

Oxygen Isotopic Measurements by Secondary Ion Mass Spectrometry in Uranium Oxide Microparticles: A Nuclear Forensic Diagnostic

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To exploit oxygen isotopic measurement by SIMS as a diagnostic tool in nuclear forensics, the magnitude and reproducibility of O-isotope instrumental mass discrimination for O-isotope standards in the SIMS laboratory at the Institute for Transuranium Elements has been evaluated. Tests for matrix-dependent discrimination effects on three different O-isotope standards with substantially different matrix compositions have been performed. The results were checked by an interlaboratory comparison of O-isotope discrimination with those obtained in the SIMS laboratory at the Lawrence Livermore National Laboratory on two standards. The results from the two laboratories are in very good agreement, indicating statistically indistinguishable instrumental mass discrimination factors for $^{18}\text{O}/^{16}\text{O}$ ratios on the Cameca 6f and 3f, when the analyses are performed under the experimental conditions described. The $2\sigma_{\text{mean}}$ uncertainties of these factors are in the range of 0.3–0.9%. In accordance with the tested methodology, O-isotope compositions were measured in three particulate uranium oxide samples of nuclear forensics interest.

The isotopic composition of oxygen is an important diagnostic for characterization of samples from a variety of research fields. Advances in secondary ion mass spectrometry (SIMS) over the last two decades have made possible precise methods for resolving small differences in $^{18}\text{O}/^{16}\text{O}$ on a microscale in solids.^{1–6}

For all practical purposes, the SIMS ion microprobe is the only mass spectrometric technique with an effective spatial resolution of a few micrometers and therefore with the capability for measurement of $^{18}\text{O}/^{16}\text{O}$ on particles and microstructures in heterogeneous samples. Typical SIMS O-isotope analyses in small

(10 ng) meteorites³ have precisions of ± 0.5 –1‰ for $^{18}\text{O}/^{16}\text{O}$. By comparison, O-isotope analysis based on laser fluorination techniques followed by gas chromatography and mass spectrometry demonstrates better precision than SIMS but has not been applied successfully to samples smaller than 0.1–0.5 mg.^{7–10}

For several years at the Institute for Transuranium Elements (ITU), SIMS techniques have been applied for the identification and characterization of radioactive microparticles (none larger than 1 ng).^{11–16} This research has been mainly focused on characterization of microparticles originating from uranium enrichment plants and from spent fuel reprocessing facilities for detection of undeclared nuclear activities. In addition, the capabilities of this methodology have been exploited in nuclear forensic science for verification of adherence to international treaties¹⁷ and for source attribution for contraband nuclear materials detected in sampling (overt and covert) by national and international authorities.¹⁵

Specifically, SIMS is used to distinguish U-bearing particles from Pu-bearing particles (as a backup to electron probe and energy-dispersive X-ray analyses) and to measure, accordingly, the U and Pu isotopic compositions.¹⁴

As demonstrated by electron microprobe analyses, the preponderance of the actinide-bearing particles are oxides. Thus, oxygen is a major element in these particles and, under properly chosen analytical conditions, offers ample signal for O-isotope analysis by SIMS. Moreover, oxygen isotopic ratios for UO_2 fuels have been observed to vary slightly with the geographical location of the fuel production facility.¹⁸ These variations exhibit a range in $^{18}\text{O}/^{16}\text{O}$ of $\sim 3\%$. This observation thus bolsters the expectation

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that SIMS measurements of $^{18}\text{O}/^{16}\text{O}$ in actinide-bearing particles can be successfully used for source attribution ("geolocation") of contraband actinide materials. Therefore, it is necessary to have a reliable, accurate, and precise analytical methodology for the determination of the oxygen isotopic composition in radioactive microparticles.

In this paper, the first results of a study to augment the particle diagnostics provided by the actinide isotope measurements with oxygen isotope (i.e., $^{18}\text{O}/^{16}\text{O}$) determinations in the same particles is presented. The major aim of this investigation was to establish the magnitude and reproducibility of O-isotope instrumental mass discriminations for O-isotope standards in the SIMS laboratory at ITU. For this purpose, tests for matrix-dependent discrimination effects were performed by analyzing three different O-isotope standards with substantially different matrix compositions. The results were checked by an interlaboratory comparison of O-isotope discriminations with those obtained in the SIMS laboratory at the Lawrence Livermore National Laboratory (LLNL), California, on two standards. In accordance with the tested methodology, O-isotope compositions were measured in three particulate uranium oxide samples of nuclear forensics interest. The results are reported in terms of ratios with uncertainties.

