Determinations of osmium isotope ratios in iron meteorites and iridosmines by ICP-MS

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Osmium isotopes in three Os reagents, four terrestrial Os-Ir alloys (iridosmine) and two iron meteorites have been measured on an inductively coupled plasma mass spectrometer (ICP-MS), with the precision of around 1% for $^{187}\text{Os}/^{192}\text{Os}$.

Comparisons are made of our isotopic ratios with the previous ones. Apart from the variation of ^{187}Os abundance as naturally expected, there seems to be a slight systematic deviation for ^{189}Os . Also some discussions are given to ^{184}Os .

The Os isotopic ratios for three iridosmine samples from Hokkaido, Japan, have been found quite similar to each other. The values for the Hokkaido iridosmines are 3-4% higher relative to the straight ^{187}Os growth line obtained by Allegre and Luck (1980). Finally, the isotopic "standard" abundances (%) for Os are presented by us: ^{184}Os , 0.019; ^{186}Os , 1.589; ^{187}Os , 1.519; ^{188}Os , 13.24; ^{189}Os , 16.37; ^{190}Os , 26.30; ^{192}Os , 40.96. These give us the Os atomic weight = 190.24.

INTRODUCTION

Herr *et al.* (1961) started Re-Os cosmochronology on the basis of the β^- decay of ^{187}Re , but the difficulty in Os isotope measurements prevented the popular use of this method. Recent developments in a variety of mass spectrometry have allowed us easier access to Os isotope measurements. Luck *et al.* (1980) and Allegre and Luck (1980) established Os isotope measurements with secondary ion mass spectrometer (SIMS) and reported Re-Os age for meteorites. Since these works, geochemical and cosmochemical studies on Re-Os systematics have proceeded on the basis of Os isotope data obtained by SIMS (Luck and Allegre, 1982, 1983, 1984; Luck and Turekian, 1983; Palmer and Turekian, 1986). Luck and Allegre (1983) reported the half life value of $(4.56 \pm 0.12) \times 10^{10}\text{y}$ based on the meteoritic isochron. On the other hand, Lindner *et al.* (1986) measured Os isotope ratios in HReO_4 by two different types of mass spectrometers, an inductively coupled plasma mass spectrometer (ICP-MS) and a laser microprobe mass analyzer (LAMMA). They

determined the ^{187}Re half-life $((4.35 \pm 0.13) \times 10^{10}\text{y})$ with these measurements. The half life of ^{187}Re is similar to that of ^{87}Rb $(4.88 \times 10^{10}\text{y})$. Further, Os isotope measurements by accelerator mass spectrometer have been reported on meteoritic and terrestrial samples (Teng *et al.*, 1986).

Re and Os are siderophile or chalcophile elements. Further, it has been pointed out that Re/Os ratio has a large fractionation factor during continental crust/mantle fractionation. These geochemical features indicate the importance of Re-Os systematics as an isotope tracer and geo- and cosmo-chronometer. Thus, it can be said that the recent developments in mass spectrometry are strongly promoting the further progress of the Re-Os method.

In this paper, we will report Os isotope ratios in iron meteorites and iridosmines as well as Os reagents measured by ICP-MS. ICP-MS uses inductively coupled plasma (ICP) as an atmospheric ion source for a quadrupole mass spectrometer (Gray, 1975, 1985; Gray and Date, 1983; Houk *et al.*, 1980). The most preliminary work of ours was presented at the 1985

Annual Meeting of the Geochemical Society of Japan.

