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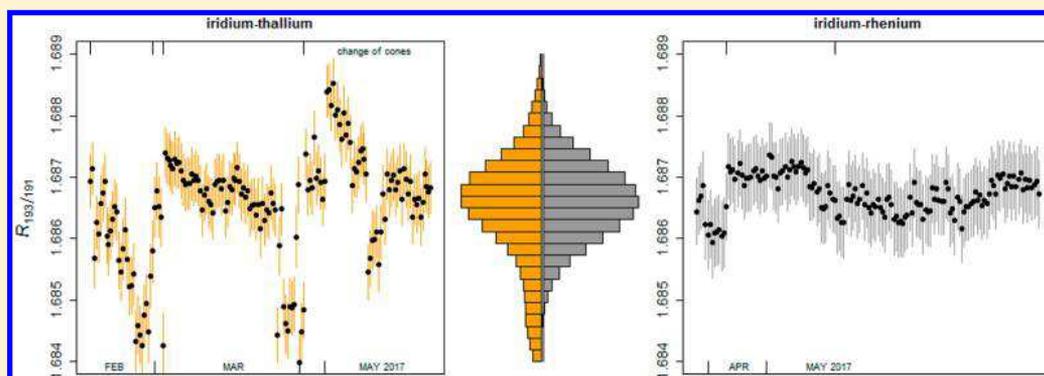


Determination of the Isotopic Composition of Iridium Using Multicollector-ICPMS

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ABSTRACT: Like many other elements, iridium is lacking a calibrated, SI traceable isotope ratio measurement. In this study, we have undertaken absolute isotope amount ratio measurements of iridium by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) using a state-of-the-art regression model to correct for the instrumental fractionation (mass bias) of isotope ratios using both NIST SRM 997 isotopic thallium and NIST SRM 989 isotopic rhenium as primary calibrators. The optimized regression mass bias correction model is based on incrementally increasing plasma power and short (10–30 min) measurement sessions. This experimental design allows fast implementation of the regression method which would normally require hours-long measurement sessions when executed under constant plasma power. Measurements of four commercial iridium materials provide a calibrated iridium isotope ratio $R_{193/191} = 1.6866(6)_{k=1}$ which corresponds to isotopic abundance $x_{191} = 0.372\ 21(8)_{k=1}$ and an atomic weight of $A_r(\text{Ir}) = 192.217\ 63(17)_{k=1}$. In addition, we present data on a new Certified Reference Material from NRC Canada IRIS-1 which fulfills the requirements of a delta zero reference for iridium isotope measurements.

Accurate knowledge of the isotopic composition of an element is essential in many branches of chemistry and physics. For several elements, however, the measurement science is not mature enough to allow for calibrated measurements of atomic weights or isotope ratios.¹ A lack of independent absolute isotope ratio measurements was most recently highlighted with the revision of the standard atomic weight of ytterbium for which only two largely discrepant calibrated measurements are available.² Although more documented measurements^{3–6} are available for iridium than for ytterbium, none of them have been fully calibrated, that is, corrected for the instrumental fractionation of the isotope ratios during mass spectrometric measurements. The interest in iridium is largely due to its anomalous levels in cretaceous-tertiary boundary sediments worldwide.⁷ In addition, industrial developments of new materials using platinum-group elements as catalysts and additives have created an increased demand for the chemical analysis of iridium.⁸

Since its commercialization in 1992, the multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) has become a powerful tool for the determination of isotope ratios with a wide range of applications.⁹ Despite this, very few

absolute isotope ratio measurements by MC-ICPMS have surpassed the traditional thermal ionization mass spectrometry (TIMS) because MC-ICPMS suffers significantly larger instrumental fractionation effects (mass bias) compared to TIMS and efforts to address these effects are not trivial.¹⁰ In this vein, the aim of this study was to develop a method for the determination of absolute isotope ratio of iridium by MC-ICPMS with the use of a state-of-the-art regression mass bias correction model and both NIST SRM 997 isotopic thallium and NIST SRM 989 isotopic rhenium as calibrators. Given that the regression model for isotope ratio measurements is not a standard method, we built from our earlier work¹¹ to further test the validity of this method while extending it to isotope ratio measurements of iridium. In addition, we are presenting a new iridium CRM IRIS-1 certified for isotopic composition which could be used as a delta zero standard for iridium isotope

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ratio measurements in environmental and geoscience applications.

EXPERIMENTAL SECTION

Instrumentation. A Thermo Fisher Scientific Neptune Plus (Bremen, Germany) MC-ICPMS equipped with nine Faraday cups was used for all isotope ratio measurements. The plug-in quartz torch with quartz injector was fitted with a platinum guard electrode. For sample introduction, a combined Scott-type on the top of a cyclonic spray chamber with a PFA self-aspirating nebulizer (Elemental Scientific, Omaha NE, USA) was used, operating at 50 $\mu\text{L min}^{-1}$. Instrument optimization was performed by following a standard procedure of the manufacturer's manual. In brief, the instrument was tuned to achieve the highest sensitivity while maintaining flat-top square peaks and stable signals. At this point, the gain calibration of the Faraday cups was performed to ensure normalization of their efficiencies. Typical operating conditions are summarized in Table 1.

