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MEASURING FLUORINE IN URANIUM OXYFLUORIDE PARTICLES USING SECONDARY ION MASS SPECTROMETRY FOR NUCLEAR FORENSICS

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Abstract

Gaseous uranium hexafluoride (UF_6) is used for the enrichment of uranium and is known to be a very reactive and volatile gas. When a small amount of UF_6 is released in the environment, it forms uranium oxyfluoride particles and hydrogen fluoride from the reaction with atmospheric moisture. The uranium oxyfluoride particles settle on various surfaces within the enrichment facility where they are collected by safeguards organizations such as the International Atomic Energy Agency (IAEA) through a technique called environmental sampling (1). Despite their small size, the IAEA uses the uranium isotopic

composition of these particles to determine whether an enrichment facility is compliant with its declarations. What makes particle samples from enrichment facilities particularly interesting is that they often contain a measurable amount of fluorine. As uranium oxyfluoride particles lose this fluorine over time, and from the exposure to certain environmental conditions, the analysis of the relative amount of fluorine can place boundaries on particle exposure history.

Expressly for the purpose this work, we prepared a set of UO_2F_2 particle samples from the hydrolysis of UF_6 and stored these samples in environmental chambers at different temperature, humidity and lighting conditions. The NanoSIMS secondary ion mass spectrometer, with a nanometer-scale spatial resolution, was used to measure the F^+/U^+ secondary ion ratio of individual particles immediately after sample preparation, and at different time intervals. NanoSIMS analysis on single particles stored up to 7 months in dry air did not detect a significant decrease in the relative amount of fluorine. The exposure to high humidity however, caused a large variability in the F^+/U^+ ratio, up to 2 orders of magnitude below that of the particles stored in dry air.

Introduction

Nuclear forensics relies on the analysis of certain sample characteristics to determine the origin and history of a nuclear material. In the specific case of uranium enrichment facilities, it is the release of trace amounts of uranium hexafluoride (UF_6) gas - used for the enrichment of uranium - that leaves a process-specific fingerprint. When this UF_6 gas interacts with atmospheric moisture, uranium oxyfluoride particles or particle agglomerates are formed with sizes ranging from several microns down to a few tens of nanometers (2). These particles are routinely collected and analyzed by safeguards organizations, such as the International Atomic Energy Agency (IAEA), allowing them to verify whether a facility is compliant with its declarations.

Spectrometric analysis on uranium oxyfluoride particles has revealed the presence of particles that contain fluorine, and particles that do not. It is therefore assumed that uranium oxyfluoride is unstable, and decomposes to uranium oxide. The rate of the decomposition is still unknown, but is suspected to be influenced by the exposure to ultraviolet radiation, moisture and elevated temperatures (3). A better understanding of the rate of fluorine loss in uranium oxyfluoride particles, and the parameters that control it, may therefore contribute to placing boundaries on the particle's exposure time in the environment.

Expressly for the purpose of this study, we prepared a set of uranium oxyfluoride particles from a static release of UF_6 in a humid atmosphere, and stored most of the samples in environmental chambers with controlled temperature, humidity and light. Individual particles or particle agglomerates from these samples were characterized by secondary ion mass spectrometry with nanometer-scale spatial resolution (NanoSIMS). The relative amount of fluorine was determined at different stages in the aging process, as well as immediately after preparation.

Experimental

Uranium oxyfluoride particle samples

The uranium oxyfluoride particles used for this study were prepared at the Institute for Reference Materials and Measurements of the European Commission (EC-IRMM) in Belgium (4). UF_6 is a highly volatile and reactive gas and hydrolyzes almost instantaneously upon contact with water.

In a 2 liter static air volume, with a relative humidity of around 70 %, an estimated 40 mg of UF_6 was released from a glass vial that was shattered by a metallic pin, allowing the UF_6 released from the vial to fully react with the atmospheric moisture. Upon its release, the UF_6 hydrolyzed to form UO_2F_2 particles and hydrogen fluoride gas (HF) (2). The UO_2F_2 particles are highly hygroscopic and are assumed to be in a hydrated form.

