High-precision Ru isotopic measurements by multi-collector ICP-MS

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Ruthenium isotopic data for a pure Aldrich ruthenium nitrate solution obtained using a Nu Plasma multi collector inductively coupled plasma-mass spectrometer (MC-ICP-MS) shows excellent agreement (better than 1 ε unit = 1 part in 10^4) with data obtained by other techniques for the mass range between 96 and 101 amu. External precisions are at the 0.5–1.7 ε level (2σ). Higher sensitivity for MC ICP-MS compared to negative thermal ionization mass spectrometry (N-TIMS) is offset by the uncertainties introduced by relatively large mass discrimination and instabilities in the plasma source-ion extraction region that affect the long-term reproducibility. Large mass bias correction in ICP mass spectrometry demands particular attention to be paid to the choice of normalizing isotopes. Because of its position in the mass spectrum and the large mass bias correction, obtaining precise and accurate abundance data for ^{104}Ru by MC-ICP-MS remains difficult. Internal and external mass bias correction schemes in this mass range may show similar shortcomings if the isotope of interest does not lie within the mass range covered by the masses used for normalization. Analyses of meteorite samples show that if isobaric interferences from Mo are sufficiently large (Ru/Mo < 10^4), uncertainties on the Mo interference correction propagate through the mass bias correction and yield inaccurate results for Ru isotopic compositions. Second-order linear corrections may be used to correct for these inaccuracies, but such results are generally less precise than N-TIMS data.

Introduction

The motivation for high-precision Ru isotopic studies of solar system materials is primarily linked to the study of the short-lived ^{98}Tc–^{98}Ru (half-life 10 Ma) and ^{99}Tc–^{99}Ru (half-life 0.21 Ma) chronometers in meteorites. Variable abundances of ^{98}Ru and ^{99}Ru in various solar system objects may yield evidence for extant ^{98}Tc and ^{99}Tc in the early solar system and time constraints on chemical fractionations involving metal phases in meteorites. Furthermore, because of its short half-life, ^{99}Tc–^{99}Ru may help to constrain the interval between production of s-process nuclides in stars and their incorporation into the solar system. Such data may also provide limits on initial abundances of ^{98}Tc and ^{99}Tc, and implications for p- and s-process models of nucleosynthesis.

High-precision Ru isotopic studies by negative thermal ionization mass spectrometry (N-TIMS) reported differences for ^{98}Ru between terrestrial Ru and magmatic iron meteorites of up to 40 ε units (1 ε = 1 part in 10^4),[1] and differences for ^{99}Ru between terrestrial Ru and chondritic metal at the 0.7 ε level.[2] However, a recent multi collector N-TIMS study conducted in our laboratory revealed no differences in the Ru isotopic composition of terrestrial materials, magmatic iron meteorites and chondrites at the 0.3–1.0 ε level.[3,4] While the N-TIMS studies yielded the highest analytical precisions so far, the drawbacks are that the analyses are time-consuming and that relatively large quantities of Ru are necessary for multiple analyses (0.5–1 μg Ru per run).

Here we report results of a study of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) for high-precision Ru isotopic measurements using the Nu Plasma at the University of Maryland. This technique has the advantage of a more efficient ionization process compared to N- or P (positive)-TIMS, thus giving potentially higher sensitivity and typically a shorter analysis time compared to TIMS. Because the isotopic composition of terrestrial Ru is now known to high precision and accuracy from N- and P-TIMS studies in several laboratories,[1–6] these data can be used as a benchmark to evaluate the performance of the MC-ICP-MS for high-precision measurements in this mass region in terms of sensitivity, precision and accuracy. Of particular interest is how well the exponential fractionation law describes mass bias for the complete mass spectrum of Ru isotopes using internal mass bias corrections in ICP-MS work. We show that it is difficult to obtain precise and accurate abundance data for ^{104}Ru (and by implication for other important r-process isotopes in this mass region) by this technique. Furthermore, systematic biases appear for isotopic ratios corrected for mass discrimination, when the masses of isotopes used for this normalization lie too far off the mass range of the isotopes of interest. Another major objective has been to evaluate the effects of small isobaric interferences from Mo on Ru isotopic ratios obtained on meteorite samples and it is shown that very efficient Mo–Ru separation is necessary to obtain precise and accurate Ru isotopic data on natural samples by the MC-ICP-MS technique.

Experimental

Reagents

All H_2O used was at least of 18.2 MΩ cm purity. $HClO_4$, HCl and HNO_3 were double quartz distilled, HBr was distilled in PFA Teflon, H_2SO_4 was double distilled (GFS). NaOH (Baker) and Na_2O_2 (Alfa Aesar), and $NaBrO_3$ (Aldrich), were reagent-grade quality, and CrO_3 was Puratronic-grade (Johnson–Matthey). The chemical separation procedures were performed in a clean room environment.

Instrumentation

All Ru isotopic measurements were performed on a Nu Instruments (Wrexham, UK) Nu Plasma MC-ICP-MS. This instrument has a double focusing Nier–Johnson geometry with

12 fixed Faraday cups and three electron multipliers. The electrostatic zoom optics permits a change in mass dispersion throughout the entire mass range.[7] Solutions of samples and reference materials were aspirated using an Aridus micro-concentric nebulizer (CETAC) refitted with a PFA spray chamber (ESI) and a PFA micro-flow nebulizer (ESI) with uptake rates of *ca.* 60–100 µl min^{-1}. Operating parameters during this study are listed in Table 1.