Table 1. MC-ICPMS Operating Conditions

Instrument Settings	
radio-frequency power, P	1240 to 1290 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	1.025 L min^{-1}
sampler cone depth (H, Ni)	1.1 mm
skimmer cone depth (Ni)	0.8 mm
lens settings	optimized for maximum and stable analyte signal intensity while maintaining a flat top peak
Data Acquisition Parameters	
Faraday cup configuration for Ir–Tl	L4 (^{191}Ir), L2 (^{193}Ir), C (^{198}Pt), H2 (^{203}Tl), H4 (^{205}Tl)
Faraday cup configuration for Ir–Re	L4 (^{185}Re), L2 (^{187}Re), C (^{191}Ir), H2 (^{193}Ir)
mass resolution, $m/\Delta m$ (at 5% and 95% peak height)	300
signal integration time	4.192 s
number of integrations, cycles, and blocks	1, 6, 5 (for Ir–Tl) and 1, 8, 4 (for Ir–Re)

Reagents and Solutions. High-purity hydrochloric and nitric acids were obtained by sub-boiling distillation (Milestone Inc., Shelton CT, USA) of reagent grade feedstocks. High-purity (18 M Ω cm) deionized water was obtained from a NanoPure mixed-bed ion exchange system with reverse osmosis domestic feedwater (Barnstead/Thermolyne Corp, Iowa USA).

Iridium materials were sourced from four commercial vendors. Two elemental iridium standard solutions (1000 $\mu\text{g L}^{-1}$) were purchased from SCP Science (Baie D'Urfé QC, Canada) and Sigma-Aldrich (Oakville ON, Canada) denoted as Ir-1 and IRIS-1 standards, respectively. The latter material was set aside to produce isotopic reference material, IRIS-1, at National Research Council Canada (NRC, Ottawa, ON Canada), which can be subsequently used as iridium delta zero standard. A third iridium standard solution (Ir-3), $w(\text{Ir}) = 2035 \text{ mg kg}^{-1}$, was prepared by dissolution of an appropriate amount of high-purity iridium bromide, $\text{IrBr}_3 \cdot 4\text{H}_2\text{O}$ ($w = 0.9999 \text{ g/g}$ purity, Johnson Matthey, Royston, United Kingdom) in 10% HCl. A fourth iridium standard solution (Ir-4), $w(\text{Ir}) = 235 \text{ mg kg}^{-1}$, was prepared by dissolution of metallic iridium powder ($w = 0.99998 \text{ g/g}$ purity, Pure Analytical

Laboratories, Sellersville PA, USA) in HNO_3 and H_2O_2 using an acid digestion vessel (Parr Instrument Company, Moline, Illinois, USA) at 220 $^\circ\text{C}$ for 3 days and diluted with water.¹²

A solution of thallium isotopic primary standard, NIST SRM 997 (National Institute of Standards and Technology, Gaithersburg MD, USA), with certified value of thallium isotope ratio, $R_{205/203} = N(^{205}\text{Tl})/N(^{203}\text{Tl}) = 2.38714(51)_{k=1}$, was prepared by dissolution of an appropriate amount of SRM 997 in HNO_3 and HCl with mild heating and diluted with water to yield mass fraction $w(\text{Tl}) = 1000 \text{ mg kg}^{-1}$. A solution of rhenium isotopic primary standard, NIST SRM 989 with certified value of rhenium isotope ratio, $R_{187/185} = N(^{187}\text{Re})/N(^{185}\text{Re}) = 1.67398(53)_{k=1}$, was prepared by dissolution of an appropriate amount of the material in *aqua regia* (mixture of HCl and HNO_3 in a volume ratio of approximately 3:1) at room temperature and diluted with water to yield mass fraction $w(\text{Re}) = 560 \text{ mg kg}^{-1}$.

Spectral Interferences. Potential spectral interferences from $^{175}\text{Lu}^{16}\text{O}^+$, $^{174}\text{Yb}^{16}\text{O}^+\text{H}^+$, $^{177}\text{Hf}^{16}\text{O}^+$, $^{176}\text{Yb}^{16}\text{O}^+\text{H}^+$, $^{176}\text{Lu}^{16}\text{O}^+\text{H}^+$, and $^{176}\text{Hf}^{16}\text{O}^+\text{H}^+$ on Ir isotopes, $^{169}\text{Tm}^{16}\text{O}^+$ and $^{171}\text{Yb}^{16}\text{O}^+$ on Re isotopes, and $^{187}\text{Re}^{16}\text{O}^+$, $^{187}\text{Os}^{16}\text{O}^+$, and $^{189}\text{Os}^{16}\text{O}^+$ on Tl isotopes could occur in samples containing these elements which would degrade the accuracy of the iridium isotope ratios and require elimination or correction. Quantitative analysis of iridium sample solutions (1 mg kg^{-1}) revealed that the mass fractions of Lu, Yb, Hf, Tm, Yb, Re, and Os were all less than 1 ng kg^{-1} . Such concentrations are insignificant to form isobaric interferences since the mass fraction of iridium, thallium, and rhenium in the analyzed samples was several orders of magnitude higher, approximately 1 mg kg^{-1} .

