LA-UR-15-27011

Title: Campaign 1.7 Pu Aging: Development of Time of Flight Secondary Ion Mass Spectroscopy

Author(s): Venhaus, Thomas J.

Intended for: Report

Issued: 2015-09-09

Campaign 1.7 Pu Aging: Development of Time of Flight Secondary Ion Mass Spectroscopy

Final Report for FY15

T. Venhaus, MST-16

9/3/15

INTRODUCTION

The first application of Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) to an aged plutonium surface has resulted in a rich set of surface chemistry data, as well as some unexpected results. FY15 was highlighted by not only the first mapping of hydrogen-containing features within the metal, but also a prove-in series of experiments using the system's Sieverts Reaction Cell. These experiments involved successfully heating the sample to ~450 °C for nearly 24 hours while the sample was dosed several times with hydrogen, followed by an *in situ* ToF-SIMS analysis. During this year, the data allowed for better and more consistent identification of the myriad peaks that result from the SIMS sputter process. In collaboration with the AWE (U.K), the system was also fully aligned for sputter depth profiling for future experiments.

MAPPING

High resolution SIMS maps were produced on the aged Pu sample (~30 years old). Figure 1 shows SIMS maps of the secondary H^- and F^- ions, as well as an intense mass 27 peak that was observed in the positive ion spectrum. This peak is likely associated with aluminum, as the mass 27 peak appears in the positive spectrum (consistent with a metal), and a map of mass 43 (Al + O) correlates exactly with the map below. It should be noted that SIMS is highly sensitive to aluminum, and quantification of the contaminants below is extremely difficult. It is possible that an alumina polishing compound had been used in the glovebox where this sample was prepared, but this is uncertain. Mapping of hydrogen is complex, as the hydrogen ions can be fragments from surface contamination, hydroxyl groups, hydrocarbons, etc. Contrast in SIMS can either be due to concentration or, often very dramatically, chemical environment (matrix effects). This is a very small subset of the total mapping data that can be obtained from the system. An entire SIMS spectrum is contained within each pixel of the 512 x 512 maps, and any peak can be mapped post-analysis from the main data file.

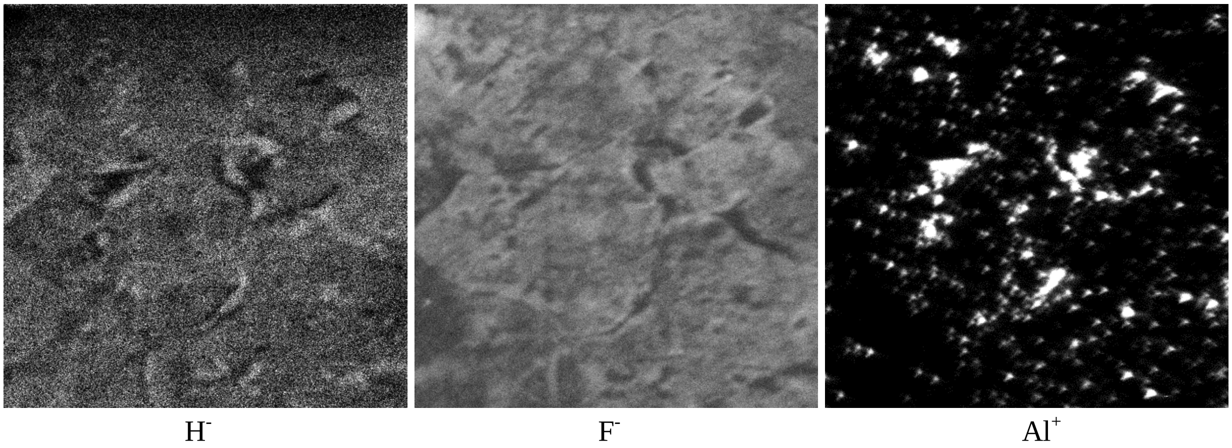

H^- F^- Al^+

Figure 1 – 500 μm² SIMS images from sputtered area on Pu sample surface, showing H^-, F^-, and Al^+

Figure 2 below shows maps from an area that was not sputter cleaned (as-received). The $^{71}Ga^{+}$ peak is mapped to exclude the ^{61}Ga isotope that is lightly deposited from the primary monoisotopic gallium ion gun. Note the variability in contrast of the gallium along grain boundaries and triple points. The contrast in PuO^{-} shows how surface oxide is chemically heterogeneous, both along grain boundaries and within the grains themselves. The Fe^{+} map shows a spatial variation that is very consistent with microprobe and Auger electrons spectroscopy results.