Reference material

No Ru standard with certified isotopic composition is available. IUPAC has adopted the single-collector N-TIMS Ru isotopic measurements on Ru from five different commercial sources by Huang and Masuda[5] as representative of average terrestrial Ru. Here, we use a Ru nitrate solution (in 2% HNO_3) prepared from Aldrich $RuCl_3$ as our terrestrial reference material. The Ru isotopic composition of this solution was determined by N-TIMS in our laboratory,[3,4] and overlaps within $<\pm1$ ε unit with the data in.[5] For ICP-MS measurements, a 500 ng g^{-1} Ru solution was used initially, but was replaced later with a 200 ng g^{-1} Ru solution because of a substantial increase in sensitivity during the course of this study (see below).

Sample preparation and digestion

Small pieces of iron meteorites (1.540–2.708 g) were cut using a Leco 'Vari-cut' saw with diamond wafering blades, using deionized water as a coolant. The iron meteorite pieces were abraded using carborundum and briefly leached in 11 M HCl. After dissolution in 20 ml concentrated HCl, trace amounts of carbon remained as insoluble residue. The supernatant was dried and re-dissolved in 0.1 M HCl. USNM (US Museum of Natural History) carbonaceous chondrite Allende standard reference powder (USNM 3529 Split 15, Pos. 8, 1.0304 g) and a piece of the ordinary chondrite Allegan (USNM 3279, 1.0463 g), ground in an agate mortar, were digested using the NaOH–Na_2O_2 fusion technique described in detail elsewhere.[8] This technique has the advantage that it results in total digestion of the chondrites, including silicates and phases that are difficult to dissolve, such as spinel, platinum group element alloys, diamond, and carbides. Because of the large amount of chondrite digested, the quantities of reagents were doubled and the temperature was held at 600 °C for 60–90 min. After digestion, the cake was dissolved in H_2O and 19 N H_2SO_4.

Ruthenium separation

The PGEs were separated from the Fe–Ni matrix of the iron meteorites using four 2 ml cation exchange columns (AG 50-X8, 100–200 mesh) and 0.1 M HCl. Ruthenium was separated from the PGE and interfering elements such as Mo using a modified micro-distillation technique. A 1:2 mixture of concentrated $HClO_4$ and dichromate solution was used as the oxidant. RuO_4 was distilled at 80 °C for 2 h and collected in 3% H_2O_2. After micro-distillation, 13.5 M HNO_3 was added to the peroxide solution and carefully evaporated to near dryness under a heat lamp. The Ru fraction was dissolved in 10 µl of 13.5 M HNO_3, transferred to another Teflon beaker and diluted with 1–2 ml 2% HNO_3; it was then homogenized and was ready for analysis.

Ru was separated from the dissolved chondrites by oxidation and distillation of RuO_4 in a conventional distillation apparatus using 10 ml of a 20% solution of $NaBrO_3$ as the oxidant and 3 ml of 8.8 M HBr as the collector solution. The Ru fraction of the chondrites was also further cleaned by micro-distillation as previously described. Total chemistry Ru blanks for the iron meteorite and chondrite chemistries were 1.8 pg and 149 pg, respectively, and are insignificant.

Multi collector ICP-MS measurements

In the course of this study, a number of experiments aimed at increasing ion transmission and sensitivity were performed. High signal intensities are crucial for obtaining precise data on the minor isotope ^{98}Ru (1.88%). These experiments are indicated and explained in Table 3. The most pronounced increases in sensitivity at a given uptake flow rate were noted for a decrease in vacuum pressure in the region of the extraction interface located between sampler and skimmer cone. This was achieved by interfacing a Leybold Trivac D65B rotary pump (65 m^3 min^{-1}) parallel with an Edwards E2M28 rotary pump (32.2 m^3 min^{-1}). The resulting pressure decrease from ~2.1 mbar to ~0.78 mbar was accompanied by nearly a factor of 2 increase in signal intensity, *e.g.*, from ~2 V to ~4 V ^{102}Ru (31.6%) for a 500 ng g^{-1} Ru solution at *ca.* 80 µl min^{-1} uptake rate (Table 3, Exp. 3). The pressures in source lens chamber and flight tube were not affected in a systematic way by the use of the big rotary pump. The instrument was tuned for a compromise of signal stability and high signal intensity, with preference of stability over intensity. The range of optimum Ar+N_2 sweep gas flow rates for the Aridus is indicated in Table 1. A further major improvement in sensitivity by *ca.* 50% was achieved by using a new-design wide-angle skimmer cone from Nu Instruments, resulting in typically ~2.4 V on ^{102}Ru for a 200 ng g^{-1} Ru solution at ~60 µl min^{-1} (Table 3, Exp. 5, 7). The new skimmer cone required a substantial change in the

