HCl	Elution

Table 4.

Uranium isotope ratios in UCLO-1, UCHI-1, UPER-1, and certified values in the SI-traceable calibrators used in this study

Material	**Lab**	$\mathbf{10^4}\boldsymbol{R}_{\mathbf{234/238}}$	$\mathbf{10^2}\boldsymbol{R}_{\mathbf{235/238}}$	$\mathbf{10^9}\boldsymbol{R}_{\mathbf{236/238}}$
UCLO-1	L1	0.529 94(27)	0.72565(11)	–
	L2	0.536(26)	0.72507(27)	–
	L3	0.5679(88)	0.717760(20)	–
	L4	0.5350(43)	0.7267(12)	–
	L5	0.530 732(63)	0.725673(58)	–
	L6	0.530 08(46)	0.72558(30)	–
	L7	–	0.742(13)	–
	L8	0.62(11)	0.736(12)	–
	L9	0.553(25)	0.7290(22)	–
	L10	–	–	–
	L11	0.5355(28)	0.72565(83)	–
	L12	–	–	–
	L13	–	–	0.0099(20)
UCHI-1	L1	0.54709(27)	0.72564(11)	–
	L2	0.553(17)	0.72500(39)	–
	L3	0.5784(95)	0.7147 93(22)	–
	L4	0.5506(32)	0.72600(67)	–
	L5	0.547518(87)	0.725641(58)	–
	L6	0.54721(58)	0.72565(28)	–
	L7	–	–	–
	L8	0.611(78)	0.729(18)	–
	L9	0.545(19)	0.7261(15)	–
	L10	0.5474(15)	0.72504(58)	–
	L11	0.5530(38)	0.72492(12)	–
	L12	0.5482(28)	0.72604(57)	–
	L13	–	–	0.1964(80)
UPER-1	L1	0.53581(25)	0.72543(11)	–
	L2	0.538(13)	0.72494(19)	–
	L3	–	–	–

L4	0.5463(38)	0.72509(57)	–
L5	0.536208(75)	0.7254 58(58)	–
L6	0.53592(53)	0.72552(21)	–
L7	–	0.720(17)	–
L8	0.594(59)	0.7057(73)	–
L9	0.543(20)	0.7251(15)	–
L10	0.5354(14)	0.72485(69)	–
L11	0.5393(44)	0.7252(12)	–
L12	0.5372(28)	0.72601(57)	–
L13	–	–	0.0216(28)
IRMM-184	0.53183(16)	0.72623(11)	–
NBL 129A	0.53350(20)	0.72614(20)	–
NBL U125A	3.9130(19)	4.2301(12.5)	–
NBL U010	0.5466(25)	1.0140(5)	–
NBL U020A	1.7683(15)	2.0687(6)	–
NBL U112A	0.52841(41)	0.72543(20)	–
IRMM-3636a	$R_{233/236}$ = 1.01906(8)		