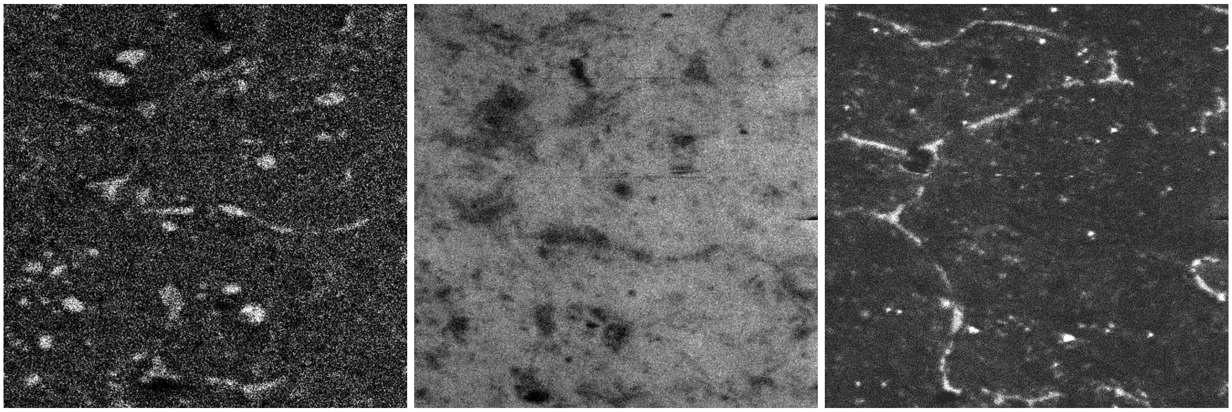


Figure 2 – 500 μm×500 μm SIMS images from the as received area on Pu sample surface, showing PuO^{-}, Ga^{+}, and Fe^{+}.

HYDROGEN

A very interesting series of negative ion peaks appear at mass 240 through 243 amu on areas that have been sputter cleaned (4kV argon ion beam) beyond the top surface. These peaks are assigned to PuH_x fragments (see Figure 3). These fragment patterns are very similar to those found by ToF-SIMS on uranium hydride particles by Morrall et al.[1] It was of interest to map this particular series of peaks on the aged sample, along with other common surface species (fluorine, hydrocarbons, gallium, etc.). The advantage of mapping these peaks rather than simply mapping the H^{-} or H^{+} peaks (as shown in Figure 1) is that it shows a direct, spatial correlation of plutonium and hydrogen, and the data is not confused with hydrogen from, say, hydrocarbons. In addition, these peaks are much more intense that those associated with the just the hydrogen ions. Figure 2 shows the series of maps taken from the 500 μm x 500 μm area that was sputter cleaned down to the oxide/metal interface.

---

[1] P. Morrall, D. W. Price, A. J. Nelson, W. J. Siekhaus, E. Nelson, K. J. Wu, M. Stratman, W. Mclean, ToF-SIMS characterization of uranium hydride, *Philosophical Magazine Letters,* **87**, 541-547, (2007)