Table 1 Nu Plasma MC-ICP-MS operating conditions

Gas flow rates—	
Ar cooling	13–14 l min^{-1}
Ar auxiliary	0.8–0.95 l min^{-1}
Ar sweep^a	2.1–3.5 l min^{-1}
N_2^{a}	7–12 ml min^{-1}
Nebuliser pressure^a	2.4–3.1 bar
Solution uptake rate^a	60–100 µl min^{-1}
ESI spray chamber^a	95 °C
Desolvation cell^a	160 °C
Vacuum—	
Expansion chamber	2.1 mbar (Exp. 2)
	0.78 mbar (Exp. 3–7)
Extraction area	~2.5 × 10^{-4} mbar
Transfer area	~3.5 × 10^{-8} mbar
Analyzer	~2–3 × 10^{-9} mbar
ICP rf, power	27.12 MHz, 1300 W
Sampler cone	Ni, 1.15 mm orifice
Skimmer cone	Ni, 0.6 mm orifice (Exp. 2,3)
	Ni, 0.6 mm wide angle (Exp. 5,7)
Extraction potentials	4000–1650 V
Sensitivity^b	12–100 V (µg g^{-1})$^{-1}$
ESA V1 Deflection	5 V
ESA V2 Deflection	90 V
ESA Plates	229 V
Zoom lens^c—	
	Cycle 1 (cycle 2)/V
Quad 1	−3 (8) Exp. 2, 3
	8 (16) Exp. 5, 7
Quad 2	43 (12) Exp. 2, 3
	32 (5) Exp. 5, 7
Lin 1	−1.5 (3.3) Exp. 2, 3
	−1.5 (0) Exp. 5, 7
Lin 2	2.2 (−0.5) Exp. 2, 3
	0.5 (0) Exp. 5, 7
Q16	0 (0) Exp. 2, 3
	−50 (−50) Exp. 5, 7
Integration time	10 s
Magnet delay time	2 s

^{a} Aridus parameter. ^{b} See Table 3 for details. ^{c} Lin corr, cubic and Q15 set to 0. Exp. are experiments in Table 3.

zoom lens potentials (Table 1). Higher aspiration rates and a new nebulizer used during the 10/22/01 session resulted in substantially higher signal intensities near 7 V ^{102}Ru.

Data were acquired in a two-cycle routine in static mode. The Faraday cup configuration and positions of the masses are indicated in Table 2. Baselines were measured for 30 s by applying 10 V ESA deflection at the beginning and end of each block (20 scans). On-peak zeros were negligible before each standard or sample introduction. For standards, typically 60–100 scans were acquired. For samples, 20–80 scans were acquired, depending on the amount of Ru available. Masses 96–102 were measured in the first cycle of each scan, with mass 97 as the monitor for Mo interferences on masses 96, 98, and 100. A second cycle (Masses 100–105) was devised to measure ^{104}Ru (as well as ^{100}Ru, ^{101}Ru and ^{102}Ru) and to monitor Pd interferences on masses 102 and 104 *via* ^{105}Pd. The data were not corrected for Faraday cup biases. Interferences from Mo and mass discrimination were corrected on-line using high-precision Mo isotopic data[9] and an exponential mass fractionation law.[10] Mass bias in cycle 1 was corrected to ^{96}Ru/^{101}Ru = 0.324851, as in most previous work. ^{104}Ru/^{101}Ru in Table 3, collected in cycle 2, was normalized to ^{100}Ru/^{101}Ru = 0.738482, which is consistent with ^{96}Ru/^{101}Ru = 0.324851 and

the data in Table 2 of ref. 5. However, as will be discussed below, this normalization does not yield optimal results for ^{102}Ru and ^{104}Ru.

Results and discussion

Terrestrial Ru reference material

Results for 26 analyses of Aldrich RuCl$_3$ ('standard') over a period of 4 months are shown in Table 3, Fig. 1 and Fig. 2. Because of higher signal intensities, in-run precisions are usually much better for MC-ICP-MS than for N- or P-TIMS. However, MC-ICP-MS shows larger fluctuations in measured and fractionation-corrected values on a day-by-day basis (Fig. 1). Improvement of the vacuum in the extraction region resulted in a minor decrease of the exponential mass fractionation factor (Exp. 3, Table 3). It also produced no systematic changes in the corrected ratios. We note, however, that a wide-angle skimmer cone not only increased sensitivity, but also significantly reduced the fractionation factor from ~ 2.5% amu^{-1} to ~ 1.9% amu^{-1}. Mass bias effects are probably created in this region and in the plasma.[11] These results suggest that changes in cone geometry and their effects on mass discrimination should be further explored. Molybdenum interferences in most of the standard runs are sufficiently small (Table 3) that corrections are insignificant or minor. Occasionally, larger Mo signals in standard runs were associated with melting in the plasma shield due to arcing in the front torch region. It is not clear if this led to vaporization of the stainless steel shield and direct con-

Table 2 Faraday cup configuration

F. cup	L4	L3	L2	L1	Ax	H1	H2	H3	H4	H5
Cycle 1	96	97	98		99		100		101	102
Cycle 2	100	101	102		103		104		105	

Table 3 Ru isotopic data for the Aldrich Ru reference solution[a]

