Isotopx

High precision Os isotope ratio measurements using Phoenix X62 TIMS.

Application Brief G10711

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Introduction

The study of Osmium isotopes is an important tool in geochemistry and cosmochemistry (e.g. Shirey and Walker 1998, Brandon et al. 2006, Ravizza and Turekian 1992). Side box 1 provides background on the two Os isotope systems of interest.

Whilst $^{187}Os/^{188}Os$ ratios can vary by several percent, the variation in $^{186}Os/^{188}Os$ is far smaller – a few hundred ppm. Consequently any meaningful $^{186}Os/^{188}Os$ measurements must be capable of attaining a precision of ~ 20ppm (2SRSD). For Faradays this implies a ^{186}Os beam intensity of 100mv or more.

Phoenix TIMS

We present here the first high precision Osmium isotope ratio data from the Phoenix Thermal Ionization Mass Spectrometer.

Side box 2 provides details of the NTIMS methodology used. The aim of the study was to provide a performance baseline using a standard Phoenix instrument situated in a factory environment. There was no temperature or environmental control.

New Developments

Phoenix includes three specific developments which make these measurements possible:-

1. A newly designed focus unit which can analyse negative ions at up to -8KV. -6KV was used throughout this work as it did not reduce the sensitivity.

2. Small Al-Ni-Co magnets have been fitted to one of the side filament (Figure 1). This facilitates the repulsion of electrons as close as possible to the filament. Large electron beams can produce irregularities in the peak shape and potentially a high voltage flashover.

3. A targeted oxygen bleed system which directs oxygen immediately adjacent to the sample bead holder.

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1. Os Isotopes

Two decay schemes are important in Os isotope analysis.

1. ^{187}Re decays to ^{187}Os with a half life ~42 Gyr.
2. ^{190}Pt decays to ^{186}Os with a half life ~ 470 Gyr.

^{187}Os and ^{186}Os are quoted as a ratio against stable ^{188}Os

Re/Os – Re is enriched in the crust relative to the mantle leading to wide variations in $^{187}Os/^{186}Os$ of surface rocks. Low Os concentrations and complex chemistry prior to NTIMS analysis remain major challenges.

Pt/Os – The extremely long half life of ^{190}Pt and a comparatively narrow range in Pt/Os means that even small variations in $^{186}Os/^{188}Os$ are significant. Very high measurement precision is therefore required.

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2. NTIMS Analysis

Osmium is measured by TIMS as a the negatively ionized OsO_3^- molecular species. This is because the ionization potential of Osmium is so high that it would evaporate before Os^+ ions could form (Creaser et. al 1991). Osmium has a high electron affinity, and will readily combine with O^-. The formation of OsO_3^- requires a high work function filament (Platinum), and a low work function activator $Ba(NO_3^-)_2$ or $Ba(OH)_2$ or a combination. The activator covers the Osmium on the filament and during thermal ionization it disassociates to combine the O^- with Os. Formation of OsO_3^- is also facilitated by bleeding a very small quantity of Oxygen close to the sample filament. Addition of oxygen from the bleed system raises the source vacuum from $1e^{-8}mbar$ to $2e^{-7}mbar$. The small magnet placed next to the Pt filament deflects electrons away from the mass spectrometer lens stack, thereby ensuring focus continuity over a range of filament currents.

Peak Shape Stability

Figure 2 shows a magnet scan over $^{192}OsO_3^-$ (the major Os oxide isotope peak at mass 240) repeated continuously for 45 minutes. The quality and stability of the peak shape highlights the performance of the new focusing electronics. The peak side stability was better than 10ppm of mass over the 45 minutes.
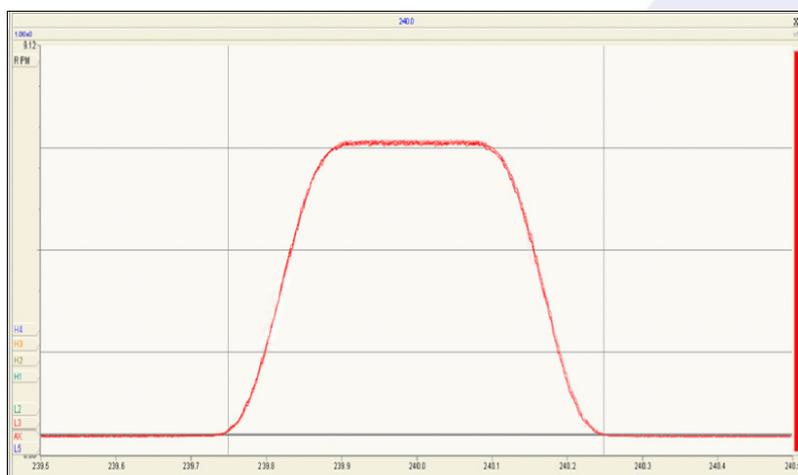