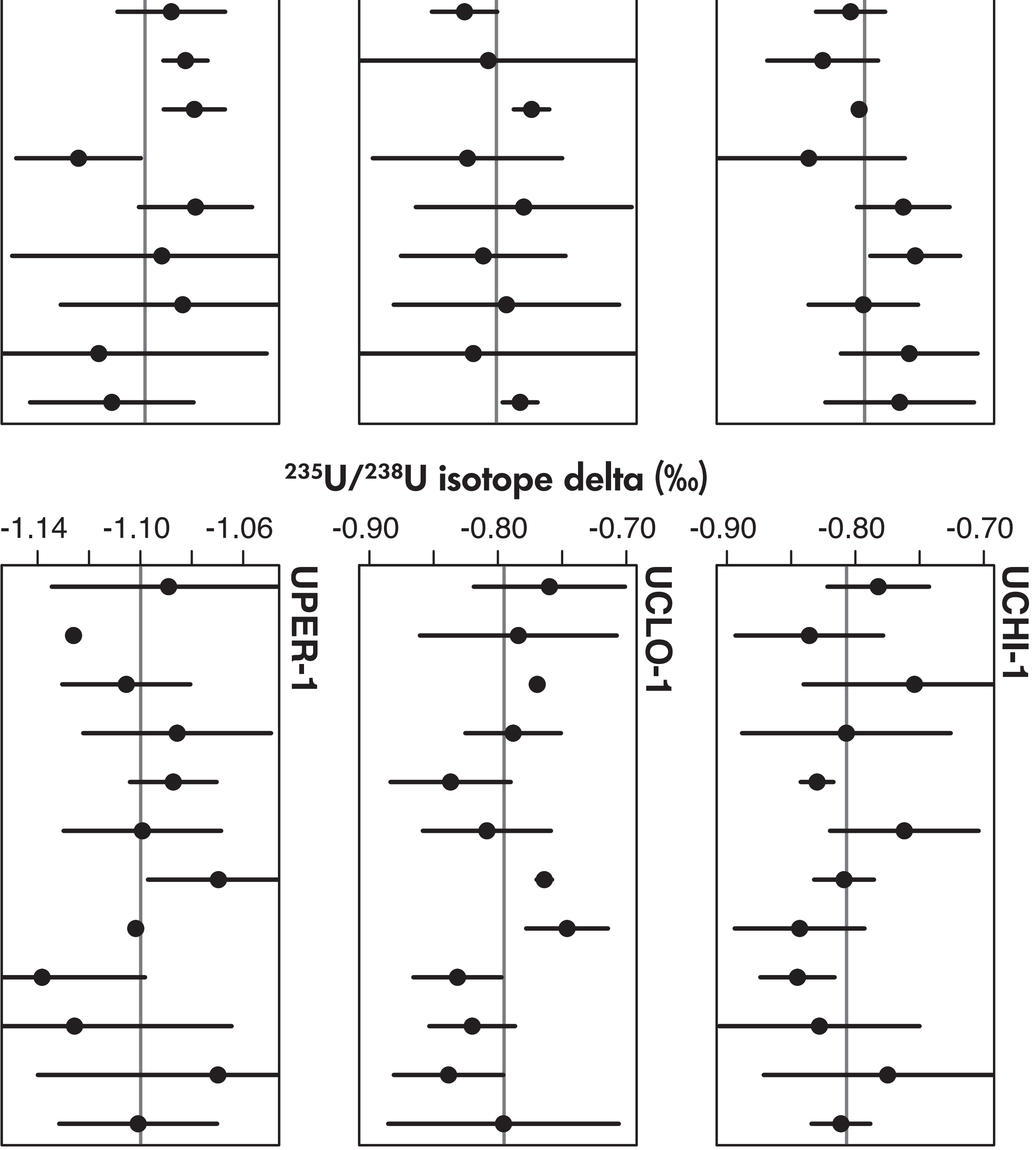
Values in parenthesis are standard uncertainties (k = 1).

Table 5.

Isotope ratios of uranium in NRC UCLO-1, UCHI-1, and UPER-1

Isotope ratio	**Material**	**Value (mol mol^{-1})**
$R_{234/238}$	UCLO-1	0.000 053 04(7)[a]
	UCHI-1	0.000 054 75(2)
	UPER-1	0.000 053 61(4)
$R_{235/238}$	UCLO-1	0.007 2563(13)
	UCHI-1	0.007 2563(10)
	UPER-1	0.007 2542(11)

[a] Expanded uncertainty (k = 2) is given in the parenthesis.



