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Determination of the isotopic composition of zirconium using MC-ICPMS

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ABSTRACT

Measurements of zirconium isotopes provide insights in the formation of planetary bodies, dating nuclear explosions or maintenance of nuclear reactors. Although many comparative measurements for the isotopic composition of zirconium have been performed using mass spectrometry, zirconium isotopic standards are lacking and only a single calibrated measurement has been reported to date by thermal ionization mass spectrometry (TIMS). In this study, we report an independent measurement of zirconium isotopic composition in a new zirconium isotopic reference material by inductively coupled plasma mass spectrometry (MC-ICPMS) using the-state-of-the-art regression method and two independent primary standards, NIST SRM 984 rubidium and SRM987 strontium. Our results agree well with the recent TIMS measurements and suggest a revision of the standard atomic weight of zirconium.

Keywords: Zirconium isotope ratios, isotopic reference material, MC-ICPMS, regression method

1. Introduction

Zirconium isotopic analysis are essential in wide-ranging applications including the study of early solar system development[1] and the formation of planetary bodies[2,3]. Besides its role in cosmochemistry, zirconium isotopes have applications in geology[3,4], life science[5], environmental science[6] and nuclear science[7-12].

Despite the numerous applications, calibrated measurements of zirconium isotopic composition have received little attention. Zirconium isotope ratio measurements are typically performed with thermal ionization mass spectrometry (TIMS)[13-15] or multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS).[16-18] As noted recently by Tompkins *et al.*[19], no standards of certified isotopic composition are available for zirconium. Hence, virtually all studies report relative measurements against in-house laboratory standards or rely on conventional values, such as $^{94}Zr/^{90}Zr = 0.3381$ from Minster and Richard[20] or $^{94}Zr/^{90}Zr = 0.3378$ from Nomura *et al.*[21] as constant input variables, in tandem with conventional correction models for instrumental isotopic fractionation such as the exponential law[17,18,22-24] or double spike method[16,25,26]. The validity of either these normalizing constants or the exponential correction models[27] has not been demonstrated for zirconium isotopes which leaves zirconium isotope ratio measurements without reliable anchors.

The aim of this study is to provide an independent calibrated measurement for all isotope ratios of zirconium by MC-ICPMS, without relying on any normalization values or instrumental isotopic fractionation models. A primary method of isotope amount ratio analysis is the full gravimetric isotope mixture model that requires weighable amounts of all near-pure (separated) isotopes of the element, which is costly and not always feasible for elements with many isotopes.[27] A low-cost alternative approach employed in this work is the state-of-the-art regression method which is increasingly employed for absolute isotope ratio measurements.[28-35] This model enables the calibration of every isotope ratio of an element by using an isotopic standard of another element. In this study, isotopic standards NIST SRM 984 rubidium and NIST SRM 987 strontium were used as primary calibrators and, in turn, a new isotopic certified reference material NRC ZIRC-1 was made available.

2. Experimental section

2.1. Instrumentation

For all zirconium isotope ratio measurements, we used a Neptune Plus MC-ICPMS (Thermo Fisher Scientific; Bremen, Germany) equipped with nine Faraday cups and a combined Scott-type cyclonic spray chamber with a PFA self-aspirating nebulizer (Elemental Scientific; Omaha, NE, USA) operated at 50 µL min^{-1}. The instrument is installed with a plug-in quartz torch with quartz injector and a platinum guard electrode. This instrument was operated under low mass

resolution mode to perform isotope ratio measurements. In brief, the instrument was tuned for high sensitivity, optimal peak shape (flat-top square) and stable signals. The gain calibration of the Faraday cups was performed weekly to ensure normalization of their efficiencies. Rotating amplifiers were chosen during the measurements, which effectively eliminate amplifier calibration biases and improve measurement precision. Typical operating conditions are summarized in Table 1.