Figure 1. The New side filament mounted magnet.

Figure 2. $^{192}OsO_3^-$ peak shape recorded continuously for 45 minutes on the axial Faraday.

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OsO$_3^-$ Coincidence

Figure 3 shows a magnet scan from m/z 233.5 to m/z 241.5 (referenced to axial collector) showing the response of all 9 Faradays on one diagram. For this scan all 9 Faradays have been set to the equivalent of 1 AMU spacing for OsO$_3^-$

At the extreme left hand side of the figure the traces for the 5 channels from Axial to H4 show coincidence of peaks from m/z 234 (predominantly ^{186}OsO$_3^-$) up to m/z 238 (predominantly ^{190}OsO$_3^-$). At this point the L5 Faraday is collecting m/z 230 (^{182}WO$_3^-$) although none is evident.

On the extreme right of Figure 3, mass 241 is on the Axial collector, mass 245 is on H4 and mass 237 (^{189}OsO$_3^-$) is on the L5 Faraday. Hence with its 9 Faradays set to OsO$_3^-$ spacing, Phoenix can achieve coincidence on isotopes from m/z 230 to m/z 245.
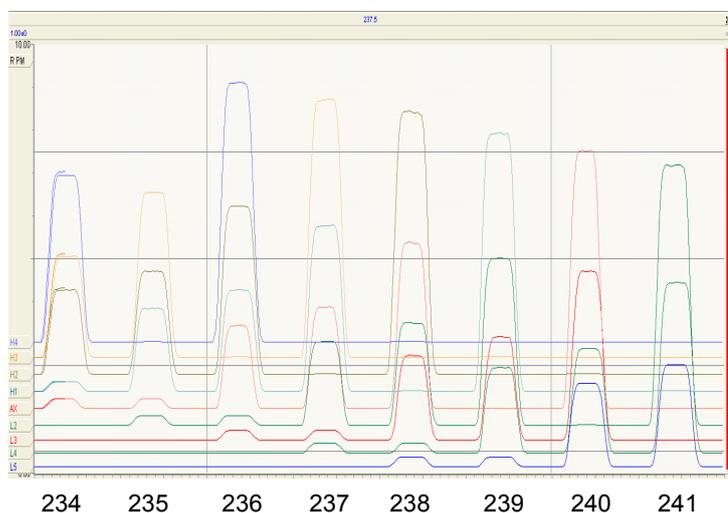

Figure 3. Scan of OsO$_3^-$ across all 9 Faradays. Mass number relates to the Axial Faraday.

Multi-static analysis

We have adopted a 4 cycle multi-static analysis routine as shown in Table 1. Multi-static is a new acquisition method currently under investigation at Isotopx.

	Cycle			
	1	2	3	4
H4	240			
H3	239	240		
H2	238	239	240	
H1	237	238	239	240
Ax	236	237	238	239
L2	235	236	237	238
L3	234	235	236	237
L4	233	234	235	236
L5	232	233	234	235

Table 1. Multi-static analysis protocol.

Multi-dynamic remains the gold standard mode as it eliminates any variations in collector efficiency or amplifier gain drift. The multidynamic method requires that normalizing isotopes are measured on the same collectors as the isotope ratios of interest. This requires the normalizing isotopes to be closely matched in mass to the isotopes of interest. For example a true multidynamic analysis which cancels all collector gains and efficiencies could be made for 235/236 (^{187}Os/^{186}Os) in cycle 1 and 2 (highlighted on Table 1) using a mass fractionation correction from 238/236 (^{190}Os/^{188}Os) in cycle 3.