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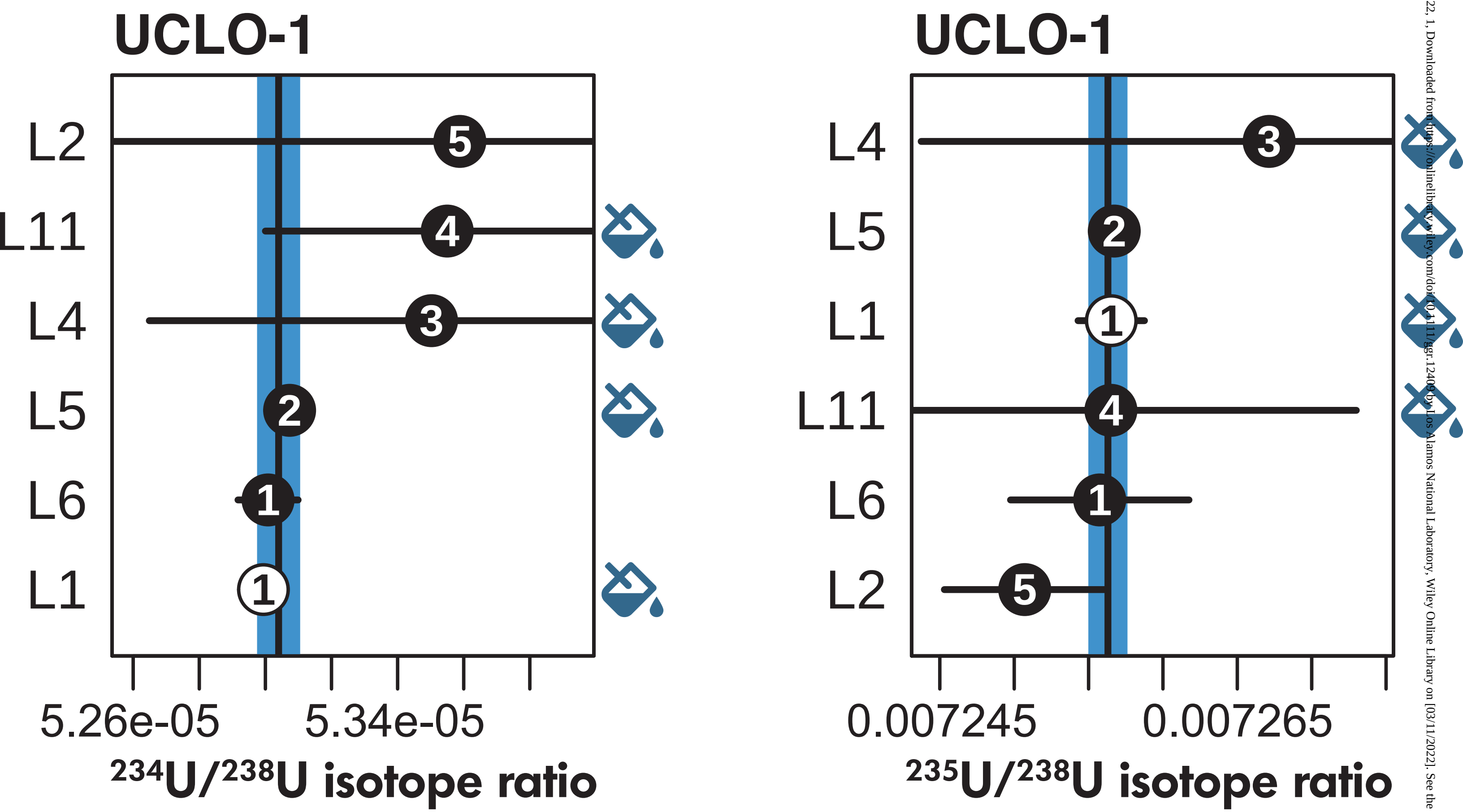

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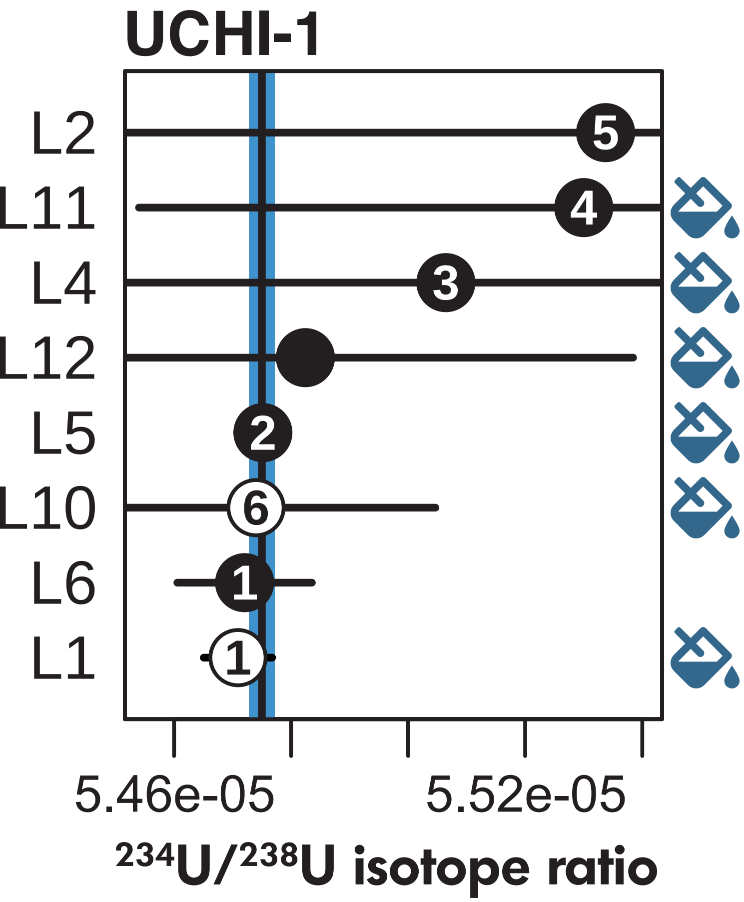

