

A double spike for osmium analysis of highly radiogenic samples

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Received 8 November 2002; accepted 27 May 2003

Abstract

Geologic samples containing highly radiogenic Os (molybdenites and low-level, highly radiogenic (LLHR) samples) have no internal means by which to correct for mass fractionation during isotopic measurement by mass spectrometry. We describe a double spike for use with highly radiogenic samples, created by combining isotopically enriched ¹⁸⁸Os and ¹⁹⁰Os. Spiking molybdenite and other highly radiogenic minerals with this tracer allows for a fractionation correction, as well as a more reliable determination of common Os relative to analysis using single spikes.

The precise isotopic composition of the double spike is determined by a calibration against natural Os, in which two separate measurements are necessary: one each for the pure double spike and the spike–standard mixture. An estimate of the true composition of the spike is obtained by least squares approximation, and the errors are obtained by Monte Carlo methods. Sample analyses are then much more straightforward than the calibration because isotopic compositions of all components are known a priori.

Results obtained with a mixed Re-double Os spike demonstrate an improved reproducibility over individual ¹⁸⁵Re and ¹⁹⁰Os spikes. For an Archean in-house molybdenite standard we now observe a reproducibility of 0.08%. The ability to make a fractionation correction is essential for Os measurements made by ion counting. With the double Os spike, young samples and those with low Re contents (i.e., LLHR) can now be accurately analyzed. The ¹⁸⁸Os–¹⁹⁰Os double spike also allows a determination of the common Os contents of highly radiogenic samples. Common Os is poorly determined for ancient samples with high concentrations of ¹⁸⁷Os, which fortunately are not sensitive to estimates of common Os. Common Os can be reasonably well determined for younger samples and those with low Re contents. We report a common Os concentration of 0.4 ± 0.1 ppb for an 11 Ma molybdenite. Consideration of common Os content is important for age determination of young samples and LLHR samples, and is not possible by other published means of Os analysis.

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Keywords: Molybdenite; Dating; Osmium; Double spike; Mass fractionation; Highly radiogenic

1. Introduction

For Os analysis of most geologic materials, there is an intrinsic means by which to correct for instrumental

mass fractionation during measurement by NTIMS. This is because natural Os is composed of six relatively abundant isotopes, of which only two are radiogenic (¹⁸⁶Os, ¹⁸⁷Os). It is possible, then, to obtain as many as three well-measured ratios not involving a radiogenic daughter (namely, ¹⁸⁹Os/¹⁸⁸Os, ¹⁹⁰Os/¹⁸⁸Os, and ¹⁹²Os/¹⁸⁸Os). Any measurement with significant Os has at least one ratio that neither includes a radiogenic isotope nor is irretrievably affected by the addition of

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large amounts of an isotopic tracer. The remaining ratios can be corrected “on line” for mass discrimination by comparing the observed value of that ratio to its accepted reference value (Luck and Allègre, 1983). This has been the method employed for Os isotope ratio and isotope dilution analysis for many years.

Some minerals, for example, molybdenite, form with very high Re/Os ratios and contain very little common or initial Os. As a result, the Os present in a typical molybdenite is almost entirely radiogenic ^{187}Os . A molybdenite sample spiked with a ^{190}Os tracer (“single spike”) therefore has no well-measured Os ratio for on-line fractionation correction. This has been the case in our high-level lab, and for this reason our molybdenite analyses are subject to a small but unknown bias on the order of a few permil for the ratio $^{187}\text{Os}/^{190}\text{Os}$ with mass difference (δ_m) = 3 AMU. In recent years, reproducibility for molybdenite ages has reached a level of precision of the same magnitude as this bias (Markey et al., 1999). Therefore, a means of measuring and correcting for mass discrimination in Os analyses of highly radiogenic samples is now required.

There are a number of ways to approach the problem. An obvious method is to spike these samples with common Os (e.g., Suzuki et al., 1992). Although this is a reasonable approach, there are a number of reasons why it is not ideal. The common Os spike contains an appreciable quantity of ^{187}Os , which must of course be accounted for in the isotope-dilution calculations. The possible presence of detectable common Os in the molybdenite itself, as well as in the analytical blank, is another complicating factor. Spiking with common Os makes it impossible to monitor common Os in the sample, and any common Os present will produce an apparent change in the proportion of “common Os” spike in the mixture. Common Os and/or analytical blank may in fact become significant when analyzing small samples (<10 mg), young samples, or samples with very low Re contents. Finally, spiking with common Os is clearly incompatible with analysis of low-level, highly radiogenic samples (LLHR samples; Stein et al., 2000), which have high ^{187}Os concentrations relative to other Os isotopes but also contain significant common Os. For these reasons, we have considered it preferable to use the ^{190}Os spike for molybdenite analysis, despite the lack of any correction for mass fractionation.

Another approach to fractionation correction would be to determine an average fractionation factor for our mass spectrometer under normal operating conditions by repeated analysis of an osmium standard. This correction factor can then be applied to measurements for all samples. In Pb analysis this is commonly done using the NIST SRM981 to estimate the fractionation factor. This is acceptable under many circumstances, but it has been observed that even with skill and care (i.e., consistent loading and run conditions), geological samples may behave differently from a standard in the mass spectrometer; indeed they are known to behave differently from one another (Woodhead et al., 1995).

