Pergamon

A gravimetric K₂OsCl₆ standard: Application to precise and accurate Os spike calibration

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Abstract—The Re-Os isotopic system is currently limited as a chronometer because of the lack of accurate gravimetric standards for Os spike calibration and uncertainty of the ^{187}Re half-life, which is also dependent on the accuracy of Os spike calibration. We demonstrate that the concentration of an Os spike can be calibrated accurately to ±0.2%. The accuracy of this calibration was achieved by using a high-purity, stoichiometric, and anhydrous K₂OsCl₆ standard. We show that (NH₄)₂OsCl₆, the standard material used by most other laboratories, is less reliable for Os spike calibration because it is hygroscopic and decomposes during heating. Nebulization and ionization in a plasma at 6500 to 8000 K does not discriminate Os of different oxidation states and chemical forms, allowing Os isotopic ratios in spike-normal mixtures to be equilibrated "on-line" and reproduced at the ~0.02% level. Multiple isotope dilution measurements reproduce Os concentrations at the 0.04% level. The Os isotopic compositions of the standards determined by multiple collector inductively coupled plasma mass spectrometry are in excellent agreement with that of negative thermal ionization mass spectrometry. A strong linear relationship between instrumental mass fractionation factors (β) for Os and Ir in MC-ICP-MS allows us to determine the isotopic composition of the Os spike with high precision and accuracy. Application of such an accurately calibrated spike is anticipated to reduce the uncertainty of ^{187}Re half-life significantly, thereby increasing the accuracy of the ^{187}Re-^{187}Os chronometer. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

The ^{187}Re-^{187}Os chronometer is potentially one of the most useful isotopic systems in geochemistry and cosmochemistry (see Shirey and Walker, 1998 for a review). In addition to being useful for many of the same problems addressed by other chronometers (such as U-Pb, K-Ar, Sm-Nd, etc.), the ^{187}Re-^{187}Os system also can be used to date the crystallization of metal in cores of parent bodies for iron meteorites as well as to date times of melting and or crystallization of olivine-rich rocks from planetary mantles (dunites, harzburgites, and lherzolites). However, since the introduction of high-precision negative thermal ionization mass spectrometry (NTIMS) for Re and Os isotopic measurements in 1991 (Creaser et al., 1991; Völkening et al., 1991; Yin et al., 1991), two problems have limited the use of the Re-Os system in absolute chronology.

The first centers on the precision and accuracy of Os spike calibrations. The main difficulties are (i) the absence of stoichiometric Os salts of high purity or Os metals of precisely known composition to serve as primary standards and (ii) the lack of isotopic equilibrium between Os of different oxidation states and of different chemical forms in the spike and standard. ^{187}Re-^{187}Os isochrons have been determined to per-mil range precision in both slope and initial ratio (Morgan et al., 1995; Shen et al., 1996; Smoliar et al., 1996; Birck and Allègre,

1998), but because the accuracy of Os spikes is currently limited to as much as 1.6% (Shen et al., 1996), the slope of the isochron may be off by as much. This may lead to errors on isochron ages that are significantly greater than the precision of the measurements.

The second problem is that the half-life of ^{187}Re has only been measured to ~3% compared to ^{238}U (0.054%), ^{235}U (0.068%), ^{40}K (~1.0%), ^{87}Rb (0.8%), ^{147}Sm (0.9%), and ^{176}Lu (4%; Steiger and Jäger, 1977; Lindner et al., 1989; Renne et al., 1998; Begemann et al., 2001). The ^{187}Re half-life was determined by purifying an accurately known quantity of Re and measuring the amount of ^{187}Os that has accumulated over a known period of time. This measurement therefore also relies on the accuracy of the Os spike calibration.

Any Re-Os isochron age thus has an uncertainty that is a combination of the uncertainties on the spike concentration and decay constant. Shen et al. (1996) concluded that this leads to an overall uncertainty of 4% on the age. If so, substantial improvement is required before the Re-Os system will be competitive with other radiogenic systems for accuracy of age determinations.

The need for an accurate Os gravimetric standard for Os spike calibration has been recognized for some time. Smoliar et al. (1996) noted that the above problems "hinder our ability to obtain precise Re-Os *absolute* ages" and that Re-Os ages can only be "used to place precise *relative* age constraints." Morgan et al. (1995) remarked, "the stoichiometry of Os standards is currently a vexed issue." Papanastassiou et al. (1994) and Shen et al. (1996) observed that neither using the certified concentrations nor heating aliquots of their salts to a fixed temperature resolved the stoichiometry problem. Birck et al. (1997) remarked, "The absence of a commercially available reference material of certified stoichiometry is a serious problem." In a more recent paper Birck and Allègre (1998) commented, "The

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absence of an Os standard is not yet resolved." Re standard-ization is also important but, in general, is considered to be less of a problem (Papanastassiou et al., 1994; Morgan et al., 1995; Shen et al., 1996; Birck et al., 1997).

This article (building on the preliminary report of Yin et al., 1999) details the methods we used to calibrate an Os spike to an accuracy of $\pm 0.2\%$, a substantial improvement over the current 1 to 2% level of accuracy. Such a spike, if employed in ^{187}Re half-life determinations, as well as in Re-Os chronome-try, will make the Re-Os system comparable in accuracy to the U-Pb system.

2. SELECTION AND PREPARATION OF Os GRAVIMETRIC STANDARDS AND SPIKE

To calibrate an Os spike precisely and accurately, an Os compound with an accurately known composition is required. The only practical choices are ultra-pure Os metal or a stoichi-ometric, stable, and nonhygroscopic Os salt. The latter can be used to make an aqueous solution in which the Os concentra-tion can be determined accurately by weighing and with min-imal processing. Because Os metal is difficult to work with, we concentrated our efforts on salts that are soluble in water or acid. We obtained pure (99.999%), anhydrous K_2OsCl_6 and $(NH_4)_2OsCl_6$ that were freshly manufactured by Electronics and Space Products Inc. (California, USA) for this work and shipped under a sealed Ar atmosphere. As we learned from the manufacturer, the Os compounds were exposed to a vacuum chamber to ensure that they were initially anhydrous before sealing under Ar. We confirmed the certified purity of these salts by ICP-AES and ICP-MS, in particular Br^- and I^- were found to be below the detection limit (<50 ppb). We also determined X-ray diffraction patterns for both substances. In both cases the diffraction patterns were in agreement with experimental and theoretical spectra for the pure substances. There was no sign of any components with different structure in these salts and the patterns suggest that the salts have less than ~ 1 to 2% of water.

Two dissolutions were made of each compound in ~ 6.7 N HCl, which served as stock solutions (named NOSY-1 and NOSY-2 for the K_2OsCl_6 standard and NOSY-3 and NOSY-4 for the $(NH_4)_2OsCl_6$ standard). The concentrations of these stock solutions are given in Table 1. From these concentrated solutions, a set of four diluted standards were prepared with concentrations of ~ 2 nmol ^{190}Os/g (Fig. 1), which were used for calibration of the Os spike.

The ^{190}Os spike (named HOST-1), obtained from Oak Ridge National Laboratory, was dissolved in two parts HNO_3 and one part HCl (reverse aqua regia) using a modified Carius tube technique (Shirey and Walker, 1995). It was then separated by solvent extraction (CCl_4), back-extracted into 9 N HBr (Cohen and Waters, 1996), and further diluted to ~ 17 nmol ^{190}Os/g in 9N HBr.

To determine the level of stoichiometry and the stability of the Os salts, we performed a number of experiments, as de-scribed below.

2.1. Relative Stability of K_2OsCl_6 and $(NH_4)_2OsCl_6$

After the glass ampoules in which the salts were shipped in an Ar atmosphere were opened in 1997, the remaining contents

Table 1. Gravimetric standards.

	Os (μg/g) concentrated	Os (μg/g) dilute	^{190}Os (nmol/g) dilute
K_2OsCl_6			
NOSY-1	83.686	1.39564	1.93680
NOSY-2	61.147	1.05533	1.46453
$(NH_4)_2OsCl_6$			
NOSY-3	93.014	1.56229	2.16768
NOSY-4	99.924	1.69790	2.35584

NOSY-1 and NOSY-2: Atomic weight = 190.244, $(^{190}Os/Os)_{Atomic}$ = 0.264011, $^{187}Os/^{188}Os$ = 0.10688, NOSY-3 and NOSY-4: Atomic weight = 190.243, $(^{190}Os/Os)_{Atomic}$ = 0.263962, $^{187}Os/^{188}Os$ = 0.10829. The nuclide masses of Os isotopes used to obtain the atomic weights are 183.952514, 185.953852, 186.955762, 187.955850, 188.958156, 189.958455, 191.961487 for ^{184}Os through ^{192}Os, respec-tively (IUPAC, 1994). Uncertainties of concentrations in this table from weighing are in the range 0.015–0.05% and assume ideal stoi-chiometry of the salts. The actual Os fraction is only known to about 2 per mil for K-salt and about 4 per mil for the NH_4-salt based on our assessment of stoichiometry.

were exposed to air. In 1999, the integrity of these remaining salts was tested by thermal gravimetric analysis (TGA) with continuous Ar gas flow through the system. When the K_2OsCl_6 standard was heated to 120°C and 140°C in a thermal gravi-metric analyzer over a 4-h period, it lost no more than 0.07% of its mass, and further heating (6 h) revealed no weight change at the level of the precision of the measurement (± 1 μg). This experiment was repeated several times and shown to be repro-ducible. One example is shown in Figure 2. We conclude that the K_2OsCl_6 salt did not absorb significant amounts of water and that it is stable up to 140°C, showing no significant weight change during heating.

