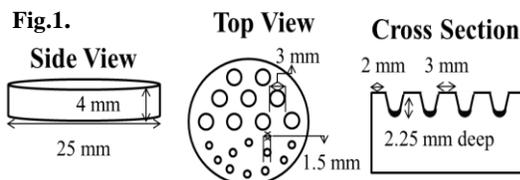


ADVANCES IN TRIPLE OXYGEN ISOTOPE ANALYSES OF TERRESTRIAL AND EXTRATERRESTRIAL SAMPLES AT WESTERN UNIVERSITY CANADA. Arshad Ali, Iffat Jabeen and Neil R. Banerjee, Deptt. of Earth Sciences, Western University, 1151 Richmond St., London, ON, N6A 5B7 Canada

Introduction: Triple oxygen isotope analyses have great significance in understanding our solar system. It is considered indispensable for meteorite classification and is routinely used for constraining primary and secondary processes in the solar nebula and on parent bodies as well as finding genetic relationships among meteorites. Western University has recently refined protocols for high precision and high accuracy analyses of triple oxygen isotopes using CO₂ laser-BrF₅ fluorination extraction mass spectrometry. Our advancements have included defining the longest terrestrial fractionation line to date and a redesigned sample holder that improves reaction efficiency (Fig.1). Our laser extraction procedures are then applied to analysis of different ordinary chondrites, achondrites and carbonaceous chondrites to determine precision and accuracy.

Analytical System Description: The laser line is equipped with a 25W CO₂ laser (New Wave Research, Bozeman, MT, USA; Model MIR10-25) and is constructed from 316 grade electropolished stainless steel based on the design of [1]. Bromine pentafluoride (BrF₅) is used as a fluorinating agent, which is doubly distilled before a set of analyses. The reaction chamber is made of 316L grade stainless steel and is fitted with a BaF₂ window (44.6mm dia. x 3.5mm thick). The sample holder is a small disc (25mm dia. x 4mm thick) made of pure nickel having ~2mm deep grooves with a rounded "V" profile of 1.5 mm and 3 mm diameters (Fig.1). This design consistently ensures complete reaction as the material gets to the bottom of the groove as it melts and improves the lasing efficiency compared to conventional square "U" profile.



Pre-dried samples of 1-2 mg size are loaded in the sample holder and placed in the reaction chamber for preheating at 110°C overnight under vacuum conditions. Pre-fluorination of the sample is conducted for at least three hours to remove any water adsorbed to the sample or interior of the reaction chamber. Laser heating is started with a defocused beam followed by stepwise increments in laser power with increased beam focusing. The liberated O₂ gas is purified from any by-products of the reaction by removing unwanted gases

stepwise using cryogenic traps and heated KCl trap down the giving yields of >95%. Finally, O₂ is adsorbed using 5Å molecular sieve cooled with liquid nitrogen, purified further using ethanol-liquid N₂ slush at -100°C and adsorbed again on the 5Å molecular sieve for analysis on a Delta V Plus isotope ratio mass spectrometer in dual inlet mode. Eight individual runs of UWG-2 provided an external precision (1σ) of ±0.04‰ in δ¹⁷O and ±0.08‰ in δ¹⁸O values. The measured δ¹⁷O=2.99‰ and δ¹⁸O=5.72‰ values for UWG-2 suggest our accuracy is better than ±0.1‰.

Terrestrial Fractionation Line (TFL): We have succeeded in defining a terrestrial fractionation line with the longest range both in terms of δ¹⁷O and δ¹⁸O values. This TFL is based on the analyses of 79 individual runs of 17 different minerals and rocks. A summarized presentation of the data is given in Fig. 2. The lower end of the TFL belongs to the minerals of a sample (K-1) from Belomorian Complex, Russia having ultralow oxygen isotope compositions due to the hydrothermal activity [2]. Our TFL has a slope of 0.5223 with intercept of -0.0103.

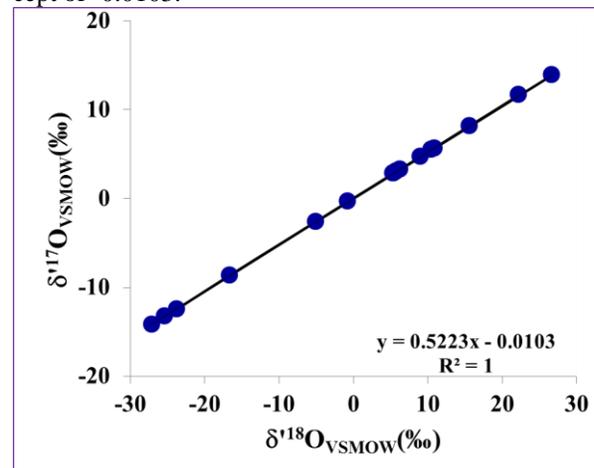


Fig.2. Plot of oxygen isotope data of terrestrial samples. The data points includes analyses of the reference materials NBS-28 quartz, UWG-2 garnet and San Carlos olivine.