Date	Exp.	A. r.	^{102}Ru (V)	α_1	^{97}Mo/^{101}Ru	^{98}Ru/^{101}Ru	^{99}Ru/^{101}Ru	^{100}Ru/^{101}Ru	^{102}Ru/^{101}Ru	^{104}Ru/^{101}Ru
Terrestrial Ru (Aldrich RuCl$_3$)—										
07/12/01	(2a)	80	1.90	−2.45	0.000009 ± 2	0.109545 ± 5	0.747687 ± 8	0.738412 ± 7	1.84987 ± 2	1.09197 ± 4
07/13/01	(2a)	80	1.94	−2.47	0.000004 ± 2	0.109546 ± 6	0.747673 ± 7	0.738413 ± 8	1.84997 ± 2	1.09203 ± 4
07/13/01	(2a)	80	1.92	−2.39	0.000004 ± 2	0.109556 ± 7	0.747717 ± 10	0.738432 ± 10	1.85019 ± 2	1.09194 ± 5
07/13/01	(2a)	80	1.88	−2.40	0.000005 ± 3	0.109543 ± 7	0.747699 ± 21	0.738405 ± 12	1.85015 ± 3	1.09192 ± 5
07/16/01	(2a)	80	1.94	−2.49	0.000005 ± 2	0.109555 ± 8	0.747706 ± 10	0.738424 ± 9	1.85016 ± 3	1.09186 ± 5
07/16/01	(2a)	80	1.96	−2.49	0.000009 ± 3	0.109536 ± 7	0.747700 ± 11	0.738423 ± 10	1.85021 ± 2	1.09187 ± 6
07/16/01	(2b)	80	2.03	−2.51	0.000012 ± 2	0.109541 ± 7	0.747702 ± 9	0.738433 ± 9	1.85022 ± 3	
07/16/01	(2a)	80	2.02	−2.48	0.000002 ± 2	0.109551 ± 6	0.747711 ± 10	0.738421 ± 8	1.85017 ± 2	1.09197 ± 6
07/17/01	(3)	80	3.70	−2.37	0.000002 ± 1	0.109563 ± 3	0.747766 ± 7	0.738437 ± 7	1.85002 ± 2	1.09175 ± 4
07/17/01	(3)	80	3.80	−2.37	0.000004 ± 1	0.109552 ± 5	0.747759 ± 8	0.738429 ± 7	1.85003 ± 2	1.09174 ± 5
07/17/01	(3)	80	3.87	−2.29	0.000004 ± 1	0.109557 ± 5	0.747792 ± 6	0.738446 ± 6	1.84997 ± 2	1.09172 ± 4
07/17/01	(3)	80	3.89	−2.29	0.000003 ± 1	0.109555 ± 4	0.747788 ± 7	0.738435 ± 6	1.84996 ± 2	1.09167 ± 4
08/16/01	(3)	80	3.61	−2.33	0.000012 ± 1	0.109551 ± 4	0.747685 ± 18	0.738442 ± 6	1.85006 ± 2	1.09275 ± 22
08/16/01	(3)	80	4.35	−2.42	0.000007 ± 1	0.109549 ± 4	0.747698 ± 18	0.738429 ± 7	1.85004 ± 2	1.09263 ± 18
08/16/01	(3)	80	4.46	−2.41	0.000006 ± 1	0.109547 ± 3	0.747714 ± 14	0.738432 ± 6	1.85002 ± 1	1.09210 ± 8
10/8/01	(5)	60	2.53	−1.97	0.000004 ± 2	0.109549 ± 5	0.747752 ± 9	0.738439 ± 10	1.85001 ± 2	1.09173 ± 6
10/9/01	(7)	60	2.40	−1.91	0.000010 ± 2	0.109557 ± 4	0.747796 ± 12	0.738432 ± 9	1.84996 ± 2	1.09165 ± 6
10/9/01	(7)	60	2.38	−1.80	0.000058 ± 14	0.109557 ± 8	0.747905 ± 16	0.738433 ± 12	1.84989 ± 3	1.09158 ± 8
10/9/01	(7)	60	2.27	−1.92	0.000009 ± 2	0.109555 ± 5	0.747962 ± 9	0.738429 ± 8	1.84998 ± 2	1.09160 ± 5
10/15/01	(7)	60	2.35	−1.86	0.000012 ± 2	0.109554 ± 7	0.747831 ± 10	0.738475 ± 8	1.84993 ± 2	1.09165 ± 6
10/15/01	(7)	60	2.46	−1.89	0.000005 ± 2	0.109565 ± 5	0.747789 ± 10	0.738433 ± 10	1.84993 ± 3	1.09164 ± 5
10/15/01	(7)	60	2.57	−1.90	0.000011 ± 2	0.109549 ± 6	0.747766 ± 11	0.738434 ± 10	1.84993 ± 2	1.09192 ± 10
10/22/01	(7)	100	7.60	−1.85	0.000016 ± 1	0.109537 ± 3	0.747753 ± 8	0.738414 ± 6	1.84996 ± 2	1.09168 ± 5
10/22/01	(7)	100	6.87	−1.92	0.000005 ± 1	0.109532 ± 5	0.747722 ± 6	0.738396 ± 5	1.85006 ± 1	1.09167 ± 5
10/22/01	(7)	100	6.65	−1.75	0.000019 ± 2	0.109532 ± 5	0.747796 ± 8	0.738446 ± 9	1.84993 ± 3	1.09155 ± 6
10/22/01	(7)	100	6.44	−1.88	0.000012 ± 1	0.109537 ± 3	0.747719 ± 6	0.738399 ± 5	1.85007 ± 1	1.09176 ± 5
7/12–10/22 Mean (excl. 10/9 data)					0.000008 ± 10	0.109548 ± 18	0.747736 ± 87	0.738428 ± 35	1.85004 ± 21	1.09189 ± 60
ε						0.02 ± 1.65	−0.57 ± 1.16	−0.29 ± 0.47	2.3 ± 1.1	3.8 ± 5.5
Becker and Walker 2002 N-TIMS refs. 3,4					0.000019 ± 7	0.109548 ± 16	0.747778 ± 44	0.738449 ± 71	1.84962 ± 16	1.09147 ± 18
Yin 1995 N-TIMS ref. 2						0.109598 ± 11	0.747769 ± 48	0.738430 ± 25	1.84968 ± 6	1.09156 ± 11
Huang and Masuda 1997 N-TIMS ref. 5						0.109543 ± 26	0.747828 ± 75	0.738482 ± 74	1.84947 ± 15	1.09150 ± 15
Smoliar 1998 N-TIMS ref. 1						0.109550 ± 10	0.747570 ± 20			
Poths *et al.* 1987 P-TIMS Ref. 6						0.109550 ± 28	0.747757 ± 49	0.738608 ± 94	1.84998 ± 6	1.09234 ± 63