In contrast, after a similar 2-year exposure to air, the $(NH_4)_2OsCl_6$ absorbed $\sim 1.0 \pm 0.1\%$, by mass of water, as documented in five repeated experiments (one example is shown in Fig. 3). Three to four hours of heating appears to have driven off nearly all of the water, as marked by a dramatic change in the rate of weight loss (Fig. 3a). Continued heating (at 120°C and 140°C) produced progressive weight loss at a slower rate (Fig. 3b). We believe this slower rate of weight loss reflects thermal decomposition of $(NH_4)_2OsCl_6$. Morgan et al. (1995) observed NH_4Cl as white condensates on the watch glass covering their standard when they heated the $(NH_4)_2OsCl_6$ salt for 24 h at 140°C. Similarly, Gilchrist (1932) observed the formation of a faint white sublimate and a con-tinual decrease in weight upon heating $(NH_4)_2OsCl_6$ at some-what higher temperatures (166–170°C). Because of this, Gil-christ (1932) did not heat the $(NH_4)_2OsCl_6$ salt for more than 7 h, whereas he heated the $(NH_4)_2OsBr_6$ salt somewhat longer (up to 14 h). The temperature at which decomposition occurs is not well determined, and there is no guarantee that thermal decomposition does not occur at lower temperatures. If the thermal decomposition of $(NH_4)_2OsCl_6$ into NH_4Cl and $OsCl_4$ indeed occurs, as Yilmaz and Içbudak (1996) also documented, the Os content of the heated product will be underestimated. Thus, even though absorbed H_2O can be driven off from $(NH_4)_2OsCl_6$ by heating, the above observations suggest that the ammonia salt decomposes into NH_4Cl and $OsCl_4$ during the heating procedures.
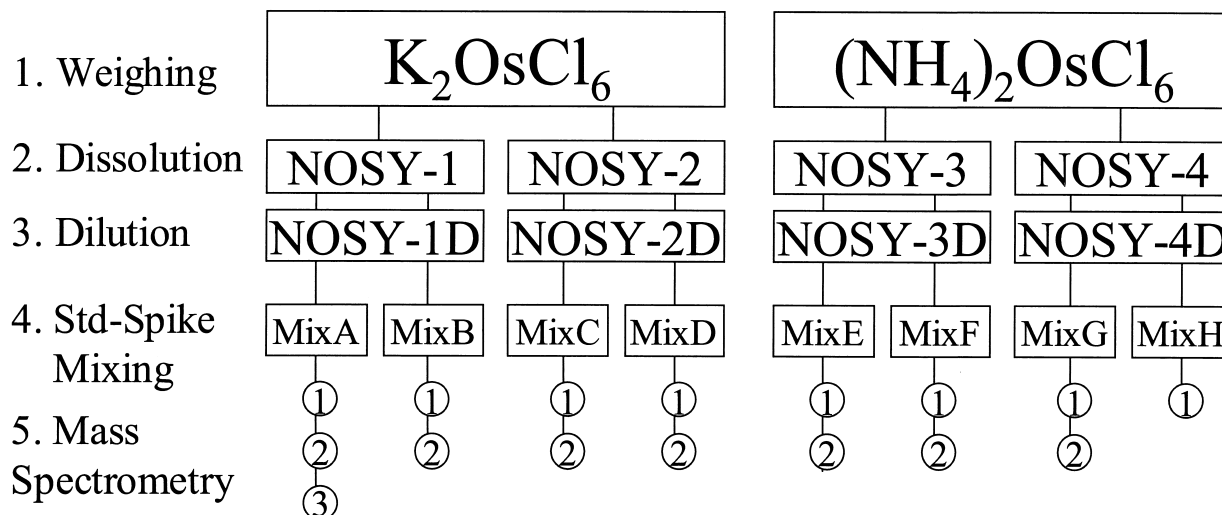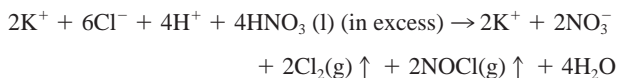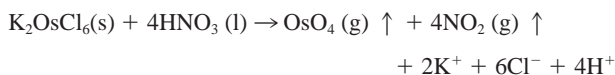
1. Weighing | K$_2$OsCl$_6$ | (NH$_4$)$_2$OsCl$_6$

2. Dissolution | NOSY-1 | NOSY-2 | NOSY-3 | NOSY-4

3. Dilution | NOSY-1D | NOSY-2D | NOSY-3D | NOSY-4D

4. Std-Spike Mixing | MixA | MixB | MixC | MixD | MixE | MixF | MixG | MixH

5. Mass Spectrometry | ① ② ③ | ① ② | ① ② | ① ② | ① ② | ① ② | ① ② | ①

Fig. 1. Flow chart for preparation of Os gravimetric standards (NOSY-1, NOSY-2, NOSY-3, and NOSY-4) from K$_2$OsCl$_6$ and (NH$_4$)$_2$OsCl$_6$, dilution of these standards, and preparation of the eight mixtures (MixA through MixH) of diluted standards with Os spike (HOST1). The isotopic composition of Os was measured by MC-ICP-MS at least twice for each mixture (except MixH).

2.2. Stoichiometry of K$_2$OsCl$_6$

We checked the stoichiometry and ideal molecular weight of the K$_2$OsCl$_6$ salt used in this work by the following procedures.

An accurately weighed amount of K$_2$OsCl$_6$ was dissolved in ultra-pure nitric acid. The reactions involved are as follows:

$$K_2OsCl_6(s) + 4HNO_3 (l) \rightarrow OsO_4 (g) \uparrow + 4NO_2 (g) \uparrow$$
$$+ 2K^+ + 6Cl^- + 4H^+$$

$$2K^+ + 6Cl^- + 4H^+ + 4HNO_3 (l) \text{ (in excess)} \rightarrow 2K^+ + 2NO_3^-$$
$$+ 2Cl_2(g) \uparrow + 2NOCl(g) \uparrow + 4H_2O$$

The Cl$_2$ gas and nitrosyl chloride (NOCl) gas are the standard gas products of an aqua regia reaction. It took about 2 weeks to complete the reaction. Once dissolved, the remaining solution was dried at 140°C under N$_2$ gas flow until no weight change was observed. By this procedure, the dark reddish K$_2$OsCl$_6$ was completely converted to white, crystalline KNO$_3$, which was accurately weighed.

To check the stoichiometry of KNO$_3$ obtained from the above reaction it was converted to KCl by adding pure HCl, which took about 1 week to complete. The reaction is:

$$2KNO_3 + 8HCl(l) \text{ (in excess)} \rightarrow 2K^+ + 2Cl^- + 2Cl_2(g) \uparrow$$
$$+ 2NOCl(g) \uparrow + 4H_2O$$
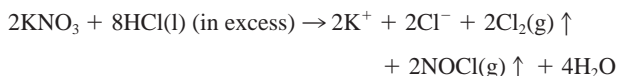
When dried at 140°C under N$_2$ gas flow to constant weight, the cubic KCl crystals were also accurately weighed. The molecular weights of KNO$_3$ and KCl are as follows: $M_{KNO3} = 101.103$, $M_{KCl} = 74.551$. The theoretically correct weight ratio of these two substances based on their molecular weights is $M_{KNO3}/M_{KCl} = 1.35616$. The experimentally determined weight ratio $m_{KNO3}/m_{KCl} = 1.3541 \pm 0.0027$ is within error of this value ($-0.15 \pm 0.20\%$). The accuracy of the weighing was established using standard weights calibrated accurately rela-

tive to weight standards certified by the National Bureau of Standards. From this excellent agreement, we conclude that both KNO$_3$ and KCl are stoichiometric. We therefore use the ideal molecular weight of KNO$_3$ for the determination of the molecular weight of our K-Os-Cl salt as described in the following.

The ideal molecular weight of K$_2$OsCl$_6$ ($M_{K2OsCl6} = 481.1568$) was calculated using our determination of the atomic weight of Os in this salt ($A_{Os} = 190.244$; see footnote in Table 1), as well as the standard atomic weights of Cl and K ($A_{Cl} = 35.4527$, $A_K = 39.0983$). The theoretical molecular weight ratio of KNO$_3$ to K$_2$OsCl$_6$ should be: $M_{KNO3}/M_{K2OsCl6} = 0.2101249$. Our experimentally determined weight ratio of these substances from reactions (1) and (2) is $m_{KNO3}/m_{K2OsCl6} = 0.41991 \pm 0.00042$. This is within error ($-0.08 \pm 0.10\%$) of 2 times the theoretical molecular weight ratio (0.4202497). The molecular weight of K$_2$OsCl$_6$ was determined using the relation: $M_{K2OsCl6} = 2M_{KNO3}/(m_{KNO3}/m_{K2OsCl6}) = 481.54 \pm 0.48$. This value is within error ($+0.08 \pm 0.10\%$) of the theoretical value for K$_2$OsCl$_6$. Therefore, the measurement is *consistent* with exact stoichiometry of this substance.

As will be shown later in this article, the use of the ideal formula of the K$_2$OsCl$_6$ salt for calibration of Os spikes leads to concentrations that are systematically higher by 1 to 2% compared with calibrations in several other laboratories using NH$_4$-based Os salts as their primary gravimetric standard material. This could mean that the mass fraction of Os in our salt is lower by this amount than that in the ideal formula. However, as shown in the Appendix, there is no reasonable composition of a K-Os-Cl salt that could account for such a difference. We conclude that the K$_2$OsCl$_6$ salt we used for our primary Os standard solutions (NOSY-1 and NOSY-2) is essentially stoichiometric and should yield Os concentrations accurate to within $\pm0.2\%$.
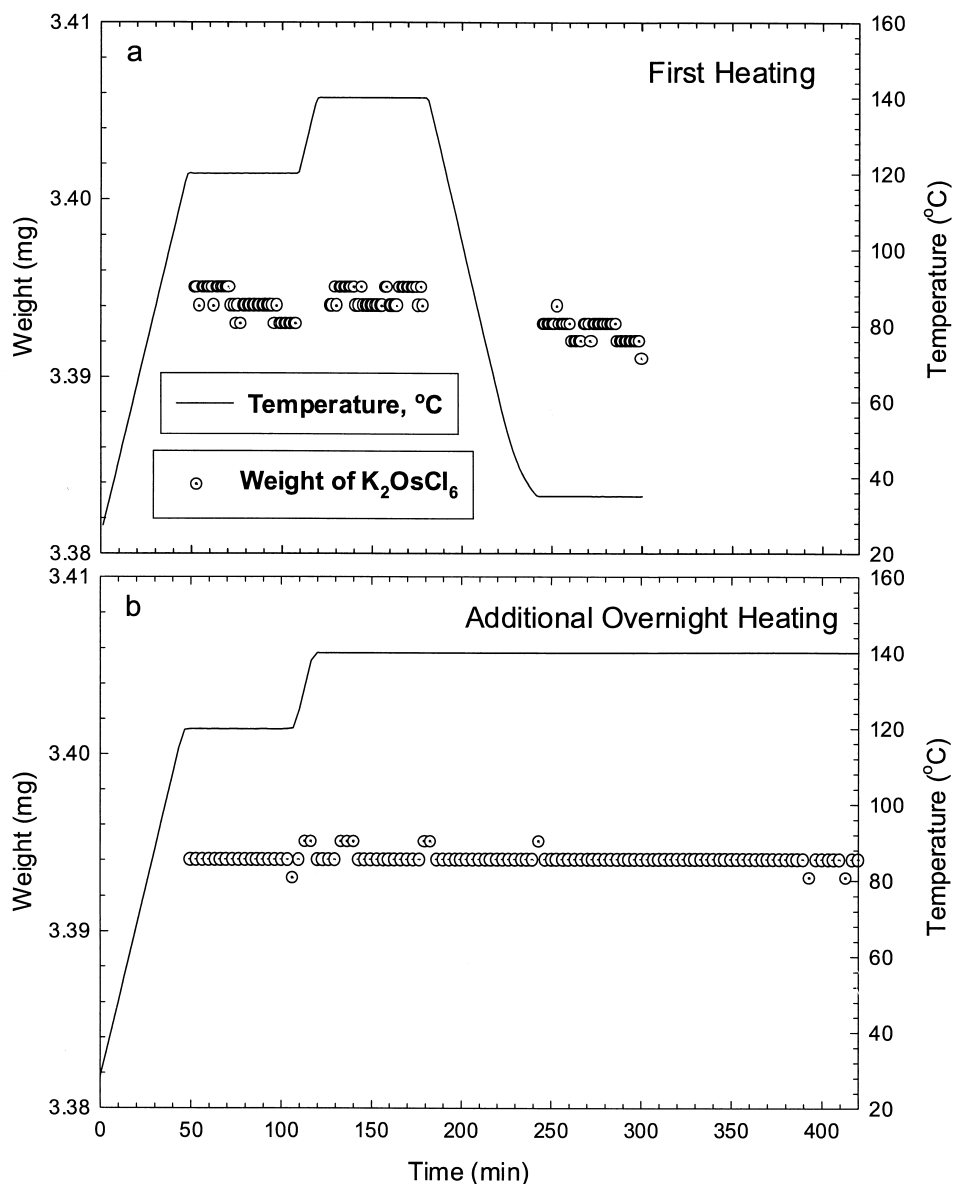
Fig. 2. Thermal Gravimetric Analysis results for K_2OsCl_6. (a) shows first 300 min of heating and (b) an additional 420 min. The lines represent the heating pattern (temperature in °C). The open circle data points record weight changes in K_2OsCl_6 in mg, measured every 3 min. The temperature range for heating (120–140°C) was selected based on the recommendation of Gilchrist (1932) and adopted by Morgan et al. (1995) and Birck and Allègre (1998).