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$$

Slightly depleted UF_6 (^{235}U = 0.704 %) was used for all particle samples. Graphite, sapphire and ZnSe substrates were placed at the bottom of the chamber to collect the solid UO_2F_2 particles through gravitational settling. 174 particle samples were prepared at the IRMM and sent to Lawrence Livermore National Laboratory (LLNL) for either storage in environmental chambers at specific humidity, temperature and light exposure levels (Table 1), or immediate analysis at LLNL or Pacific Northwest National Laboratory (PNNL) to provide a reference measurement for the relative amount of fluorine right after formation (time = 0 measurement). The uranium oxyfluoride particles deposited on 9.25 mm diameter graphite planchets (3/8 inch) were analyzed by NanoSIMS at the LLNL. The sapphire and ZnSe substrate samples were shipped to PNNL where they were characterized by cryogenic total-reflection laser-induced fluorescence spectroscopy (CTRLIFS), Raman spectroscopy and Fourier-transform infrared spectroscopy (FTIR), as well as secondary ion mass spectrometry.

	ETS 1		ETS 2	ThF1	ThF2	
Temperature (°C)	24	25	40	25	41	30
Rel. Humidity (%)	< 15	30	< 15	76	77	43
Light	simulated daylight/dark		diffuse/ dark	diffuse	diffuse	

Table 1: Overview of the temperature, relative humidity and light settings for the four environmental chambers that were used for particle storage at LLNL. The conditions for chambers ETS1 and ThF2 were changed to more moderate temperature and humidity levels (right column) after the first experiment (left column) was finished.

Secondary ion mass spectrometry (SIMS)

The Cameca NanoSIMS 50 secondary ion mass spectrometer at LLNL is able to measure the elemental composition of individual uranium oxyfluoride particles. NanoSIMS is a destructive technique in which a 16 keV beam of either O^- (from a duo-plasmatron) or Cs^+ ions is rastered onto the sample, generating secondary ions that are detected by a double-focusing mass spectrometer (Fig. 1). The combination of a short working distance, normal ion beam incidence and high brightness ion sources results in a lateral resolution in the order of a few hundred nanometer. Up to 5 ion species can be detected simultaneously over a mass range of a factor of 12 through an array of secondary electron multipliers. For the large mass difference between fluorine (m/z = 19) and uranium oxide (m/z = 254), however, the magnetic field setting needed to be adjusted (peak jumping). A bulk UF_4 sample was used for mass calibration. Variations in the ion intensities with sputtering were monitored by collecting 6 µm x 6 µm ion images, while cycling the magnet through the masses of interest to obtain a depth profile. Specific image-processing software (L'Image, Larry Nittler) was used for data reduction.

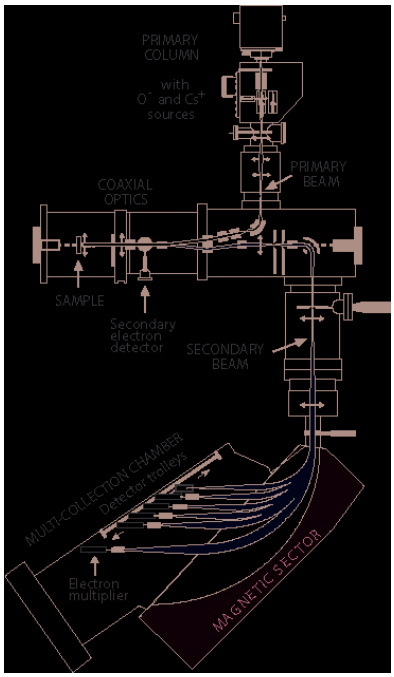

Fig 1: Schematic of the NanoSIMS secondary ion mass spectrometer at LLNL

Scanning electron microscopy (SEM)

Although NanoSIMS is a very powerful tool for the analysis of individual particles, sample characterization using scanning electron microscopy (SEM) remains indispensable, both before and after NanoSIMS analysis. Images and compositional information are obtained by rastering a highly-focused electron beam across the sample. At the IRMM, a tungsten filament FEI Quanta 200 3D SEM was used to examine the particle loading and morphology for a subset of freshly-prepared uranium oxyfluoride samples. This instrument has a spatial resolution of 3.5 nm at 20 kV at a working distance of 8 mm. An FEI Inspect F field-emission type SEM equipped with an EDAX Si(Li) detector was used at LLNL to monitor particle morphology and composition during storage in the environmental chambers, and after NanoSIMS analysis.