A third option is to simulate the presence of a non-radiogenic isotope ratio by adding a spike enriched in two isotopes. This is the basis of the “double spike” method, which was proposed in the early 1960s (Dodson, 1963, and references therein). Isotopic tracers composed of multiple isotopes have been used to this effect for isotopic analysis of several elements (Dodson, 1969 and references therein). The double spike method was first applied to Pb isotopic analyses (Compston and Oversby, 1969). Many subsequent workers have developed a mathematical treatment for double-spike data and error analysis (Dodson, 1970; Russel, 1971; Hamelin et al., 1985; Powell et al., 1998). Morgan (1999) proposed the use of a double spike for Os analysis of highly radiogenic samples, and presented preliminary results. Qu et al. (2001) presented molybdenite Re–Os results using an ^{186}Os – ^{188}Os spike created by irradiation of Re metal with a large fluence of neutrons. The present paper is a continuation of the work initiated by Morgan (1999) and describes further the chemical and mathematical treatments involved in the double spike method as it applies to analysis of highly radiogenic Os samples.

2. Preparation of the double spike

2.1. Design of the double spike

The ^{188}Os – ^{190}Os double spike in this study was designed to simultaneously perform three functions: (1) determine the concentration of ^{187}Os in the sample, (2) monitor the common Os component, and (3) provide a fractionation correction. Fig. 1 illustrates

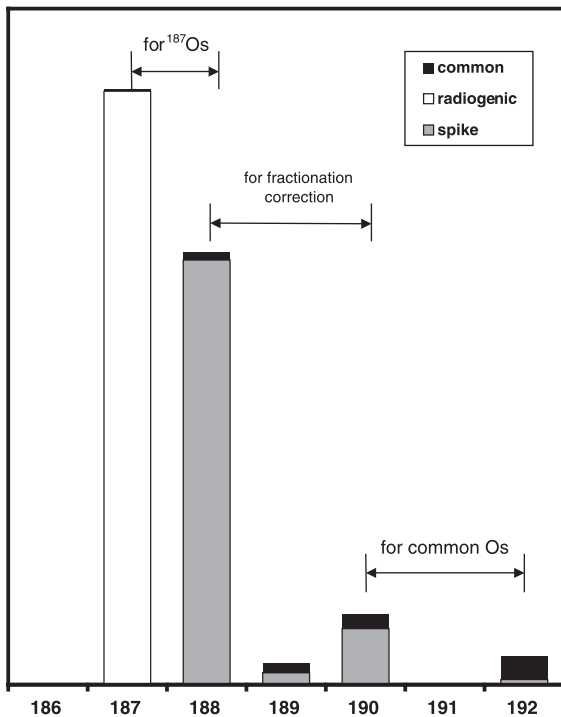


Fig. 1. A graphical representation of a hypothetical mixture of osmium from molybdenite with a double Os spike. The isotope dilution calculations for radiogenic Os are based on the $^{187}\text{Os}/^{188}\text{Os}$ in the mixture, the common Os ID is based on the $^{192}\text{Os}/^{190}\text{Os}$ ratio, and the fractionation correction is based on the $^{190}\text{Os}/^{188}\text{Os}$.

the systematics of double spiking Os for highly radiogenic samples.

The ^{187}Os from the sample is determined from the $^{187}\text{Os}/^{188}\text{Os}$ in the spike–sample mixture. Even without a fractionation correction, this decreases by a factor of three the effect of mass fractionation on the ^{187}Os determination, relative to spiking with ^{190}Os . We use the $^{190}\text{Os}/^{192}\text{Os}$ of the mixture to determine the abundance of common Os in the sample. Considering the much lower abundance of common Os relative to ^{187}Os in these samples, the spike was designed with a factor of 10 less ^{190}Os than ^{188}Os , resulting in a better-determined $^{190}\text{Os}/^{192}\text{Os}$ of the mixture (i.e., closer to unity). Finally, the ^{188}Os and ^{190}Os in the spike–sample mixture are overwhelmingly provided by the spike. This provides us the basis to determine the magnitude of mass fractionation during measurement.

Os analysis of highly radiogenic samples using a double spike is much more straightforward than is the

case for Pb analysis, where the isotopic composition of the sample is not known a priori. In practical terms, we know the composition of our samples: although we must assume an initial composition for the common Os, the bulk of the Os in the samples we are concerned with is radiogenic ^{187}Os .

2.2. Chemical preparation

Enriched ^{188}Os and ^{190}Os were obtained from Oak Ridge National Laboratory (ORNL). Aliquots of these powders (about 50 mg ^{188}Os and 6 mg ^{190}Os) were weighed into a zirconium crucible along with 2 g NaOH. This was fused at 350, 375, and 400 °C for 20 min each. Two grams of Na_2O_2 were added to the crucible, and the mixture was fused at 550, 575, and 600 °C for 20 min each. Another 2 g Na_2O_2 were added, and the mixture was fused an additional 30 min at 650°. The products were allowed to cool overnight in a desiccator.

The fusion product was dissolved in ultra-pure H_2O , transferred to a 100 ml boiling flask, and acidified to roughly 5 N H_2SO_4 . A distillation apparatus was fitted to the boiling flask (Morgan and Walker, 1989), 5 ml 30% H_2O_2 were added, and the flask was heated gently to about 105 °C. Os was distilled from the H_2SO_4 solution and trapped in 35 ml of quartz-distilled 9 N HBr chilled in an ice bath. Distillation proceeded for about 2.5 h, changing the HBr trap periodically, until no further color change in the HBr was observed with further distillation. The HBr darkened on warming to room temperature, as OsO_4 converted to OsBr_6^{-2} . The OsBr_6^{-2} was converted to OsCl_6^{-2} by combining the traps and repeatedly ($3\times$) drying to a small volume after addition of 10 ml distilled 12 N HCl.

Upon cooling, the solution was transferred to a 100 ml volumetric flask and brought to 100 ml volume with 50 ml distilled 12 N HCl and the remainder ultra-pure H_2O . The calculated concentration of Os in this solution (referred to as MS-1) was $521\ \mu\text{g g}^{-1}$. A roughly 100-fold dilution was made and labeled MS-2.