Table 1. MC-ICPMS operating conditions

Instrument setting	
Radio-frequency power, *P*	1220 to 1280 W
Argon plasma gas flow rate	16.0 L min^{-1}
Argon auxiliary gas flow rate	1.00 L min^{-1}
Argon carrier gas flow rate	1.015 L min^{-1}
Sampler cone orifice (Ni)	1.1 mm
Skimmer cone orifice (H, Ni)	0.8 mm
Lens settings	Optimized for maximum and stable analyte signal intensity while maintain flat top peak
Data acquisition parameter	
Faraday cup configuration #1 (Rb-Zr)	L3 (^{85}Rb), L1 (^{87}Rb), C (^{88}Sr), H1 (^{90}Zr), H2 (^{91}Zr)
Faraday cup configuration #2 (Sr-Zr)	L3 (^{86}Sr), L1 (^{88}Zr), C (^{89}Y), H1 (^{90}Zr), H2 (^{91}Zr)
Faraday cup configuration #3 (Zr-Zr)	L2 (^{90}Zr), L1 (^{91}Zr), C (^{92}Zr), H1 (^{94}Zr), H2 (^{95}Mo), H3 (^{96}Zr)
Faraday cup configuration #4 (Sr-Zr)	L4 (^{87}Sr), L3 (^{88}Zr), L1 (^{90}Zr), C (^{91}Zr), H1 (^{92}Zr), H2 (^{94}Zr), H3 (^{95}Mo), H4 (^{96}Zr)
Mass resolution	Low
Signal integration time	2.097 s
Number of integrations, cycles, and blocks	1, 8, 6 for Zr-Zr (#3); 1,10,5 for Rb-Zr (#1) and Sr-Zr (#2); 1, 6, 8 for Sr-Zr (#4)
Sensitivity	12 V/ppm for $^{90}Zr^{+}$

2.2. Reagents and solutions

Reagent grade nitric and hydrochloric acids (Fisher Scientific; Ottawa, ON, Canada) were purified via a sub-boiling distillation system (Milestone; Shelton, CT, USA) before use. The deionized water (DIW, 18.5 MΩ cm) was obtained from a Milli-Q ion exchange system (Sigma Aldrich; Oakville, ON, Canada).

Four zirconium materials were obtained from different commercial vendors. One zirconium standard solution (Zr-1) at 1005 mg L^{-1} in 5 % HNO_3 was sourced from SCP Science (Baie-D'Urfé, QC, Canada). The second Zr standard solution (Zr-2) at 999 mg L^{-1} in 4 % HNO_3 was purchased from Delta Scientific (Ottawa, ON, Canada). The third Zr standard solution (Zr-3), NIST SRM 3169 Zr at 10 000 mg kg^{-1} in 10 % HNO_3 and 2% HF, was obtained from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). A fourth Sigma Zr standard solution at 10 018 mg L^{-1} in 5 % HNO_3 and 0.5 % HF was sourced from Sigma Aldrich (Oakville, ON, Canada). This solution

was diluted 10-fold in 2 % HNO_3 and 0.1 % HF, bottled in 2 mL glass ampules as candidate zirconium isotopic standard, NRC ZIRC-1.

The primary calibrators of NIST SRM 984 with certified value of rubidium isotope ratio, $R_{85/87}$ = $N(^{85}Rb)/N(^{87}Rb)$ = 2.593 with expanded uncertainty U = 0.002 (k = 2) and NIST SRM 987 with certified value of strontium isotope ratio, $R_{88/86}$ = $N(^{88}Sr)/N(^{86}Sr)$ = 8.378 61 with expanded uncertainty U = 0.003 25 (k=2) were obtained from NIST.

2.3. Sample preparation and analysis

For absolute isotope ratio measurements, test solutions containing mixture of Zr (ZIRC-1) and Rb (SRM 984), Zr (ZIRC-1) and Sr (SRM 987) or Zr (ZIRC-1) alone with w(Zr) = 2.5-4.0 mg kg^{-1}, w(Rb) = 1.0-1.5 mg kg^{-1} and w(Sr) = 1.5-2.0 mg kg^{-1}, were prepared by diluting the individual stock solutions in 1 % HNO_3. A self-aspiration nebulizer was used for sample introduction to ICPMS. Similar to previous studies,[29-35] the instrument plasma radio frequency (RF) power was increased stepwise (four steps) from the optimum value P_0 (which corresponds to the high sensitivity region, stable signal and flat top peak, typically at 1220 W) to P_{max} (typically at 1280 W) wherein Zr, Rb and Sr signals decreased by approx. 25–30 % compared to their values at P_0. The purpose of this deliberate change of RF power during the measurement session is to induce a fast drift in the mass bias. Each session of measurement takes ca. 15 min compared to several hours at the optimum P_0[27]. The isotope ratios of all samples were measured by incrementally increasing the RF power with values from 1220 to 1280 W for each measurement session which constitute a single data set. Signals of all measured isotopes obtained from a blank solution of 1 % HNO_3 at the optimum RF power were subtracted from all measurement results for simplicity. In principle, the corresponding blank should be subtracted for the sample at each RF value. Since intensities of all measured isotopes in the blank at P_0 were very small (0.05–11 mV) compared to intensities in the samples (5–45 V), both blank subtraction approaches yielded identical isotope ratios. Static run was employed for isotope ratio measurements using Faraday cup configurations 1-3, respectively, as shown in Table 1. The quality of each data set was monitored via the linear correlation coefficient (R^2). From the 850 regressions used in this work, the average R^2 was 0.9999 and the lowest R^2 was 0.9993. Results reported in this study were collected at the NRC between Jun 2019 and Jan 2020.