2.3. The Nonstoichiometry of $(NH_4)_2OsCl_6$

Papanastassiou et al. (1994) pointed out some of the problems with the stoichiometry of $(NH_4)_2OsCl_6$. We know of no improved methods for determining the Os content of $(NH_4)_2$ $OsCl_6$ since the original work of Gilchrist (1932). We therefore followed his method for evaluating the stoichiometry of the $(NH_4)_2OsCl_6$ salt used to make our NOSY-3 and -4 standards. Because this is an extremely dangerous experiment, which requires heating a toxic substance under H_2 gas flow at very high temperatures (800°C), only one experiment was performed. The $(NH_4)_2OsCl_6$ salt was reduced to Os metal as follows: A quartz boat containing an accurately weighed

amount of $(NH_4)_2OsCl_6$ was placed in a quartz reaction tube in a tube furnace. The tube was swept with dry purified Ar for 1 h while the temperature of the tube furnace was gradually raised to 120°C at the rate of 2°C/min. While maintaining isothermal conditions of 120°C, the Ar was replaced by pure, dry H_2 for 2 h at the rate of 100 mL/min. At the end of this step, the temperature of the tube furnace continued to be heated gradually at a rate of 5°C/min to 725°C. The temperature was maintained at this point for 1 h while the H_2 was displaced by dry purified Ar. The furnace was allowed to cool to room temperature in Ar (without any exposure to air, so as to avoid oxidative Os loss as OsO_4 gas). The boat was then transferred
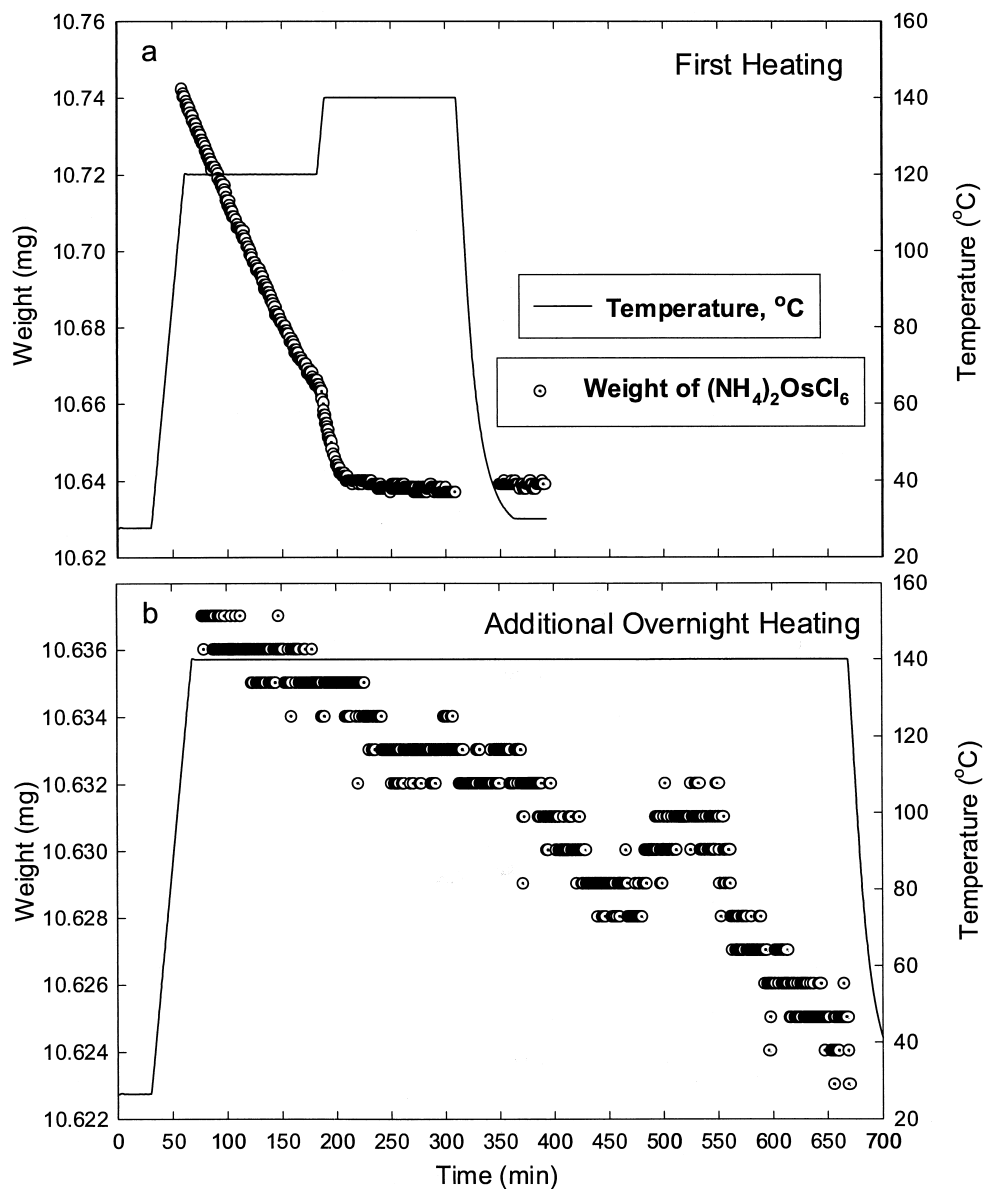
Fig. 3. Thermal gravimetric analysis results for (NH$_4$)$_2$OsCl$_6$. (a) shows rapid weight loss of ~1.0 ± 0.1% within first few hours. This is interpreted to reflect evaporation of absorbed water. After ~3 hours, the rate of change is much less. (b) Further heating results in continuous weight loss at a much slower rate. Each data point represents the weight recorded every 30 seconds.

to a balance and allowed to equilibrate with the ambient temperature before being weighed. The Os weight fraction in the (NH$_4$)$_2$OsCl$_6$ salt was determined by comparing the weight of the reduced metallic Os sponge to the amount of initial (NH$_4$)$_2$OsCl$_6$ salt. We obtained 0.43096, which is 0.5% lower than the theoretical value of 0.43328. Thus, it appears that the stoichiometry of the (NH$_4$)$_2$OsCl$_6$ salt used in this study is further from ideal than that of the K$_2$OsCl$_6$ salt, both from this experiment as well as the TGA measurements of the salt.

We conclude that only NOSY–1 and NOSY-2, produced from the K$_2$OsCl$_6$ salt, should be used for precise calibration of our Os spike. However, we also report results for the standards produced from the (NH$_4$)$_2$OsCl$_6$ salt because this is currently the salt most widely used in calibration of Os spikes.

3. THE ISOTOPIC COMPOSITION OF STANDARDS AND SPIKE

The isotopic composition of several Os standards was determined by multiple collector (MC) NTIMS (the Finnigan MAT262 at Harvard) and multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS; the Micromass IsoProbe at Harvard). The NTIMS methods follow those described in Creaser et al. (1991), Völkening et al. (1991), and Yin (1995). The MC-ICP-MS methods used here were developed in this laboratory. For all the high-precision Os isotope ratios reported here, we used a high-efficiency-nebulizer interfaced with a cyclonic spray chamber, which was water-chilled to 2°C. The much smaller internal surface area of the cyclonic

Table 2. Comparison of the Os isotopic composition obtained for the OsM standard by negative thermal ionization mass spectrometry and multiple collector inductively coupled plasma mass spectrometry with published values for a variety of other standards.