[a] All errors on ratios from individual runs are $2\sigma_m$ uncertainties on the last digits of the number. Errors on the means and the literature data are 2σ. Exp., experiments; (2a) no D65B pump, 500 ng g^{-1} Ru; (2b) like 2a, but 1-cycle experiment; (3) D65B pump, 500 ng g^{-1} Ru; (5) wide-angle skimmer cone, no D65B pump, 200 ng g^{-1} Ru; (7) wide-angle skimmer cone, D65B pump, 200 ng g^{-1} Ru. A. r., approximate aspiration rate in μl min^{-1}; α_1, cycle 1 exponential fractionation factor, calculated using ^{96}Ru/^{101}Ru = 0.324851. ^{104}Ru/^{101}Ru was measured during cycle 2, and mass discrimination was corrected to ^{100}Ru/^{101}Ru = 0.738482. ε = (Ratio$_{ICP-MS}$/Ratio$_{N-TIMS}$ −1) × 10^4). Uncertainties on ε are 2σ errors for MC-ICP-MS data only.

tamination of the plasma. A more likely explanation for the enhanced Mo signals could be indirect contamination from the deposits that develop on the sampler cone in the course of failed ignition due to a burned shield. As a consequence of these problems, deteriorated stability may have affected Ru isotopic ratios and mass bias correction on 10/9/01 (Fig. 1, Table 3). For this reason, standard data obtained on 10/9/01 were excluded from long-term means and 2σ reproducibility in Table 3. Interferences from ^{102}Pd and ^{96}Zr (monitored on mass 91 before each run) were insignificant. The interference from ^{104}Pd on average comprised about 0.6 ε (range between 0.3 and 1.3 ε) and was corrected using ^{105}Pd. We found no evidence for

significant production of Ar molecular ions (e. g., $^{56}Fe^{40}Ar$, $^{60}Ni^{40}Ar$) that might cause interferences in this mass region.

In Table 3, the mean of the data on 23 runs of Aldrich Ru are normalized to our N-TIMS data[3,4] and shown in the ε notation [$\varepsilon = (ratio_{ICP-MS}/ratio_{N-TIMS} - 1) \times 10^4$]) as parts in 10^4 deviations from our N-TIMS data. The agreement of the MC-ICP-MS data with N-TIMS and P-TIMS data are better than $\pm$ 1 ε unit for $^{98}Ru/^{101}Ru$ and $^{99}Ru/^{101}Ru$ (Table 3, Fig. 1) and, by implication, also for the normalizing ratio $^{96}Ru/^{101}Ru$. (The origin of the high $^{98}Ru/^{101}Ru$ in ref. 2 and the low $^{99}Ru/^{101}Ru$ in ref. 1 is not clear). Long-term external precisions are comparable to N-TIMS for $^{98}Ru/^{101}Ru$ (±1.65 ε), but poorer by a factor of 2 for $^{99}Ru/^{101}Ru$ (±1.16 ε) in MC-ICP-MS. Low relative precision of $^{98}Ru/^{101}Ru$ compared to $^{99}Ru/^{101}Ru$ reflects the low abundance of ^{98}Ru. The agreement with N-TIMS is also excellent for $^{100}Ru/^{101}Ru$, with a factor of 2 better external precision for MC-ICP-MS (±0.47 ε) than for N-TIMS. Compared to N-TIMS data, $^{102}Ru/^{101}Ru$ and $^{104}Ru/^{101}Ru$ are too high by +2.3 and +3.8 ε units in MC-ICP-MS, respectively, with relatively large 2σ uncertainties (Fig. 2, Table 3). It should be noted that P-TIMS data for $^{100}Ru/^{101}Ru$, $^{102}Ru/^{101}Ru$ and $^{104}Ru/^{101}Ru$ are also too high by +2 to +8 ε units. This has been attributed to possible isobaric interferences from complex ions.[6] Agreement between MC-ICP-MS data obtained for the mass range 96–101 and other techniques indicates that no interferences other than Mo affected this mass range. Because isobaric interferences from Pd are insignificant for mass 102, and were corrected for 104, the most plausible explanations for the deviations found for these Ru masses in MC ICP-MS are either unknown interferences or, more likely, inappropriate mass bias correction.