However, the current consensus is that mass fractionation should use the stable isotope ratio pair with the largest mass difference, i.e. 240/236 (^{190}OsO$_3^-$/^{186}OsO$_3^-$) as this produces more precise normalised osmium isotope ratios (Brandon et. al. 2006). It is evident from Table 1 that (for example) the 235/236 does not have a multi-dynamic solution using mass fractionation correcting with 240/236.

The multi-static approach is relatively simple. Static ratios are measured in each collector pair, an average is calculated and a fractionation correction applied using the average 240/236 ratio from each of the 4 sequences.

The method provides partial cancellation of gain and collector efficiency variations by measuring the same isotope ratios on different collector pairs. A rigorous comparison with multi-dynamic analysis is under investigation as the methodology will have application to other isotope systems such as Nd and Sr.

Sample loading Method

Two samples were used. An Osmium Standard kindly provided by Dr. Richard Walker from the University of Maryland, and an ICP Osmium standard from Alfa chemicals.

Both samples were in an HCl matrix. Sample sizes for the UMd standard were typically 140ng, while the Alfa standard was 500ng.

Samples were loaded onto Platinum ribbon and dried down with no filament current. 2 microlitres of Barium hydroxide was placed onto the Osmium and dried down at 1A.

Mass Spectrometry

The filament current was increased steadily to 2 Amps over the course of 2 hours. The ^{35}Cl isotope was monitored until it had grown to ~6 volts. At this stage the Osmium ion beam started to appear. The filament current was then raised slowly over the course of 1 hour to ~2.4A, by this time the Osmium ion signal had grown to >3volts.

Data collection started at ~720C and continued for 150 cycles. Each cycle consisted of 4 mass jumps with an integration of 15 seconds for each mass. Baselines were taken at the start of each block. These were measured for 30 seconds at 0.5amu either side of the peak. The ion beam was focussed and peak centred at the start of each block of data. Generally the ion beam remained steady during the course of the measurement with no requirement to increase the filament current.

During the measurement, oxygen was bled into the source of the Phoenix to provide a source vacuum of 2e^{-7} mbar. The base source vacuum was <1e^{-8} mbar, no cryo-cooling of the source was required. Analyser vacuum remained at <5e^{-9} mbar during this process. Each analysis took ~ 6 hours, with data collection taking 50% of the time.

Following correction for ^{187}Re on ^{187}Os, all the isotopes were corrected for oxygen isotopes. Side box 3 provides details on the O_2 correction used. The corrected ratios were then fractionation corrected using an exponential law and a ^{192}Os/^{188}Os ratio of 3.083,(Brandon et al. 2006).

Results

The results are shown in Table 3 and in Figures 4 and 5.

^{186}Os/^{188}Os – Results for both samples show excellent external precision in range 17-25ppm (2σ). Internal precision correlates with ion beam intensity (second column) with Consistently sub 10 ppm (2σ) for ion beams greater than 4V of ^{192}Os.

^{189}Os/^{188}Os Provides an example of how precise the multi-static method is. Both samples produce the same isotope ratio. Ion beams are typically 1-2 volts for both isotopes and the ratio reproduces to 7ppm 2 RSD for all data. This precision cannot be obtained for single static isotope ratio measurements without performing an on-line amplifier calibration method. It can be obtained using a multi-dynamic method, but this is not possible using the ^{192}Os/^{188}Os mass fractionation correction.

Comparison with other studies

Table 2 shows a comparison between the UMd data collected in this study and in three other studies which used either NTIMS or ICP-MC-MS. (Luguet et. al 2008)

Although within the 2σ of the other NTIMS values, the Phoenix ^{184}Os/^{188}Os is slightly higher. It is definitely higher than the ICP-MC-MS value which is the lowest of all the datasets. This is perhaps consistent with a small but constant PtO$_2$ interference being present beneath the ^{184}OsO$_3^-$ at mass 232 on NTIMS but not in the ICP. Since the 184 intensity is small (~1-2mv), even interferences at the microvolt level will have a significant effect. There is a suggestion within the data in Table 2 that ^{184}Os/^{188}Os and the beam intensity are negatively correlated which adds support to the suggestion of an uncorrected interference at mass 232.