Natural variations of zirconium isotope ratios in shelf reagents were measured using the combined standard-sample bracketing method (C-SSBIN) with strontium as an internal standard. Faraday cup configuration #4 (Table 1) was used for this purpose at optimum instrument conditions with RF at P_0. Test solutions with mass fractions w(Zr) = 3.0 mg kg^{-1} and w(Sr) = 1.5 mg kg^{-1} were prepared in 1 % nitric acid.

2.4. Spectral interferences

NRC ZIRC-1, NIST SRM 984 Rb, and NIST SRM 987 Sr standards are made from high purity materials, thus polyatomic or double charged interferences from matrix elements are negligible.

However, isobaric interferences from other elements could occur. Isobaric interferences from impurities of molybdenum ($^{92}Mo^+$, $^{94}Mo^+$, $^{96}Mo^+$) and ruthenium ($^{96}Ru^+$) could occur on Zr isotopes. We prepared four zirconium solutions (Zr-1, Zr-2, Zr-3, and ZIRC-1) and two calibrator solutions (SRM984 Rb and SRM987 Sr) at 5 mg kg^{-1} Zr, Rb, and Sr, respectively and analyzed them with HR-ICPMS (Element XR) using external calibration.

The Zr solutions revealed Ru, Rb and Sr below 5 ng kg^{-1} and Mo at 80 ng kg^{-1}. The SRM 987 solution revealed Rb below 5 ng kg^{-1} and the SRM 984 solution revealed Sr below 2 ng kg^{-1}.

The mass fraction of these impurities were insignificant to form isobaric interferences. Although the mass fraction of Mo was somewhat higher in ZIRC-1, it only produced 0.2 mV for the test solutions, insignificant compared to intensities of 39.1, 8.7, 13.6, 14.4, and 2.4 V for ^{90}Zr, ^{91}Zr, ^{92}Zr, ^{94}Zr, and ^{96}Zr, respectively. Such interferences on Zr isotopes were observed to be insignificant; nevertheless, these isobaric interferences of $^{92}Mo^+$, $^{94}Mo^+$, and $^{96}Mo^+$ on Zr isotopes were corrected by subtracting its contribution based on the following equation:

$$I(^{A}\mathrm{Zr}) = I(A) - r(^{A/95}\mathrm{Mo}) \times I(^{95}\mathrm{Mo}) \quad (1)$$

where $I(A)$ is the observed net intensity at mass A, $I(^{A}\mathrm{Zr})$ is the signal intensity from ^{A}Zr, $r(^{A/95}\mathrm{Mo})$ is the measured molybdenum isotope ratio from a 1 mg kg^{-1} Mo standard solution, and $I(^{95}\mathrm{Mo})$ is the signal intensity for ^{95}Mo.

3.1. Correction for instrumental isotopic fractionation

The regression model effectively calibrates each isotope ratio of the analyte element from the known isotope ratio of a calibrator element without assuming identical instrumental fractionation for both elements (they are indeed different)[27]:

$$\ln(r_{\mathrm{Analyte}}) = a + b \cdot \ln(r_{\mathrm{Standard}}) \quad (2)$$

The regression parameters a and b are obtained using the ordinary least squares fitting and are used to obtain the calibrated isotope ratio R_{Analyte}:[36]

$$R_{\mathrm{Analyte}} = e^{a} \cdot (R_{\mathrm{Standard}})^{b} \quad (3)$$

Although the regression model does not require identical mass bias between the analyte and calibrator isotope ratios, better results are obtained when both elements are close in mass[29,35]. Thus, rubidium and strontium were selected as calibrators for zirconium (molybdenum is not suitable as it shares isobaric nuclides with zirconium).

Because of the Faraday cup arrangement in our MC-ICPMS instrument, it was impossible to simultaneously collect all five isotopes of zirconium, ^{95}Mo (for interference correction) along with ^{86}Sr and ^{88}Sr (or ^{85}Rb and ^{87}Rb) in a static mode (which provides best performance). Hence, zirconium 91/90 isotope ratio in ZIRC-1 was first calibrated against rubidium and strontium standards using Faraday cup configurations #1 and #2 (see Table 1) which was then used to

calibrate all other zirconium isotope ratios using Faraday cup configuration #3. A total of 327 linear regression (Figure 1) sets were obtained, 161 sets of Rb → Zr and 166 sets of Sr → Zr, over the course of six months from Jun 2019 to Dec 2019.