EXPERIMENTAL SECTION

Instrumentation. A Cameca IMS-6f ion microprobe and a modified Cameca IMS-3f ion microprobe were used at the ITU (Karlsruhe, Germany) and at the LLNL (Livermore, CA), respectively. At both laboratories, the analyses were performed with a Cs^+ sputtering beam, and the sputtered $^{16}\text{O}^-$ and $^{18}\text{O}^-$ were measured as singly charged, negative ions, according to analytical conditions already described by other authors as giving high-precision O-isotope measurements on Cameca ion microprobes.^{19–24}

Some of the samples investigated here are known to exhibit severe charging when analyzed as macroscopic samples ($\geq 100\ \mu\text{m}$ in size) under Cs^+ bombardment. However, the experimental approach is to measure these materials as microscopic particles (i.e., $< 100\ \mu\text{m}$). Previous work¹² has shown that careful sample preparation eliminates charging for such microscopic samples. The sample preparation used (see below) has been designed to achieve freedom from such sample charging and was successful.

Instrumental Analytical Conditions at ITU. The $^{133}\text{Cs}^+$ primary sputtering beam was operated with an accelerating voltage of +10 kV and was mass-separated with a mass filter to ensure mass spectral purity of the primary ions. Primary beam currents were in the range of 5–10 nA. The primary beam resolution was a few micrometers, always smaller than the analyzed particles. To homogenize the collection of the secondary signal, the primary beam was slightly defocused and beam rastering was not used.

The secondary ion beam accelerating voltage was –5 kV. The energy band-pass of the secondary mass spectrometer was 50 V. Oxygen isotopes ($^{18}\text{O}^-$ and $^{16}\text{O}^-$ only) were measured with a

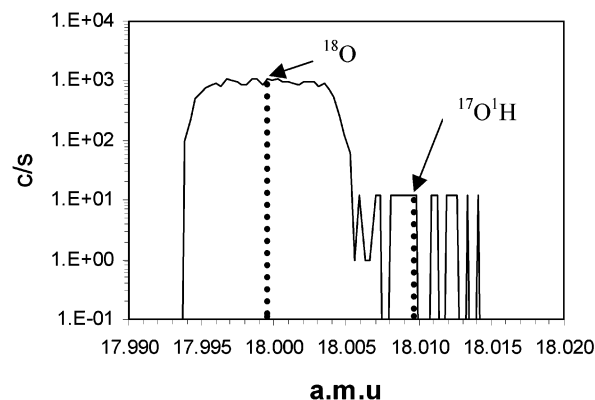


Figure 1. 2500 resolving power for the peaks ^{18}O and $^{17}\text{O}^1\text{H}$.

resolving power of 2500. This resolving power was sufficient to eliminate a possible contribution from the $^{17}\text{O}^1\text{H}^-$ ion to the $^{18}\text{O}^-$ signal (Figure 1). The secondary ions $^{18}\text{O}^-$ and $^{16}\text{O}^-$ were measured by peak switching on an ETP 133H electron multiplier pulse-counting system. The measured dead time of the pulse-counting system was 25 ns, and the data reported here have been corrected for dead time losses according to a nonparalyzable dead time correction algorithm.²⁵

The secondary ion analyses were performed according to a vendor-supplied software protocol entitled Depth Profile. The $^{16}\text{O}^-$ signal had an integration time of 1 s; that of $^{18}\text{O}^-$ was 10 s. The primary beam intensity and the acquisition time were chosen to achieve 10^6 total counts for $^{18}\text{O}^-$; i.e., such that the counting statistics for the $^{18}\text{O}/^{16}\text{O}$ ratio were nominally 0.1%. Under these conditions, the $^{16}\text{O}^-$ count rate was typically 5×10^5 counts/s, and the $^{18}\text{O}^-$ count rate was 1×10^3 counts/s.

Instrumental Analytical Conditions at LLNL. The $^{133}\text{Cs}^+$ primary beam with a typical current of 0.60 nA was operated with an accelerating voltage of +10 kV. It was mass-filtered, defocused, and not rastered.