The fractionation factors, α_1 in Table 3, show that MC-ICP-MS is characterized by a relatively large mass bias (1.8–2.5% amu^{-1}), compared to N-TIMS (typically between 0.1 and 0.25% amu^{-1}). Excellent agreement of the MC-ICP-MS data with data obtained by other techniques for Ru isotopes in the mass range between $m = 96$ and 101 (Fig. 2) indicates that for these masses the exponential law and the normalizing ratio $^{96}Ru/^{101}Ru$ provide an accurate description of instrumental mass discrimination. Using a power law instead of the exponential law results in ratios that are too high ($^{98}Ru/^{101}Ru$, $^{99}Ru/^{101}Ru$, $^{100}Ru/^{101}Ru$) or too low ($^{102}Ru/^{101}Ru$, $^{104}Ru/^{101}Ru$) by +4 to +8 ε units compared to N-TIMS data. The mass bias correction employed in the first cycle is optimized for ^{98}Ru and ^{99}Ru, and hence does not cover ^{102}Ru appropriately because the mean of the masses covered by the normalizing ratio is 98.5 amu. Consequently, $^{102}Ru/^{101}Ru$ measured in the first cycle is 2.3 $\pm$ 1.1 ε units too high and slightly less precise than the N-TIMS data. The effects of improper mass bias corrections are more pronounced in MC-ICP-MS because of the large mass bias. It is less evident in our N-TIMS data in the form of a correlation of long-term 2σ errors and mass number in the numerator of Ru isotopic ratios between ^{99}Ru and ^{104}Ru.[12] The fractionation-corrected $^{104}Ru/^{101}Ru$ data in Fig. 2 and Table 3
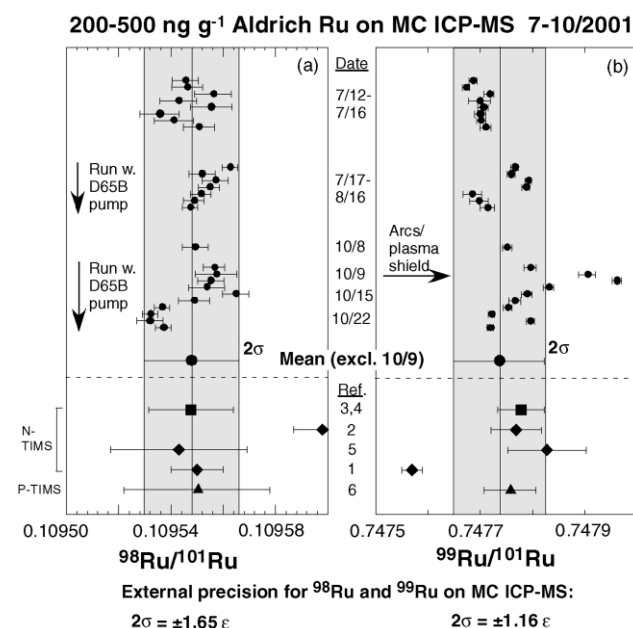

Fig. 1 $^{98}Ru/^{101}Ru$ (a) and $^{99}Ru/^{101}Ru$ (b) data obtained by MC-ICP-MS for 200–500 ng g^{-1} of Aldrich Ru in 2% HNO$_3$, analyzed between 7/2001 and 10/2001. Small symbols are individual runs and their $2\sigma_m$ errors. Large circles are means and and gray band $\pm$ 2σ external precision over this period (excluding the data collected on 10/9). 'D65B pump' refers to additional use of a large-volume mechanical pump to improve the vacuum pressure in the sampler–skimmer cone area. Also shown are data obtained by N-TIMS[1–5] and P-TIMS.[6] Analysis dates are indicated between the two panels.
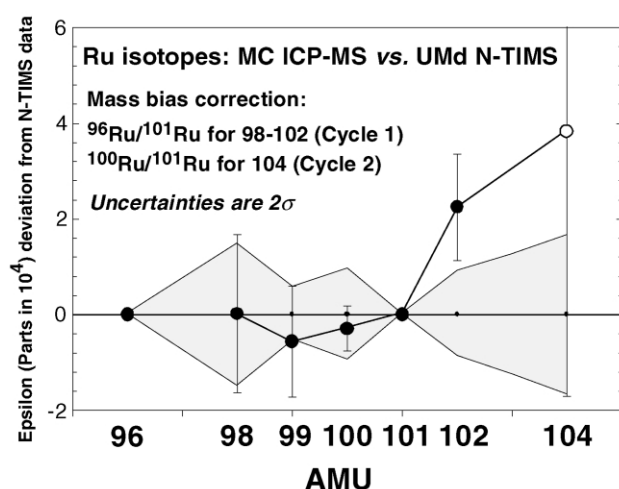

Fig. 2 Epsilon (parts in 10^4) deviations of the means of Ru isotopic data measured by MC ICP-MS from N-TIMS data obtained on the UMD SECTOR 54 instrument.[3,4] The gray field indicates the $\pm$ 2σ uncertainties of the N-TIMS data in ε units. Note that ε 96 and ε 101 are 0 because these are used for normalization in both N-TIMS and the first cycle of the MC-ICP-MS measurements. ^{104}Ru (open circle) was normalized to $^{100}Ru/^{101}Ru$ in cycle 2.

Table 4 Results for alternative normalization procedures of cycle 2 raw data (Aldrich Ru standard)[a]

	$^{100}Ru/^{101}Ru$	$^{102}Ru/^{101}Ru$	$^{104}Ru/^{101}Ru$
A. Normalization to $^{104}Ru/^{100}Ru = 1.47804$[b]			
	0.738547 ± 102	1.84997 ± 32	
ε	1.32 ± 1.39	1.90 ± 1.71	
B. Normalization to $^{102}Ru/^{101}Ru = 1.84947$[b]			
	0.738751 ± 224		1.090719 ± 42
ε	4.1 ± 3.0		−6.9 ± 3.9

[a] The isotopic ratios are the means and associated 2σ uncertainties (last digits) collected during cycle 2 of the Aldrich Ru standard runs in Table 3, using different corrections for mass discrimination. [b] Consistent with $^{96}Ru/^{101}Ru = 0.324851$ and the data in Table 2 of ref. 5. ε calculated as in Table 3.