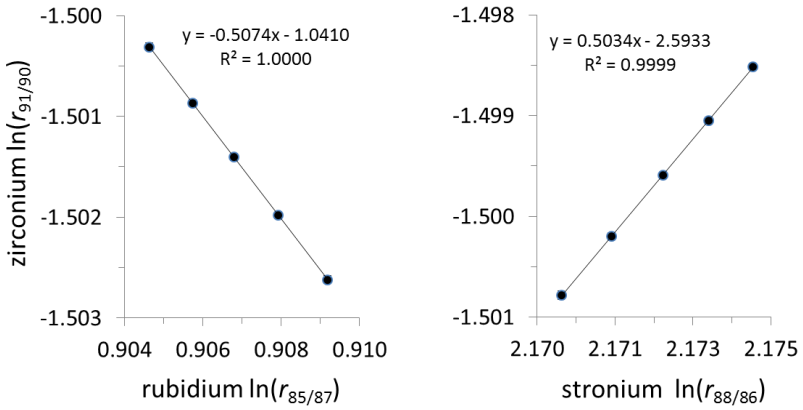

Figure 1. Typical log-linear regression plots of Rb → Zr and Sr → Zr isotope ratios. Repeatability uncertainty of isotope ratio is smaller than the symbols.

The typical uncertainty of individual zirconium $R_{91/90}$ isotope ratio estimates in ZIRC-1 from the SRM984 Rb calibrator is similar to that from the SRM987 Sr, equalling 2 parts in 10^4. Fig. 2 shows the results of calibrating $^{91}Zr/^{90}Zr$ isotope ratio by two independent routes. It is evident that the individual consensus values of $R_{91/90}$ from Rb → Zr and Sr → Zr differ by 1 part in 10^3 and this difference is significant (p = 0.01). Put differently, the value of $^{85}Rb/^{87}Rb$ in NIST SRM 984 would have to be 2.588 instead of 2.593 (5-sigma lower) for the results of both regression approaches to agree with each other. We note that the accuracy of the certified strontium $^{88}Sr/^{86}Sr$ isotope ratio in NIST SRM 987 has been verified independently[28] by the full gravimetric isotope mixture method to be correct within 1 part in 10^3. However, such level of precision is not sufficient to trust strontium SRM 987 over the rubidium SRM 984. Since we are not willing to challenge the values assigned to either of these isotopic standards, the resulting combined value of $R_{91/90}$ was obtained by linear pooling of the two estimates.

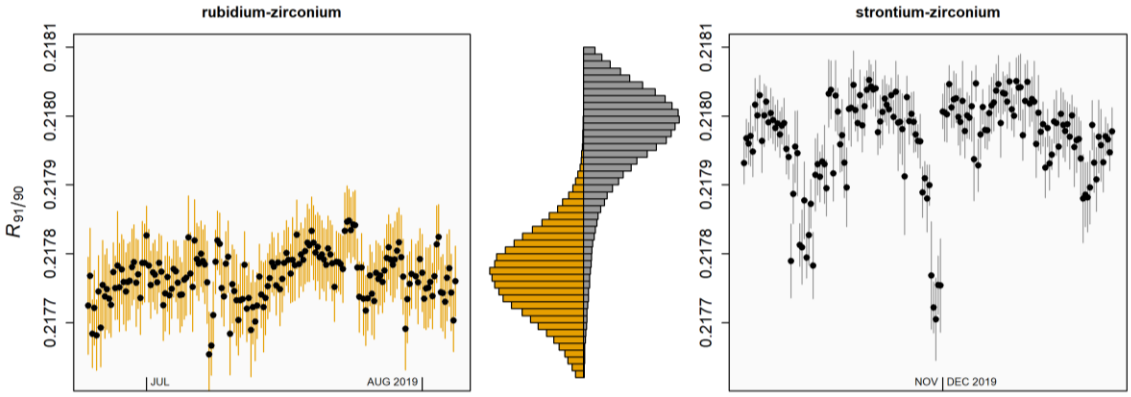

Figure 2. Measurement of zirconium isotope ratio $R_{91/90}$ in NRC ZIRC-1 using regression method with two independent calibrators. Vertical error bars represent standard uncertainty which includes contributions from the primary isotopic standards (SRM 984 Rb and SRM 987 Sr). The corresponding consensus isotope ratios of zirconium are $R_{91/90}$ = 0.217 77(5) from Rb → Zr and $R_{91/90}$ = 0.217 97(7) from Sr → Zr.

3.2. Uncertainty evaluation

Uncertainty evaluation of zirconium isotope amount ratios was done as outlined in our previous studies.[34,35] In brief, the ordinary least squares fit was applied to each regression set; the corresponding intercept, slope and their uncertainties were obtained. The obtained regression parameters were then transformed into the corresponding isotope ratios as per Eq. 2. Individual isotope ratio estimates, such as the 161 values from Rb → Zr regressions or 166 values from Sr → Zr regressions were combined into a single consensus values using random effects model. Monte Carlo method was used to draw samples from the resulting consensus values which are represented as histograms in Fig. 2. The standard deviation of the resulting distribution represents the predictive uncertainty on the $R_{91/90}$ value.