Standard[a]	Method[b]	$^{186}Os/^{188}Os$[c]	$^{187}Os/^{188}Os$[c]	$^{189}Os/^{188}Os$[c]	$^{190}Os/^{188}Os$[c]	Reference[d]
OsM	SC-NTIMS	0.11994 ± 4	0.14920 ± 2	1.21974 ± 5	1.98402 ± 7	This work
OsM	MC-NTIMS	0.11991 ± 1	0.14911 ± 1	1.21974 ± 3	1.98397 ± 4	This work
OsM	MC-ICP-MS	0.11994 ± 10	0.14914 ± 7	1.21969 ± 7	1.98406 ± 16	This work
TIT	MC-ICP-MS	0.11986 ± 1	0.13988 ± 3	1.21974 ± 5	1.98375 ± 18	1
UP	MC-NTIMS	0.11997 ± 1	0.17391 ± 1	1.21967 ± 8	1.98375 ± 3	2
UM	MC-NTIMS	0.11985 ± 1	0.11379 ± 1	1.21966 ± 14	*1.98448 ± 16*	3
DTM	MC-NTIMS	0.11999 ± 1	0.17395 ± 5	1.21973 ± 4	1.98376 ± 3	4
DTM	MC-NTIMS	0.12000 ± 5	0.17393 ± 6	1.21967 ± 4	1.98379 ± 2	5
LLNL	SC-NTIMS	0.12007 ± 5	0.17444 ± 1	1.21960 ± 7	1.98400 ± 11	6
WHOI	SC-NTIMS		0.17403 ± 30	1.21969 ± 10	1.98397 ± 80	7
R1	SC-NTIMS	*0.11969 ± 34*	0.14830 ± 10	1.21954 ± 22	1.98380 ± 31	8
R2	SC-NTIMS	0.12005 ± 5	0.14925 ± 10	1.21959 ± 13	1.98373 ± 19	9
CIT2	SC-NTIMS	0.11995 ± 3	0.14911 ± 3	1.21967 ± 6		10
CIT1	SC-NTIMS	*0.12022 ± 6*	0.12411 ± 6	*1.21911 ± 18*	1.98403 ± 18	11
Grand mean		0.11996 ± 14	Variable	1.21966 ± 12	1.98389 ± 26	

[a] TIT = Tokyo Institute of Technology Standard; UP = University of Paris Standard; DTM = Department of Terrestrial Magnetism Standard; LLNL = Lawrence Livermore National Laboratory Standard; WHOI = Woods Hole Oceanographic Institution Standard; R1 = Regensburg Standard #1, R2 = Regensburg Standard #2; CIT2 = CalTech Standard; CIT1 = Natural iridosmine.

[b] SC = single collector; MC = static multiple collector.

[c] Normalized to $^{192}Os/^{188}Os$ = 3.08261 (Nier, 1937). For NTIMS measurements the following oxygen composition was used: $^{18}O/^{16}O$ = 0.002045 and $^{17}O/^{16}O$ = 0.0003708 (Nier, 1950). Obvious outliers are italicized and excluded from the grand mean values. $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ are naturally variable because of radioactive decay from ^{190}Pt or ^{187}Re, respectively. All errors in this table and the following table are quoted at the 2 sigma level.

[d] 1 = Hirata et al. (1998), 2 = Birck and Allègre (1998), 3 = Shirley and Walker (1998), 4 = Finnigan (1995), 5 = Tuttas (1992), 6 = Yin (1995), 7 = Hauri and Hart (1993), 8 = Völkening et al. (1991), 9 = Walczyk et al. (1991), 10 = Creaser et al. (1992), 11 = Creaser et al. (1991).

spray chamber in comparison to a Scott double-pass spray chamber minimizes washout time and cross-contamination from previous samples, resulting in a lower blank. Initially, we found substantial memory during the MC-ICP-MS measurements of Os solutions prepared in 2% HNO_3 or 2% HCl. We solved this problem by using ultra-pure 10% HCl to clean the sample introduction system between Os samples. The Os solutions were also prepared in 10% HCl. Using this approach, we observed that Os signals from prior samples dropped almost instantaneously to the level of background. Without this cleaning step, significant residual Os signals were observed even hours after a sample was analyzed. To test the effectiveness of our procedure, we alternated measurements of the Os spike, Os normal, and Os spike-normal mixtures with 10% HCl washout for about 3 min between the samples. By repeating the full cycle, we found that the three samples with extremely different Os isotopic compositions were reproducible to within 0.02%, demonstrating that there was negligible Os cross contamination in our measurements.

Both NTIMS and MC-ICP-MS Os isotopic measurements were corrected for mass fractionation using the exponential law of Russell et al. (1978). The exponential law fractionation factor

$$\beta = \frac{\ln(R_{uv}^N/R_{uv}^{Meas})}{\ln(m_u/m_v)} \qquad (1)$$

is obtained from a measurement of the ratio (R_{uv}^{Meas}) of two isotopes u and v relative to the accepted normal ratio (R_{uv}^N). Here m_u and m_v are the masses of isotopes u and v. For Os, β_{Os} is calculated using ($^{192}Os/^{188}Os)_N$ = 3.08261 as the normalizing ratio (Nier, 1937). The average Os isotopic composition determined by MC-ICP-MS for 12 repeat measurements of one

of our standards (OsM) is given in Table 2. A comparison of Os isotopic compositions obtained by NTIMS and MC-ICP-MS is also given in Table 2. Our NTIMS data were obtained both in single collector (SC) mode as well as in static multicollection mode. These are generally in excellent agreement with each other. As shown, the Os isotopic composition obtained by static MC-ICP-MS and NTIMS methods are also in excellent agreement for all measured isotope ratios. Our results are also compared with the literature values in Table 2. The table emphasizes the necessity to establish a common Os standard and the need to characterize its isotopic composition precisely and accurately. Nd standards such as Ndβ or La Jolla or Hf standards such as JMC 475 have proven to be very valuable in the past two decades.

We also designed experiments to explore the possibility of using normal Ir for mass fractionation correction of Os isotopes in ICP-MS measurements. This method may potentially be important for correcting mass fractionation in Os spike-normal mixtures and is essential for Os spike measurements where none of the isotopic ratios are known a priori for internal normalization. Similar methodology has been applied to Pb isotope measurements with ICP-MS, using $^{205}Tl/^{203}Tl$ for mass fractionation corrections (e.g., Longerich et al., 1987; Walder et al., 1993a,b).

All the Os standards measured by MC-ICP-MS were mixed with normal Ir. The Os blank in the Ir solution was found to be at background level. A β_{Os}-value can be calculated using each of the Os-isotopic ratios, and one β_{Ir}-value can be calculated using the normal Ir isotope composition ($^{193}Ir/^{191}Ir)_N$ = 1.6830 ± 10; (Walczyk and Heumann, 1993). Figure 4a shows a plot of β_{Os}-values calculated from $^{192}Os/^{188}Os$ (β_{192Os}) and $^{190}Os/^{188}Os$ (β_{190Os}), respectively. This yields an excellent fit
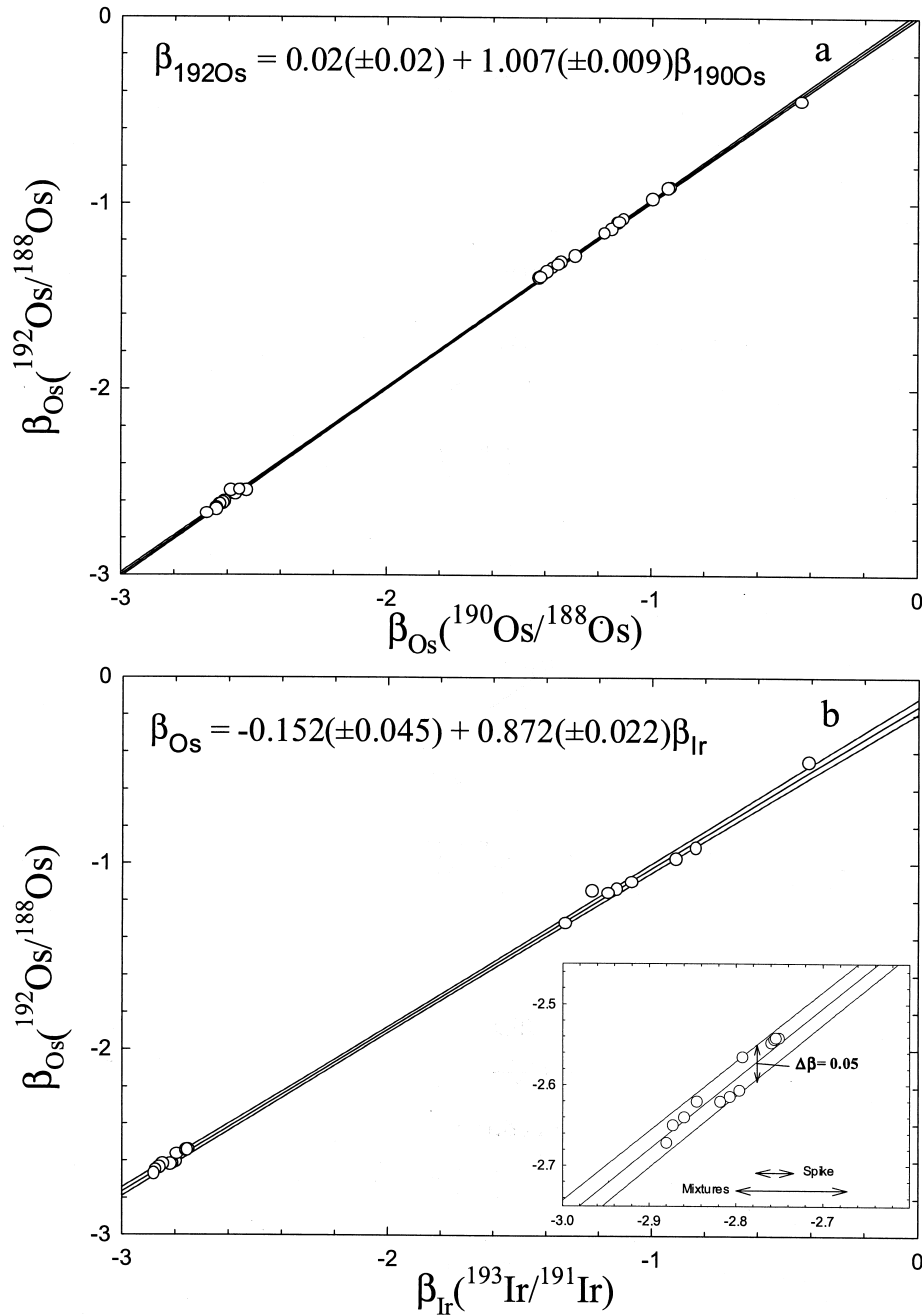
Fig. 4. Plot of exponential law mass fractionation factors (β) calculated from MC-ICP-MS measurements of ^{192}Os/^{188}Os, ^{190}Os/^{188}Os, and ^{193}Ir/^{191}Ir in mixtures of normal Os and Ir. The cluster of data points with β-values ~ -2.7 were obtained using a new high-efficiency nebulizer interfaced with a cyclonic spray chamber. The data with β-values in the range -0.4 to -1.4 were obtained on a variety of other standards using a standard Meinhard nebulizer or an MCN 6000 microconcentric nebulizer. (a) shows a plot of β_{Os}-values calculated from ^{192}Os/^{188}Os (β_{192Os}) and ^{190}Os/^{188}Os (β_{190Os}), respectively. This yield an excellent fit to a line with a slope close to 1 and near zero intercept, as expected if the exponential law is a good description of mass fractionation in Os (i.e., $\beta_{192Os} = \beta_{190Os}$). A similar plot using ^{189}Os/^{188}Os instead of ^{190}Os/^{188}Os is essentially identical (not shown). (b) shows that there is also a strong linear relationship ($R^2 = 0.99898$) between calculated β_{Os} and β_{Ir} values. Note, however, that in this case the slope is significantly lower than 1 (~ 0.87), and the intercept is not zero (~ -0.15, see text for discussion). The inset shows the 2 sigma error band for this linear relationship in the range of β_{Ir} values for the spike and mixtures measured in this work. For a single value of β_{Ir} a range of β_{Os} corresponding to $\Delta\beta_{Os} = 0.05$ is obtained, with resulting uncertainty of 2.5 ε-units per mass unit for Os isotope ratios. This linear relationship is useful for determining the instrumental mass fractionation during measurements of samples with nonnormal Os isotope composition such as our Os spike.

to a line with a near zero intercept and a slope close to 1, as expected if the exponential law is a good description of mass fractionation in Os (i.e., $\beta_{192Os} = \beta_{190Os}$).