3. Calibration of the double spike

The principles by which we calibrate the double spike were adapted from those developed for Pb

double spiking (Dodson, 1970; Hamelin et al., 1985; Powell et al., 1998). For the initial calibration of our spike, both the isotopic composition and the concentration were unknown. In this sense, with respect to the isotope dilution calculations it is appropriate to treat the Os standard as the tracer, and our double spike as the unknown sample. To simultaneously determine both the isotopic composition and the concentration of the double spike, it is necessary to perform two separate measurements: one for the pure unknown (double spike) and one for the mixture.

Preparation of the spike–standard mixtures followed routine methods for spike–sample equilibration by alkaline fusion and Os distillation (Morgan and Walker, 1989). Spike (MS-2) and standard (B₁-IA; $^{187}\text{Os}/^{188}\text{Os} = 0.17398$) were pipetted into Teflon vials and capped tightly, so that weights could be measured several times to ensure accuracy. This procedure also permitted mixing of spike and standard solutions prior to addition to the zirconium crucible and drying down. We note here that an experiment to prepare a simple spike–standard mixture by carefully weighing and mixing the two solutions, without subsequent alkaline fusion, produced inconsistent and erratic isotopic ratios. This result reconfirms the importance of isotopic equilibration by extreme oxidation to obtain reliable results in isotope dilution studies of Os.

After alkaline fusion and Os distillation, isotope ratios were measured by NTIMS under similar operating conditions for the standard, the double spike, and the spike–standard mixture. The samples were loaded onto outgassed single filaments of zone-refined Pt ribbon, previously cleaned in HNO₃. Filaments with the double spike were loaded into a VG Sector 54 multicollector instrument and measurements were taken in static mode on faraday cup collectors at the University of Maryland. Measurements of the spike–standard mixtures were collected on NBS Shields-type single collector mass spectrometers at Colorado State University. Osmium was measured as OsO₃⁻. The oxygen isotope correction was based on the abundances reported by Nier (1950). Blocks were trimmed for outliers ($\pm 3\sigma$) before summary statistics were calculated.

Three filaments of double spike were analyzed, and the raw data were pooled. The composition of our Os isotopic standard is known from multiple previous measurements. The data for the Os standard are

corrected for fractionation on-line to $^{192}\text{Os}/^{188}\text{Os} = 3.08271$ (Luck and Allègre, 1983).

The calculations necessary to obtain the concentration and true isotopic composition of the double spike follow the approach outlined by Hamelin et al. (1985). For osmium, however, we consider five isotopic ratios and solve the equations by least squares approximation. Errors are obtained by Monte Carlo methods. This is described in more detail in Appendix A. The results of the spike calibration are shown in Table 1.

3.1. Secondary calibrations

The stock solution MS-2 was used along with our Re spikes to create a series of mixed Re-double Os spikes with Re/Os ratios suitable for analysis of highly radiogenic samples of a variety of ages. Spike–standard mixtures were created in the manner described above, and equilibrated in Carius tubes (Shirey and Walker, 1995). The Os was separated by solvent extraction into CCl₄ (Cohen and Waters, 1996) and purified by microdistillation (Birck et al., 1997), and

Table 1
Results of the spike calibration for the double Os spike MS-2 (see Appendix A)

		Corrected ratio	Weighted average
$^{186}\text{Os}/^{188}\text{Os}$	X-1	0.001267 ± 0.000094	
	X-2	0.001265 ± 0.000094	
	X-3	0.001266 ± 0.000094	0.00127 ± 0.00011
$^{187}\text{Os}/^{188}\text{Os}$	X-1	0.0012496 ± 0.0000052	
	X-2	0.0012488 ± 0.0000052	
	X-3	0.0012491 ± 0.0000052	0.0012492 ± 0.0000059
$^{189}\text{Os}/^{188}\text{Os}$	X-1	0.0280092 ± 0.0000083	
	X-2	0.0280262 ± 0.0000083	
	X-3	0.0280194 ± 0.0000083	0.0280182 ± 0.0000093
$^{190}\text{Os}/^{188}\text{Os}$	X-1	0.131659 ± 0.000059	
	X-2	0.131819 ± 0.000059	
	X-3	0.131755 ± 0.000059	0.13174 ± 0.00020
$^{192}\text{Os}/^{188}\text{Os}$	X-1	0.012288 ± 0.000014	
	X-2	0.012318 ± 0.000014	
	X-3	0.012306 ± 0.000014	0.012304 ± 0.000016
		Atomic weight	188.2432 ± 0.0002
		Concentration (weighted average)	4749.8 ± 3.3 ng/g

the Re was recovered by ion exchange chromatography (Morgan et al., 1991; Markey et al., 1998), following standard procedures. Isotope data were collected on the NBS mass spectrometers at CSU.

There are two ways to approach the data collection and reduction for the calibration of these dilutions. We can of course apply the matrix solution method described in Appendix A. Alternatively, with the isotopic composition of the spike now known, we can use a more conventional approach and apply a fractionation correction directly to each scan of the measurement: the so-called “on-line” fractionation correction. The matrix solution effectively calculates a fractionation factor for the entire block, whereas the fractionation factor almost certainly varies over the course of the measurement. The on-line correction calculates and applies a fractionation factor for each scan; consequently the correction is applied with a finer resolution using the on-line method. In addition, error calculations are much simpler using this approach to data reduction. The on-line method was therefore used for these secondary calibrations. Three replicates of each mixed Re-double Os spike calibration were made, and the weighted mean Re and Os content of the three replicates were taken as the values for each spike.

Dilutions of these mixed spike solutions were then made to match samples of various Re contents for each age range. Concentrations of Re and Os in the dilutions were calculated based on the gravimetric data for each dilution. We consider it unnecessary to repeat the calibration for each dilution since it is unlikely that the Re/Os ratio of the solution changes during dilution, and it is essentially the Re/Os ratio for the spike that determines the age of the sample.