Isotopic abundances and the atomic weight of zirconium were obtained from the corresponding isotope ratio consensus values and their uncertainties while taking into the account covariances between the isotope ratios.[37,38] The results of this study are traceable to NIST SRM 984 rubidium and NIST SRM 987 strontium isotopic standards which have been prepared and characterized independently decade apart from one another. We estimate that the uncertainty of $^{91}Zr/^{90}Zr$ isotope ratio in ZIRC-1 is largely due to the inconsistency between the two primary employed followed by the session-to-session reproducibility as shown in table 2. Indeed, if we were to rely only on rubidium primary standard, the uncertainty of $^{91}Zr/^{90}Zr$ in ZIRC-1 material would be cut in half. The MC-ICPMS results reported in this study are traceable to the International System of Units through the NIST SRM 984 rubidium and SRM 987 strontium isotopic standards.

Table 2. **Uncertainty sources for zirconium isotope ratio $R_{91/90}$ in NRC ZIRC-1 standard**

Source of uncertainty	Contribution
Primary standard (NIST SRM 984 Rb)	12 %
Primary standard (NIST SRM 987 Sr)	3 %
Linear regression fits (Rb → Zr)	6 %
Linear regression fits (Sr → Zr)	7 %
Inconsistency between the primary standards	44 %
Reproducibility of Rb → Zr regression results	2 %
Reproducibility of Sr → Zr regression results	25 %

3.3. Measurement results for the NRC ZIRC-1 standard

With the consensus value for $^{91}Zr/^{90}Zr$ isotope ratio in ZIRC-1 standard, $R_{91/90}$(ZIRC-1) = 0.217 87(12)$_{k=1}$, we calibrated all other zirconium isotope ratios using additional measurement sequences involving only zirconium isotopes. Replicate solutions containing w(Zr) = 2.5–4.0 mg kg^{-1} were prepared and each was measured under the optimized experimental conditions during a three-month period from Jun to Aug 2019. During this time, four sets of ICP cones were. A total of 162 sets of Zr → Zr regressions were obtained (Figure 3).

The calibrated isotope ratios of zirconium were used to calculate the corresponding isotopic abundances and atomic weight:

$$x(^{i}\mathrm{Zr}) = \frac{R_{i/90}}{\sum_j R_{j/90}} \quad (4)$$

$$A_\mathrm{r}(\mathrm{Zr}) = \sum_i A_\mathrm{r}(\,^{i}\mathrm{Zr}) \cdot x(\,^{i}\mathrm{Zr}) \quad (5)$$

The atomic masses of zirconium isotopes are from the 2016 Atomic Mass Evaluation report[39] and the resulting isotopic composition is summarized in Table 3.

