Nu TIMS

Nu TIMS Note **TI06**

THERMAL IONISATION MS
High precision Molybdenum isotopes

- **Excellent reproducibility of 1ug Molybdenum**
  - **^{92}Mo/^{96}Mo (25.7ppm 2RSD)**
  - **^{94}Mo/^{96}Mo (9.5ppm 2RSD)**
  - **^{95}Mo/^{96}Mo (5ppm 2RSD)**
  - **^{97}Mo/^{96}Mo (3.4ppm 2RSD)**
  - **^{100}Mo/^{96}Mo (25.9ppm 2RSD)**
- **Excellent peak shape and alignment**
- **Multi-Static and Multi-Dynamic live results**
  - **With online oxide corrections**
- **Measured ^{17}O/^{18}O vs Extrapolated ^{17}O/^{18}O**

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Introduction

Molybdenum (Mo) isotope anomalies in extra-terrestrial materials hold important clues about the provenance of Earth's building material and help characterize the earths late-stage accretionary assemblage. These small deviations in Mo isotopes against terrestrial values are well suited to the high precision often associated with a TIMS instrument.

The isotopic measurement of Mo has been performed using the $Mo^{16}O_3^-$ negative ion. It is generated using double rhenium filaments with a Lanthanum coating to enhance signal emission as described in the paper (*Worsham et al.,2016*).

The Nu TIMS instrument with Zoom Optics allows ultimate peak alignment of isotopes (Figure 1), accompanied with 16 faradays a 4-cycle routine (Table 1) has been used to collect all isotopes on each magnet position. Optional ion counters can be fitted within either side of the detector array, in this case ion counters were situated between L5 and L4. These can be repositioned allowing 6 possible cycles further reducing the errors from small signals.

Each measurement line can be tuned for best alignment and instantly switched electronically to the next line in milliseconds during the measurement. The collection of all isotopes on each

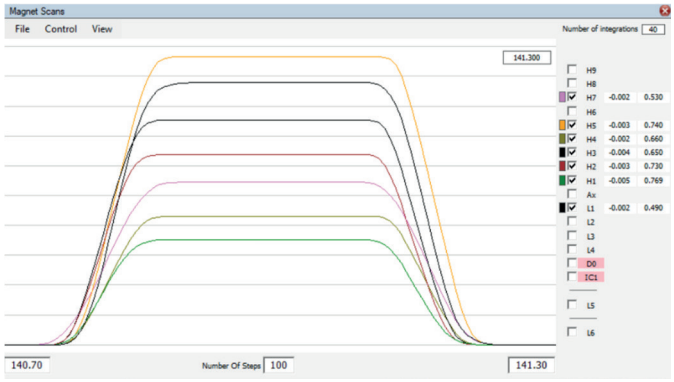

Figure 1: Alignment of Mo Peaks

line allows for an average $^{100}Mo^{16}O_2{}^{18}O$, $^{98}Mo^{16}O_2{}^{17}O$ or $^{92}Mo^{16}O_2{}^{17}O$ to be taken, reducing the error associated with the small signals. Accompanied with Multi-Static or Multi-Dynamic results this ensures the highest accuracy and precision, live results can be seen within run for oxides, Multi-Static or Multi-Dynamic ratios amongst other useful data.