Results and discussion

The analysis of the relative amount of fluorine in submicron-sized particles requires the use of highly sensitive and selective instrumentation. The Cameca NanoSIMS 50 has the unique capability of sampling 3-6 atomic mono-layers in depth at any given time, with nanometer-scale spatial resolution. The measurement of uranium oxyfluoride particles presents a number of additional challenges to this technique, however. In order to quantify the amount of fluorine in a single particle, the fluorine secondary ion intensity should be compared to the intensity of an ion characteristic of the uranium oxide matrix, preferably atomic uranium ions. Then again, the primary ions used for sputtering the sample surface are generated by either a duoplasmatron (O^- primary ions) or a Cs^+ primary ion source. A primary beam of O^- ions is typically used to chemically enhance the production of electropositive secondary ions, such as U^+, whereas bombardment using Cs^+ primary ions stimulates the generation of electronegative secondary ions, including F^-. The choice of primary ions will therefore always imply a less than optimal secondary ion yield for one of the ion species. Although the use of Cs^+ primary ions produces ion images with a spatial resolution of 100 nm (compared to 200-300 nm for O^- primary ions) and has the additional advantage of generating electron images of the sputtered area in addition to ion imaging, the difference in count rate for U^- and F^- ions was found to be too large. For a freshly-prepared particle sample that was measured with a primary ion current of 1.8 pA, the fluorine count rate nearly reached the secondary electron multipliers operation limits, while the count rate for U^- did not exceed more than 100 cps. By switching the primary ion bombardment from Cs^+ to O^-, and under optimized tuning conditions with a primary current of around 80 pA, the secondary ion yield for the uranium ions was greatly increased, up to a few ten thousand cps, while the F^+ count rate was still as high as a few thousand counts per second at the start of the analysis. Real-time imaging of the UO^+ secondary ions on a larger area, typically 30 µm x 30 µm, was used to locate and center the uranium particles for analysis. At 80 pA primary current, the beam was measured to have a spot size of 300-400 nm. The raster size for the analysis was set to 6 µm x

6 µm, with an image resolution of 32 x 32 pixels. This was calculated to be sufficient for a 300-400 nm spot size and a 30 % overlap.

The ion species collected per cycle were limited to F^+, U^+ and UO^+ to minimize the cycle time and maximize the number of data points during particle sputtering. An energy scan (secondary ion intensity as a function of sample voltage) was performed for each of the ion species and showed that they were well-aligned and centered around 0 V. Depth profiles for the F^+, U^+ and UO^+ ions were collected while changing the magnetic field of the mass analyzer for each of these ions in a series of cycles (peak jumping). The depth profile for a sample stored in an argon atmosphere (to preserve its chemical composition) for 9 months since its preparation at IRMM is shown in Figure 2. The total counts for F^+, U^+ and UO^+ integrated over the 6 µm x 6 µm raster were plotted against the cycle number. This analysis was stopped after the count rate of F^+ was reduced to background. The analysis shown in Figure 2 was completed in 25 minutes. By collecting the F^+ ions in electron multiplier number 2 (lower radius), and the uranium ion species in secondary electron multiplier 5 at higher radius (each at a different magnetic field value), the overall change in magnetic field was limited to less than 25 %. As a result, the magnetic hysteresis was found to be negligible and the peak position did not shift significantly during depth profiling. Angular and energy aberrations were corrected for through the use of an entrance and aperture slit and flat-top peaks were obtained for the uranium species at a mass resolving power of around 5000. At these measurement conditions, the transmission (secondary ion intensity reduction after insertion of the entrance slit) and conversion factor (percent secondary ions produced per primary ion) for Al^+ on an Al-Cu grid was around 60 % and slightly higher than 2 %, respectively.