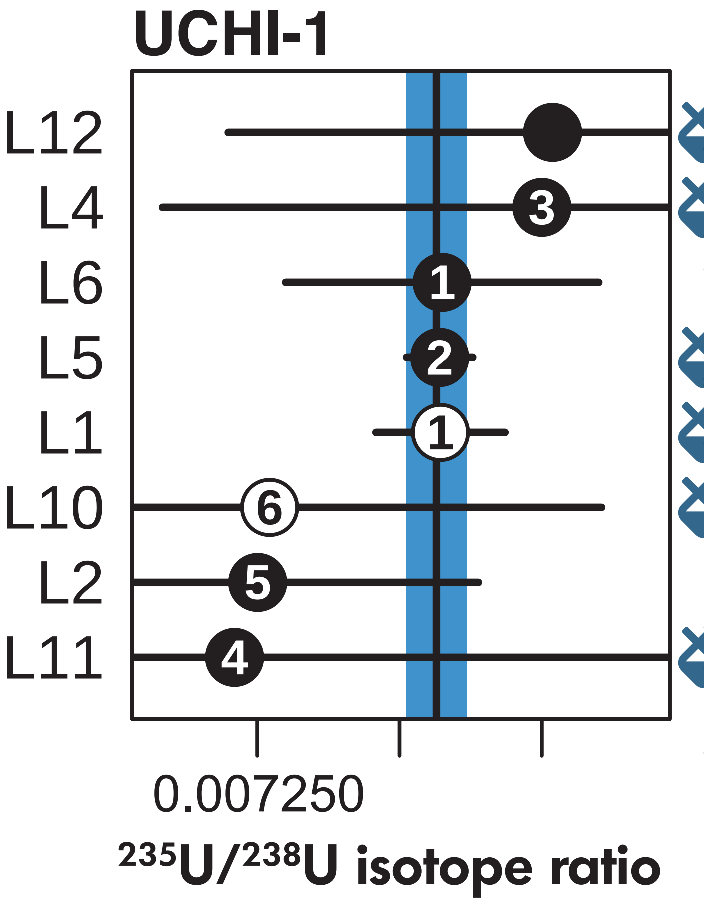

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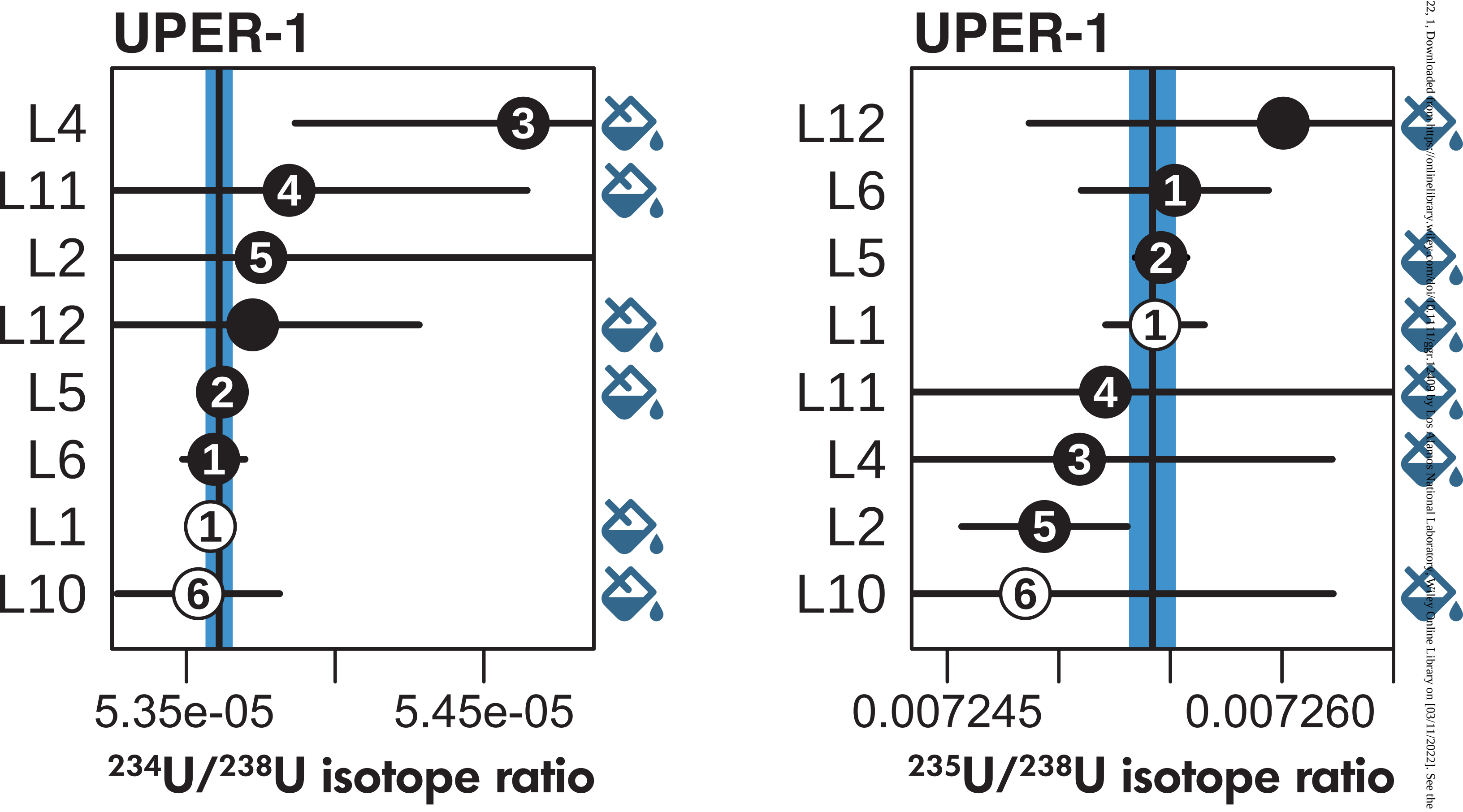