Magnet Position	H9	H8	H7	H6	H5	H4	H3	H2	H1	Ax	L1	L2	L3	L4	L5	L6	Quad 1	Quad 2
Line 1	$^{100}Mo^{16}O_2{}^{18}O$	$^{100}Mo^{16}O_2{}^{17}O$	$^{100}Mo^{16}O_3$	$^{98}Mo^{16}O_2{}^{17}O$	$^{98}Mo^{16}O_3$	$^{97}Mo^{16}O_3$	$^{96}Mo^{16}O_3$	$^{95}Mo^{16}O_3$	$^{94}Mo^{16}O_3$	$^{92}Mo^{16}O_2{}^{17}O$	$^{92}Mo^{16}O_3$						-50	382
Line 2		$^{100}Mo^{16}O_2{}^{18}O$	$^{100}Mo^{16}O_2{}^{17}O$	$^{100}Mo^{16}O_3$	$^{98}Mo^{16}O_2{}^{17}O$	$^{98}Mo^{16}O_3$	$^{97}Mo^{16}O_3$	$^{96}Mo^{16}O_3$	$^{95}Mo^{16}O_3$	$^{94}Mo^{16}O_3$	$^{92}Mo^{16}O_2{}^{17}O$	$^{92}Mo^{16}O_3$					-50	384
Line 3			$^{100}Mo^{16}O_2{}^{18}O$	$^{100}Mo^{16}O_2{}^{17}O$	$^{100}Mo^{16}O_3$	$^{98}Mo^{16}O_2{}^{17}O$	$^{98}Mo^{16}O_3$	$^{97}Mo^{16}O_3$	$^{96}Mo^{16}O_3$	$^{95}Mo^{16}O_3$	$^{94}Mo^{16}O_3$	$^{92}Mo^{16}O_2{}^{17}O$	$^{92}Mo^{16}O_3$				-50	387
Line 4				$^{100}Mo^{16}O_2{}^{18}O$	$^{100}Mo^{16}O_2{}^{17}O$	$^{100}Mo^{16}O_3$	$^{98}Mo^{16}O_2{}^{17}O$	$^{98}Mo^{16}O_3$	$^{97}Mo^{16}O_3$	$^{96}Mo^{16}O_3$	$^{95}Mo^{16}O_3$	$^{94}Mo^{16}O_3$	$^{92}Mo^{16}O_2{}^{17}O$	$^{92}Mo^{16}O_3$			-50	415

Table 1: Detector configuration for the measurements of Mo isotopes.

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Experimental

A double filament arrangement using zone refined rhenium ribbon was used and the filaments had been degassed two weeks prior to loading of the standard. A parafilm well was formed on the sample/evaporation filament prior to loading 1ug of Molybdenum (SPEX certiprep), this was then dried at 0.8A followed by holding at 1A for 5minutes. The current was then reduced to 0.8A and 10ug of lanthanum (La) was loaded on top of the dried Mo standard. After the La had dried the current was slowly raised until a dull glow was visible on the filament.

The ionization filament also had 10ug of La added but does not utilize a parafilm well and covers 50% of the filament length. This was dried the same as the sample/evaporation filament described above.

An oxygen bleed valve attached to the source chamber was used to provide a source of oxygen with the pressure being set to 4e-7mbar for the duration of the experiment. Different bleed rates have not been tested for the effects on the $Mo^{16}O_3^-$ signal emission.

Ramp Rate (mA/Sec)	Target Current (mA)	Total Ramp Time (min)
2	1200	10
0.5	1900	33
0.2	2175	56
0.1	2350	85
0.003	2600	

Table 2: Cumulative ramp time

Pyro (.C)	Sample Filament (mA)	Ionisation Filament (mA)	Signal After Tune (v)
1220	1950	2150	0.05
1245	2000	2250	0.30
1270	2050	2350	0.70
1280	2050	2400	1.00
n/a	n/a	n/a	n/a

Table 3: Tuning parameters

The filaments were ramped to the currents in Table 3 before optimizing the intensity at Mass 146 ($^{98}Mo^{16}O_3$) using the ramp rates shown in Table 2, the actual signal intensities and temperature are shown at each optimization point. After 90minutes the analysis was started with peak centering and tuning occurring after every block, more parameters are shown in Table 4.

Sample	Filament Type	Analysis Mode	Magnet Delay	Target Beam (v)	Measurement Duration	Baselines
1ug Mo (SPEX)	Zone Refined Rhenium Double Filaments	34 blocks of 20 measurements with 17 sec integrations	3 Seconds	$^{98}Mo^{16}O_3$ at 1V	20 hours	240 Seconds at the start of each block

Table 4: Measurement parameters for the negative ion Mo runs

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Results

Online data corrections for oxides were made within run measuring the average $^{100}Mo^{16}O_2{}^{18}O$, $^{98}Mo^{16}O_2{}^{17}O$ or $^{92}Mo^{16}O_2{}^{17}O$ and fractionation corrected with an exponential correction to $^{98}Mo/^{96}Mo$ = 1.453171. Little to no difference is seen in using a measured $^{17}O/^{16}O$ vs an extrapolated $^{17}O/^{16}O$ (Table 5 n=9).