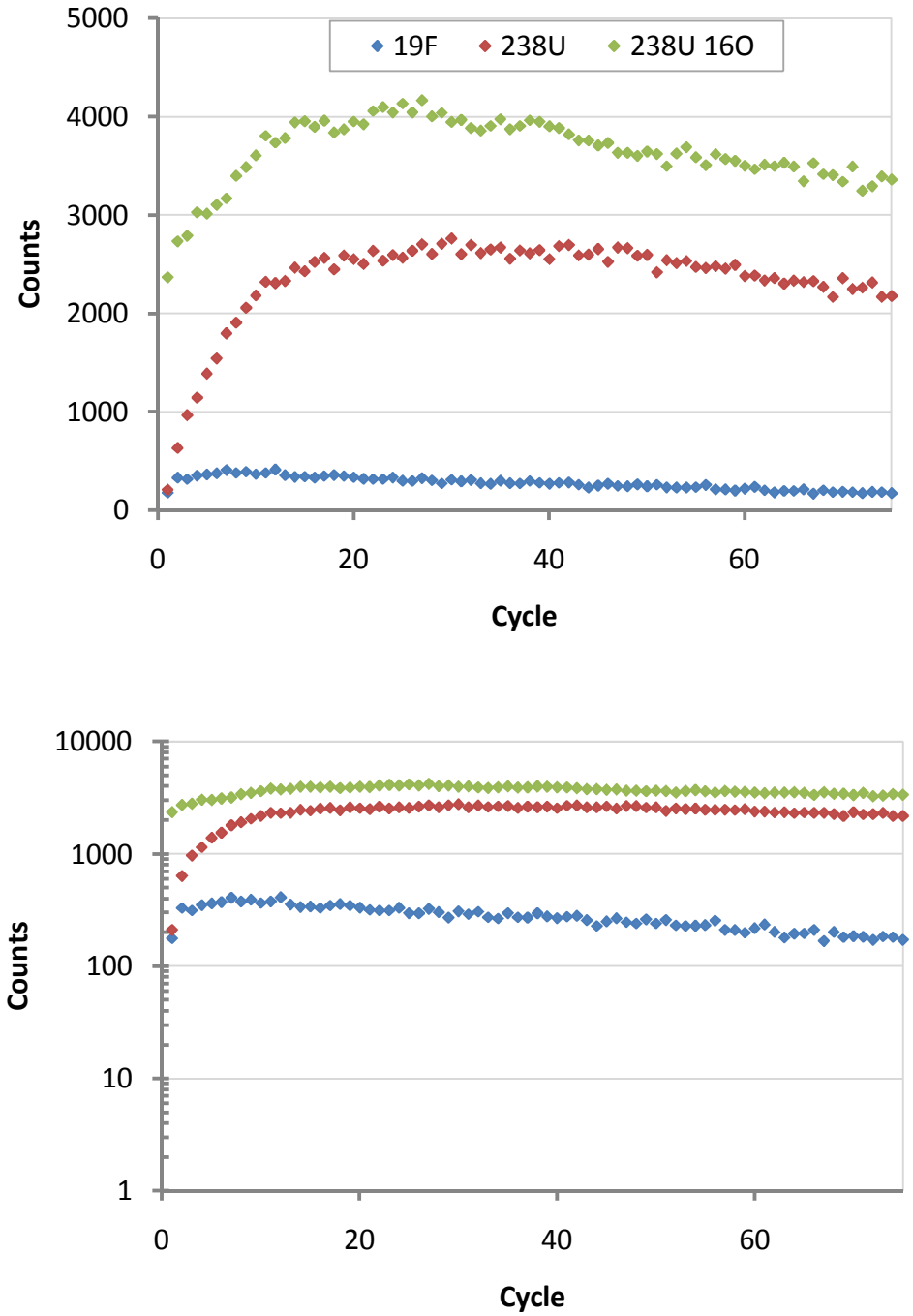

Fig 2: Depth profile of the F^+, U^+ and UO^+ secondary ions on a linear (top) and logarithmic (bottom) scale as generated by O^- primary ion bombardment of a uranium oxyfluoride particle stored in an argon atmosphere for 9 months

The UO^+ ions were generally the most abundant at the start of each measurement and varied around a few thousand counts per second. The U^+ ions tracked the UO^+ ratio as soon as the surface became implanted with oxygen. This point in the analysis is also referred to as sputtering equilibrium and occurred around cycle 11 in the depth profile of Figure 2. The particle was estimated to be eroded at a rate of approximately 1 nm/s, resulting in a steady decrease of U^+ as sputtering of the particle progressed. The intensity for F^+ was several orders of magnitude lower than that of U^+ due to its low ion yield. The count rate attained its maximum within the first few cycles of the analysis, starting at around a few thousand counts per second, and finally decreasing to around 100 cps.