4. Sample analyses

Samples run using the mixed Re-double Os spike were processed using Carius tube digestion with Os separation either by solvent extraction or by a small-scale distillation directly from the Carius tube, using 9 N HBr as a trap. In either case, Re was separated from the residuum by ion exchange chromatography, and the Os was further purified by microdistillation. All isotopic measurements were made by NTIMS on two NBS mass spectrometers housed at AIRIE. Os-isotope

ratios were corrected on-line for mass fractionation using $^{190}\text{Os}/^{188}\text{Os}=0.13174$, after subtraction of preliminary “total common Os” (explained below) contributions to the peaks for ^{190}Os and ^{188}Os .

By “total common Os”, we refer to the combination of common Os from the sample plus Os from the analytical blank. For highly radiogenic minerals, common Os is by definition very low. In addition, sample sizes used for these samples can be quite small. Therefore, contributions to the common Os from the blank can be significant. Because the isotopic composition of the blank is different from that of the sample, we compute a combined isotopic composition for the total common Os for use in correcting the measured peaks and subsequent ID computations from the final ratios. This is carried out on-line, before any corrections to peaks and calculation of ratios.

We must of course know or assume the initial $^{187}\text{Os}/^{188}\text{Os}$ for the sample. We must also know the amount and composition of our blank. Finally, we must begin by making an estimate of the amount of common Os in the sample. We can then calculate a first-pass composition of the combined common+blank Os. With this we obtain a revised, blank-corrected concentration for common Os in the sample. After three iterations of this process, the computed common Os is essentially constant, regardless of the original estimate of common Os. The combined composition is recalculated, and it is this composition that is used for correcting the peaks for the fractionation correction and for subsequent ID determinations.

Re and common Os concentrations are calculated according to the basic ID equation

$$\text{smpl} = N_t \frac{(t - m) \sum W_x t_{xj}}{(m - d) \sum W_x d_{xj}} \quad (1)$$

where *smpl* is the amount in ng from the sample (plus blank); N_t is the amount in ng of the spike element; *t*, *m*, and *d* are the ratios in the spike, mixture and natural element, respectively; and the terms $\sum W_x t_{xj}$ and $\sum W_x d_{xj}$ represent the mass of isotope *x* times its ratio to the reference isotope *j*, summed over all isotopes of the element, for the spike and natural compositions, respectively (Crouch and Webster, 1963). These latter terms are effectively the atomic weights divided by the fractional abundance of the

Table 2

Natural abundances of Re and Os isotopes (Gramlich et al., 1973; Luck and Allègre, 1983). Other terms are defined in the text

Isotope	Mass	Abundance	$d_{x/187}$	$W_x d_{x/187}$		
¹⁸⁵ Re	184.953	0.374	0.59739	110.490		
¹⁸⁷ Re	186.956	0.626	1	186.956		
	Atwt	186.207	$\Sigma W_x d_{xi}$	297.445		
Isotope	Mass	Abundance ^a	$d_{x/188}$	$W_x d_{x/188}$	$d_{x/192}$	$W_x d_{x/192}$
¹⁸⁴ Os	183.953	0.0002	0.00150	0.275930	0.00049	0.089509
¹⁸⁶ Os	185.954	0.0158	0.11880	22.091335	0.03854	7.166206
¹⁸⁷ Os	186.956	0.0160	0.12 ^a	22.434720	0.03893	7.277597
¹⁸⁸ Os	187.956	0.133	1	187.956000	0.32439	60.97103
¹⁸⁹ Os	188.958	0.161	1.21053	228.739328	0.39268	74.20073
¹⁹⁰ Os	189.958	0.264	1.98496	377.059032	0.64390	122.3141
¹⁹² Os	191.961	0.410	3.08271	591.760094	1	191.961
	Atwt	190.240	$\Sigma W_x d_{x/188}$	1430.3164	$\Sigma W_x d_{x/192}$	463.9802

^a These abundances are based on an assumed ¹⁸⁷Os/¹⁸⁸Os of 0.12. Changing this ratio to reflect a different initial composition (for example) will of course change all abundances, though it will not change any other ratio.

reference isotopes, which allows us to work with isotope ratios rather than abundances as a matter of convenience. The ratio m is calculated from peaks *not* corrected for total common Os contributions. We use data in Table 2 for the natural compositions for sample analyses. It is necessary to assume a value for the common or initial ¹⁸⁷Os/¹⁸⁸Os in the sample before calculating the atomic weight and related terms for Os. As stated above, we compute a combined common Os + blank composition for Os ID calculations. For Re, we use ¹⁸⁷Re as the reference isotope; for common Os calculations, we use ¹⁹²Os.

Re blanks are treated in the conventional way; that is, they are subtracted in bulk from the sample amount (Eq. (1)) before dividing by the sample weight to get the concentration. For common Os, blank can be subtracted from the ID result on an isotope-by-isotope basis to arrive at the corrected concentration and composition. In practical terms, the blank-corrected composition of common Os must of course be the original assumed initial. It is also the case that simply subtracting the blank in bulk from the ID result will give the corrected sample common Os concentration.

Blanks in our molybdenite lab have been variable, depending on the chemical procedure used. Carius tube digestion plus solvent extraction with CCl₄ gave blanks of 20 ± 5 pg for Re, and 5 ± 2 pg with a

¹⁸⁷Os/¹⁸⁸Os of 1.8 ± 1.8 for Os. We now separate Os by distillation directly from the Carius tubes in a manner similar to that described by Brauns (2001), except that we trap the Os in 5 ml chilled HBr. This method yields blanks of 5 ± 3 pg for Re and 3.2 ± 0.6 pg with a ¹⁸⁷Os/¹⁸⁸Os of 1.5 ± 0.9 for Os in our high-level lab.