The secondary accelerating voltage was –4.5 kV, and the value of the energy band-pass of the secondary mass spectrometer was 39 V. The contrast diaphragm was $300\ \mu\text{m}$ in diameter, the transfer optics setting was $150\ \mu\text{m}$, and the field aperture was $400\ \mu\text{m}$ in diameter. The resolving power of the secondary mass spectrometer was 2300. The mass positions of $^{16}\text{O}^-$ and $^{18}\text{O}^-$ were checked during each run by dynamic peak centering and were corrected if necessary, ensuring that there were no significant contributions to the $^{18}\text{O}^-$ signal from the $^{17}\text{O}^1\text{H}^-$. Dynamic energy offset compensation ("autovoltaging") was employed for all analyses. The resulting energy offset was typically 0 V and in no case was greater than +2 V. The $^{18}\text{O}^-$ and $^{16}\text{O}^-$ signals were measured on an electron multiplier (ETP133H) pulse-counting system, whose dead time was experimentally determined to be 15 ns. The data reported here have been corrected for dead time losses according to a nonparalyzable dead time correction algorithm.²⁵

The secondary ion analyses were performed with in-house developed software. The integration time for the $^{16}\text{O}^-$ signal was set to 1 s, that for $^{18}\text{O}^-$ 10 s. The acquisition time was adjusted by the operator such that the total counts of $^{18}\text{O}^-$ were greater than 10^6 counts. Typical count rates for $^{16}\text{O}^-$ and $^{18}\text{O}^-$ were 8×10^5 and 1.6×10^3 counts/s, respectively.

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Sample Description and Preparation. The set of materials analyzed in this study includes three standard samples with well-known $^{18}\text{O}/^{16}\text{O}$ ratios. Two of them are Burma spinel and UO_2 standards whose oxygen isotopic composition was previously determined by stable-isotope mass spectrometry at the University of Chicago.²⁶ The third is a Cu_2O control sample whose O-isotope composition was characterized by the French National Center for Scientific Research in Meudon-Belvue, France, and supplied to the Cameca Corp., France.²⁷

Burma spinel is a naturally occurring Mg–Al spinel (MgAl_2O_4) from Burma. The sample consists of small gem-quality crystals (1–3 mm in diameter). Individual particles were obtained in a broad range of sizes by crushing of the sample. The smallest pieces (1–20 μm) were obtained in an alcoholic suspension by stirring the crushed sample in alcohol and allowing the larger particles to settle for a short time. While the smallest particles were suspended, the alcohol was then pipetted and the solution containing the finest particles (slurry) was deposited on a conductive polished carbon planchet (Fullam Inc., grade A carbon planchets No. 17680). The particles adhered to the planchet after the alcohol had evaporated, and they did not cause any significant charging in the SIMS instrument.

Larger particles ($\geq 20 \mu\text{m}$) were obtained by adding more alcohol to the remaining crushed sample, stirring, and immediately taking up the slurry with a pipet. This slurry was sprinkled on either gold or indium foil substrates, and the particles were pressed into the substrates using a glass rod or a flat quartz disk. In some cases, coating the surface with a thin layer of carbon or gold alleviates charging of the largest particles.

The UO_2 O-isotope standard was prepared for analysis with the same procedure as for the Burma spinel standard. The Cu_2O O-isotope control sample was furnished from Cameca as a polished ceramic disk. It was analyzed with no further sample preparation.

Three uranium oxide samples with unknown O-isotopic compositions were investigated: “Morille” U_3O_8 powder, a standard for metallic impurities obtained from Cetama (France); “NBL_6”, an uranium oxide U-isotopic standard from the U.S. National Institute of Standards and Technology; “FFSU”, a UO_2 fuel pellet from the former Soviet Union. These samples were prepared by the same procedure as for the Burma spinel.

ITU investigated the complete series of samples. At LLNL, only the finest fraction (smaller than 20 μm) of the Burma spinel and UO_2 standard were analyzed. The Burma spinel particles were deposited on a high-purity Au sheet substrate. The UO_2 standard particles were deposited on a vitreous graphite substrate.

RESULTS AND DISCUSSION

Matrix Effects on Measured O-Isotope Composition. Isotopic analysis by SIMS can exhibit matrix-dependent mass discrimination effects. The main sources of instrumental mass discrimination occurring in geological materials are secondary ion sputtering and ionization, secondary ion transmission, and detection.¹⁹ However, in studies on oxygen isotopic composition measured by SIMS, no significant differences in instrumental mass discrimination among silicate and oxide phases have been observed.^{2,3,20–22} From these and other previous studies,^{23,24} it can

Table 1. $^{18}\text{O}/^{16}\text{O}$ Ratio Results in Standards

standard	$^{18}\text{O}/^{16}\text{O}$ true value	$^{18}\text{O}/^{16}\text{O}$ mean	uncertainty 2σ mean	no. of analysis
(A) Measured at ITU				
Burma spinel	0.002 049 9	0.001 984	$\pm 0.000\ 012$	7
Cu_2O	0.002 036 0	0.001 974	$\pm 0.000\ 004$	15
UO_2	0.001 959 1	0.001 886	$\pm 0.000\ 006$	12
(B) Measured at LLNL				
Burma Spinel	0.002 049 9	0.001 986	$\pm 0.000\ 017$	6
UO_2	0.001 959 1	0.001 888	$\pm 0.000\ 007$	12