The standardization protocols for reporting oxygen isotope data differ at different laboratories. Some use one-point standardization using an international standard reference [3], [4], [5] to calculate δ¹⁸O_{VSMOW} values from raw data and others correct their raw values by a scaling factor obtained by analysing O₂ gas extracted from VSMOW or VSMOW-SLAP meteoric waters [6], [7], [8].

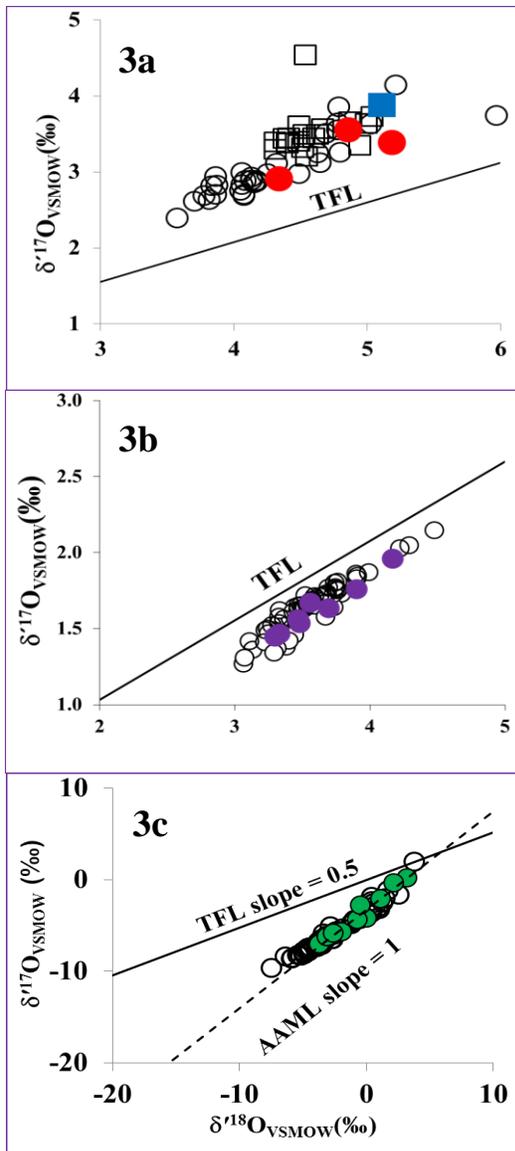


Fig.3. The open circles and squares represent data of H-type (whole rock & chondrules) and L-type (whole rock & chondrules) respectively from [10]; solid circles and square represent H-type (fragments) and L-type (fragments) respectively from this study (3a). The open circles are data from [11] and [12] for HEDs and solid circles are from this study (3b). In 3c, open circles represent data of Allende CV3 chondrules compiled from [13], [14] and [15] while solid circles are from this study.

We report $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ data based on the calibration curve of raw values (measured) obtained from the mass spectrometer against recommended or expected values ($\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$) of international standards and widely analyzed laboratory reference materials. Our calibration curve includes international silicate standard NBS-28 [9] and Gore

Mountain garnet UWG-2 [5]. We used the slopes and intercepts of the calibration curves to calculate $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ values from raw data of different rocks and minerals.

Oxygen Isotope Analyses of Meteorite Samples:

After TFL construction various known meteorites were analysed for oxygen triple isotopes and the results compared with previous studies. We have analyzed some HED meteorites (Juvinas, Stannern and Tatahuoine) from the achondrite category, some ordinary chondrites (Jumapalo, Gladstone, Densmore and Bath) and some Allende CV3 chondrules for triple oxygen isotope ratios using our analytical protocols. The $\delta^{17}\text{O}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ values are plotted in Fig. 3. The data agree well with the literature data [10-15] confirming that our method provides increased accuracy and precision for meteorite analyses of triple oxygen isotope ratios in order to characterize unidentified meteorite falls or finds.

Conclusions: Our CO_2 laser fluorination mass spectrometry protocols at Western University provide enhanced precision and accuracy. The calibration method for reporting triple oxygen isotope data provided precision and accuracy better than $\pm 0.1\%$. Our newly constructed TFL ranges from -27 to $+27\%$ in $\delta^{18}\text{O}$ and -14% to $+14\%$ in $\delta^{17}\text{O}$, which is the longest in terms of range of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values so far reported in the literature. The data obtained for ordinary chondrites, achondrites and carbonaceous chondrites is in excellent agreement with literature values. Our system is fully capable of characterization of unclassified meteorites.

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