Sample Preparation and Analysis. Replicate solutions with $w(\text{Ir}) = 0.75\text{--}2.00 \text{ mg kg}^{-1}$ were prepared by diluting the stock solution in 1% HCl followed by spiking with the stock solutions of thallium or rhenium isotopic standards yielding mass fraction of 0.75–2.00 mg kg^{-1} for Tl or Re, respectively. Samples were introduced into the plasma in a self-aspiration mode at a flow rate of 50 $\mu\text{L min}^{-1}$. The plasma radio frequency (RF) power was increased from the optimum value of P_0 (which corresponds to the highest sensitivity, typically 1245 W) until the iridium isotope signal decreased by approximately 25% compared to its value at P_0 . The obtained RF power (P_{max}) was then used for measurement sessions whereby the RF power was increased at equal increments from P_0 to P_{max} in order to induce larger temporal mass bias drift in a short measurement time (10–30 min) as compared to normal measurements at fixed P_0 which require long measurement times (6–15 h for each measurement session).^{11,13–16} Intensities of all isotopes of interest (see Table 1) obtained from a blank solution of 1% HCl at optimum RF power, P_0 , were subtracted from those of all samples measured at P_0 to P_{max} . A static run was employed for simultaneous collection of the isotope signals using the Faraday cup configuration as shown in Table 1. Each measurement session yields 5 to 11 pairs of isotope ratio measurements for the sample solution which are preceded by a measurement of a blank solution. All data sets reported here were collected between February and May of 2017.

RESULTS AND DISCUSSION

Correction for Instrumental Fractionation (Mass Bias). Calibrated isotope ratio measurements are typically performed

with the use of gravimetric mixtures of near-pure isotopes.¹⁷ This primary measurement method requires access to separated isotopes in weighable quantities which is not always feasible. The regression method presents itself as an alternative secondary method for absolute isotope ratio measurements, and it relies on the availability of primary isotope reference material of another element. The regression mass bias correction model is based on correlated temporal mass bias drift occurring in MC-ICPMS through the use of an approach pioneered by Maréchal et al.¹⁸ in 1999 for the determination of absolute zinc isotope ratio $R_{68/64}$ using copper, $R_{65/63}$, as the primary reference. Since then, this model has successfully been applied to other elements such as mercury,^{13,14,19} germanium,¹⁵ indium,¹¹ antimony,¹¹ silver,¹¹ copper,¹⁶ molybdenum,^{20,21} iron,²² and lead.^{23,24} This, so-called regression model, is based on observing a loglinear relationship between the temporally drifting isotope ratios of two elements (see Figure 1).^{9,18} This model relies on the observed correlated drift

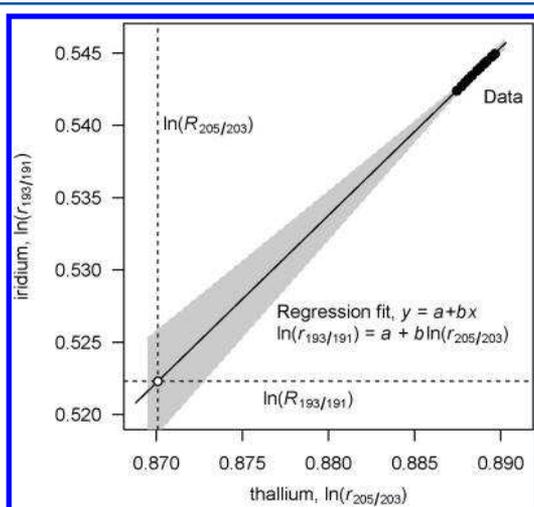


Figure 1. Concept of the regression model for correcting instrumental isotope ratio fractionation, exemplified for measurement of the iridium isotope ratios using thallium as the primary standard. Data from this study are used, and the shaded area represents the confidence interval of the regression (the 95% confidence bands are magnified ten times for visual impact).

between two isotope ratios of the same or distinct elements. One typically observes a linear array of the codrifting isotope ratios in logarithmic coordinates:

$$\ln(r_{i/j}) = a + b \times \ln(r_{\text{ref}}) \quad (1)$$

Assuming that the true isotope ratio is directly proportional to the measured ratio, $R_{\text{ref}} = K_{\text{ref}} \times r_{\text{ref}}$ and $R_{i/j} = K_{i/j} \times r_{i/j}$, eq 1 can be used to deduce the isotope ratios free from instrumental fractionation:²⁵

$$R_{i/j} = e^a \times R_{\text{ref}}^b \quad (2)$$

Coefficients a and b are the intercept and slope of the corresponding linear regression which are obtained using the (unweighted) least-squares fitting of data, $\ln(r_{i/j})$ vs $\ln(r_{\text{ref}})$. It is important to note that this calibration model is not derived from either exponential or the Russell's isotope ratio fractionation law as it is commonly perceived (and originally presented).¹⁸ Rather, the regression model relies on the invariability of the ratio of the fractionation coefficients and is

capable of correcting both mass-dependent and mass-independent isotope ratio fractionation occurring in MC-ICPMS.²⁶ In this vein, the regression model does not invoke traditional mass fractionation assumptions and it allows one to compare isotope ratio measurements between various elements regardless of the fact that each element undergoes slightly different isotope ratio fractionation. Taking advantage of these features, in this study, we test the reliability of the regression model using two independent primary isotope ratio calibrators, NIST SRM 997 thallium and NIST SRM 989 rhenium, for the characterization of iridium isotopic composition.