A plot of β_{Os} versus β_{Ir} (Fig. 4b) also shows a strong linear relationship, but in this case the best-fit line yields both a nonzero intercept and a slope differing from unity. The nonzero intercept for the β_{Os}-β_{Ir} correlation could be due to incompatible values used for the normal Ir (Walczyk and Heumann, 1993) and Os (Nier, 1937) isotopic compositions. For example, lowering the normal ^{193}Ir/^{191}Ir by 1.8 per mil results in a zero intercept value. In contrast, however, there is no change in Os or Ir reference isotope compositions that can produce a slope significantly different from 1. That the slope is <1 reflects different fractionation behavior between Os and Ir, due to differing physiochemical behavior of the two elements (e.g., ionization potential, volatility, oxidation state). For example, Hirata (1996) observed differences in the fractionation behavior of Os and Ru relative to other neighboring elements in his ICP-MS measurements, which he attributed to the greater volatility of these elements. Maréchal et al. (1999) also have observed different fractionation behavior between Cu and Zn using ICP-MS.

From the above observations, it is clear that one cannot simply assume $\beta_{Os} = \beta_{Ir}$ to correct for mass fractionation in Os isotopic analyses by ICP-MS. Doing so would lead to Os isotopic ratios that are incorrect by as much as 1 per mil per mass unit. A substantial improvement is achieved by using the linear relationship found between β_{Os} and β_{Ir}, with resulting uncertainty of ~2.5 ε-units per mass unit for Os-isotope ratios (Fig. 4b). By adding Ir to our spike and using the β_{Os}-β_{Ir} correlation we obtained an estimate of β_{Os}, which we used to correct the HOST1 spike for mass fractionation (see footnote Table 3).

4. SPIKE-NORMAL MIXTURES

Two aliquots were taken from each diluted standard solution (NOSY 1D, 2D, 3D, and 4D) and mixed with the Os spike (HOST1), generating eight mixtures altogether, as illustrated in Figure 1. The purpose was to determine how well the ^{190}Os concentration in the spike could be reproduced based on all these mixtures.

4.1. Error Magnification

The range of spike:normal ratios chosen for these mixtures was based on standard techniques for estimating the error magnification factor for isotope dilution as a function of ^{190}Os/^{192}Os in the spike-normal mixture. In an isotope dilution measurement, the uncertainty of the ratio of ^{190}Os contributed by the spike (S) and the normal (N) (e.g., $(^{190}$Os$)_S/(^{190}$Os$)_N$) is related to the uncertainty of the isotopic ratio determined for the spike-normal mixtures, R_{Mix}, (for example, $(^{192}$Os/^{190}Os$)_{Mix}$, $(^{189}$Os/^{190}Os$)_{Mix}$, or $(^{188}$Os/^{190}Os$)_{Mix}$) by an error magnification factor of $\gamma = R_{Mix}(R_S - R_N)/[(R_S - R_{Mix})(R_{Mix} - R_N)]$; (Webster, 1960). The minimum value for γ using HOST1 is 1.2 at ^{190}Os/^{192}Os = 7.918. The mixtures, MixA, MixC, MixE, and MixG ($\gamma \sim 1.2$) were all made to be closest to the "optimum spiking" level, whereas MixB, MixD, MixF, and MixH ($\gamma \sim 1.4$–1.9) were deliberately underspiked to observe

the influence of error propagation in the isotope dilution. Because the isotopic ratios in the spike-normal mixtures (R_{Mix}) are measured to the 0.02% level or better, this will translate into an uncertainty in the $(^{190}$Os$)_S/(^{190}$Os$)_N$ ratio of 0.024 to 0.038%. This is a factor of five better than the final uncertainty of our Os spike concentration (0.2%), which is primarily due to uncertainty of the Os concentration in the standard salt. We therefore conclude that the error magnification is insignificant.

4.2. Isotopic Equilibration

Each mixture was analyzed by MC-ICP-MS at least two times (MixA three times), with the exception of MixH, which was only measured once (see Table 3). These repeat measurements were performed to insure the reproducibility of isotopic ratios in spike-normal mixtures. In previous efforts, Os spike-normal isotopic equilibrium is achieved either by alkaline fusion (Morgan et al., 1995) or Carius tubes (Shen et al., 1996). In our work, the Os spike-normal isotopic equilibrium is achieved "on-line" in the plasma of the MC-ICP-MS. The data in Table 3 show that by simply mixing the Os spike with the standard, and, diluting to the desired concentration for ICP analysis, the measured Os isotopic ratios involving ^{190}Os in the mixtures are reproducible to within ~0.02%. Thus, we demonstrate that nebulization and ionization in a plasma (~6500–8000 K) results in excellent isotopic equilibration between different chemical solutions of Os that are likely to have Os in different oxidation states (cf. Papanastassiou et al., 1994).

4.3. Correction of Instrumental Mass Fractionation

To correct for instrumental mass fractionation in spike-normal mixtures, we need an estimate of the ^{192}Os/^{188}Os in the mixture (R_{uv}^{Mix} where $u = 192$ and $v = 188$) corrected for contribution from impurities of ^{192}Os and ^{188}Os in the ^{190}Os spike ($R_{uv}^{Corr} = (^{192}$Os/^{188}Os$)_{Corr}$). The corrected (Corr) ratio may be obtained from a measurement of this ratio as well as the ^{190}Os/^{188}Os (R_{jv}^{Mix} where $j = 190$) ratio in the mixture and precise estimates of normal (R_{uv}^N and R_{jv}^N) and spike (R_{uv}^S and R_{jv}^S) isotope ratios using the following equation:

$$R_{uv}^{Corr} = R_{uv}^{Mix} + (R_{jv}^N - R_{jv}^{Mix}) \frac{R_{uv}^{Mix} - R_{uv}^S}{R_{jv}^{Mix} - R_{jv}^S} \tag{2}$$

This is solved by an iterative procedure because the correction term (the second term on the right-hand side of the equation) requires knowledge of the fractionation factor. This procedure converges to within 10 ppm of the true value after two iterations and to within 1 ppm after four iterations.

5. SPIKE CALIBRATION RESULTS

The mass fraction of the spike isotope j (in this case ^{190}Os) in a spike-normal mixture (x_j^S) can be calculated from a fractionation corrected ratio of some other Os isotope (i; here ^{192}Os, ^{189}Os, or ^{188}Os) relative to j (we call this ratio R_{ij}^{Mix}) from the following simple mass balance relationship:

$$R_{ij}^N = R_{ij}^{Mix} - x_j^S(R_{ij}^S - R_{ij}^N) \tag{3}$$

where the superscripts S and N refer to the spike and normal isotope ratios. The resulting ^{190}Os concentrations in the Os

Table 3. Multiple collector inductively coupled plasma mass spectrometry measurements of Os and Ir in spike-normal mixtures and calibration of the Os spike (HOST1).

Mixture	^{189}Os/^{188}Os	^{190}Os/^{188}Os	^{192}Os/^{188}Os	^{193}Ir/^{191}Ir	^{190}Os in Standard nmol/g	Std. Wt. (g)	Spike Wt. (g)	^{190}Os in HOST1 (nmol/g)
MixA-1	1.24658 ± 0.00018	19.7915 ± 0.0020	3.16740 ± 0.00032	1.731418 ± 0.000016	1.93680	1.10057	1.18119	17.317 ± 11
MixA-2	1.24690 ± 0.00016	19.7674 ± 0.0020	3.16430 ± 0.00028	1.731296 ± 0.000019	1.93680	1.10057	1.18119	17.302 ± 11
MixA-3	1.24534 ± 0.00015	19.7679 ± 0.0018	3.16323 ± 0.00029	1.731348 ± 0.000017	1.93680	1.10057	1.18119	17.306 ± 11
MixB-1	1.23934 ± 0.00009	5.97712 ± 0.00041	3.23362 ± 0.00021	1.731709 ± 0.000019	1.93680	2.200731	0.49014	17.287 ± 13
MixB-2	1.23855 ± 0.00007	5.97543 ± 0.00034	3.23277 ± 0.00020	1.731585 ± 0.000023	1.93680	2.200731	0.49014	17.283 ± 13
MixC-1	1.24497 ± 0.00038	19.7068 ± 0.0058	3.16406 ± 0.00092	1.731946 ± 0.000033	1.46453	1.103927	0.89302	17.295 ± 11
MixC-2	1.24625 ± 0.00033	19.7148 ± 0.0049	3.16651 ± 0.00075	1.732114 ± 0.000029	1.46453	1.103927	0.89302	17.295 ± 10
MixD-1	1.23978 ± 0.00009	7.2315 ± 0.0004	3.22465 ± 0.00018	1.730738 ± 0.000022	1.46453	2.190771	0.48930	17.302 ± 7
MixD-2	1.24002 ± 0.00008	7.2369 ± 0.0004	3.22682 ± 0.00017	1.730758 ± 0.000022	1.46453	2.190771	0.48930	17.312 ± 7
MixE-1	1.24828 ± 0.00012	21.6660 ± 0.0015	3.16132 ± 0.00023	1.730515 ± 0.000017	2.16768	1.10126	1.484451	17.217 ± 7
MixE-2	1.24863 ± 0.00012	21.6450 ± 0.0021	3.15790 ± 0.00034	1.730552 ± 0.000026	2.16768	1.10126	1.484451	17.209 ± 7
MixF-1	1.23761 ± 0.00007	4.40954 ± 0.00023	3.23966 ± 0.00020	1.731942 ± 0.000016	2.16768	3.31251	0.49501	17.230 ± 8
MixF-2	1.23777 ± 0.00008	4.40741 ± 0.00025	3.23910 ± 0.00021	1.731990 ± 0.000010	2.16768	3.31251	0.49501	17.225 ± 8
MixG-1	1.24822 ± 0.00031	19.9786 ± 0.0043	3.17879 ± 0.00064	1.732649 ± 0.000036	2.35584	1.101905	1.45902	17.230 ± 9
MixG-2	1.24550 ± 0.00024	19.9395 ± 0.0037	3.17170 ± 0.00061	1.732576 ± 0.000036	2.35584	1.101905	1.45902	17.212 ± 8
MixH-1	1.23816 ± 0.00007	5.29162 ± 0.00030	3.23734 ± 0.00018	1.732060 ± 0.000024	2.35584	2.20423	0.491881	17.275 ± 6