SAMPLES AND EXPERIMENTAL METHOD

Osmium tetroxide (OsO_4) reagents prepared by Strem Chemicals Inc., E. Merck Co. Inc. and Nakarai Chemicals Ltd. were used for our examination. Os isotopes in these reagents were measured for 1 ppm Os solution (1% HNO_3 solution). Besides, Os isotopes were measured on two iron meteorites, Canyon Diablo and Tlacotepec. The iron meteorites were decomposed by aqua regia (1:3 mixture of HNO_3 and HCl) at 80–100°C. In the decomposition process, Os was oxidized to volatile OsO_4 . The evaporated OsO_4 was trapped with distilled water. The trapped OsO_4 solution was free from Pt, W and Re. Four iridosmine samples were also studied for Os isotope ratios; three samples are from Hokkaido, Japan and another is from the Urals, USSR. Iridosmine is a terrestrial Os-Ir alloy. Iridosmine samples were decomposed by sodium peroxide (Na_2O_2) in a zirconium crucible. After decomposition, Os concentration of each sample solution was adjusted to about 1 ppm. We have confirmed that $(\text{Zr}_2)^+$ ions do not appear, but very weak Zr^+ ions are recognized in such a product. If $(\text{Zr}_2)^+$ appear, they

affect Os^+ mass spectrometry.

ICP-MS used in this study was VG Isotopes PlasmaQuad. Sample solution of 1% HNO_3 was introduced to ICP-MS through the nebulizer. All of Os isotopes were measured; 184, 186, 187, 188, 189, 190 and 192. ^{192}Os was used as a reference isotope in this study. Os isotopic abundance obtained by Nier (1937) was used for correction of mass discrimination, which is currently inevitable as shown later. The mass discrimination as observed in ICP-MS rests mostly on the temperature of RF/DC generator of quadrupole mass spectrometer and on the condition of electrode bias supplied to the ion lens system. Generally, for the quadrupole mass spectrometer like this, the mass discrimination effect is inevitable and is not a strictly linear function with the mass number. However, for the rather short mass range dealt with here and within the precision under consideration, one can assume the mass discrimination effect as a linear function with the mass number.

RESULTS AND DISCUSSION

Os reagent

Figure 1 shows two examples of Os isotopic measurement for Strem Os reagent. Ordinate in

Fig. 1. Mass discrimination factor relative to Os isotope ratios of Nier (1937), employing ^{192}Os as a "reference" nuclide.

Fig. 1 refers to ratios of $^m\text{Os}/^{192}\text{Os}$ ($m = 184, 186, 187, 188, 190$ and 192) divided by the corresponding Os isotope ratios obtained by Nier (1937). Three points of $^{186}\text{Os}/^{192}\text{Os}$, $^{188}\text{Os}/^{192}\text{Os}$ and $^{190}\text{Os}/^{192}\text{Os}$ fall close to a straight line and a point of $^{189}\text{Os}/^{192}\text{Os}$ appears to deviate from this line to a certain extent. This can be understood as implying that ^{189}Os isotopic abundance obtained here differs from that by Nier.

Correction factors of mass discrimination for each isotope can be obtained from the straight line drawn by a least-squares method with respect to points of $^{186}\text{Os}/^{192}\text{Os}$, $^{188}\text{Os}/^{192}\text{Os}$ and $^{190}\text{Os}/^{192}\text{Os}$ as shown in Fig. 1. When dividing the actually observed ratios by the correction factors mathematically given by the least-square line, one can obtain the corrected ratios. Figure 2 shows $^{187}\text{Os}/^{192}\text{Os}$ and $^{186}\text{Os}/^{192}\text{Os}$ ratios thus corrected, for Strem OsO_4 reagent during this work. In this diagram, the precision of $^{187}\text{Os}/^{192}\text{Os}$ is about 0.4% ($2\sigma_m$). From Fig. 2, it can be seen that the precision for $^{187}\text{Os}/^{192}\text{Os}$ is much worse than that for $^{186}\text{Os}/^{192}\text{Os}$. This is due to a memory effect, because, while measuring the Strem Os reagent, we measured intermittently other two reagents having different $^{187}\text{Os}/^{192}\text{Os}$ ratios from that of Strem. If more caution is taken against such an effect, better data will be obtained. Table 1 lists Os isotopic ratios against ^{192}Os