Methodological Improvements. One of the key disadvantages of the regression mass bias correction model is the time required to observe a well-defined regression of the two isotope ratios. The high stability of the MC-ICPMS instruments (after the warm-up) is directly at odds with the implementation of the regression model which relies on the temporal instability (drift) in the observed isotope ratios. As a result, regression model generally demands long measurement time to establish a linear relationship between $\ln(r_{i/j})$ and $\ln(r_{\text{ref}})$, up to 15 h per session. This, in turn, requires large sample sizes. Alternative strategies have been reported to induce larger mass bias drift in a shorter duration by either adding matrix elements^{27,28} or applying small incremental changes to the plasma RF power.²¹ In this work, we adopt the latter approach using the regression mass bias correction model based on a number of short-time measurements with incremental changes applied to the MC-ICPMS plasma RF power.

As shown in Figure 2, the relationship between $\ln(r_{193/191})$ and $\ln(r_{205/203})$ or $\ln(r_{187/185})$ is linear and with high coefficient

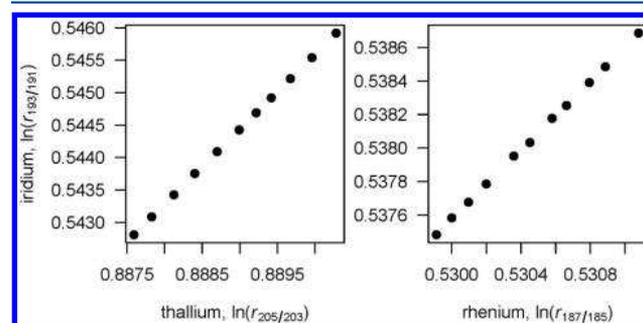


Figure 2. Regression mass bias model. The measured isotope ratio regressions of iridium–thallium (left) and iridium–rhenium (right) isotope ratios during a 30 min measurement session.

of linear determination, $R^2 > 0.9995$. Given that the regression model for isotope ratio determination relies on the linearity in the observed isotope ratio drifts, method development and optimization has to involve the minimization of the overall deviations from the linearity. We have acquired 100+ iridium–thallium regressions each containing 11 points (as in Figure 2), and deviations of the $r_{193/191}$ values from the linear fit are within 2 parts in 10^5 (95% of the time) and scattered around zero under the optimum experimental conditions. Histograms of all regression residuals follow normal distribution thus confirming that an adequate linear relationship between $\ln(r_{193/191})$ and $\ln(r_{205/203})$ or $\ln(r_{187/185})$ has been achieved.

Optimal isotope ratio regressions were obtained as long as the induced relative sensitivity drop at P_{max} is within 15–50% (with ca. 8 V iridium-191 signals at P_{max}). Thus, daily P_{max} which induces 25% sensitivity drop, was selected for all

subsequent experiments. This condition induces an adequate temporal mass bias drift to form a good linear relationship between $\ln(r_{193/191})$ and $\ln(r_{205/203})$ or $\ln(r_{187/185})$ while maintaining suitable sensitivity for the observed isotope signals.

As noted above, a measurement session consists of 11 measurement points in a Ir–Tl standard solution starting from P_0 to P_{\max} with equal increments of $(P_{\max} - P_0)/10$ and takes approximately 30 min (including time for a blank measurement at P_0). In an attempt to further shorten the session measurement time, five-point measurements were chosen. A single measurement session consisting of five points between P_0 and P_{\max} with equal increments of $(P_{\max} - P_0)/4$ and one blank measurement at P_0 takes approximately 13 min. This is significantly shorter compared to earlier studies^{11,13–16} which utilized measured strategies at constant plasma power (P_0). The optimized regression model is particularly suitable for applications requiring small sample sizes.

Uncertainty Evaluation. Uncertainty estimations for the calibrated iridium isotope ratio as well as isotopic abundances and atomic weight were done in accordance with the JCGM “Guide to the Expression of Uncertainty in Measurement”²⁹ and its Supplement 1.³⁰ Iridium isotope ratio values for each regression were calculated using eqs 1 and 2 and ordinary least-squares fitting. The uncertainty of the resulting isotope ratio was evaluated using Monte Carlo Method with proper accounting for the uncertainty due to the primary calibrator. Although trivial, this aspect is not widely appreciated.³¹ For this purpose, the values for the three variables in eq 1 (R_{ref} , a , and b) were modeled as random numbers drawn from the probability distributions representing the available knowledge about them. In particular, R_{ref} was modeled as normal distribution with the mean R_{ref} and standard deviation $u(R_{\text{ref}})$ whereas a and b for each measurement set is modeled jointly as a bivariate normal distribution with the mean estimates and covariance matrix deriving from the least-squares fitting of the data. This procedure was repeated many (10^5) times, and the best estimate of the calibrated iridium isotope ratio and its uncertainty is obtained from the resulting histogram. The same procedure was applied for the iridium–rhenium regressions. The inverse-variance weighted mean was used to combine the values from iridium–thallium and iridium–rhenium calibrations.