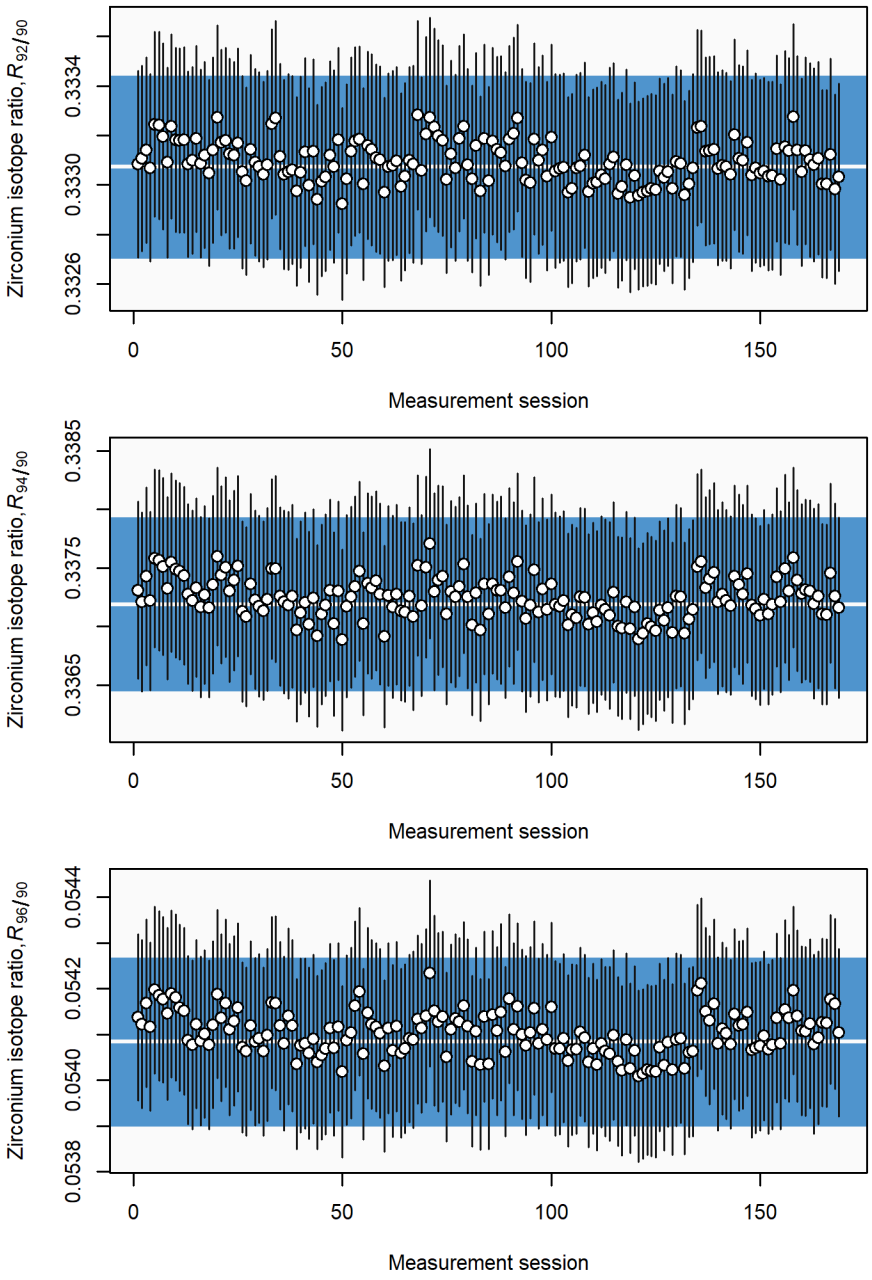

Figure 3. Zirconium isotope ratios in NRC ZIRC-1 standard measured using MC-ICPMS and parallel two-step regression approaches: $^{85}Rb/^{87}Rb \rightarrow {}^{91}Zr/^{90}Zr \rightarrow {}^{A}Zr/^{90}Zr$ and $^{88}Sr/^{86}Sr \rightarrow {}^{91}Zr/^{90}Zr \rightarrow {}^{A}Zr/^{90}Zr$ to correct instrumental isotopic fractionation. Error bars represent combined standard uncertainties which include contributions from both rubidium (NIST SRM 984) and strontium (NIST SRM 987) primary standards. Horizontal line and blue rectangles represent the consensus values and their standard uncertainty.

Table 3. **Isotopic composition of zirconium in the NRC ZIRC-1 isotopic standard**[a]

Mass number, A	Isotope ratio, $R_{A/90}$	Isotopic abundance, $x(^{A}Zr)$
90	1(exact)	0.514 87(22)
91	0.217 87(12)	0.112 18(7)
92	0.333 07(37)	0.171 49(17)
94	0.337 19(73)	0.173 61(32)
96	0.054 08(18)	0.27 85(9)

a. Values in parenthesis are standard uncertainties.

3.4. Comparison with other studies

While the isotopic composition of zirconium was first measured by Aston in the 1930s[40], not many high-quality independent studies have been reported since. Furthermore, Rosman criticized several zirconium isotopic measurements made in the 1970s and 80s on the basis that the instrumental isotopic fractionation is not corrected in these studies[41]. In light of this, we find only a single contemporary study reporting all zirconium isotope ratios without relying, directly or indirectly, on the conventional values (such as $^{94}Zr/^{90}Zr$ = 0.3381) to correct instrumental isotopic fractionation. In their study, Quemet *et al* employed total evaporation TIMS.[13] Total evaporation TIMS is an established method for accurate isotope ratio measurements and has the ability to provide absolute isotope ratio measurements without the need to correct for instrumental isotopic fractionation as isotopic signals are collected during the entire evaporation process[42-53].

As shown in Table 4, our MC-ICPMS results are in excellent agreement with the TE-TIMS results recently reported by Quemet *et al* [13]. The agreement is within few parts in 10^4 and within the stated uncertainties for all zirconium isotope ratios and is encouraging sign of confidence for the isotope ratios assigned to the ZIRC-1 isotopic standard. We also note that the regression method provides a mechanism to employ several independent isotope standards thereby improving the overall reliability of the isotopic composition of zirconium. The weighted average of the results shown in Table 4 gives $R_{94/90}$ = 0.3373(5) which differs by 0.25 % from the commonly used fixed value $^{94}Zr/^{90}Zr$ = 0.3381.

