

STATE-OF-THE-ART LASER FLUORINATION FOR OXYGEN ISOTOPE RATIO ANALYSIS OF EXTRATERRESTRIAL MATERIALS. I. E. Kohl¹, P.H. Warren¹ and E. D. Young¹, ¹UCLA EP&SS Dept. 595 Charles E young Dr. East, Los Angeles, 90095 (ikohl@epss.ucla.edu, eyoung@epss.ucla.edu)

Introduction: High-precision triple-oxygen isotope analysis of O₂ ($\Delta^{17}\text{O}$) acquired by laser-fluorination are among the best diagnostic tools applied to extraterrestrial rock samples. Using oxygen isotopes and differences among whole rock and mineral separate samples has enriched our understanding of the processes leading to planet formation in the early solar system.

Shortcomings of Laser Fluorination: We have identified two principle sources of systematic errors when collecting high-precision fluorination data for $\Delta^{17}\text{O}$. One is the difficulty in removing adsorbed water and the other is the presence of trace amounts of NF₃. Here we compare our procedures and tests for the effects of these two sources of error with those of previous studies. In brief, we demonstrate the efficacy of our procedures for eliminating adsorbed H₂O and residual NF₃ at the ppm level using experiments and a novel mass spectrometer.

Mass Interference Due to NF₃: All of the high-precision fluorination studies of triple-oxygen isotopes are done by reacting samples with F₂ or BrF₅ in a vacuum system. Because N₂ is always present at some level in vacuum lines, trace quantities of NF₃ form as a byproduct during the fluorination process. In the electron impact sources of the mass spectrometers used to measure the oxygen isotope ratios NF₃⁺ fragments to NF₂⁺ and NF⁺, with NF₂⁺ being the dominant species. NF⁺ is a mass spectrometric isobar for ³³O₂⁺ (i.e., ¹⁷O¹⁶O⁺ + ¹⁶O¹⁷O⁺) and if present in ppm or greater quantities can artificially increase the $\Delta^{17}\text{O}$ of the sample O₂.

No previously published studies comparing extraterrestrial rocks with terrestrial rocks have presented clear evidence that their analyses were free of ppm levels of NF⁺ interfering with ³³O₂⁺. Until recently it has been commonplace to report that NF₂⁺ at $m/z = 52$ was not “detected”. However, we would like to emphasize that lack of detectable NF₂⁺ is not *a priori* evidence for lack of interference by NF⁺ at the ppm level. As an example, Rumble et al. [1] showed that in their laboratory the ratio of $\Delta^{17}\text{O}$ effect to NF₂⁺ ion current on a $3 \times 10^{11} \Omega$ resistor on the Faraday-cup amplifier is 16.5 ‰/V. Similar values are reported by Pack et al. [2]. We infer that the search for NF₂⁺ in the earlier study by Weichert et al. was made under the same conditions as it was done in the same laboratory [3]. Scaling these results for a 10 ppm effect on $\Delta^{17}\text{O}$, the NF₂⁺ ion current required for detection of a 10 ppm

contribution to a measured $\Delta^{17}\text{O}$ would be $0.01/4.95 \times 10^{12} = 2 \times 10^{-15}$ amps (or 0.6 mV). Such small ion currents are not detectable with Faraday collectors used on normal gas-source isotope ratio mass spectrometers.

Experiments Demonstrating Removal of NF₃:

We use three experiments to demonstrate that NF⁺ due to fragmentation from NF₃⁺ is not affecting our results: (1) double distillation of O₂ liberated from SC olivine in which we applied our cleanup procedure twice to search for a difference in measured $\Delta^{17}\text{O}$ values; (2) analysis of O₂ liberated by fluorination of SC olivine without our usual purification procedure in order to demonstrate the efficacy of the Panorama mass spectrometer for resolving NF⁺ from O₂⁺; and (3) additional analyses of a lunar sample with the highmass-resolution Panorama instrument.

We found no difference between results using our usual analytical procedure and those from the double-distillation experiment, suggesting that NF₃ is eliminated during our normal purification procedures (Figure 1).

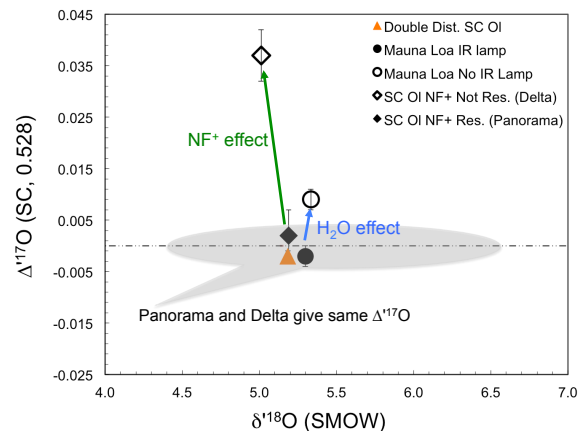


Figure 1: Summary of results for experiments outlined above. The hashed line indicates $\Delta^{17}\text{O}=0$ with a slope of 0.528 relative to SC Ol.