To calculate ¹⁸⁷Os concentrations we use an isotope dilution equation that accounts for common Os contributions to all masses, using the calculated total common Os composition. As for all isotope dilution equations, the derivation begins with the basic relationship

$$m_{187/188} = \frac{z_{187}^r + z_{187}^t + z_{187}^c}{z_{188}^t + z_{188}^c} \quad (2)$$

where the superscripts r , t , and c refer to the radiogenic, spike, and total common Os components of the mixture. This differs from typical isotope dilution equations (e.g., Eq. (6) in Appendix A) in the addition of the third term in the numerator for the radiogenic component of the ¹⁸⁷Os; therefore the total common ¹⁸⁷Os component refers only to the amount contributed by the combined initial Os plus blank Os. Because

$$z_i^t = \frac{N_t t_{ij}}{\sum W_i t_{ij}}, \quad z_i^c = \frac{N_c c_{ij}}{\sum W_i c_{ij}}, \quad \text{and} \quad z_{187}^r = \frac{N_r}{W_{187}} \quad (3)$$

where N is the amount in nanograms of the subscripted component, we can substitute Eqs. (3) and (1) into Eq. (2) and rearrange to obtain

$$\begin{aligned}
 N_r = & \frac{N_t W_{187}}{\text{splwt}} \\
 & \times \left(\frac{1}{\sum W_i t_{i/188}} (m_{187/188} - t_{187/188}) \right) \\
 & + \frac{\sum W_i c_{i/192}}{\sum W_i c_{i/188} \sum W_i t_{i/192}} \\
 & \times \frac{(m_{190/192} - t_{190/192})}{(c_{190/192} - m_{190/192})} \\
 & \times (m_{198/188} - c_{187/188}) \quad (4)
 \end{aligned}$$

There is no need to blank-correct the radiogenic Os because blank is effectively accounted for in the total common Os composition. Errors on sample analyses are computed using a first-order Taylor series expansion of the isotope dilution and age equations (Taylor and Kuyatt, 1994). The errors on all isotope ratio measurements, spike calibrations, and error magnifiers for Re and common Os (Heumann, 1988) are included. Sample and spike weighing errors are not included in

the concentration error calculations because these cancel out for the determination of the error on the age. Finally, there is no error magnifier for radiogenic ^{187}Os because it is mono-isotopic.

5. Results and discussion

A comparison of results between the single-spike and double-spike method is instructive. For the past few years we have used the Archean molybdenite A996B from Aittöjärvi, Finland as one of our in-house standards (Fig. 2). Seventeen replicates using separate ^{185}Re and ^{190}Os spikes yield a mean age of 2804 ± 4 Ma (0.14%, 1 S.D.). Using the mixed Re-double Os spike, six replicates yield 2797 ± 2 Ma (0.079%, 1 S.D.). [We note that we have previously published a result of 2809 Ma for A996B ($n=9$) using the ^{190}Os spike (Markey et al., 1999). The mean of 2804 Ma reported here represents the addition of several new analyses and a recalculation of all ^{190}Os -spike results using the same isotopic composition for the standard as the double spike analyses reported here.]

It is tempting to attribute the difference in age between the two methods entirely to the fractionation effect. The fractionation effect is diminished by a

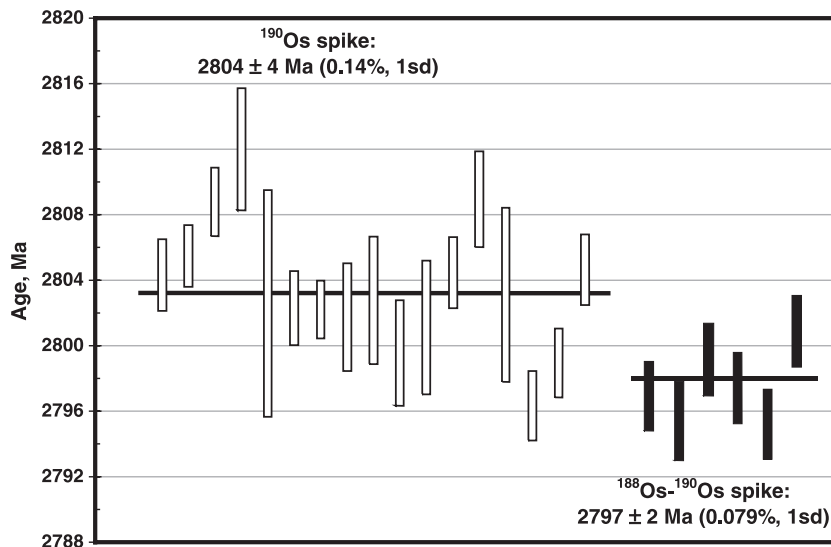


Fig. 2. Replicates of the in-house standard A996B using both the single spike and double spike methods. Summary statistics are the arithmetic mean and standard deviations for the replicates, to illustrate the repeatability of the method. Errors on each analysis do not include error on the decay constant. Differences in age and reproducibility between the two methods are discussed in the text.

factor of three simply by spiking with ^{188}Os rather than ^{190}Os . Including the fractionation correction in our data reduction makes an additional adjustment to the data, but also has the unintended effect of introducing a new component of error, in some cases. For example, when we remove the on-line fractionation correction from the data reduction, the six analyses of A996B cited above yield a mean age of $2798.1 \pm 0.06\%$. This is because the uncertainty on the spike $^{190}\text{Os}/^{188}\text{Os}$ (the ratio to which we fractionation correct on the spike–sample measurements) is sometimes greater than the fractionation effect for Faraday cup measurements, which average 0.05% per AMU for these analyses. For example, the measured $^{190}\text{Os}/^{188}\text{Os}$ for run MD-1 of A996B is 0.13179, within error of the spike ratio of 0.13174 ± 0.00020 (Table 1). It is unlikely, therefore, that mass fractionation alone is responsible for the slight difference in age between the single-spike and double-spike methods.