Table 4. Comparison of zirconium isotope ratio results[a]

$R_{91/90}$	$R_{92/90}$	$R_{94/90}$	$R_{96/90}$	Reference, method
0.217 85(23)	0.333 04(40)	0.337 34(79)	0.054 16(25)	Quemet[13] (2015) TE-TIMS
0.217 87(12)	0.333 08(29)	0.337 21(59)	0.054 09(14)	This work, regression MC-ICPMS

a. Values in parenthesis are standard uncertainties.

3.5. Instrumental isotopic fractionation in MC-ICPMS

In MC-ICPMS, many isotopes are known to exhibit instrumental isotopic fractionation that cannot be fully explained by the mass difference of the nuclide masses alone.[27] Hence, it is not possible to fully eliminate the instrumental isotopic fractionation (commonly known as the mass bias) using simple mathematical models such as the exponential law or the Russell's law. In particular, if the $^{94}Zr/^{90}Zr$ isotope ratio is known, or its value is assumed to be known, then other isotope ratios can be obtained using simple relationship:

$$R_{92/90} = r_{92/90} \times K_{92/90} \quad (6)$$

The correction factor $K_{94/90}$ is obtained from the known ($R_{94/90}$) and measured ($r_{94/90}$) values of $^{94}Zr/^{90}Zr$ and the Russell's law is used to relate the two correction factors:

$$\ln(K_{92/90}) = \ln(K_{94/90}) \times \ln(m_{92}/m_{90})/\ln(m_{94}/m_{90}) \quad (7)$$

Fig. 4 shows the slopes of the observed three-isotope plots and their agreement with the values expected from the exponential model (Eq. 7). In all cases we observed that the exponential (or Russell's) law will consistently lead in biased isotope ratios. The most significant is the plot of $\ln(r_{96/90})$ against $\ln(r_{94/90})$ giving, on average, a slope of 1.499 (with 90 % of values varying from 1.492 to 1.502) in contrast to $\ln(m_{96}/m_{90})/\ln(m_{94}/m_{90}) = 1.484$. This is equivalent to a 0.14 % bias in the $^{96}Zr/^{90}Zr$ isotope ratio if one uses the Russell's law and $^{94}Zr/^{90}Zr$ ratio as the calibrator (in addition to the errors introduced by choosing a certain conventional value for $^{94}Zr/^{90}Zr$). This observation demonstrates the limited utility of conventional mass bias correction for absolute isotope ratio measurements.

