Application note | 000969

TIMS

High precision tungsten isotopes analyzed via thermal ionization mass spectrometry

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Keywords

Tungsten isotopes, TIMS

Goal

To demonstrate the high precision achievable for tungsten isotope measurements using the negative mode of the Thermo Scientific™ Triton™ XT thermal ionization mass spectrometer.

Introduction

The short-lived ^{182}Hf-^{182}W isotopic system [^{182}Hf→ ^{182}W + 2β$^-$, half-life (t½) = 8.9 million years][1] is a powerful tool for studying planetary differentiation processes that occurred within the first 60 million years of solar system history. Given that tungsten (W) is moderately siderophile and hafnium (Hf) is strongly lithophile, the system is particularly sensitive to metal-silicate segregation. The most widely used application for this system has been dating core formation of planetary bodies.[2–4] By measuring W isotopic compositions of iron meteorites, ages can be calculated, assuming chondritic Hf/W. The ^{182}Hf-^{182}W isotopic system has also been used for terrestrial applications. ^{182}W/^{184}W is used for measuring ^{182}W ingrowth from lithophile Hf. For example, the W isotopic compositions of mantle-derived rocks have been used to investigate mantle evolution.[5–8] Isotopic variations in ^{182}W/^{184}W can be smaller than 10 ppm,[6,9] requiring high precision W isotope measurements.

Here we demonstrate the capabilities of the Thermo Scientific Triton XT thermal ionization mass spectrometer equipped with 10^{13} Ω Amplifier Technology to measure W isotopes at high precision of better than 2 ppm (2 RSD) for 0.3–1.25 µg W loadings.

Experimental

Sample preparation

Single Re filaments (99.99% purity) were used in these measurements. Filaments were outgassed at 4.5 A for at least 48 hours prior to loading, ideally several weeks.

Filament loading procedures generally followed Archer at al.[10] Specifically, W was loaded in HCl matrix on the filament followed by a brief heating of the filament to a dull glow. To enhance ionization, 1 µL of activator solution containing 20 µg of La and 5 µg of Gd in 1 M Teflon double-distilled HCl was then added in 2–3 aliquots to the standard.

Instrumentation

Analyses were performed at the University of Vienna on a Triton XT system in negative ion mode. A combination of 10^{11} and 10^{13} Ω amplifiers were used during analysis (Table 1). Specifically, the low noise 10^{13} Ω amplifiers were used to measure the small ion beams of $^{180}W^{16}O_3$, $^{181}Ta^{16}O_3$, $^{186}W^{16}O_2{}^{18}O$, $^{187}Re^{16}O_2{}^{18}O$, and $^{190}Os^{16}O_3$ during the multi-static method.

A total of 18 blocks were measured with 20 cycles per block for a total measurement time of ~11 hours. The six 10^{11} Ω amplifiers were rotated after every block (a total of three full amplifier rotations across the run). Peak centering was performed every 6th block, a lens focusing every 2nd block and a 6 minute baseline was performed every block. High-precision 160 min amplifier gains were determined before every other sample run; however, in the data reduction, an average of the last three gain measurements was used to correct each 10^{11} Ω amplifier.

Oxide production was enhanced using a Varian™ leak valve to bleed oxygen (P_{source} = 1.2 × 10^{-7} mbar) into the source[9].

Data reduction

Data reduction procedures follow a three-step iterative process[10] including interference correction of Re and Ta isotopologues and oxygen corrections. Potential Os interferences were also monitored via the measurement of $^{190}Os^{16}O_3$ using 10^{13} Ω amplifiers on H4 in line 2 (Table 1). All ratios were corrected for instrumental mass fractionation using a $^{186}W/^{183}W$ ratio of 1.9859. A two-sigma outlier rejection was made based on cycles.

Results and discussion

The internal precision of the individual measurements is between 2.1 ppm and 2.6 ppm (2 RSE) and close to the limit of counting statistics (Table 2). The results of two independent analytical sessions have $^{182}W/^{184}W$ external precisions of 2.1 and 1.8 ppm (2 RSD; n = 7 for each session; Table 2; Figure 1).