To better compare the two methods, we recalculated our double-spike analyses to yield radiogenic $^{187}\text{Os}_r$ concentrations based on the ratio $^{187}\text{Os}/^{190}\text{Os}$ without a fractionation correction, as is used in single-spike analyses. The results of the two methods of data reduction are plotted in Fig. 3, where they are also compared with true single spike analyses. The weight-

ed average age (not including error on the decay constant) for the six replicates recalculated in this way is 2799.4 ± 2.6 Ma. This is within error of the weighted average of all 17 single spike runs of 2803.3 ± 1.9 Ma (we use the weighted average here to represent our best estimate of the actual age, whereas we use the arithmetic mean and standard deviation to give a measure of repeatability of replicates, e.g., Fig. 2). The major component of the uncertainty in these analyses is the error on the spike calibrations, so although we emphasize that the two sets of analyses are indistinguishable within error, we conclude that a major portion of the difference in age is due to the difference in the spike calibrations. Further differences are due to the decrease in the effect of mass fractionation, due to both the decrease in δ_m associated with spiking with ^{188}Os rather than ^{190}Os , and the fractionation correction itself.

Another set of double spike replicates of a Proterozoic sample also dated repeatedly in our labs by the single spike method is presented in Table 3. Once again we see excellent reproducibility for the double spike runs. For the Archean–Proterozoic samples, the age is relatively insensitive to either blank or assumed initial ratio of the common Os. The improved reproducibility in ages can probably be attributed to using a

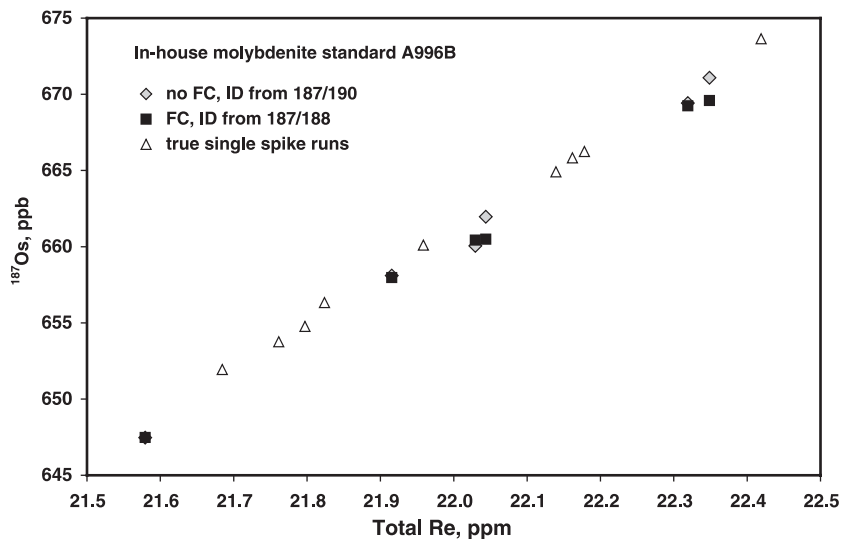


Fig. 3. Six replicates of A996B spiked with the double spike, calculated two ways. Also shown for reference are those true single spike analyses that fall within the same range in Re concentrations (open symbols). The grey symbols are calculated in the same manner as single spike runs; that is, the $^{187}\text{Os}_r$ concentrations are based on $^{187}\text{Os}/^{190}\text{Os}$, with no fractionation correction applied. The black symbols are based on $^{187}\text{Os}/^{188}\text{Os}$, with a fractionation correction.

Table 3
Replicates of two molybdenites using the double-spike method.
Errors on individual runs are at the 2σ level

Sample (run #)	Re, ppm (2σ)	$^{187}\text{Os}_r$, ppb (2σ)	Common Os, ppb (2σ)	Age, Ma (2σ)
<i>B-25</i>				
Single spike runs (mean, 1 S.D., $n=8$)	38.0 (4)	744 (10)	0.4 (3)	1842 (5)
Double spike:				
MD-5	37.88 (3)	739.8 (4)	0.1 (3.6)	1837 (2)
MD-6	38.69 (3)	756.5 (4)	0.1 (2.2)	1839 (2)
MD-9	37.35 (2)	729.6 (2)	0.0 (6.9)	1837 (2)
<i>CH02-LP13</i>				
MD-23	303.4 (2)	36.59 (7)	0.5 (1)	11.516 (25)
MD-24	312.7 (2)	37.71 (6)	0.43 (9)	11.519 (21)
MD-28	396.0 (2)	35.68 (6)	0.38 (9)	11.513 (22)
Weighted average			0.4 (1)	11.516 (12)
Blanks: Re = 5 ± 3 pg; Os = 3.2 ± 0.6 pg with $^{187}\text{Os}/^{188}\text{Os} = 1.5 \pm 0.9$. Assumed initial ratio for common Os = 1.5 ± 1.0 .				

mixed Re–Os spike as well as to the reduction or elimination of the fractionation effect due to using the ^{188}Os – ^{190}Os for Os. From run-to-run, the Re–Os ratio of the mixed Re–Os spike is invariant, whereas using individual Re and Os spikes the Re–Os ratio is subject to weighing errors for the separate spike solutions.