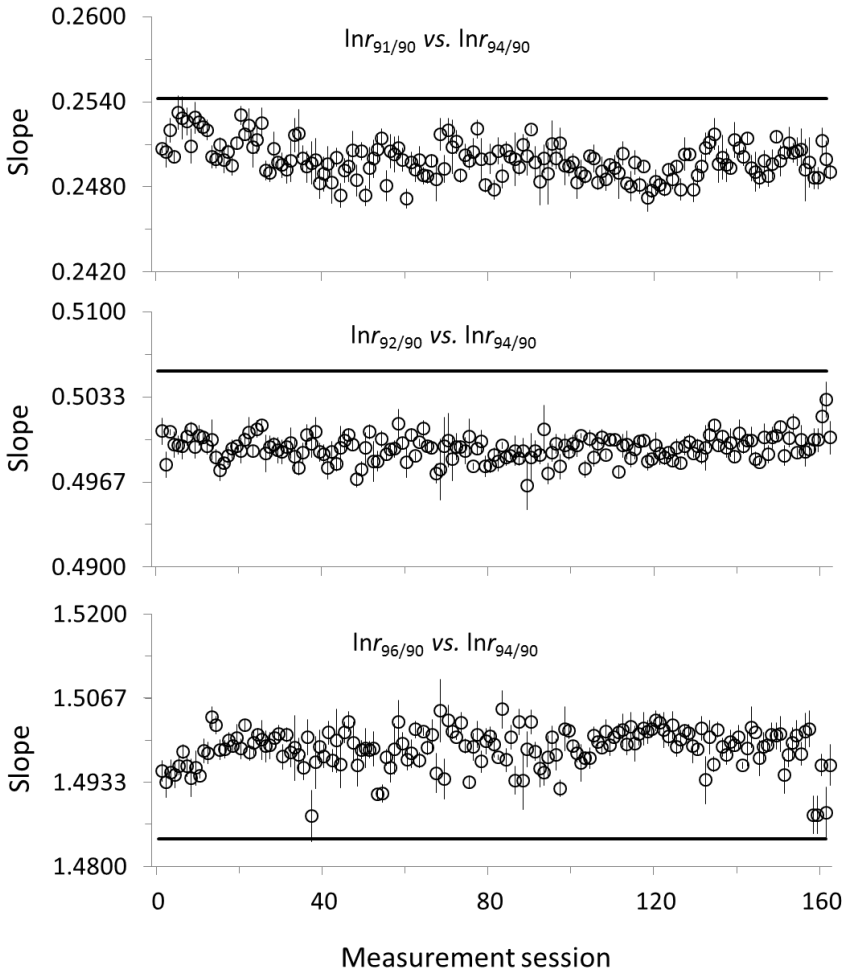

Figure 4. Deviations from the Russell's law in MC-ICPMS measurements of NRC ZIRC-1 (162 datasets collected between Jun and Aug 2019) as evidenced from the systematic offset of the three-isotope plot slopes from the values predicted by the Russell's law (horizontal lines), e.g., $b(96/90, 94/90) = \ln(m_{96}/m_{90})/\ln(m_{94}/m_{90}) = 1.484$.

3.6. Isotope delta measurements of zirconium

Given the infancy of the zirconium isotopic measurements, it is not surprising that first reports on stable isotope variations between zirconium standards appeared only in the last decade[22,54]. To further take advantage of the absolute isotopic composition of zirconium in NRC ZIRC-1, we have performed high-precision measurements of three zirconium commercial standards, including the commonly used NIST 3169 material, using the combined standard-sample bracketing with strontium internal standard[27]. This method provides relative isotope ratios with precision to few parts in 10^6. Results are presented in Table 5, showing small yet discernable variations in the zirconium isotope ratios between the four materials. All results show mass-dependent relationships in the observed isotope deltas which can be summarized in the form $\delta_{\text{ZIRC-1}}(^{A/90}\text{Zr})$ ‰ ≈ $d\times(A - 90)$ where d = 0.056, 0.013, and 0.046 for NIST Zr, SCP Zr, and ISOSPEC Zr, respectively.

Table 5. Isotope ratios of zirconium in several commercial materials relative to the NRC ZIRC-1 standard, $\delta_{ZIRC\text{-}1}(Zr)$[a]

Material	$^{91}Zr/^{90}Zr$	$^{92}Zr/^{90}Zr$	$^{94}Zr/^{90}Zr$	$^{96}Zr/^{90}Zr$
NRC ZIRC-1	0 (exact)	0 (exact)	0 (exact)	0 (exact)
NIST SRM 3169 Zr	0.06(1) ‰	0.11(2) ‰	0.24(3) ‰	0.32(4) ‰
SCP Zr	0.02(1) ‰	0.03(1) ‰	0.06(2) ‰	0.07(3) ‰
ISOSPEC Zr	0.05(1) ‰	0.09(1) ‰	0.19(3) ‰	0.27(5) ‰

a. Standard deviation is given in parentheses using shorthand notation, e.g., 0.27(5) means 0.27 with standard deviation 0.05.

In two recent studies, Inglis *et al* and Feng *et al* report variations of $^{94}Zr/^{90}Zr$ isotope ratio in numerous geological reference materials, zircons, and shelf reagents from approx. –0.15 ‰ to +0.50 ‰ relative to the NIST 3169.[54,55] We recognize that there are more extreme recent observations of an order of magnitude larger fractionation of $^{94}Zr/^{90}Zr$ ratio in some zircons[56]. In most cases this observed natural variation is within the standard uncertainty of the absolute $^{94}Zr/^{90}Zr$ isotope ratio, the latter being 1.4 parts in 10^3. Consequently, the weighted average of the results from Quemet *et al.*[13] and this study leads to an atomic weight of zirconium $A_r(Zr)$ = 91.222 ± 0.002 (k = 3). This estimate is significantly lower than the current standard atomic weight of zirconium, 91.924 ± 0.002, that was adopted in 1983[57]as an average value of the results by Nomura *et al*[21], Minster *et al*[20] and Shima[58] – none of which are, in fact, free from instrumental isotopic fractionation effects[41].

4. Conclusion

Despite numerous applications of zirconium isotopes in nuclear and geological sciences, a single calibrated measurement of its isotopic composition has been reported prior to this study. In this work we employed entirely different mass spectrometry (MC-ICPMS) and calibration approach (regression model). Our results are in excellent agreement with the recent total evaporation TIMS data which lends further credibility to both total evaporation TIMS and the cost-effective regression MC-ICPMS for the determination of absolute isotope ratios. In addition, we show that the instrumental isotopic fractionation of zirconium isotopes in MC-ICPMS follows the traditional mass-dependent models only to within few parts in 10^3 thus seriously limiting the utility of such models in precise isotope ratio measurements. Our results suggest that the current standard atomic weight of zirconium needs to be revised.

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