Isotopic Abundances and Atomic Weight. The obtained calibrated isotope ratios of iridium, $R_{193/191}$, were used to calculate the corresponding isotopic abundances and atomic weight of iridium:

$$x_{191} = \frac{1}{1 + R_{193/191}} \quad (3)$$

$$x_{193} = 1 - x_{191} \quad (4)$$

$$A_r(\text{Ir}) = x_{191}m_{191} + x_{193}m_{193} \quad (5)$$

The uncertainty of isotopic abundances, x_{191} and x_{193} , and the atomic weight of iridium, $A_r(\text{Ir})$, is propagated from the isotope ratio $R_{193/191}$ as follows:³¹

$$u(x_{193}) = u(x_{191}) = \frac{u(R_{193/191})}{(1 + R_{193/191})^2} \quad (6)$$

$$u^2(A_r(\text{Ir})) = (m_{193} - m_{191})^2 \times u^2(x_{191}) + x_{191}^2 \times u^2(m_{191}) + x_{193}^2 \times u^2(m_{193}) \quad (7)$$

The atomic masses of iridium isotopes (m_{191} and m_{193}) used for calculations in this report are from the 2016 Atomic Mass Evaluation³² where $m_{191} = 190.960\,5915(14)_{k=1}$ Da and $m_{193} = 192.962\,9238(14)_{k=1}$ Da.

Measurement Results. Effect of the Concentration. Initially for the measurements of Ir and Tl isotope ratios, four different sample solutions containing both iridium (Ir-1) and thallium at two levels, 0.75 and 2.00 mg kg⁻¹, were prepared and each was measured under the optimized experimental conditions to investigate the effect of mass fractions of measurand and calibrant on the determined absolute isotope ratio of iridium using the regression mass bias correction model. As shown in Table 2, no significant difference in mass bias corrected ratios $R_{193/191}$ in the Ir-1 standard solutions was observed due to varying mass fractions of iridium and thallium.

Table 2. Calibrated Iridium Isotope Ratios, $R_{193/191}$, Obtained Using Ir-1 Standard Solutions with Different Mass Fractions of Iridium and Thallium^a

	$w(\text{Tl}) = 0.75 \text{ mg kg}^{-1}$	$w(\text{Tl}) = 2.00 \text{ mg kg}^{-1}$
$w(\text{Ir}) = 0.75 \text{ mg kg}^{-1}$	1.686 92(42)	1.686 76(41)
$w(\text{Ir}) = 2.00 \text{ mg kg}^{-1}$	1.686 79(53)	1.686 88(41)

^aAll measurements were performed on the same day (10 March 2017). Results are the average of three measurements. Average standard uncertainty is given in the parentheses.

Similarly, subsequent experiments were conducted for the measurements of Ir and Re isotope ratios in sample solutions containing Ir and Re at varying mass fractions between 0.75 and 1.5 mg kg⁻¹. No significant difference in mass bias corrected iridium isotope ratios $R_{193/191}$ (from 1.686 71(54) to 1.686 77(54)) in the Ir-1 standard solutions was observed.

Effect of the Sample Matrix. Since the measurand and calibrator isotope ratios are acquired simultaneously from the sample, the sample matrix should exert no effect on the measurement results. Nevertheless, we investigated the robustness of the regression model with respect to the sample matrix, and use of either calibrator would give the needed information. Sodium, iron, indium, and uranium were selected as matrix elements, simply representing low, medium, and high mass matrix effects. For this purpose, isotope ratio of iridium was measured from five solutions at optimized experimental conditions using the regression mass bias correction model. All solutions contained iridium and thallium each at 1 mg kg⁻¹, and matrix elements were added as shown in Table 3. As shown in Table 3, no significant difference in mass bias corrected iridium isotope ratios was found in the presence of these matrix elements.

Measurement Results for Ir-1 Standard. It was observed that absolute isotope amount ratios of iridium obtained from same day measurements show no significant difference between each other, but measurements from different days may show some difference as a result of different daily optimization conditions, similar to that observed previously.^{11,13–16} Thus, iridium isotope ratio measurements in Ir-1 standard were performed with replicate solutions containing 0.75 to 2.00 mg kg⁻¹ of Ir and Tl during a four-month period (February to May of 2017) with five different sets of cones used.