The ^{186}Os/^{188}Os is higher for the Phoenix than the other studies. Reproducibility is as good as other the studies. The higher ratio could be due to an uncorrected ^{186}W^{16}O$_3^-$ interference, but this would have to be very consistent and unlike the ^{184}Os/^{188}Os there is no suggestion of a correlation with ion beam intensity which may indicate that this

interference is in the sample. It is noteworthy that the Alfa standard has a lower ^{186}Os/^{188}Os ratio though the Pt/Os history of this sample is not known.

We would also discount a collector efficiency or gain effect since these ratios were measured on multiple collector sets. Peak tailing (abundance sensitivity) can be excluded as analyser vacuum was always <5e-9mbar during analysis. This would give rise to an uncorrected peak tail of 5ppm of intensity of <5ppm at mass 237 with respect to 238, and <2ppm at mass 236 (^{184}Os).

The ^{187}Os/^{188}Os is identical within error of other studies. Since the ^{187}Os/^{188}Os are measured on the same collectors as ^{186}Os, the reason for the high ^{186}Os is still unclear.

^{189}Os/^{188}Os is of higher precision than other TIMS studies, while the ^{190}Os/^{188}Os is about 2 times more precise. It is noteworthy that the ^{190}Os/^{188}Os is lower than the other studies, as is perhaps the ^{189}Os/^{188}Os. This may suggest that some of the discrepancy is due to subtleties in the mass fractionation correction, and that the exponential law is not quite correct. This has also been suggested by Luguet et.al, 2008. More data is required to confirm this.

UMd Osmium isotope comparison										
	^{184}Os/^{188}Os	2SD	^{186}Os/^{188}Os	2SD	^{187}Os/^{188}Os	2SD	^{189}Os/^{188}Os	2SD	^{190}Os/^{188}Os	2SD
PHOENIX	0.001313	4	0.119859	3	0.113782	8	1.219676	10	1.983746	8
N-TIMS (TRITON) a	0.001304	13	0.119843	7	0.113787	8	1.219710	17	1.983801	26
N-TIMS (TRITON)b	0.001309	6	0.119847	2	0.113791	4	1.219692	15	1.983793	19
MC_ICP-MS c	0.001300	1	0.119830	4	0.113790	9	1.219717	11	1.983836	122

Table 2. Comparison of UMd data with other studies (Luguet et. al 2008)

Summary

- High precision Osmium isotopes have been measured on the Phoenix TIMS at Isotopx in negative ion mode with the 2σ errors being comparable with the best literature values.
- ^{186}Os/^{188}Os precisions of ~20ppm 2RSD can be obtained providing there is sufficient ion beam.
- The multi-static analysis mode produces <sub 10ppm 2RSD precision for major isotopes of Osmium without requiring gain calibration between detectors over the analytical campaign of 3 weeks. This is not a multi-dynamic analysis method, and it may have interesting capabilities for other isotope systems.

Umd Os Standard

Analysis	240 (volts)	^{184}Os/^{188}Os	%1se	^{185}Re/^{188}Os	%1se	^{186}Os/^{188}Os	PPM 1se	^{187}Os/^{188}Os	PPM 1se	^{189}Os/^{188}Os	PPM 1se	^{190}Os/^{188}Os	PPM 1se
1	4.7	0.001313	0.04	0.000005	9	0.119860	5	0.113786	6	1.219672	1	1.983749	1
2	3.3	0.001312	0.05	0.000006	8	0.119861	8	0.113784	10	1.219672	2	1.983738	2
3	3.0	0.001313	0.04	0.000005	10	0.119860	6	0.113783	8	1.219681	2	1.983745	2
4	0.8	0.001315	0.23	0.000010	26	0.119860	19	0.113777	38	1.219683	5	1.983746	4
5	1.9	0.001309	0.09	0.000005	22	0.119857	10	0.113783	15	1.219671	3	1.983745	2
6	0.9	0.001314	0.17	0.000012	16	0.119858	23	0.113776	30	1.219676	4	1.983750	4
mean		**0.001313**		**0.000007**		**0.119859**		**0.113782**		**1.219676**		**1.983746**	
2SD		**0.000004**		**0.000006**		**0.000003**		**0.000008**		**0.000010**		**0.000008**	
2RSD		**0.3%**		**88%**		**25 PPM**		**69 PPM**		**8 PPM**		**4 PPM**	