We analyzed a sample known to have significant NF⁺ interference with the Panorama gas-source mass spectrometer. This instrument has more than sufficient mass resolution to reliably resolve NF⁺ (33.001473 amu) from ³³O₂⁺ (32.994050 amu). The latter two species define an $m/\Delta m$ of 4,450 where m is molecular mass, implying that an instrumental $m/\Delta m$ (mass resolving power) of at least ~12,000 is required for clear separation. The Panorama routinely runs with an $m/\Delta m$

of 60,000. An example of the separation achievable between these species is shown in Figure 2. We fluorinated SC olivine and collected the O_2 without the usual purification by distillation on two molecular sieves. Results for analyses of this gas using the conventional Delta instrument where NF^+ and $^{33}O_2^+$ are not resolved, and with the Panorama, where they are resolved, are clearly different (Figure 1).

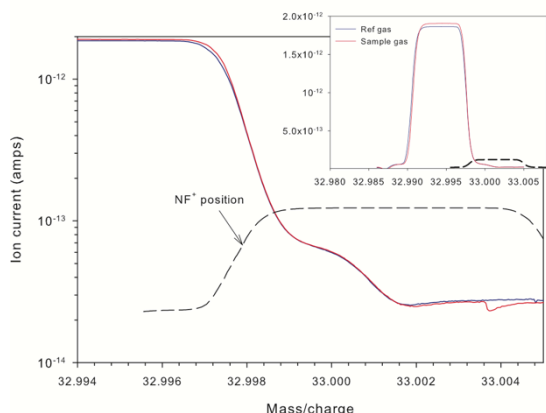


Figure 2: Panorama mass scan over the $^{33}O_2^+$ peaks for sample and reference gases showing the position of NF^+ (dashed line) if it were detectable. The scan shows that $^{33}O_2^+$ and NF^+ are resolved when measurements are made at the center of the $^{33}O_2^+$ ion beams. Inset shows the full width of the beams at larger scale.

The anomalously high $\Delta^{17}O$ value of 37 ± 5 ppm for the conventional mass spectrometric analysis suggests that NF^+ was present in the sample. The lack of this anomalously high $\Delta^{17}O$ value for the Panorama analysis of the same gas, with a $\Delta^{17}O$ value of 2 ± 5 ppm, indicates that the source of the high value was indeed NF^+ interference on $^{33}O_2^+$.

We used the instrument to demonstrate further that NF_3 is not an explanation for our finding that $\Delta^{17}O$ for Earth and Moon are indistinguishable (see abstract, this volume). For this purpose we performed replicate analyses of a single sample of Apollo 17 high-Ti basalt (70215) both on the Panorama mass spectrometer at high mass resolution and at low mass resolution using the conventional Delta instrument. Results show no difference between the data obtained using the two instruments.

Adsorbed Water: Because SC olivine has lower $\Delta^{17}O$ values than terrestrial waters by ~ 80 to 100 ppm [4, 5], spuriously high $\Delta^{17}O$ values can result if adsorbed water remains in fluorination samples. Most laboratories remove water and other contaminants using “pre-fluorination” in which the sample is exposed to F_2 or BrF_5 gas prior to heating with the infrared laser. Our experience is that oven drying and prefluorination alone are not adequate for very high precision $\Delta^{17}O$ determinations. Instead, we have found that an

infrared-lamp heating step is necessary for complete removal of the effects of water.

Experiments on the Effects of Water: In order to demonstrate the effects of lingering adsorbed water on $\Delta^{17}O$ measurements, we analyzed a sample of Mauna Loa basalt powder without our infrared heating step and compared the $\Delta^{17}O$ values with those obtained with the infrared heating step.

For this experiment we powdered a fragment of Mauna Loa basalt. A fraction of the powder of Mauna Loa basalt was set out on the lab bench in an unsealed plastic container for two months. Two aliquots of the “wet” powder were loaded directly into the fluorination chamber under N_2 purge gas and pumped over night. After pre-fluorination, the samples were analyzed by CO_2 laser heating in the usual way. As a control experiment, five fractions of the same Mauna Loa basalt powder were subjected to oven drying prior to loading followed by infrared-lamp heating until the baseline pressure was $< 10^{-6}$ mbar following our usual procedures. The wet basalt powders subjected to pre-fluorination but not infrared-lamp heating have an average $\Delta^{17}O$ value of $+9 \pm 2$ ppm while the dry samples subjected to prefluorination following infrared-lamp heating have an average $\Delta^{17}O$ value of -2 ± 1 ppm (Figure 1).

Oven-drying of three aliquots of lunar sample 70215.380 resulted in 10% weight loss, corresponding to a fraction of oxygen present as water of 0.166. The effect of this water on measured $\Delta^{17}O$ values if not removed is $0.166 (+80 \text{ ppm}) + (1.000 - 0.166)(0 \text{ ppm}) = 13.3 \text{ ppm}$ based on a water $\Delta^{17}O$ value of $\sim +80$ ppm (which could be conservative) relative to SC olivine. From this we conclude that if sufficient steps are not taken to remove adsorbed water, especially for powders, $\Delta^{17}O$ values can be too high by 10 ppm or more. This is similar to the recently measured difference between Earth and Moon reported by Herwartz et al. [6].

References: [1] Rumble, D. et al., (1997) *Geochimica Et Cosmochimica Acta* 61, 4229-4234. [2] Pack, A. et al., (2007) *Rapid Communications in Mass Spectrometry* 21, 3721-3728. [3] U. H. Wiechert et al., (2001) *Science* 294, 345-348. [4] Tanaka, R.; Nakamura, E.; (2013) *Rapid Communications in Mass Spectrometry* 27, 285-297. [5] Pack, A.; Herwartz, D.; (2014) *Earth and Planetary Science Letters* 390, 138-145. [6] Herwartz, D. et al., (2014). *Science* 344, 1146-1150

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