A total of 164 sets of iridium–thallium regressions were acquired for Ir-1 standard, each yielding the respective intercepts and slopes (in all cases, the coefficient of

Table 3. Calibrated Iridium Isotope Ratios Obtained Using Standard Solutions of Iridium (Ir-1) and Thallium at 1 mg kg⁻¹ with Various Amounts of Matrix Elements^a

matrix	$R_{193/191}$
none (control)	1.686 88(43)
$w(\text{Na}) = 20 \text{ mg kg}^{-1}$	1.687 08(42)
$w(\text{In}) = 20 \text{ mg kg}^{-1}$	1.686 72(43)
$w(\text{U}) = 20 \text{ mg kg}^{-1}$	1.687 32(44)
$w(\text{Na}) = w(\text{Fe}) = w(\text{In}) = w(\text{U}) = 5 \text{ mg kg}^{-1}$	1.687 04(43)

^aAll measurements were performed on the same day (12 May 2017). Results are the average of three measurements along with the average standard uncertainty.

determination was $R^2 > 0.9995$). For, iridium–rhenium regressions, a total of 151 regression sets were acquired for Ir-1 standard ($R^2 > 0.9997$). Results are summarized in Figure 3 and Table 4. It is evident that the absolute isotope ratio, isotope abundances, and atomic weight obtained in Ir-1 standard using the optimized regression mass bias correction model and SRM 997 Tl as calibrator are in close agreement with results obtained using SRM 989 Re, confirming the accuracy of the method. Primary calibrators remain a major source of uncertainty in the isotope ratio of iridium: SRM 997 (Tl) contributes approximately 90% toward the combined uncertainty in iridium–thallium calibration whereas SRM 989 (Re) accounts for approximately 50% of the combined uncertainty.

Effect of the Calibrator Element. The measured isotope ratios of iridium vary by 2% (from $r_{193/191} = 1.70$ to 1.74) whereas the fractionation corrected (calibrated) isotope ratios of iridium show spread to within 0.3% (from $R_{193/191} = 1.684$ to 1.689). Comparison of the average isotope ratios before and after the correction for the instrumental fraction shows that, on average, iridium and rhenium isotope ratios are biased to a nearly identical extent, by approximately 2.25%, whereas thallium isotope ratios are biased, on average, by 1.95% (Figure 4). The causes of mass bias within ICPMS are not fully understood but likely arise during supersonic expansion of ions through the sampler cone and from space charge effects in the skimmer cone regions.^{33–36} Both of these processes favor transmission of the heavier isotope into the mass spectrometer and generate different transmission efficiencies for ions of different m/z to yield nonuniform response across the mass range. Therefore, mass bias generally decreases as mass of isotope increases; thus, higher mass Tl has smaller mass bias

compared to that of Ir and Re. Unlike other mass dependent fractionation models, such as exponential or the Russell law, which impose a monotonous function to describe the mass bias behavior for all isotopes regardless of the element, the regression model calibrates each isotope pair separately while allowing for the different mass bias between elements. Consequently, the regression model is capable of correcting both mass-dependent and mass-independent fractionations.^{11,26} Despite markedly different mass fractionation behavior between thallium and iridium, compared to the rhenium and iridium, both systems produce identical results within a few parts in 10⁴, thus confirming the accuracy of the method.

The agreement between the iridium isotope ratios calibrated using thallium and rhenium isotopes provides an independent verification that the regression model is able to provide absolute isotope ratio of iridium with a relative uncertainty of few parts in 10⁴. Note also that the rhenium isotopic reference material (NIST SRM 989) was characterized in 1973³⁷ whereas the thallium isotopic reference material (NIST SRM 997) was characterized in 1980,³⁸ both using thermal ionization mass spectrometry and near-pure (enriched) isotopes for calibration. Our measurements of iridium are done using an entirely different mass spectrometric technique and using an entirely different calibration strategy than was used to characterize the primary isotopic standards. Thus, the overall level of orthogonality is quite high thereby providing a high level of confidence to both our measurement results and to the regression model itself.

Effect of the Sample Provenance. In addition to the SCP iridium (Ir-1), relative isotope ratios (isotope deltas) of three other sources of iridium standards were measured against the Ir-1 standard using the combined standard-sample bracketing and thallium internal standard approach as detailed elsewhere.^{39–41} The results, summarized in Table 5, show a maximum observed variation of isotope ratio $R_{193/191}$ from $\delta(^{193/191}\text{Ir})_{\text{Ir-1}} = -0.21 \text{ ‰}$ to $+0.01 \text{ ‰}$ relative to the Ir-1.

This isotope ratio variation is incorporated in the best estimate of the iridium isotope ratio in Ir-1, isotopic composition of $R_{193/191,\text{Ir-1}}$, as follows:

$$R_{193/191} = (1 + \delta_{\text{Ir-1,X}}(^{193/191}\text{Ir})) \times R_{193/191,\text{Ir-1}} \quad (8)$$

where $R_{193/191}$ is the “average” isotope ratio of iridium across the four materials. For the sake of simplicity, we model $\delta_{\text{Ir-1,X}}(^{193/191}\text{Ir})$ as a random variable distributed uniformly between -0.25 ‰ and $+0.25 \text{ ‰}$. Using $R_{193/191,\text{Ir-1}} = 1.6866(5)$