Table 5 Ru isotopic data for iron meteorites and chondrites[a]

Date	Sample	A. r.	^{102}Ru(v)	α_1	^{97}Mo/^{101}Ru	^{98}Ru/^{101}Ru	^{99}Ru/^{101}Ru	^{100}Ru/^{101}Ru	^{102}Ru/^{101}Ru
Iron meteorites—									
07/16/01	CM1a	80	0.48	−2.49	0.000073 ± 11	0.109566 ± 29	0.747619 ± 30	0.738405 ± 25	1.85029 ± 6
07/16/01	CM1b	80	0.32	−2.50	0.000253 ± 19	0.109462 ± 44	0.747546 ± 50	0.738380 ± 37	1.85045 ± 8
10/9/01	C1A1	60	1.21	−1.98	0.000165 ± 4	0.109524 ± 14	0.747653 ± 14	0.738341 ± 16	1.85007 ± 4
10/22/01	C1A1	100	3.72	−1.95	0.000155 ± 3	0.109508 ± 8	0.747659 ± 18	0.738324 ± 9	1.85005 ± 5
10/9/01	C1A2	60	2.60	−1.98	0.000074 ± 5	0.109537 ± 12	0.747760 ± 17	0.738397 ± 14	1.84995 ± 5
10/9/01	C1A2	60	2.57	−1.98	0.000062 ± 2	0.109551 ± 6	0.747784 ± 11	0.738410 ± 10	1.84991 ± 3
10/15/01	BC1a	60	2.06	−1.83	0.000051 ± 5	0.109542 ± 14	0.747780 ± 25	0.738432 ± 24	1.84979 ± 7
10/22/01	BC1a	100	5.72	−1.93	0.000047 ± 1	0.109530 ± 6	0.747769 ± 11	0.738385 ± 10	1.84995 ± 2
10/22/01	BC1b	100	4.39	−1.94	0.000085 ± 1	0.109518 ± 5	0.747716 ± 9	0.738362 ± 10	1.85001 ± 2
Chondrites—									
08/16/01	Alg1	80	0.45	−2.31	0.000363 ± 12	0.109263 ± 44	0.746699 ± 52	0.737697 ± 31	1.85186 ± 8
08/16/01	All1	80	1.09	−2.44	0.000125 ± 6	0.109461 ± 17	0.747332 ± 41	0.738064 ± 22	1.85068 ± 4

[a] Meteorites: CM, Central Missouri; C, Coahuila; BC, Bennett County; Alg, Allegan; All, Allende. Other abbreviations, see Table3. All errors on ratios from individual runs are $2\sigma_m$ uncertainties on the last digits of the number.

were obtained by normalization to ^{100}Ru/^{101}Ru in cycle 2. This normalizing ratio is clearly inappropriate, because ^{104}Ru is neither included in the mass range covered by the normalizing ratio (mean mass 100.5 amu), nor does it lie close to these masses. Table 4 shows results for long-term reproducibilities of the Aldrich standard in the mass range $m = 100$–104, using alternative normalization schemes for data collected in cycle 2. Normalization to ^{104}Ru/^{100}Ru covers a large enough mass range that should allow the acquisition of precise data for ^{101}Ru and ^{102}Ru. Thus normalized, ^{100}Ru/^{101}Ru and ^{102}Ru/^{101}Ru collected in cycle 2 overlap with the N-TIMS data, albeit with relatively large 2σ errors (Table 4). This implies that there are no interferences on ^{104}Ru, other than the corrected interference from Pd. An alternative normalization scheme that employs ^{102}Ru/^{101}Ru (Table 4) works less well. It overestimates ^{100}Ru/^{101}Ru by 4.1 ± 3.0 ε units and underestimates ^{104}Ru/^{101}Ru by -6.9 ± 3.9 ε units, most likely because the mean mass covered by both ratios is lower or higher than that of ^{102}Ru/^{101}Ru. A recent high-precision study of Nd isotopes using MC-ICP-MS also reported systematic inaccuracies and degradation of precisions of isotopic abundances for masses significantly different from the mean mass covered by the ratio used for mass bias correction.[13] These results highlight the limitations imposed by the large mass bias in MC-ICP-MS for high-precision isotopic measurements. This requires much more attention towards the proper choice of normalizing isotopes than in most TIMS studies. In some cases such inaccuracies may be corrected by second-order mass bias corrections.[13] We note that some isotopes of cosmochemical relevance, such as ^{142}Nd, ^{96}Zr, ^{100}Mo and ^{104}Ru, lie either at the lower or upper end of the mass range of multi-isotopic elements. Because of the mass bias effects in MC-ICP-MS, these isotopes are more difficult to measure to high precision and accuracy than other isotopes of the same elements.

Meteoritic Ru

The samples analyzed here (Table 5) are the Group IIAB magmatic iron meteorites Bennett County (BC1a and b), Coahuila (C1A1 and 2), and Central Missouri (CM1a and b), the H5 ordinary chondrite Allegan (Alg1) and the CV3 carbonaceous chondrite Allende (All1). Except for CM, all samples were analyzed before at least once or multiple times by N-TIMS.[3,4] Signal intensities on ^{102}Ru (0.3–3.7×10^{-11} A) for samples were comparable or lower than for standards. All samples show a small and variable Mo interference that is significantly larger than the Mo interference in standard runs. This is surprising since all samples were micro-distilled and care was taken to collect only liquid from the tip of the conical area of the beaker. The source of the Mo may be either the