The isotope ratios in columns 2 through 5 are uncorrected for mass fractionation. We used the normal Os composition measured by negative thermal ionization mass spectrometry in this laboratory (see Table 2; ^{189}Os/^{188}Os = 1.21974, ^{190}Os/^{188}Os = 1.98402, ^{192}Os/^{188}Os = 3.08261) and the Os spike composition (^{189}Os/^{188}Os = 1.35139, ^{190}Os/^{188}Os = 210.333, ^{192}Os/^{188}Os = 2.15904) to reduce the data in this table. Uncertainties in Os standard concentrations are given in Table 1. Uncertainties in standard weights and spike weights are conservatively estimated at <0.05%. The average Os spike composition of six repeat measurements of the Os spike (HOST1) is ^{186}Os = 0.000150 ± 4, ^{187}Os = 0.000184 ± 8, ^{188}Os = 0.004653 ± 3, ^{189}Os = 0.006288 ± 6, ^{190}Os = 0.97868 ± 2, ^{192}Os = 0.010046 ± 4, ^{192}Os/^{190}Os = 0.010265 ± 5. The atomic weight of the spike is: 189.96182 ± 3. The spike composition was corrected for mass fractionation using the β_{Os}-β_{Ir} correlation (see text and Fig. 4).
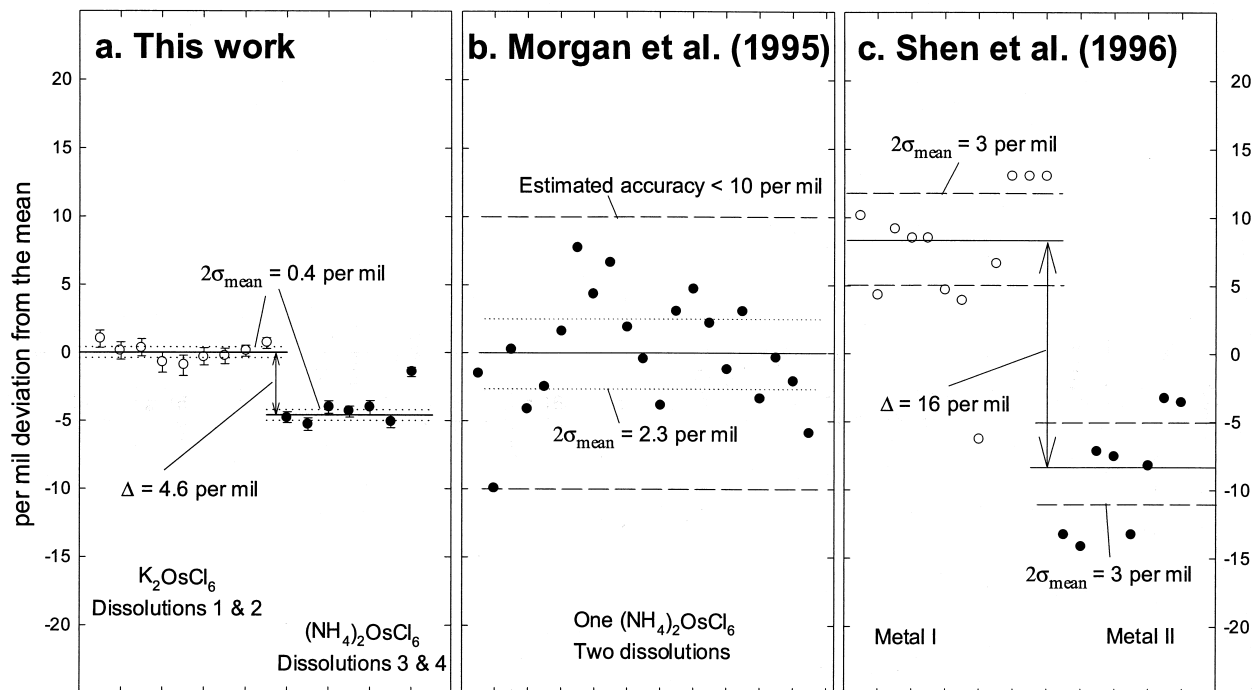
Fig. 5. Comparison of reproducibility of our spike calibrations with that in two other laboratories: (a) shows the results of all our individual spike calibrations. They are shown as per mil deviations from the grand mean value of the ^{190}Os concentration in HOST1 determined with K_2OsCl_6 standard. The standards prepared from K_2OsCl_6 reproduced at the 0.42 per mil level, whereas the standards prepared from $(NH_4)_2OsCl_6$ reproduced at the 1 per mil level (excluding the outlier MixH-1 improves the reproducibility to 0.43 per mil). However, a difference of 4.6 per mil exists between the two groups of measurements, which we attribute to nonstoichiometry in the $(NH_4)_2OsCl_6$ salt (see text). The two panels to the right show a comparison with two recently published Os spike calibrations. (b) Morgan et al. (1995) used two dissolutions of one salt ($(NH_4)_2OsCl_6$) to calibrate their Os spike repeatedly and pooled the results, obtaining $2\sigma_m$ precision at the level of 2.3 to 3.6 per mil. However, the accuracy of the Os spike was estimated at ~10 per mil. (c) Shen et al. (1996) used two Os metal chips to calibrate their Os spike. The resulting concentration varied from 3.9 to 13 per mil for Metal I and −3.3 to −14.1 per mil for Metal II. The offset between the two metals is 16 per mil.

spike (HOST1) were obtained from each of the spike-normal mixtures discussed above and are presented in Table 3 and Figure 5. The errors quoted on the final result in this table include both weighing and mass spectrometric errors propagated through the equations used for the concentration calculation. The reproducibility obtained with two dissolutions of K_2OsCl_6 (NOSY-1 and NOSY-2) is 0.42 per mil ($2\sigma_m$), whereas the reproducibility obtained with two dissolutions of $(NH_4)_2OsCl_6$ (NOSY-3 and NOSY-4) is 0.43 per mil ($2\sigma_m$; excluding the last data point MixH-1, which appears to be an outlier; including that data point will increase the spread to 0.11%). This level of uncertainty reflects our handling errors for the entire procedure of spike calibration, including weighing, dissolution, mixing, dilution, evaporation, and mass spectrometry. This indicates that the reproducibility of the techniques we used to determine the Os spike concentrations is at the 0.43 per mil level. Comparison of the results based on the two standards show that the Os spike concentration calibrated against NOSY-1 and -2 and NOSY-3 and -4 are offset by ~0.46% (Fig. 5, entirely consistent with a 0.31% offset in the same direction from the Os assay provided by the manufacturer for these two salts. This offset suggests nonstoichiometry with one or both of the Os compounds used in this work. As

discussed in section 2, the problem lies primarily with the $(NH_4)_2OsCl_6$ standard, and therefore all our data in Figure 5a are shown as deviations from the average spike concentration determined using the K_2OsCl_6-based standards.

We obtained much improved reproducibility compared with previous studies (Fig. 5b: Morgan et al., 1995; Fig. 5c: Shen et al., 1996). We also obtained better agreement between dissolutions of our two different salts (4.6 per mil difference), than that measured by Shen et al. (1996) for their two metal standards (16 per mil).

We show in Figure 6 that concentrations obtained by inversion of data for $^{188}Os/^{190}Os$, $^{189}Os/^{190}Os$, and $^{192}Os/^{190}Os$ agree to within 0.3 per mil (in most cases much better) with the results based on the $^{192}Os/^{188}Os$ ratio itself, as explained above. We carried out the inversion by generalizing Eqn. 3 to include the possibility that the ratio in the mixture (R_{ij}^{Mix}) was fractionated according to the exponential law (Eqn. 1):

$$\frac{R_{ij}^{N}}{R_{ij}^{Mix}} = \left(\frac{m_i}{m_j}\right)^{\beta} - x_j^S \frac{R_{ij}^S - R_{ij}^N}{R_{ij}^{Mix}} \qquad (4)$$