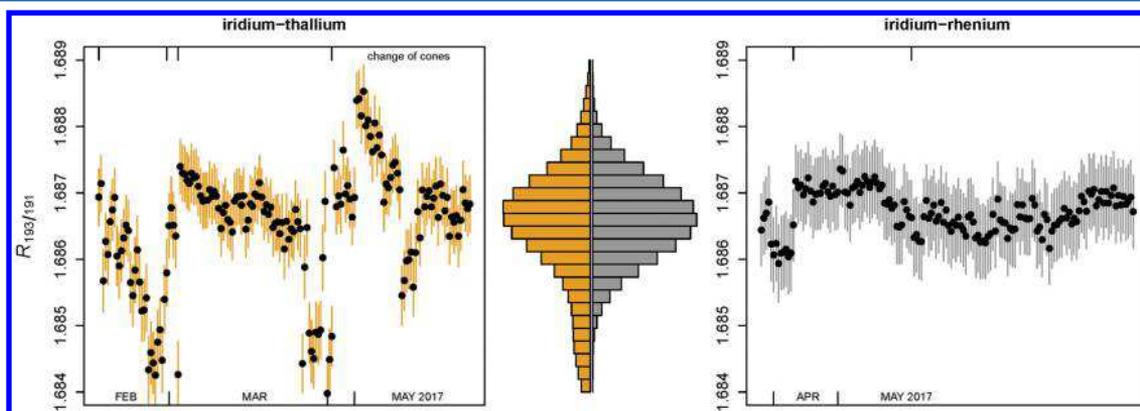


Figure 3. Calibrated iridium isotope ratio measurement results for sample Ir-1. Summary data are shown in Table 4. The vertical error bars represent combined standard uncertainties, and back-to-back histograms are obtained from Monte Carlo simulation as described in Uncertainty Evaluation.

Table 4. Results for Isotopic Composition of Iridium in Ir-1 Standard^a

iridium standard	calibrator	$R_{193/191}$	x_{191}	$A_r(\text{Ir})$
Ir-1	SRM 997 Tl	1.6865(10)	0.372 23(14)	192.217 59(28)
Ir-1	SRM 989 Re	1.6867(6)	0.372 20(9)	192.217 65(18)
Ir-1	combined	1.6866(5)	0.372 21(8)	192.217 63(15)

^aValues are presented in a concise notation whereby the combined standard uncertainty is given in parentheses next to the least significant digits to which it applies.

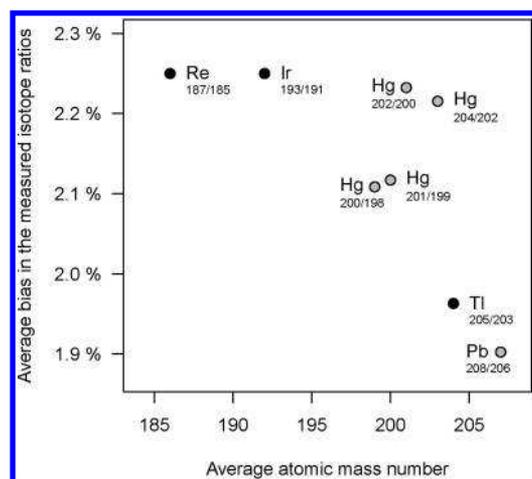


Figure 4. Typical mass bias for iridium, rhenium, and thallium isotope ratio measurements using MC-ICPMS. The open circles show earlier measurement results for mercury²¹ and lead (2010, unpublished) for comparison (the observed mass biases in these historical measurements are scaled relative to the thallium mass bias exhibited in this study).

Table 5. Iridium Isotope Ratios Relative to the Ir-1 Standard^a

iridium sample (X)	isotope delta, $10^3 \delta_{\text{Ir-1}, X} (^{193}/^{191}\text{Ir})$
Ir-1	0 (exact)
NRC IRIS-1	+0.009(3)
Ir-3	-0.207(13)
Ir-4	-0.084(11)

^aValues are presented in a concise notation whereby the repeatability standard deviation ($N = 5$) is given in parentheses next to the least significant digits to which it applies.

from Table 4, the uncertainty propagation⁴² yields $R_{193/191} = 1.6866(6)$. Table 6 displays other cognate data that follows from this isotope ratio value. Similarly, iridium isotope ratio in IRIS-1 is obtained from data shown in Tables 4 and 5 (using eq 8), and they are indistinguishable from Ir-1 (see Table 6). Note

Table 6. Average Isotopic Composition of Iridium from Four Commercial Materials Studied in This Work and in IRIS-1 Material

quantity	IRIS-1 ^a	average value ^a
isotope ratio, $R_{193/191}$	1.6866(5)	1.6866(6)
isotope ratio, $R_{191/193}$	0.592 90(18)	0.592 90(21)
isotopic abundance, x_{191}	0.372 21(8)	0.372 21(8)
isotopic abundance, x_{193}	0.672 79(8)	0.672 79(8)
atomic weight, $A_r(\text{Ir})$	192.217 63(15)	192.217 63(17)

^aValues are presented in a concise notation whereby the combined standard uncertainty is given in parentheses next to the least significant digits to which it applies.

that the measurement uncertainty is the dominating source of uncertainty and natural variations between the studied samples contribute marginally, as indicated by a slight increase in uncertainties for the average values, shown in Tables 4 and 6.