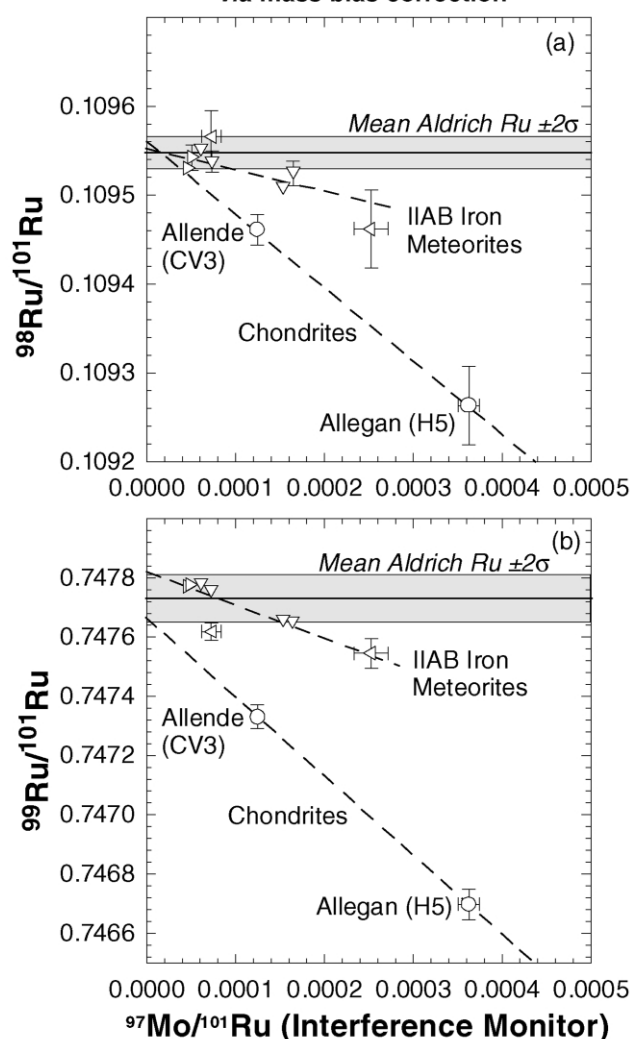**Effect of interfering ^{96}Mo on Ru isotopic ratios *via* mass bias correction**

Fig. 3 Interference- and mass discrimination-corrected ^{98}Ru/^{101}Ru (a) and ^{99}Ru/^{101}Ru (b) data for chondrites and iron meteorites *vs.* ^{97}Mo/^{101}Ru (see Table 5). The meteorite data shows negative correlations with different slopes for chondrites *vs.* iron meteorites. The intercept at ^{97}Mo/^{101}Ru = 0 indicates that these meteorites have normal Ru isotopic compositions.

sample itself, or the oxidant mixture, fine drops of which may have contaminated the trap area, or the H_2O_2. We note that the same techniques were used for Ru separations in our N-TIMS study, without resulting in enhanced Mo signals. This is most

certainly a result of the different ionization conditions for Ru *vs.* Mo in N-TIMS.

Because the amounts of sample Ru were limited, the data were collected in a single-cycle routine on masses 96–102, without ^{104}Ru (Table 5), but other conditions were identical to standard runs. Analyses of sample aliquots with the lowest ^{97}Mo/^{101}Ru such as C1A2 or BC1a show mass bias- and interference-corrected ratios that are close to or overlap with the values for the Aldrich standard. Precise N-TIMS measurements of the Ru isotopic composition of these samples are consistent with these results.[3,4] However, corrected ratios for other aliquots of samples measured by MC-ICP-MS are either too low (^{98}Ru/^{101}Ru, ^{99}Ru/^{101}Ru, ^{100}Ru/^{101}Ru) or too high (^{102}Ru/^{101}Ru). Fig. 3 shows that interference- and fractionation-corrected ^{98}Ru/^{101}Ru and ^{99}Ru/^{101}Ru ratios of meteorites show negative correlations with the magnitude of the Mo interference as monitored by ^{97}Mo/^{101}Ru. Similar relationships exist for ^{100}Ru/^{101}Ru and ^{102}Ru/^{101}Ru (positive correlation). Even at a very modest level of Mo in the sample, the interference correction on ^{96}Mo and associated uncertainties propagate into the mass bias correction, resulting in systematic offsets of the corrected isotopic ratios. In Fig. 3, the slopes for the chondrite and iron meteorite lines are different. Because the amount of data is limited, it is unknown whether this represents a matrix effect or just an increase in scatter at higher ^{97}Mo/^{101}Ru. Linear extrapolation towards ^{97}Mo/^{101}Ru = 0, using separate linear regressions, yields ^{98}Ru/^{101}Ru = 0.10956 ± 4 and 0.10955 ± 1, ^{99}Ru/^{101}Ru = 0.74766 ± 7 and 0.74783±1, ^{100}Ru/^{101}Ru = 0.73826 ± 4 and 0.73843 ± 1, ^{102}Ru/^{101}Ru = 1.85006 ± 9 and 1.84985 ± 3, for the chondrite and iron meteorite data, respectively. These values are close to or indistinguishable from the terrestrial Ru isotopic composition. In the case of samples of unknown isotopic compositions, Mo must either be separated nearly quantitatively (Ru/Mo > 10^4), or a number of aliquots must be measured that show some variability in ^{97}Mo/^{101}Ru to permit linear regression of the data. The latter approach will introduce additional uncertainties. The results suggest that Mo impurities in the Ru fraction represent the largest obstacle to obtaining precise and accurate Ru isotopic data on natural samples by MC-ICP-MS.

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