and Table 2 shows Os isotopic abundances. The Os isotopic data by Nier (1937) and Luck and Allegre (1983) are also presented in Tables 1 and 2. Figure 3 shows Os isotope data for Os reagents, corrected by mass discrimination factor as defined by the least-square line for $^{186}\text{Os}/^{192}\text{Os}$, $^{188}\text{Os}/^{192}\text{Os}$ and $^{190}\text{Os}/^{192}\text{Os}$. As shown in Fig. 3 and Table 1, our data for $^{186}\text{Os}/^{192}\text{Os}$, $^{188}\text{Os}/^{192}\text{Os}$ and $^{190}\text{Os}/^{192}\text{Os}$ agree well with those obtained by Nier (1937) and Luck and Allegre (1983). As for $^{189}\text{Os}/^{192}\text{Os}$ ratio, our value is close to that of Luck and Allegre, but it is 1.7% higher than that of Nier. Precision of $^{184}\text{Os}/^{192}\text{Os}$ ratio is worse than those for other Os isotope ratios, because of very low isotopic abundance of ^{184}Os . Anyhow, $^{184}\text{Os}/^{192}\text{Os}$ ratio obtained here is close to the value by Nier (1937), but $^{184}\text{Os}/^{192}\text{Os}$ value obtained by Luck and Allegre (1983) is about 20-40% higher than that obtained by Nier and in this study. It is noted here that ^{184}W is the major isotope (30.7%) in tungsten and ^{184}Os (0.018%) is subject to the interference by W. The data cited in Table 1, from the work by Luck and Allegre (1983) is for their Merck standard.

Specifically, in our measurements, any W^+ peaks have not been observed for Os reagents. However, when using the solutions simply prepared by dissolving the iridosmines from Nuppu River and Nizhni Tagil, we could recog-

Fig. 2. $^{187}\text{Os}/^{192}\text{Os}$ and $^{186}\text{Os}/^{192}\text{Os}$ ratios in repeated measurements of Strem Os reagent. Errors are $2\sigma_m$.

Table 1. Os isotope ratios against ^{192}Os for Os reagents, together with isotopic ratios by Nier (1937) and Luck and Allegre (1983)

	^{184}Os	^{186}Os	^{187}Os	^{188}Os	^{189}Os	^{190}Os
Strem	0.00042 ± 0.00002	0.03881 ± 0.00002	0.04862 ± 0.00022	0.3238 ± 0.0005	0.4002 ± 0.0005	0.6428 ± 0.0017
Nakarai	0.00050 ± 0.00010	0.0388 ± 0.0014	0.0463 ± 0.0010	0.3223 ± 0.0016	0.4002 ± 0.0028	0.6421 ± 0.0020
Merck	0.00045 ± 0.00008	0.0387 ± 0.0002	0.0371 ± 0.0010	0.3237 ± 0.0012	0.3992 ± 0.0038	0.6416 ± 0.0016
Average* (I)	0.00046 ± 0.00004	0.0388 ± 0.0001	—	0.3233 ± 0.0009	0.3998 ± 0.0006	0.6422 ± 0.0007
Average** (II)	0.00042 ± 0.00002	0.0388 ± 0.0001	—	0.3237 ± 0.0006	0.4000 ± 0.0002	0.6421 ± 0.0007
Nier	0.00049	0.0388	0.0393	0.3244	0.3927	0.6439
Luck & Allegre	0.00059 ± 0.00006	0.03904 ± 0.00002	0.03687 ± 0.00002	0.32439***	0.39679 ± 0.00011	0.64382 ± 0.00026

Errors are $2\sigma_m$.

* Average (I): arithmetical mean.

** Average (II): weighted mean, taking into account the statistical fluctuations in measurement.

*** Luck and Allegre (1983) used $^{192}\text{Os}/^{188}\text{Os} = 3.08271$ for normalization.

nize the W^+ peaks. Their peak heights were such as to affect to some extent only ^{184}Os . In the case a reliable value for ^{184}Os relative abundance is needed for iridosmine, we are currently employing the separation of Os vapor from the simply dissolved sample solution. For meteorites, we also carried out the Os vapor separation.