Historical Values of Iridium Isotope Ratios. Iridium has two stable isotopes, both of which were discovered by Venkatesachar and Sibaiya⁴³ in 1935 (and soon thereafter confirmed by Dempster⁴⁴). Venkatesachar and Sibaiya noted that “there is considerable disagreement in the values of atomic weight given by several investigators, which range from 192.59 to 193.40”.⁴³ Indeed, the first iridium isotope ratio measurement by Sampson and Bleakney⁴⁵ in 1936 gave the atomic weight of 192.2 with very poor agreement with the chemical value of 193.1 (both in $O = 16$ scale). Currently, the best available mass spectrometric measurement of iridium isotopic composition is derived from a noncalibrated negative ion TIMS measurements performed in 1993^{6,46} whereas our measurements yield nearly twice lower uncertainty and a value that is 3s away from this value. The available five mass spectrometric iridium isotope ratio measurements (1954–2017) have been performed on many terrestrial materials using a variety of measurement techniques, as shown in Table 7.

Table 7. Summary of Iridium Isotope Ratio Measurements since 1935^a

year	lead author	$R_{191/193}$	notes	ref.
1935	Venkatesachar	ca. 0.5		43
1936	Sampson	0.626		45
1954	Howard	0.5949(25)		3
1991	Creaser	0.5948(1)	(-)TIMS, not calibrated	4
1992	Chang	0.593 99(103)	(+)TIMS, partially calibrated with Re	5
1993	Walczyk	0.594 18(37)	(-)TIMS, not calibrated	6
2017	Zhu	0.592 90(21)	MC-ICPMS, calibrated with Re and Tl	this study

^aValues are presented in a concise notation whereby the combined standard uncertainty is given in parentheses next to the least significant digits to which it applies.

Iridium Isotope Ratio Consensus Value. The available iridium isotope ratio measurements can be reduced into a single representative consensus value, as described by Meija and Possolo.⁴⁷ In short, the meta-analysis of the results reported by the (five) individual studies are modeled using the random-effects statistical model:

$$R_i = \mu + \lambda_i + \varepsilon_i \quad (9)$$

Here, R_i is an observed isotope ratio value from the i th study, μ is the consensus value from all studies, λ_i denotes the random effect of the i th study which is modeled as a normal random variable with mean 0 and variance τ^2 , and ε_i denotes

measurement error which is modeled as normal random variable with mean 0 and variance $u(R_i)^2$. The within-study variances, $u(R_i)^2$, are known beforehand whereas the between-study variance, τ^2 , and the consensus value, μ , must both be estimated from the data.

Results obtained for the four commercial iridium samples in this study, combined with the historical mass spectrometric determinations (1954–1993), provide a consensus iridium isotope ratio $R_{191/193} = 0.5940(6)_{k=1}$ with 94% of the uncertainty in this consensus value deriving due to heterogeneity between the results of individual studies. This isotope ratio consensus value corresponds to $R_{193/191} = 1.6835(17)_{k=1}$, isotopic abundance $x_{191} = 0.372\ 65(23)_{k=1}$, and the atomic weight $A_r(\text{Ir}) = 192.2167 \pm 0.0009$ ($k = 2$). We suggest that this estimate replaces the current standard atomic weight of iridium, 192.217 ± 0.003 , which has been in effect since 1993 (see Figure 5).⁴⁸

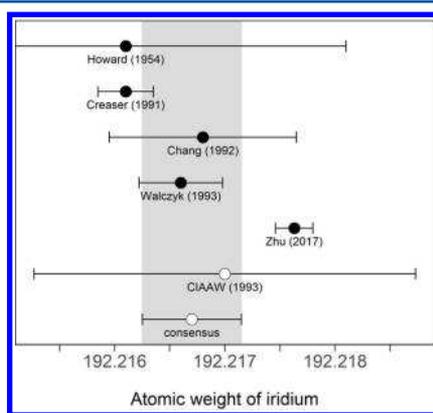


Figure 5. Meta-analysis of isotopic measurements of iridium presented as the corresponding atomic weights (black circles). The current standard atomic weight (CIAAW 1993) and the consensus value from the random-effects model are also given (white circles). Error bars represent standard uncertainties (CIAAW estimate is given as standard uncertainty which is calculated from the standard atomic weight uncertainty by dividing it by $\sqrt{3}$).

CONCLUSIONS

The regression mass bias correction model can provide absolute iridium isotope amount ratio measurements with MC-ICPMS with the highest precision and accuracy. To the best of our knowledge, this is the first report of calibrated isotope ratio measurements for iridium using mass spectrometry. We report iridium isotope ratio $R_{193/191} = 1.6866(5)_{k=1}$ on a single commercial material of iridium (NRC IRIS-1) with the relative uncertainty of a few parts in 10^4 and traceability to two independent isotope ratio certified reference materials. This value corresponds to an atomic weight $A_r(\text{Ir}) = 192.217\ 63(15)_{k=1}$ and isotopic abundance of iridium-191 $x_{191} = 0.372\ 21(8)_{k=1}$. Our work has further demonstrated the applicability of the regression model for calibrated measurements of isotope ratios using MC-ICPMS. Our results for four commercial iridium reagents, combined with the historical mass spectrometric determinations reported for iridium, provide a consensus isotope ratio $R_{191/193} = 0.5940(6)_{k=1}$ along with the corresponding (rounded) atomic weight of iridium, $A_r(\text{Ir}) = 192.217 \pm 0.001$ ($k = 2$), which we suggest as a revision of the current standard atomic weight, 192.217 ± 0.003 .

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Notes

The authors declare no competing financial interest.

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