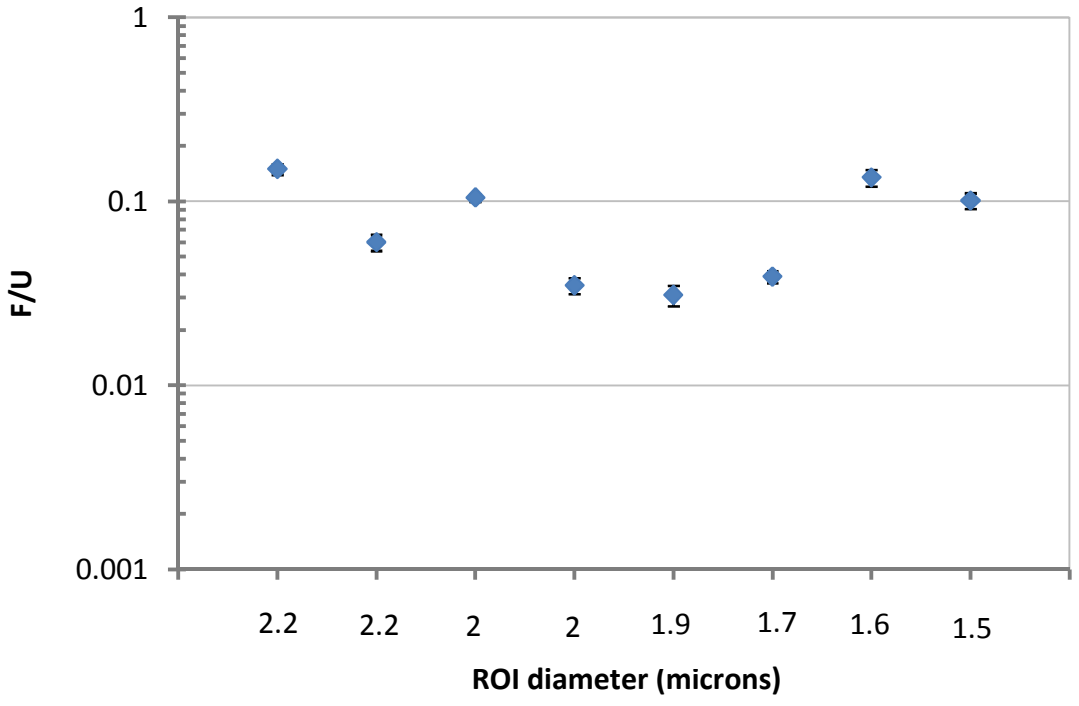

Fig 3: F^+/U^+ ratio for 8 particles from a sample stored for 2 months in 43 % relative humidity at 30 °C plotted as a function of the diameter of the region of interest (ROI) selected on the total uranium oxide ion image, as a measure for particle size

In order to evaluate the relative amount of fluorine in single particles, the total number of counts collected for F^+ was ratioed to the total number of counts for U^+. The resulting F^+/U^+ ratio provided a means to compare differences in composition between particles from the same sample and between samples that