A major benefit of the double Os spike is the improved ability to analyze low-Re and young samples using the electron multiplier as the ion detector. A set of three replicates was made of the Chilean molybdenite CH02-LP13 from Los Pelambres (Table 3). Os measurements were made using the electron multiplier, and a fractionation correction was applied. Errors on each individual age for these young samples are on the order of 0.2%, not including error on the ^{187}Re decay constant. These errors primarily reflect the uncertainty in our Os blank, our estimate of the assumed initial ratio for the common Os, and the precision on the measured $^{190}\text{Os}/^{192}\text{Os}$, which is the least well-measured of all the ratios because of the small peak size for ^{192}Os . If the error on the decay constant is included (Smoliar et al., 1996), that error overwhelms the analytical uncertainty and controls the final reported error on the age. The weighted average for these replicates yields a best estimate for the age of this sample at 11.516 ± 0.012 Ma (0.11%).

These results demonstrate that use of the double Os spike provides for precise, reproducible age determinations on young molybdenites.

The double ^{188}Os – ^{190}Os spike was also designed to make possible a more precise measurement of common Os in the sample. Table 3 shows calculated common Os contents. As for single spike analyses, it is still necessary to assume an isotopic composition for the common Os (i.e., the initial $^{187}\text{Os}/^{188}\text{Os}$). It is clear from the our double spike data that common Os measurements are difficult for older molybdenites, as is also the case for the single ^{190}Os spike. If an old sample is spiked appropriately for its ^{187}Os content, then the mixture is grossly over-spiked for its common Os content. The result is that the measured $^{190}\text{Os}/^{192}\text{Os}$ is very close to the spike value, and the isotope dilution error magnifier is very high (Heumann, 1988). Fortunately, knowledge of the common Os content in these samples is not critical to calculation of the ^{187}Os content and age.

For younger samples and those with low Re contents, however, our ability to measure common Os is somewhat improved. The lower ^{187}Os content of these samples allows for more appropriate spiking for common Os. For the Chilean sample in Table 3, for example, error on the common Os concentration is in the range of 25%. Once again, this error is controlled by our knowledge of the Os blank and our assumed initial isotopic composition for the common Os. From the three replicates, we obtain a weighted average of 0.43 ± 0.14 ppb. We see with a reasonable degree of certainty, therefore, that at least some molybdenites may contain a determinable amount of common Os, but this is an important consideration only when analyzing young samples or samples with very low Re contents.

6. Conclusions

The ^{188}Os – ^{190}Os double spike is a convenient and useful means for Os isotopic analyses in molybdenites. It is an improvement over the ^{190}Os single spike method because it provides a means for fractionation correction to the isotopic measurements. Indeed, the fractionation effect is reduced by a factor of three when using ^{188}Os as the reference isotope rather than ^{190}Os . The ^{186}Os – ^{188}Os spike of Qu et al. (2001) provides similar benefits. The utility of our ^{188}Os – ^{190}Os double spike is greatest for samples with low concentrations

of ^{187}Os (i.e., young samples and/or those with very low Re contents). For these samples, accurate determination of the common Os concentration and its isotopic composition will influence calculated Re–Os ages. Spiking with natural Os or with a ^{186}Os – ^{188}Os spike will not address common Os in molybdenite and mass fractionation effects as well as a ^{188}Os – ^{190}Os double Os spike.

From a practical standpoint, the precision on the age and common Os content for young samples will be improved by decreasing the magnitude and the error on Os analytical blanks. We also note that mass fractionation in the Re measurements is not addressed by NTIMS; the use of a separate element (e.g., Ir) and MC-ICP-MS has been explored as a solution to this issue (Pearson et al., 2002). The double-Os spike described in this paper could be improved in two ways. First, the error magnifier for common Os could be reduced if the spike could be constructed from purer ^{188}Os and ^{190}Os powders. This would increase the final $^{190}\text{Os}/^{192}\text{Os}$ of the spike and broaden the range of acceptable spike–sample ratios. Second, it is theoretically preferable to use a ^{186}Os – ^{190}Os combination, since this would provide for a more precise fractionation correction, based on $\delta_m=4$ rather than $\delta_m=2$, while not compromising any of the other functions of the spike.

Acknowledgements

We are deeply grateful to Phil Chapman and Richard McNally of the Franklin A. Graybill Statistical Laboratory at CSU for advice and SAS programming for error propagation for the least squares regression. We are responsible for any inaccuracy in other aspects of the statistics presented. We thank Richard Walker for isotopic measurements made at UMD. Thanks also to Anders Scherstén for helpful discussions. The comments of Stephen Galer and two anonymous reviewers improved the manuscript. This work was supported by NSF grant EAR-0087483 to HJS. [RR]

Appendix A. Data reduction for spike calibration

Dodson (1970) reports a simple method for the simultaneous solution of the double spike equations by

substitution and back-calculation. The matrix approach of Hamelin et al. (1985) gives identical results and includes a method for propagation of errors. In both cases, a first order (linear) fractionation effect is assumed. For the present study, we too assume a linear fractionation law. This greatly simplifies the equations, and is likely to give the same result as would use of an exponential law, for example, in all except the most extremely fractionated cases (Wasserburg et al., 1981; Galer, 1999). Measurements of our standard have an average fractionation factor of 0.06% per AMU, certainly within the range where this approximation is valid (Galer, 1999).

Two mass spectrometer runs are necessary to obtain the true (fractionation-corrected) isotopic composition of our spike and determine its concentration. The “composition run” (U) represents measurements of pure spike (the unknown); the “concentration run” (M) represents measurements of the mixture of spike plus standard. There will be $i=n-1$ ratios in each run, where n is the number of isotopes measured. The lower case letter t will be used to refer to the standard, which for the purposes of spike calibration is effectively the tracer. The true values for the ratios t_i are assumed to be known. To fully solve the following equations, a minimum of three ratios (four isotopes) is required. Since five ratios are in fact available for Os measurements, we have a set of five equations in three unknowns, which will be solved by least squares approximation.