It might merit notice that ^{190}Pt decays into ^{186}Os with the half-life of 5.9×10^{11} y. The isotopic abundances of ^{190}Pt (0.0127%) and ^{186}Os (1.59%) and the decay constant concerned suggest that the possible isotopic variation of the latter nuclide should be far smaller than the current detection limits but can be detected in unusually Pt-rich minerals. Hence

some uneasiness may remain in discussing ^{187}Os relative to ^{186}Os . At present, however, discussions about ^{187}Os will be given in terms of $^{187}\text{Os}/^{186}\text{Os}$, following the way currently adopted.

Isobaric effect on ^{186}Os (1.59%) by ^{186}W (28.4%) could not be so serious as the similar one on ^{184}Os by ^{184}W so long as the ordinary caution is taken in separation of Os from W. The W-Os interference can be detected by sweeping the mass range involving tungsten isotopes. But the effect as noted here might become an additional reason to let us prefer $^{187}\text{Os}/^{188}\text{Os}$ ratio to $^{187}\text{Os}/^{186}\text{Os}$ in geochemical discussions.

Table 2. Osmium isotopic abundances (%)

	^{184}Os	^{186}Os	^{187}Os	^{188}Os	^{189}Os	^{190}Os	^{192}Os
This study*							
A	0.019	1.582	1.982	13.18	16.30	26.18	40.76
B	0.019	1.589	1.519	13.24	16.37	26.30	40.96
Nier**	0.018	1.59	1.64	13.2	16.1	26.4	41.0
Luck & Allegre***	0.024	1.599	1.510	13.29	16.25	26.37	40.96

* These isotopic abundances were calculated from the arithmetical mean of the Os ratios in Table 1, except for $^{187}\text{Os}/^{192}\text{Os}$; "A" was based on the $^{187}\text{Os}/^{192}\text{Os}$ ratio for Strem Os reagent and "B" on the $^{187}\text{Os}/^{192}\text{Os}$ ratio for Merck Os reagent.

** Nier (1937).

*** Luck and Allegre (1983) for Merck Os reagent.

Iron meteorites and iridosmines

Os isotopic ratios for iron meteorites and iridosmines are shown in Table 3. $^{187}\text{Os}/^{186}\text{Os}$ ratios are 1.066 and 1.033 for Canyon Diablo and Tlacotepec, respectively. Luck and Allegre (1983) reported $^{187}\text{Os}/^{186}\text{Os}$ ratios of 1.115 and 1.113 for Canyon Diablo and of 0.980, 0.994 and 1.008 for Tlacotepec. We cannot rule out a possibility that the numerical differences between those by Luck and Allegre and ours may be due to the heterogeneity in Re/Os ratios in the iron meteorite specimens.

Three iridosmine samples from Hokkaido (Kodaira, Nuppu River and Usotannai) are considered to be associated with ultra-mafic rocks in the Kamuikotan metamorphic belt. Metamorphic age for the Kamuikotan belt is thought to be about 100m.y. Iridosmine from the Urals (Nizhni Tagil) is associated with ultra-mafic rocks (300-400m.y.) in the "Hercynian ophiolite belt". Allegre and Luck (1980)

Table 3. Osmium isotopic ratio for iron meteorites and iridosmines

	$^{186}\text{Os}/^{192}\text{Os}$	$^{187}\text{Os}/^{192}\text{Os}$	$^{187}\text{Os}/^{186}\text{Os}$
<i>Iron Meteorite*</i>			
Canyon Diablo	0.0391 ± 0.0012	0.0417 ± 0.0008	1.066 ± 0.038
Tlacotepec	0.0389 ± 0.0006	0.0402 ± 0.0008	1.033 ± 0.020
<i>Iridosmine*</i>			
Kodaira, Hokkaido	0.0387 ± 0.0002	0.0415 ± 0.0006	1.072 ± 0.016
Nuppu River, Hokkaido	0.0388 ± 0.0010	0.0414 ± 0.0006	1.067 ± 0.032
Usotannai, Hokkaido	0.0387 ± 0.0004	0.0412 ± 0.0004	1.065 ± 0.016
Nizhni Tagil, The Urals	0.0388 ± 0.0002	0.0393 ± 0.0005	1.013 ± 0.006

Errors are $2\sigma_m$.