were stored under different environmental conditions. Figure 3 shows a plot of the F^+/U^+ ratio for 8 particles, or possibly particle agglomerates, measured on a sample that was exposed to diffuse light at 43 % relative humidity and 30 °C for 2 months. The error bars were obtained from Poisson statistics on the total number of counts. The x-axis shows the diameter of the region of interest (ROI) that was selected on the UO^+ image, which is typically larger, yet directly correlated to the particle diameter. Redeposition of sputtered ions and atoms, as well as "knock on" effects, where the heavier atoms such as uranium are more susceptible to atom displacements upon impact of the primary ions, are the cause of this offset. This logarithmic plot shows considerable variation in the F^+/U^+ ratio for the different analysis sites, although no correlation between the particle size or the number of cycles, which varied between 34 and 100 cycles, could be established. Differences in particle morphology, topography or charging of the sample which may result in local variations in the extraction field could also have affected the relative secondary ion yield and caused this variation. If this variation in the F^+/U^+ ratio is not caused by the sputtering and measurement process however, then it is either characteristic of the particle formation process (gas-phase condensation), the result of a spread in the rate of fluorine loss between individual particles, or a combination of both. Measurements on particle samples carried out immediately after preparation indicated that a certain variation already exists within 2-3 weeks after preparation. The average F^+/U^+ ratio calculated for two of these samples obtained from 7 particles resulted in 0.14 ± 0.05 and 0.09 ± 0.01 respectively.

The average F^+/U^+ ratios for these freshly-prepared samples were compared to those of a set of samples stored in the environmental chambers at LLNL under different humidity, temperature and lighting conditions, and this for various amounts of time. An overview is presented in Figure 4 (log scale). The sample labels indicate the time in the environmental chamber (7m = 7 months, 3m = 3 months, 1d = 1 day, etc), while the letter L or D denotes whether they were exposed to diffuse or sunlight simulated light (L), or stored in the dark (D), and finally the B number at the end of the labels represents the particle

production batch number. The plotted ratio is the average of 4-8 particles for each of the samples and the error bars represent 1 sigma standard error.