Here β is the exponential fractionation factor and m_i amd m_j are the masses of isotopes i and j. For an element with at least three
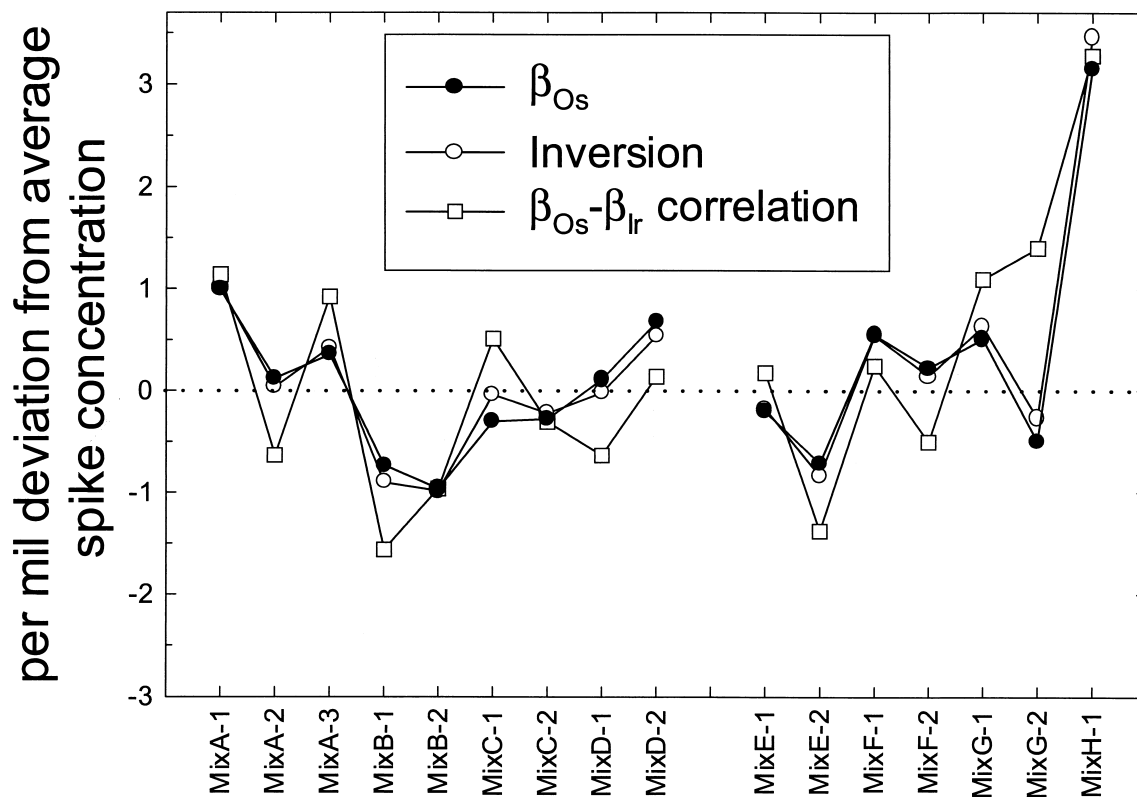
Fig. 6. Comparison of ^{190}Os concentrations in the HOST1 spike calculated using different methods. The results are given in per mil deviations relative to the average values given in Table 3 for MixA through MixD (K$_2$OsCl$_6$ standard) and MixE through MixH ((NH$_4$)$_2$OsCl$_6$ standard) so that the systematic difference of 4.6 per mil between the two standards is removed from this plot. The different calculation methods are (1) ^{190}Os/^{188}Os internally normalized to ^{192}Os/^{188}Os using the exponential law and a simple spike unmixing formula (solid circles); (2) inversion based on a simultaneous solution of the ^{190}Os concentration and the β_{Os}-value using measured ^{188}Os/^{190}Os, ^{189}Os/^{190}Os, and ^{192}Os/^{190}Os ratios (open circles, see text); and (3) using the β_{Os}-β_{Ir} correlation shown in Figure 4 (open squares). The Os concentration values obtained from methods 1 and 2 agree to within 0.3 per mil and in most cases much better. The concentrations based on method three (the β_{Os}-β_{Ir} correlation) show more variability but in general confirm the results obtained using the internal normalization.

nonradiogenic isotopes, there exists at least two such equations, allowing the system of equations to be solved for both x_j^S and β. For our Os isotope measurements, we have three such equations (one for each of the ratios ^{188}Os/^{190}Os, ^{189}Os/^{190}Os, and ^{192}Os/^{190}Os) and both x_j^S and β were obtained using the total inversion algorithm of Tarantola and Valette (1982). Lee et al. (in press) discussed the application of inversion techniques for this type of spike unmixing problem in detail. The values obtained for β using this technique are in excellent agreement with those obtained using Eqn. 2 above.

A comparison of concentration results using different correction procedures is shown in Figure 6 and demonstrates that internal fractionation correction based on Os isotope ratios are less scattered than the results based on the β_{Os}-β_{Ir} correlation.

6. DISCUSSION

6.1. Comparison of the K$_2$OsCl$_6$ Standard with Os Standards Based on Ammonia Salts

Because the comparison in Figure 5 is based on a relative scale, it only shows how precise the spike calibrations are in each

laboratory and does not address the question of interlaboratory biases. In Figure 7a we compare our standard, based on the K$_2$OsCl$_6$ salt, with Os standards based on ammonia salts from several laboratories (see Fig. 7a). The anhydrous and stoichiometric nature of the K$_2$OsCl$_6$ salt was demonstrated in section 2 and shown in Figure 2. After our initial calibration in 1999 we repeated our calibration with K$_2$OsCl$_6$ 1 year later (2000) and obtained excellent agreement to within 0.06% (Fig. 7a).

We have obtained Os standard solutions from the University of Paris and the University of Maryland, which were prepared from (NH$_4$)$_2$OsBr$_6$ and (NH$_4$)$_2$OsCl$_6$, respectively. With the intention of driving off any absorbed water, the Paris and Maryland groups heated their ammonia salts to 120°C and 140°C, respectively, before dissolution. Figure 7a shows the relative deviation of the standards of different laboratories as measured relative to the Harvard K$_2$OsCl$_6$ standard by the spike, HOST-1. In both cases, the concentrations we determined for the standards are higher than those determined by the original investigators, who based their concentrations on assumed stoichiometry of the salts.

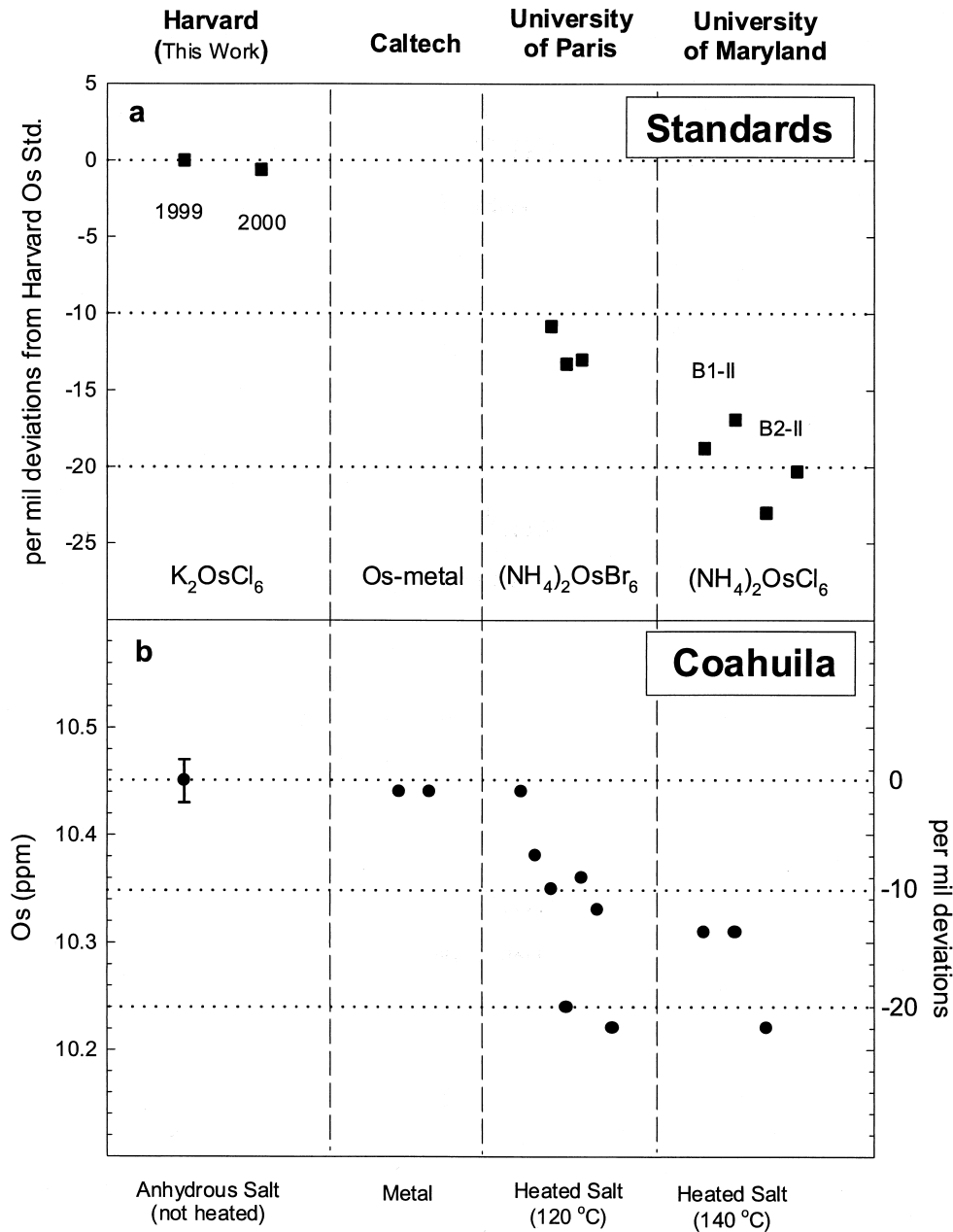These differences may reflect evaporative loss of solution in

Fig. 7. (a) Comparison of relative concentrations of Os salt standards from three different laboratories as measured by the same spike. The per mil deviation is calculated as the reported concentration divided by the concentration determined using our spike, HOST-1, calibrated relative to our K_2OsCl_6 standard. We attribute the negative offsets to the breakdown of the $(NH_4)_2OsCl_6$ salt upon heating (note the correlation between offset and temperature to which the salts were heated). Note that these deviations are larger than the accuracy originally suggested from gravimetry. (b) Comparison of Os concentration measurements of the Coahuila (IIAB) iron meteorite measured by isotope dilution. The error bar is the range of Os concentration permitted in our sample of this meteorite and based on the K_2OsCl_6 standard (Os = 10.45 ± 0.02 ppm for a 179-mg sample). Data from Caltech (Shen et al., 1996) average 10.44 ppm for 77- to 93-mg samples. Data from the University of Maryland (Morgan et al., 1995; Smoliar et al., 1996) for 109- to 251-mg samples yield Os concentrations in the range 10.22 to 10.31 ppm. Data from the University of Paris (Birck and Allègre, 1998; Birck et al., 1997) for 2- to 296-mg samples yield Os concentrations in the range 10.22 to 10.44 ppm. The same general "temperature trend" observed with the standards in (a) is clearly visible in the Coahuila data as well.

the Paris and Maryland standards over the years since the original preparations (assuming Os is preferentially retained) or nonstoichiometry of the salts used in preparation of the Paris and Maryland standards. The fact that the deviations broadly correlate with the temperature at which these salts were heated suggests that the "temperature trend" is due to decomposition of the ammonia-based Os salts at high temperature, which would result in underestimation of the Os content of the stan-

dard. The observed biases are somewhat larger than the estimated accuracy of the Paris and Maryland standards (~1%). Morgan et al. (1995) used one standard based on $(NH_4)_2OsCl_6$ (two dissolutions of the same salts, B1 and B2) to calibrate their Os spike, obtaining $2\sigma_m$ precision at the level of 0.23 to 0.36% based on repeat measurements (Smoliar (1996) achieved a slightly better precision (0.16%)). However, the accuracy of the Os spike calibration was ascertained to be 1% or better based on three lines of evidence as described in Morgan et al. (1995), including cumulative heating of the $(NH_4)_2OsCl_6$ salt at 140°C for 24 h.