For development of the mathematical treatment of the data used here, we follow the notation and general approach of Hamelin et al. (1985). The linear fractionation law applies to both runs, each run having its own fractionation factor ε

$$u_i = U_i(1 + \varepsilon_u \delta m_i); \quad m_i = M_i(1 + \varepsilon_m \delta m_i) \quad (5)$$

where u_i and m_i are the true values of the ratios in the spike and mixture, respectively, and δm_i is the mass difference between the isotopes in the ratio.

By definition,

$$m_i = \frac{z_u^i + z_t^i}{z_u^j + z_t^j} \quad (6)$$

where m_i is the ratio of isotope i to the reference isotope j in the mixture, and z represents the contribution of the isotopes from the spike (u) and standard

(*t*). Following Compston and Oversby (1969), Eq. (6) can be rearranged to give the useful quantity q :

$$q = \frac{z_i^j}{z_u^j} = \frac{u_i - m_i}{m_i - t_i} \quad (7)$$

The quantity q describes the mixture in terms of the ratio of the reference isotope from the tracer to that from the spike. For the isotope-dilution determination of the concentration of the spike, it would be theoretically more convenient to use the inverse of q as defined above (for example $Q = z_u^j/z_i^j$; Compston and Oversby, 1969); however, the matrix solution to the current problem is more elegant if we solve for q and invert afterward. Thus, in terms of q , we have

$$m_i = \frac{u_i + t_i q}{1 + q}. \quad (8)$$

Combining Eq. (5) with Eq. (8) results in the system of linear equations

$$q(M_i + t_i) + (1 + q)\varepsilon_m \delta m_i M_i - U_i \delta m_i \varepsilon_u = U_i - M_i \quad (9)$$

arranged in such a way as to produce a set of equations in three unknowns (namely, q , ε_m and ε_u ; Hamelin et al., 1985). Any three equations could be used to obtain a unique solution. For Os, however, five equations are available that can be solved simultaneously by least squares approximation of the following matrix expression:

$$\begin{bmatrix} M_1 - t_1 & \delta m_1 M_1 & -\delta m_1 U_1 \\ M_2 - t_2 & \delta m_2 M_2 & -\delta m_2 U_2 \\ M_3 - t_3 & \delta m_3 M_3 & -\delta m_3 U_3 \\ M_4 - t_4 & \delta m_4 M_4 & -\delta m_4 U_4 \\ M_5 - t_5 & \delta m_5 M_5 & -\delta m_5 U_5 \end{bmatrix} \begin{bmatrix} q \\ \varepsilon_m \\ \varepsilon_u \end{bmatrix} = \begin{bmatrix} U_1 - M_1 \\ U_2 - M_2 \\ U_3 - M_3 \\ U_4 - M_4 \\ U_5 - M_5 \end{bmatrix}, \quad (10)$$

or

$$\mathbf{AB} = \mathbf{D}.$$

In Eq. (10), the subscripts 1–5 refer to different ratios of each measurement, namely $^{186}\text{Os}/^{188}\text{Os}$, $^{187}\text{Os}/^{188}\text{Os}$, $^{189}\text{Os}/^{188}\text{Os}$, $^{190}\text{Os}/^{188}\text{Os}$ and $^{192}\text{Os}/^{188}\text{Os}$; and $r = (1 + q)\varepsilon_m$. We may solve for the vector \mathbf{B} using the least squares approximation

$$\mathbf{B} = (\mathbf{A}^T \mathbf{A})^{-1} \mathbf{A}^T \mathbf{D} \quad (11)$$

The errors on the quantities in \mathbf{B} are obtained by Monte Carlo simulation. The covariance matrices for each set of measurements are obtained conventionally from the output of the mass spectrometer runs (c.f. Powell et al., 1998). These covariance matrices are used with a set of random numbers from the standard normal distribution to simulate 2000 replicates of these measurements, and subsequently calculate 2000 simulated replicates of \mathbf{B} . From these simulated replicates we then calculate the standard errors for q and ε_u (we are not interested in ε_m for the present purposes). This method is far simpler than a Taylor expansion of Eq. (10) and furthermore avoids making any assumption of linearity in the relationships between the dependent and independent variables. The simulation was carried out with a program written in the statistical software package SAS. The final errors on the corrected ratios u_i are calculated using the relationship

$$\sigma_i^2 = (T\delta m)^2 \sigma_{\varepsilon_u}^2 + (1 + \delta m \varepsilon_u)^2 \sigma_T^2, \quad (12)$$

where σ_i^2 , $\sigma_{\varepsilon_u}^2$, and σ_T^2 are the variances of the corrected ratio, the fractionation factor, and the measured ratio, respectively. Eq. (12) is simply an application of the law of propagation of error (Taylor and Kuyatt, 1994) to Eq. (5).

A separate fractionation factor ε_u was obtained from each of the mixtures. The pooled measurements U_i were corrected with each of these fractionation factors as separate replicates. A weighted average of the three replicates of each ratio was calculated and together the set of weighted averages represents our best knowledge of the true isotopic composition of the double spike.

The concentration of the double spike was then calculated from q , using the usual isotope dilution equation and the isotopic composition determined above. The errors on each replicate are based principally on the error on q . Again, a weighted mean represents our best knowledge of the concentration of the double Os spike MS-2. We note that the q that characterizes the spike–standard mixture is not a parameter of consequence for molybdenite analyses, therefore we are not concerned with the calculated spike concentration as a function of q . The main consideration for samples is the $^{178}\text{Os}/^{188}\text{Os}$ ratio, where the numerator is heavily dominated by sample and the denominator is heavily dominated by spike.

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