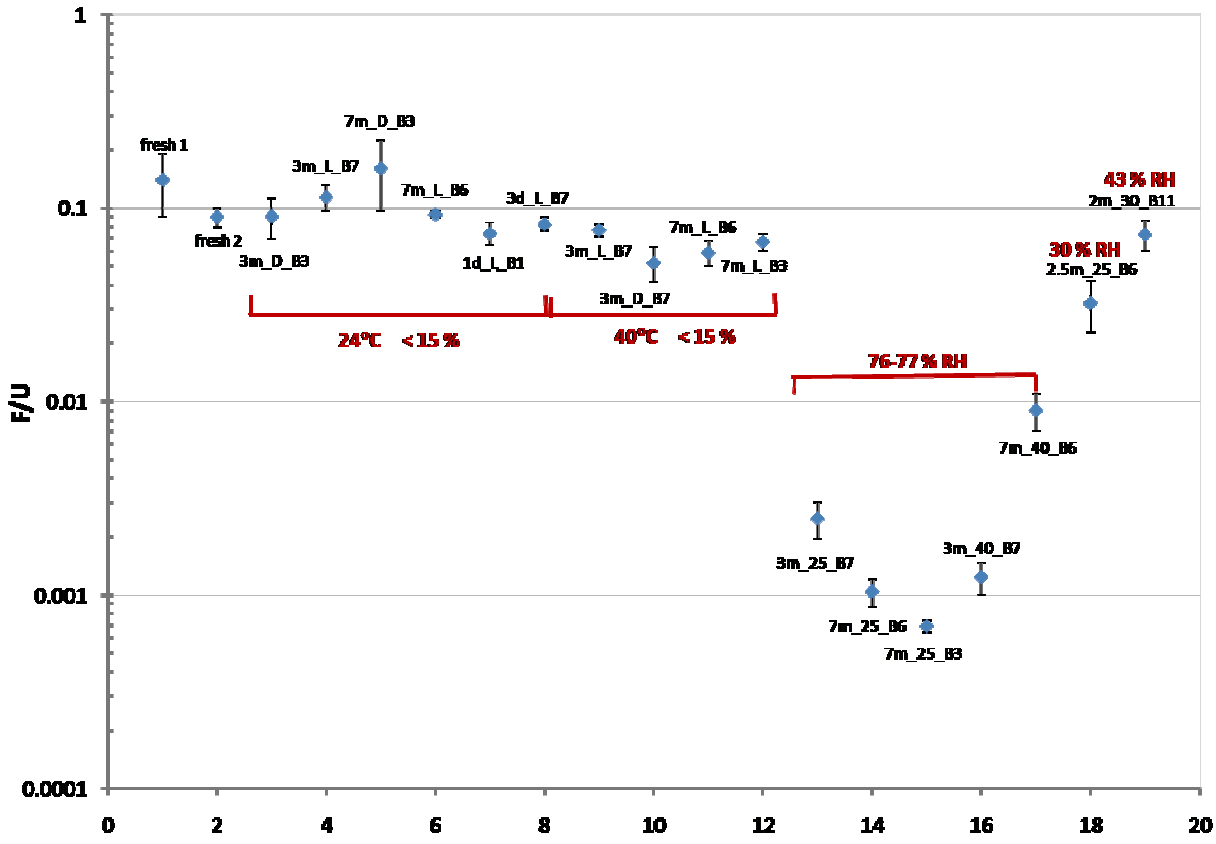

Fig 4: Overview of the F^+/U^+ ratios of 19 uranium oxyfluoride particle samples measured by NanoSIMS using O^- primary ion bombardment

Despite the variation between samples, the average F^+/U^+ ratio for the samples stored in low relative humidity air showed no significant decrease compared to the freshly-prepared samples, indicating that little or no ageing occurred after 7 months of storage under these conditions. In addition, single-factor ANOVA analysis ($\alpha = 0.05$) concluded that the F^+/U^+ variance associated with the different temperature and lighting conditions in these dry air samples did not exceed the variance expected from random error.

The exposure to high humidity seemed to be the main factor promoting the loss of fluorine in uranium oxyfluoride particles. The F^+/U^+ ratio for the samples stored in high humidity air (76 - 77 %) at both 25

°C and 40 °C varied between one and two orders of magnitude below the values of those samples kept in a dry atmosphere. The count rates for fluorine started off at around 10-50 cps, compared to several hundred cps for the samples stored in dry air, and were typically reduced to only a few counts per second after less than 10 cycles. The large spread in the F^+/U^+ ratio for these samples was partially attributed to changes in particle morphology as result of the exposure to moisture. For samples stored at intermediate relative humidity levels (30 % and 43 %) for 2-2.5 months, the decrease in the relative amount of fluorine was much less pronounced.

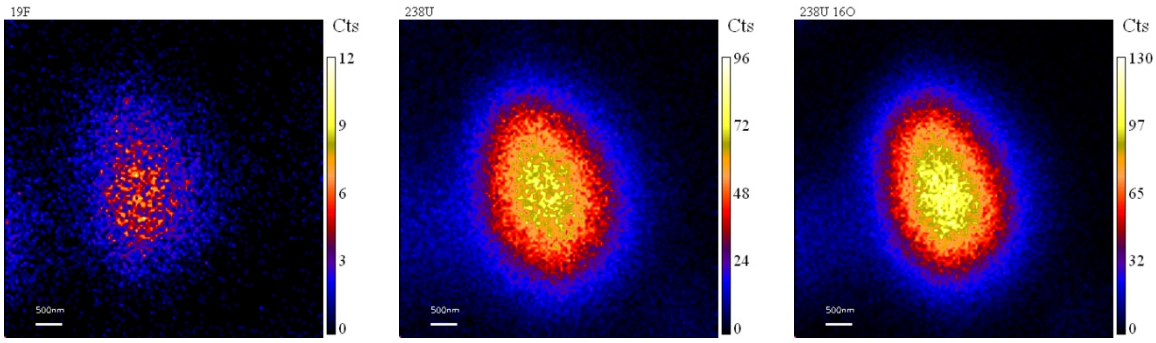

Fig 5: 6 µm x 6 µm ion images of F^+ (left), U^+ (middle) and UO^+ (right) from a uranium oxyfluoride particle measured by NanoSIMS. The color scaling represents the variation in ion intensity

Information on how the fluorine is distributed throughout the particle will provide more insights on how the fluorine is lost from these particles (surface reaction, diffusion,...). Ion images represent a map of the intensity of the secondary ion species across the NanoSIMS raster. The 6 µm x 6 µm ion images of a uranium oxyfluoride particle stored in dry air is depicted in Figure 5 and were recorded within the first 5 minutes of the analysis. These ion images, together with the fluorine depth profile in Figure 6 indicate that the fluorine is located in the center of the particle. However, because of atomic mixing during sputtering and the small difference between the beam spot size and the particle diameter, further experiments are required to confirm this statement.