Table 2. Instrumental Mass Discrimination Factor (IMF) Results

samples	IMF_ITU	uncertainty (2σ)	IMF_LLNL	uncertainty (2σ)
Burma spinel	1.033	± 0.007	1.032	± 0.009
UO_2	1.039	± 0.003	1.038	± 0.004
Cu_2O	1.032	± 0.002		

be inferred that instrumental mass discrimination for oxygen isotope analysis might not require any matrix-dependent corrections. To validate this inference, it is subtracted from the ^{16}O and ^{18}O count rates; then the background-corrected $^{18}\text{O}/^{16}\text{O}$ ratio was calculated.

Oxygen Isotope Blanks for Sample Substrates. Concerning the ITU analyses, the carbon planchets used for the particle analyses were found to have negligible O-isotope blanks. Thus, no substrate–blank corrections were applied to the reported $^{18}\text{O}/^{16}\text{O}$.

At LLNL, the gold substrate for the Burma spinel analyses was also found to have a negligible O-isotope blank. Therefore, no substrate–blank corrections were made to the reported $^{18}\text{O}/^{16}\text{O}$ ratios for these analysis.

The O-isotope blank of the carbon planchet substrate for the UO_2 standard particles was larger than that of the gold substrate. However, the effect of blank corrections to $^{18}\text{O}/^{16}\text{O}$ ratios for this substrate were generally in the range of 0.05–0.3‰; the worst case being 0.5‰. Since these corrections amounted to 1 order of magnitude less than the uncertainties on the $^{18}\text{O}/^{16}\text{O}$ ratios of the UO_2 particles, substrate–blank corrections to the reported $^{18}\text{O}/^{16}\text{O}$ ratios of these particles were not made.

Instrumental Intercomparison between ITU and LLNL. The results of composition of the $^{18}\text{O}/^{16}\text{O}$ measurements of standards at ITU and LLNL are listed in Table 1. As can be seen, the results from the two laboratories are in very good agreement. This is also evident when these data are reported, as in Table 2 in terms of instrumental mass discrimination factors (IMFs), where the IMF is defined as

$$\text{IMF} = (^{18}\text{O}/^{16}\text{O})_{\text{true value}} / (^{18}\text{O}/^{16}\text{O})_{\text{mean measured value}}$$

The LLNL results for the Burma spinel and UO_2 standards are essentially identical to those measured at ITU, for both the IMF's and the uncertainties. At both laboratories, the sample preparations, the optics of the instruments, and the analytical conditions were similar. Therefore, we conclude that this congruence of results indicates a statistically indistinguishable IMF for $^{18}\text{O}/^{16}\text{O}$

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Table 3. $^{18}\text{O}/^{16}\text{O}$ Ratio Results on Three Different Uranium Oxide Samples^a

samples	$^{18}\text{O}/^{16}\text{O}$ mean ITU	uncertainty (2σ)
NBL_6	0.002 080	$\pm 0.000\ 005$
Morille	0.002 049	$\pm 0.000\ 002$
FFSU	0.002 008	$\pm 0.000\ 003$

^a Mean values given over 10 measurements of different particles.

ratios on the Cameca 6f and 3f, when the analyses are performed under the conditions cited above and the $2\sigma_{\text{mean}}$ uncertainties are in the range of 0.3–0.9%.

The difference between the IMF results (Table 2) for the two particle-based standards, Burma spinel and UO_2 , is statistically insignificant at the $2\sigma_{\text{mean}}$ level. Therefore, there is no statistically significant matrix effect on the mean $^{18}\text{O}/^{16}\text{O}$ ratios of the Burma spinel and UO_2 particle-based standards. In other words, the findings of this study indicate that, if a matrix effect is present, experimental precisions of $\leq 0.2\%$ on the IMFs will be required to detect it.

The IMF for the Cu_2O standard, which is a flat and polished sample, has the smallest uncertainty of the IMFs for the three standards. The Cu_2O IMF is in statistical agreement with that of Burma spinel but is distinct from that of UO_2 standard at the $2\sigma_{\text{mean}}$ level. This could be an indication that variations in sample “topography” from particle to particle in the particle-based samples may be responsible for the larger variance of the mean $^{18}\text{O}/^{16}\text{O}$ ratios when compared to the variance for this ratio on the flat, polished sample measured under the same instrumental conditions. A test of this hypothesis will require more careful sample microcharacterization than was done for the present study.