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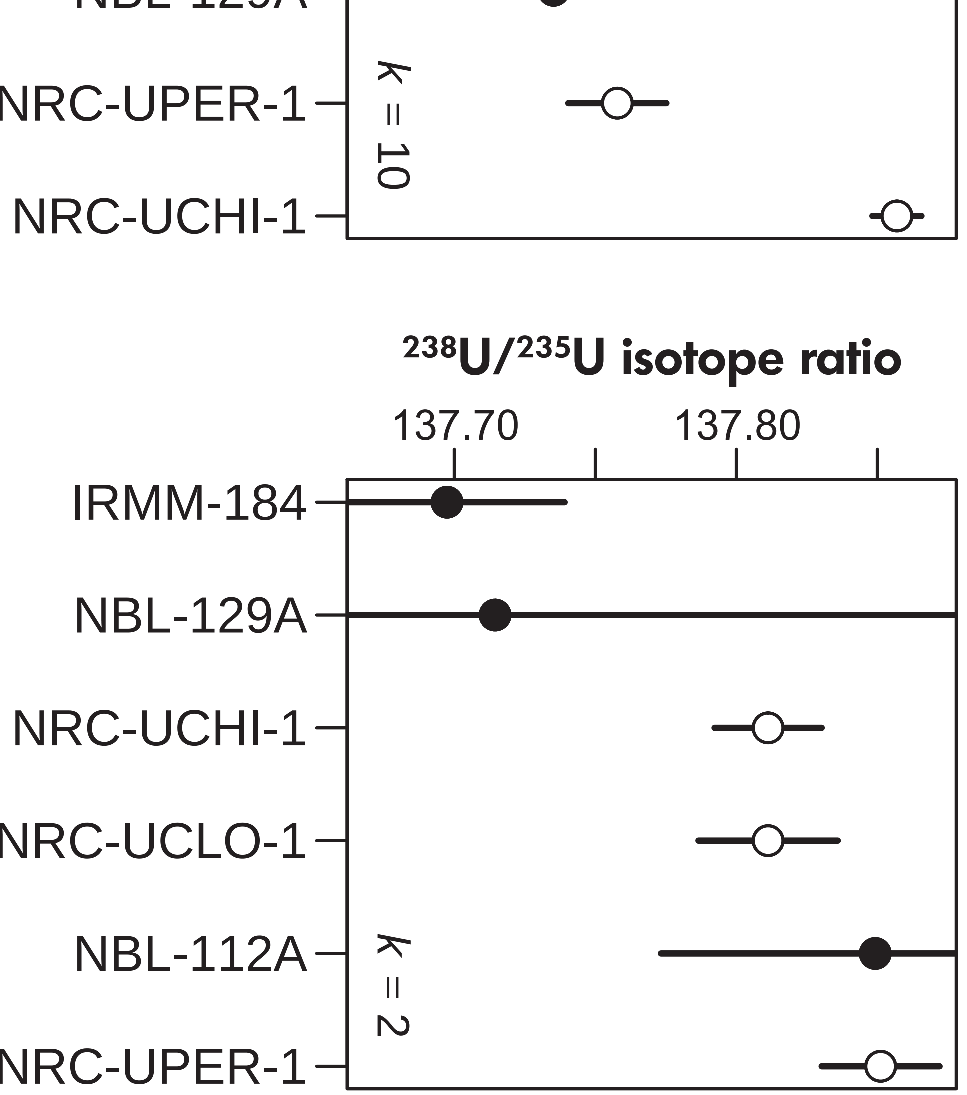

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