We also compared our standard with the Lawrence Livermore National Laboratory (LLNL) standard of Lindner et al. (1989) that was used to calibrate their Os spike and was in turn used to determine the Re decay constant. Lindner et al. (1989) also used ammonium hexachloroosmate to prepare this standard. However, unsatisfied with a consistent bias of 2.5% between two spikes, the Os content of the standard solution was checked for accuracy by potentiometric titration. This method cannot be considered absolute, however, because the reagent itself had to be standardized with an independent source of chloroosmate or chloroplatinate. At best, the method provides an indication of confidence on accuracy at the precision of the quadrupole ICP-MS that was used in Lindner's (1989) work. The Os concentration in our aliquot of the LLNL standard was found to be low by ~6% relative to the value provided for the standard. Again, this may reflect problems with the aliquot we measured, such as evaporative loss over the years or nonstoichiometry of the LLNL Os standard.

6.2. Os Metal Standards

Shen et al. (1996) used Os metal as a primary standard, which eliminates problems of stoichiometry in the Os salts. They used two Os metal chips with 0.2 to 0.4% estimated metal impurities. Each metal was dissolved in a glass ampoule under a strongly oxidizing medium, then converted to stable hexachloroosmate, dried, and redissolved in 4N H_2SO_4 as stock solution. The resulting Os spike concentration varied from 0.39 to 1.3% (Metal I) and -0.33 to -1.41% (Metal II) relative to the average value of both metal standards (Fig. 5c). The offset between the two metals is 1.6%, which was ascribed by Shen et al. (1996) to O and C impurities in the metal.

We have obtained Os metal with total metal impurities of <0.05%, and have also characterized its impurities of O, N, C, and H. Two measurements of the same metal yield good agreement for total nonmetal impurities (O, N, C, and H) of 0.132% and 0.139%. Oxygen is the major impurity (~0.098%). However, we did not check for rare gas impurity. If the metal was melted under Ar, this could be a problem. The good agreement between these measurements suggests that these are indeed the major impurities in our Os metal and that such impurities can be accounted for.

Although the choice of metal as a standard may eliminate the stoichiometric problems that plague ammonium salt standards, obtaining good reproducibility in preparation of an Os standard from the metal is exceedingly difficult. It requires initial dissolution of the metal in a highly oxidizing medium, followed by a reduction step, in which the oxidized Os is converted to a reduced stable form. From our own experience and from Shen et al. (1996), quantitative recovery of Os in this multistep process is very difficult. With our own metal standards, as well as the Os standard used by Shen et al. (1996), we were only able to obtain reproducibility at the 1 to 2% level. These measurements suggest that we are in agreement with the Caltech standard to within ~1 to 2%.

6.3. Interlaboratory Comparisons Using the Coahuila Iron Meteorite

Another way to compare our spike calibration results with those of other laboratories is to compare results for the same natural sample, measured in each laboratory. For this purpose, we determined the Os concentration in a piece of the Coahuila (IIAB) iron meteorite. Comparison of results for natural samples always involves uncertainty with regard to intrinsic sample heterogeneity. This meteorite was chosen because it is considered to be chemically homogeneous. The average Os concentration obtained by recent isotope dilution measurements for samples of the Coahuila meteorite, obtained from different museums, is 10.34 ± 0.14 ppm. The $\pm 1.4\%$ spread is within the range of uncertainty for earlier Os spike calibrations (Morgan et al., 1995; Shen et al., 1996; Smoliar et al., 1996; Birck and Allègre, 1998). Thus, this meteorite appears, by all accounts, to be the best choice for an interlaboratory comparison.

We performed no chemical leaching before the dissolution of the meteorite sample because of the potential danger of electrodeposition of Re and Os (cf. Smoliar, 1996; Smoliar et al., 1996), which would result in erroneous concentrations. The sample was cut by a low-speed diamond saw into a small rectangular chunk, which was physically abraded to get a clean surface and then ultrasonically cleaned using distilled alcohol and water to remove the dust particles before dissolution. The sample was dissolved (in reverse aqua regia) and equilibrated with the HOST1 ^{190}Os spike using the modified Carius tube technique (Shirey and Walker, 1995) and then measured by NTIMS.

Figure 7b shows a comparison of our results with those of other laboratories. We measured an Os concentration of 10.45 ± 0.02 ppm on a 179-mg sample, which is nearly identical to the 10.44 ppm value obtained by Shen et al. (1996). Our results are also consistent with some of the data from Birck and Allègre (1998) and Birck et al. (1997), within the 1% uncertainty of their Os spike calibration. The data of Morgan et al. (1995) and Smoliar et al. (1996) are, however, significantly lower, beyond their stated accuracy. The lower values obtained by the Paris and Maryland groups for Coahuila match the "temperature trend" observed for the standards (Fig. 7a). This suggests that the concentration differences for Coahuila may be due to nonstoichiometry in the ammonium salts used to prepare the Os standards in these laboratories. However, unless the same pieces of Coahuila used by different laboratories are remeasured by isotope dilution using the same spike, we are unable to determine how much of the spread in Os concentration might be due to intrinsic chemical heterogeneity.

7. CONCLUSIONS

The Re-Os system has been shown by others to be one of the worst in terms of accuracy among commonly used isotopic

dating methods, highlighting the need for a major undertaking to solve this chronic problem. Although solutions of $(NH_4)_2OsCl_6$ have been widely adopted as gravimetric standards and served the Os community well up to now, we recommend that it be abandoned as a primary gravimetric standard in preference to K_2OsCl_6. Using this standard, we show that Os concentrations can be determined accurately at the 0.1 to 0.2% level. This will be of great utility in the future, both for precise determination of the [187]Re half-life as well as in the application of [187]Re-[187]Os chronometry.

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APPENDIX

The use of the ideal formula of the K_2OsCl_6 salt for calibration of Os spikes leads to concentrations that are systematically higher by 1 to 2% compared with calibrations in several other laboratories using NH_4-based Os salts as their primary gravimetric standard material (as shown in Fig. 7a). This could mean that the mass fraction of Os in our salt ($\zeta_{Os-real}$) is lower than that in the ideal formula ($\zeta_{Os-ideal}$), and we express this difference as $\xi_{Os} = (\zeta_{Os-real}/\zeta_{Os-ideal}) -1$. For example, a 2% difference results in $\xi_{Os} = -0.02$. Therefore, we also considered whether there are *other* permissible compositions of our K-Os-Cl salt, given the constraints discussed above.

First the K-Os-Cl salt contains 2 mol of K per formula unit as determined by the experiment described in section 2.2. If Os is present in several oxidation states in this salt, then it is conceivable that the remaining part is $Y\Sigma_i X_i OsCl_{n_i}^{m_i-}$ to charge balance 2 mol of K, where Y is a number close to 1 (because most of the salt is K_2OsCl_6 with Os in the +4 oxidation state) and X_i is the fraction of each species $OsCl_{n_i}^{m_i-}$ ($\Sigma_i X_i = 1$) in the mixture, where $n_i = Z_{Os(i)} + m_i$ and Z_{Os} is the valence state of Os (in addition to the main Os oxidation state of +4, we may possibly have +1, +2, +3, +5, +6, +7, or +8 and an average valence of $\bar{Z}_{Os(i)} = \Sigma_i X_i Z_{Os(i)}$). From charge balance, it follows that $\bar{m} = \Sigma_i X_i m_i = 2/Y = (K/Os)$, and thus the formula for this salt can be written as $K_2Os_YCl_{Y\bar{n}}$, where $\bar{n} = \Sigma_i X_i n_i = (Cl/Os)$.

Mass balance considerations require that the molecular weight of this salt be very close to the ideal molecular weight for K_2OsCl_6, (within $1 + \delta$ where δ is a small number that is measured equal to 0.0008 ± 0.0010 as discussed in section 2.2). This results in the following relationships between these parameters:

$$\xi_{Os} = \left[\frac{\zeta_{Os-real}}{\zeta_{Os-ideal}} \right] - 1 = \frac{1}{1 + \delta} \left[\left(\frac{2}{\bar{m}} - 1 \right) - \delta \right] \quad (A1)$$

From mass balance considerations we obtain,

$$\frac{2}{\bar{m}} - 1 = \frac{[2(A_K/A_{Cl}) + (A_{Os}/A_{Cl}) + 6]\delta - (\bar{Z}_{Os} - 4)}{(A_{Os}/A_{Cl}) + \bar{Z}_{Os}} \quad (A2)$$

and because $\bar{Z}_{Os}$ is close to 4, we may simplify to:

$$\xi_{Os} = \frac{1}{1 + \delta} \left[0.45\delta - \frac{(\bar{Z}_{Os} - 4)}{9.37} \right] \quad (A3)$$

First, for two special cases: (i) $\bar{m} = 2$, we obtain $\xi_{Os} = -\delta/(1+\delta)$, (ii) $\bar{Z}_{Os} = 4$ we obtain $\xi_{Os} = 0.45\delta/(1+\delta)$. For a δ value of 0.0008 ± 0.0010, as measured for our salt, we obtain a difference in the Os mass fraction of only -0.8 ± 1.0 and $+0.4 \pm 1.0$ per mil, respectively, from the mass fraction in the ideal substance.

Considering more general cases, for $\bar{Z}_{Os} < 4$, we always have $\xi_{Os} > 0$, which would produce a discrepancy opposite to that observed. For $\bar{Z}_{Os} > 4$, the +5 state is the most likely additional oxidation state, and to obtain a 2% discrepancy ($\xi_{Os} = -0.02$), we need $\bar{Z}_{Os} = 4.19$ (i.e., we would thus need 19% of such a component to explain this effect). Such a large component should have been easily detected by the XRD measurements. For $\xi_{Os} < 0$, we must have $\bar{Z}_{Os} > 4$. Given that $\delta = 0.0008$ and that the mass fraction of the impurity is at most 2% ($X_2 + X_3 + \ldots < 0.02$), we obtain $-0.002 < \xi_{Os} < 0$. Thus, we conclude that our K-Os-Cl salt exhibits essentially the ideal stoichiometry of K_2OsCl_6.

These results are all due to the simple fact that if we start with the molecular weight determined for our K-Os-Cl salt of 481.54, it is clear that after subtracting the weight of 2 K and one Os, then the remaining weight of 213.099 yields 6.011 Cl in the formula (i.e., in this case $\bar{n} = (Cl/Os) = 6.011$), very close to the theoretical value of 6.