Table 1. Cup configuration for W isotope measurements

10^{13} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{11} Ω	10^{13} Ω	10^{13} Ω	Integration time	Idle time
L4	L3	L2	L1	CC	H1	H2	H3	H4	[s]	[s]
$^{180}W^{16}O_3$	$^{181}Ta^{16}O_3$	$^{182}W^{16}O_3$	$^{183}W^{16}O_3$	$^{184}W^{16}O_3$	$^{185}Re^{16}O_3$	$^{186}W^{16}O_3$	$^{186}W^{16}O_2{}^{18}O$	$^{187}Re^{16}O_2{}^{18}O$	33.554	10
$^{181}Ta^{16}O_3$	$^{182}W^{16}O_3$	$^{183}W^{16}O_3$	$^{184}W^{16}O_3$	$^{185}Re^{16}O_3$	$^{186}W^{16}O_3$	$^{187}Re^{16}O_3$	$^{187}Re^{16}O_2{}^{18}O$	$^{190}Os^{16}O_3$	33.554	10

Table 2. $^{182}W/^{184}W$ ratios for 14 analyses from two analytical sessions of a 0.3-1.25 µg Alfa Aesar™ W standard

Wheel	Sample	Average ^{184}W signal [V]	$^{182}W/^{184}W$ multi static	2σ	2 RSE (ppm)	Theoretical limit of precision 2 RSE (ppm)
1	1	1.4	0.864861	2.10E-06	2.4	2.0
1	2	1.2	0.864861	2.27E-06	2.6	2.2
1	3	1.3	0.864863	2.47E-06	2.9	2.1
1	4	1.3	0.864860	2.23E-06	2.6	2.1
1	5	1.1	0.864862	2.07E-06	2.4	2.3
1	6	1.2	0.864861	2.14E-06	2.5	2.2
1	7	1.1	0.864860	2.25E-06	2.6	2.2
		Average	**0.864861**	**1.78E-06**	**2.1**	
2	1	1.2	0.864861	2.19E-06	2.5	2.2
2	2	1.1	0.864860	2.60E-06	3.0	2.2
2	3	1.2	0.864860	2.37E-06	2.7	2.2
2	4	1.2	0.864860	2.11E-06	2.4	2.2
2	5	1.2	0.864858	2.11E-06	2.4	2.2
2	6	1.2	0.864860	2.27E-06	2.6	2.2
2	7	1.1	0.864860	2.23E-06	2.6	2.3
		Average	**0.864860**	**1.59E-06**	**1.8**	

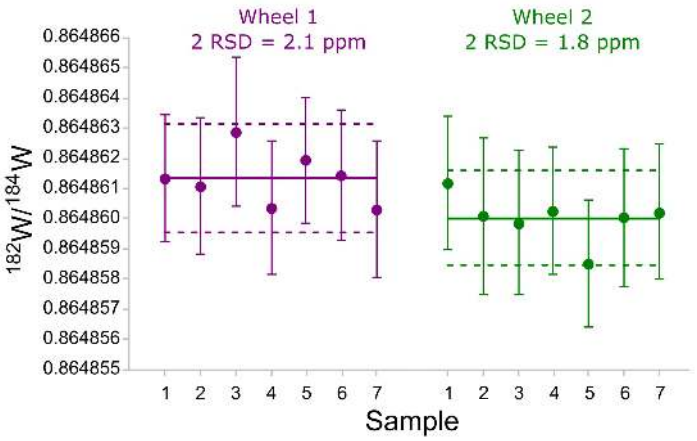

Figure 1.^{182}W/^{184}W ratios for 14 analyses from two analytical sessions of a 0.3-1.25 µg Alfa Aesar W standard. Mean ^{182}W/^{184}W and 2 SD for each session shown by solid and dashed lines. Error bars represent 2 SE internal precisions.

Based on the average signal intensity of each filament (given a measurement time of 402 min = 2 lines x 33.554 s * 18 blocks * 20 cycles), the theoretical limit on internal precision of the measurement can be determined:

$$2\text{RSE (ppm)} = \sqrt{\left(\frac{2\text{x}10^6}{\sqrt{\text{Tot.counts}_{^{184}\text{W}}}}\right)^2 + \left(\frac{2\text{x}10^6}{\sqrt{\text{Tot.counts}_{^{182}\text{W}}}}\right)^2}$$

Table 2 shows that the measurements made on the 14 W samples were within 40–50% of the theoretical limit of internal precision based on counting statistics. This demonstrates that the precision of the method is not limited by the instrument noise but rather by signal intensity and total measurement time.

Conclusion

The Triton XT TIMS system equipped with 10^{13} Ω Amplifier Technology is capable of analyzing ^{182}W/^{184}W isotope ratios at precisions of ≤2 ppm for 0.3–1.25 µg W loadings. This allows small W isotopic variations to be identified, opening up new possibilities for exploring small-scale heterogeneities resulting from early planetary differentiation processes. These isotopic differences can help in constraining the timing of mantle homogenization in Early Earth or tracing core-mantle interactions, ultimately giving a better understanding of geodynamic processes and composition of mantle reservoirs.

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