Oxygen Correction Details:	$^{17}O/^{16}O$	2SD	$^{92}Mo/^{96}Mo$	2RSD(ppm)	$^{94}Mo/^{96}Mo$	2RSD(ppm)	$^{95}Mo/^{96}Mo$	2RSD(ppm)	$^{97}Mo/^{96}Mo$	2RSD(ppm)	$^{100}Mo/^{96}Mo$	2RSD(ppm)
$^{17}O/^{16}O$ Extrapolated from measured $^{18}O/^{16}O$	0.0003838	0.0000029	0.883421	25.9	0.552522	9.5	0.953253	5.0	0.573941	3.4	0.581482	5.6
$^{17}O/^{16}O$ Measured from $^{92}MO^{16}O_2{}^{17}O$	0.0003840	0.0000031	0.883422	25.8	0.552523	10.8	0.953253	5.0	0.573940	3.8	0.581482	5.5
$^{17}O/^{16}O$ Measured from $^{98}MO^{16}O_2{}^{17}O$	0.0003854	0.0000034	0.883436	34.7	0.552526	12.9	0.953256	4.3	0.573938	2.7	0.581482	5.4
$^{17}O/^{16}O$ Measured average of $^{92}MO^{16}O_2{}^{17}O$ + $^{92}MO^{16}O_2{}^{17}O$	0.0003847	0.0000032	0.883426	27.1	0.552525	11.6	0.953255	4.9	0.573939	3.5	0.581482	5.4
Difference on ratio (ppm)			17.0		7.9		2.9		6.0		0.8	

Table 5: Comparison of various methods for correcting $^{17}O/^{16}O$

Compared to some published values, Table 6 shows superior external reproducibility using the Nu TIMS, especially for $^{92}Mo/^{96}Mo$.

Details:	$^{92}Mo/^{96}Mo$	$^{94}Mo/^{96}Mo$	$^{95}Mo/^{96}Mo$	$^{97}Mo/^{96}Mo$	$^{100}Mo/^{96}Mo$
Alfar Aesar (1ug)	n=13	n=13	n=13	n=13	n=13
Worsham et al 2016 (IJMS)	0.88319	0.55243	0.95318	0.57395	0.58146
[1] (2RSD ppm)	110	36	18	5.2	33
Kanto-Mo (1ug)	n=21	n=21	n=21	n=21	n=21
Yuichiro Nagai et al 2016 (JAAS)	0.88323	0.55248	0.95326	0.57396	0.58148
[2] (2RSD ppm)	47	16	10	13	33
Aldrich (1ug)	n=7		n=7	n=7	n=7
Lu and MASUDA et al 1992 (JASMS)	0.88343	n/a	0.95323	0.57393	0.58146
[3] (2RSD ppm)	42.8		39.6	35.4	60
SPEX (1ug)	n=20	n=20	n=20	n=20	n=20
this data	0.88342	0.55252	0.95325	0.57394	0.58148
(2RSD ppm)	25.4	10.2	6.9	5.1	5.6

Table 6: Multi-Dynamic and Multi-Static measurements

1: E.A. Worsham, et al., High-precision molybdenum isotope analysis by negative thermal ionization mass spectrometry, Int. J. Mass Spectrom. (2016), International Journal of Mass Spectrometer., 2: Yuichiro Nagai, et al. J. Anal. At. Spectrom, 2016, 31, 948, 3: Qi Lu et al, J Am Soc Mass Spectrom 1992, 3, 10-17.