Alfa Os ICP standard solution

Analysis	240 (volts)	^{184}Os/^{188}Os		^{185}Re/^{188}Os	%1se	^{186}Os/^{188}Os	PPM 1se	^{187}Os/^{188}Os	PPM 1se	^{189}Os/^{188}Os	PPM 1se	^{190}Os/^{188}Os	PPM 1se
1	4.7	0.001310	0.03	0.000006	6	0.119850	4	0.120226	6	1.219680	1	1.983725	1
2	4.7	0.001309	0.02	0.000005	5	0.119847	5	0.120223	5	1.219675	1	1.983728	1
3	4.7	0.001310	0.02	0.000005	6	0.119847	5	0.120221	5	1.219674	1	1.983731	1
4	4.7	0.001308	0.03	0.000004	8	0.119848	5	0.120222	6	1.219679	2	1.983735	1
5	4.7	0.001309	0.04	0.000006	10	0.119849	6	0.120230	8	1.219672	2	1.983736	2
6	4.7	0.001310	0.03	0.000005	7	0.119850	5	0.120223	6	1.219672	2	1.983737	2
7	4.7	0.001310	0.03	0.000006	7	0.119849	5	0.120214	6	1.219672	2	1.983744	1
8	3.1	0.001309	0.05	0.000006	8	0.119847	6	0.120214	7	1.219669	2	1.983743	1
9	3.1	0.001310	0.05	0.000006	9	0.119849	7	0.120212	7	1.219675	2	1.983749	2
10	6.6	0.001307	0.02	0.000004	6	0.119847	4	0.120232	5	1.219683	1	1.983728	1
mean		**0.0013093**		**0.000005**		**0.119848**		**0.120222**		**1.219675**		**1.983736**	
2SD		**0.0000018**		**0.000002**		**0.000002**		**0.000014**		**0.000008**		**0.000016**	
2RSD		**0.14%**		**28%**		**17 PPM**		**114 PPM**		**7 PPM**		**8 PPM**	

Table 3. Data collected for UMd and Alfa Os standards

Figure 4. ^{186}Os/^{188}Os ratios

Figure 5. ^{189}Os/^{188}Os ratios
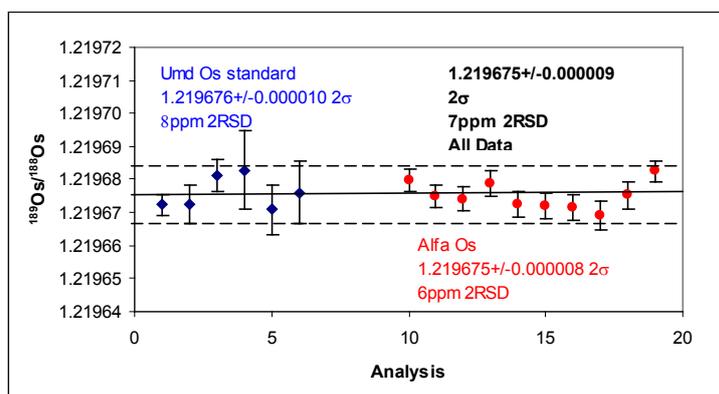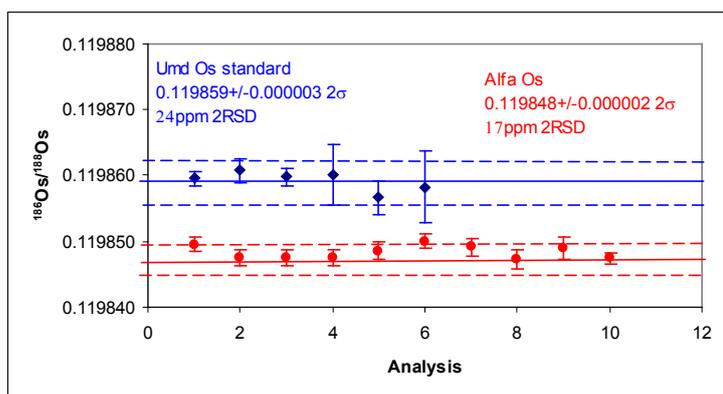
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