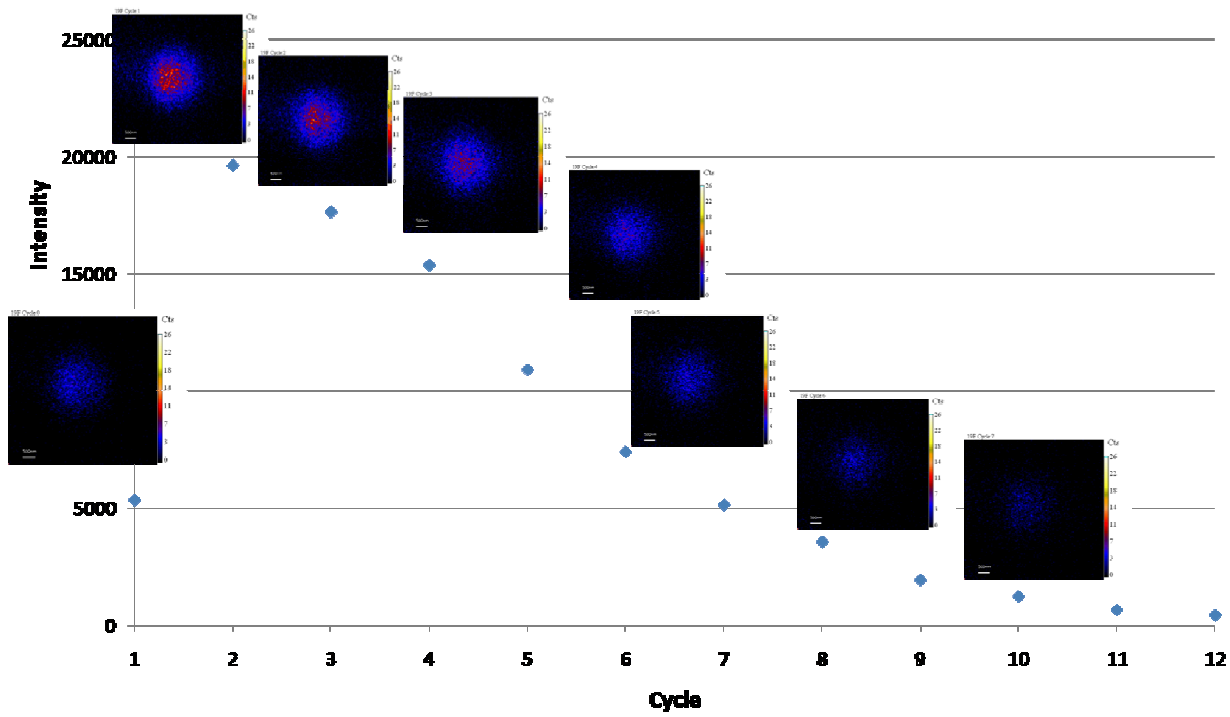

Fig 6: NanoSIMS depth profile and corresponding 6 µm x 6 µm F^+ ion images of a uranium oxyfluoride particle measured after 3 days of storage in <15 % relative humidity at 24 °C

Conclusions

After their preparation in January 2009, a set of fresh and aged uranium oxyfluoride particles has been analyzed by a suite of micro-analytical techniques.

At LLNL, NanoSIMS analysis on single particles stored up to 7 months in dry air did not detect a significant decrease in the relative amount of fluorine. The exposure to high humidity however, caused a large variability in the F^+/U^+ ratio, up to 2 orders of magnitude below that of the particles stored in dry air. Storage in 76 % removed most of the fluorine within 3 months after preparation. The relative humidity for two of the four chambers was therefore changed to 30 % and 40 % to study the effect of moderate humidity levels on particle composition. The effect of UV-light on particle composition will also be investigated.

Acknowledgements

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