$^{18}\text{O}/^{16}\text{O}$ Results for Uranium Oxide Particle Samples of Different Origins. The oxygen isotope results of the three “unknown” uranium oxide samples in this study are summarized in Table 3. The tabulated values for the $^{18}\text{O}/^{16}\text{O}$ ratios have been corrected with the IMF for the UO_2 standard measured at ITU (see Table 2). The mean $^{18}\text{O}/^{16}\text{O}$ values for these samples differ significantly from one another, thus demonstrating that SIMS measurements of the $^{18}\text{O}/^{16}\text{O}$ ratio of uranium oxide particles can be used as a discriminator for nuclear forensic investigations.

As was found for the particle-based oxygen isotope standards, particle-to-particle variations in the $^{18}\text{O}/^{16}\text{O}$ ratio are larger than the counting statistics uncertainties determined for each individual particle of a given sample (see Figure 2). The overall precision for the mean $^{18}\text{O}/^{16}\text{O}$ ratio of these three samples ranged from 0.1 to 0.25%, whereas the precision due to counting statistics was always $<0.1\%$ for each individual particle measurement.

The $^{18}\text{O}/^{16}\text{O}$ results for 12 uranium oxide samples measured by thermal ionization mass spectrometry (TIMS) have been recently reported.²⁸ The TIMS results compared with the SIMS ones of this study for the three samples are plotted in Figure 3. As can be seen, the relative oxygen isotope differences between the TIMS data set and the SIMS data set are in good agreement.

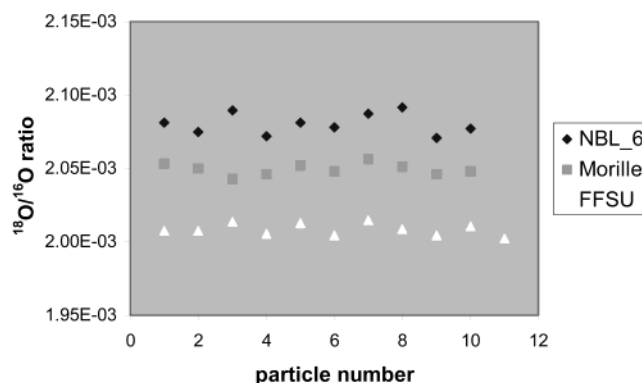


Figure 2. $^{18}\text{O}/^{16}\text{O}$ isotopic ratio results on the three “unknown” uranium oxide samples as obtained by SIMS measurements for different particles.

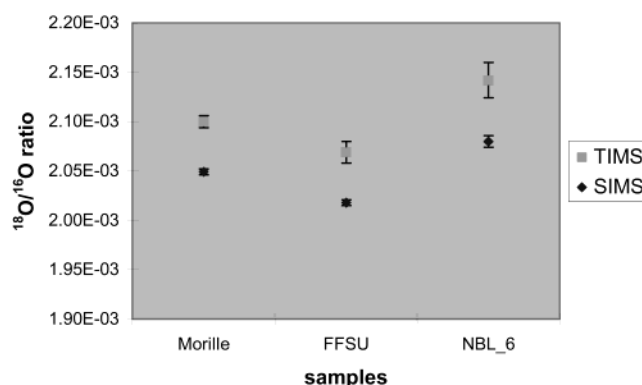


Figure 3. $^{18}\text{O}/^{16}\text{O}$ mean SIMS and TIMS results on the three “unknown” uranium oxide samples.

However, the TIMS data have not been referenced to an absolute isotopic standard, as the SIMS data have been; therefore, there is no substantive basis for further comparison and discussion of the absolute differences between the two data sets.

CONCLUSIONS

In this paper, the attention has been focused on the $^{18}\text{O}/^{16}\text{O}$ ratio in the final UO_2 products. Research is ongoing to find out whether the $^{18}\text{O}/^{16}\text{O}$ ratio of the uranium ore might be significantly changed during the fabrication process, as a result of isotopic exchange with the oxygen of the water or solutions used during the hydrolysis step. From the results so far obtained, it has been demonstrated—with O-isotope standards, an interlaboratory calibration, and “unknown” uranium oxide samples whose relative O-isotope ratios have been measured independently by TIMS—that SIMS measurements of these small oxygen isotope variations can also be made on single microparticles of uranium oxide. Furthermore, it has been shown that the accuracy and reproducibility of such measurements are sufficient to make SIMS-based O-isotope determinations a reliable and efficient tool for robust discrimination in nuclear forensics applications.

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