* Amounts of samples used are ca. 1g for iron meteorite and ca. 1mg for iridosmine.

Fig. 3. Relative Os isotope ratios to ^{192}Os for Os reagents, together with Os isotope ratios obtained by Luck and Allegre (1983). Errors are $2\sigma_m$. (For corrections for mass discrimination, see text.)

reported $^{187}\text{Os}/^{186}\text{Os}$ ratio for "osmiridium" samples of various ages from 90 to 2,700m.y. Their conclusion is that the $^{187}\text{Os}/^{186}\text{Os}$ variation with time can be fitted by a straight line corresponding to $^{187}\text{Re}/^{186}\text{Os} = 3.15$ for the mantle, comparable to CI carbonaceous chondrites.

Our $^{187}\text{Os}/^{186}\text{Os}$ ratio (1.013) for the sample from the Urals is somewhat lower than that (1.036 ± 0.004) reported by Allegre and Luck (1980). Our value appears to fall on the straight line mentioned above, while their value deviates somewhat from it.

As seen in Table 3, the $^{187}\text{Os}/^{186}\text{Os}$ ratios (1.065-1.072) for three Hokkaido iridosmines are quite similar to each other. Assuming the fixation of $^{187}\text{Os}/^{186}\text{Os}$ ratio 100m.y. ago corresponding to the metamorphic age, we consider that the Hokkaido iridosmine ratio is 3-4% higher as compared with the Allegre-Luck's straight line. If the fixation age is older than the metamorphic age, the difference from the straight line would tend to increase. This difference could be explained either as reflecting some possible variation of $^{187}\text{Os}/^{186}\text{Os}$ ratio in the mantle source, or as due to a small extent of contamination by the crustal source. The explanation in terms of the latter effect might be unfavorable in view of the considerably high homogeneity for three samples studied

here, but it would be premature to give conclusive words to this matter yet. One cannot rule out a third possibility such as double-stage evolution of the mantle and even a fourth one related with the systematic aberration in measurements. But, in view of the variation in meteoritic $^{187}\text{Os}/^{186}\text{Os}$ ratios as observed by Luck and Allegre (1983) and in the present study for Canyon Diablo and Tlacotepec, it is most likely that the deviation observed here is due to some heterogeneity of Re-Os ratio in the mantle source.

Meanwhile, Morgan (1985) discussed the Os/Re ratios for the mantle source, in relation with the Os/Re ratios in classified chondrite groupings. He maintains that the appropriate Os/Re value for the earth's mantle source should be 12.06 by weight, corresponding to $^{187}\text{Re}/^{186}\text{Os} = 3.32$. If similar calculation is made for the Hokkaido iridosmine, we can get $^{187}\text{Re}/^{186}\text{Os} = 3.27$, which falls between 3.15 (Allegre and Luck, 1980) and 3.32 (Morgan, 1985).

In summary, isotope ratios of osmium for osmium tetroxide reagents, iridosmines and iron meteorites have been measured by ICP-MS, with the relative precision of around 1% for $^{187}\text{Os}/^{192}\text{Os}$ ratio. Some minor differences have been observed in Os isotopic abundances among the data by Nier (1937), Luck and Allegre (1983) and this study; slightly lower abundance of ^{189}Os in the data of Nier and higher abundance of ^{184}Os in the data of Luck and Allegre. We think that the isotopic abundances indicated by B in Table 2 are recommendable as standard values. Based on this data, one can obtain the atomic weight for Os to be 190.24.

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