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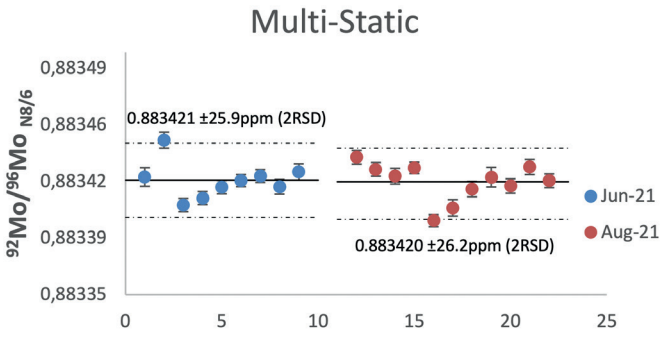
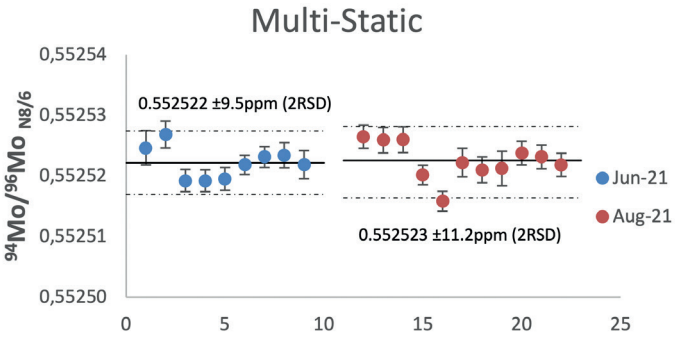
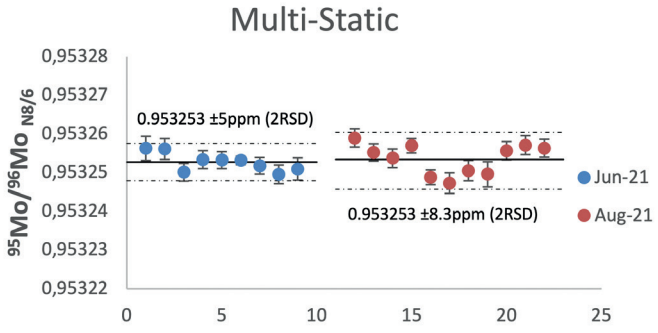
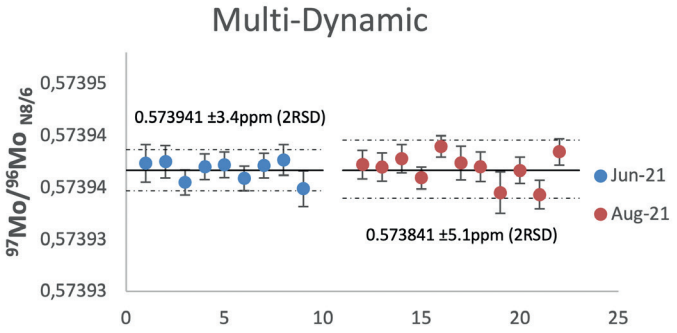
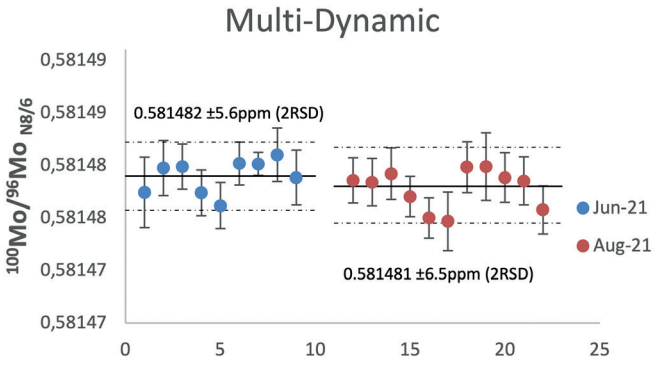
Graphical results are shown below, black line represents the mean value with the dotted lines indicating +/-2SD. All data was fractionation corrected to $^{98}Mo/^{96}Mo = 1.453171$. Error bars are reported as ±2SE.

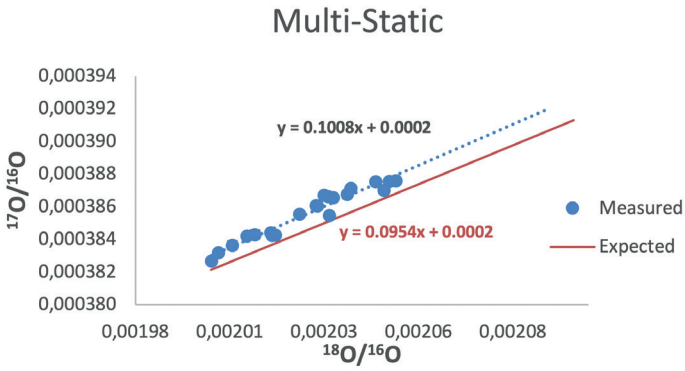












Conclusion

Isotopic measurements of high precision Mo have been performed in the negative ion mode using a Nu TIMS.

Utilizing the larger number of collectors and unique zoom lens capabilities found on the Nu TIMS instrument, extremely high precision results can be achieved.

The graphs shown to the left indicate little to no change over a two-month period on faradays that have been in use for over 1yr prior.