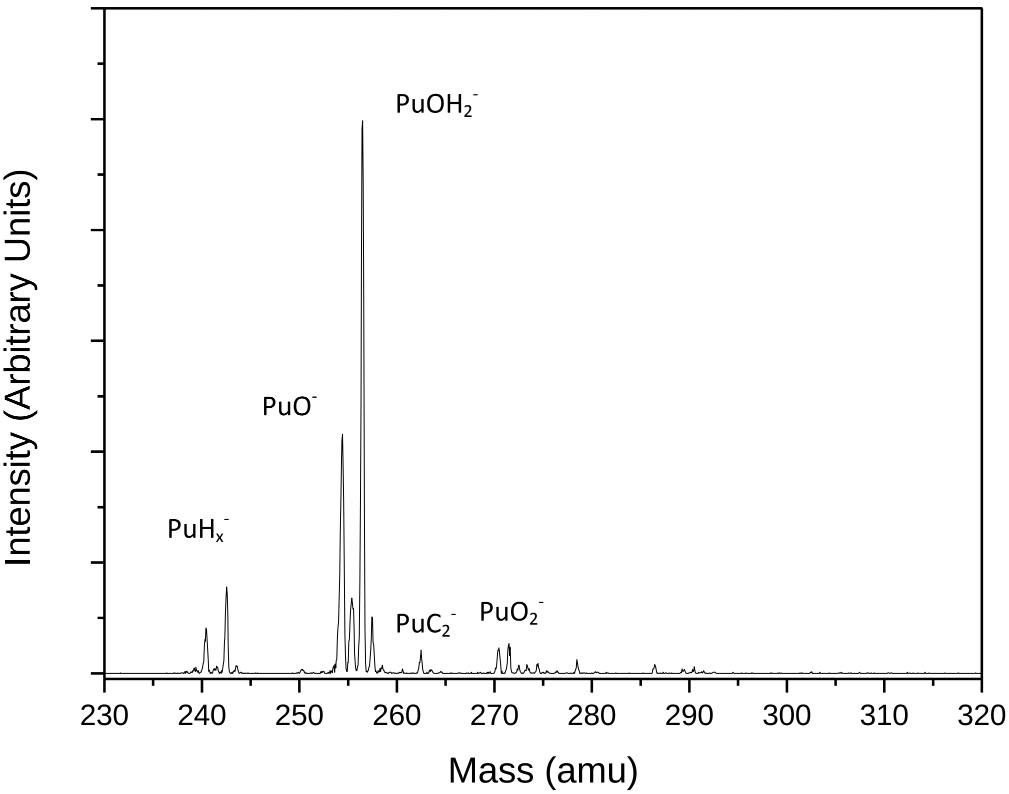
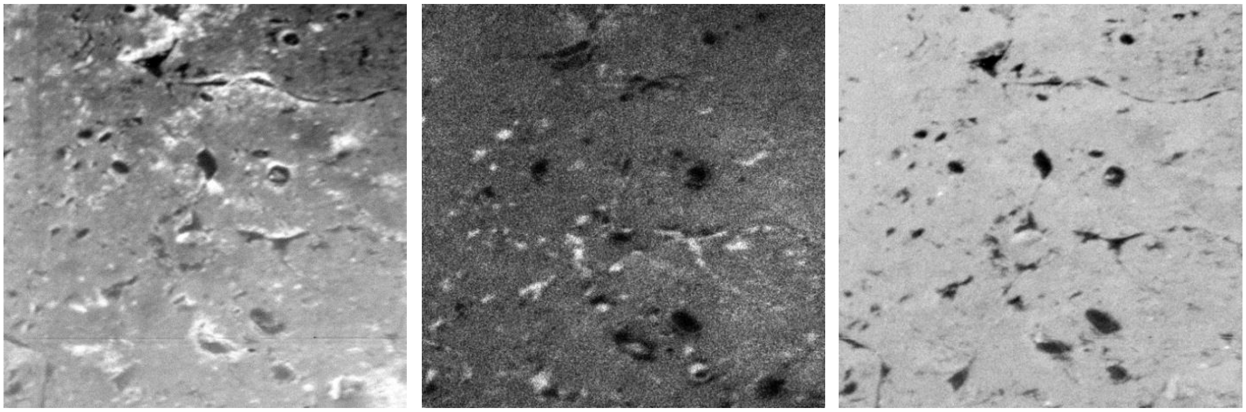
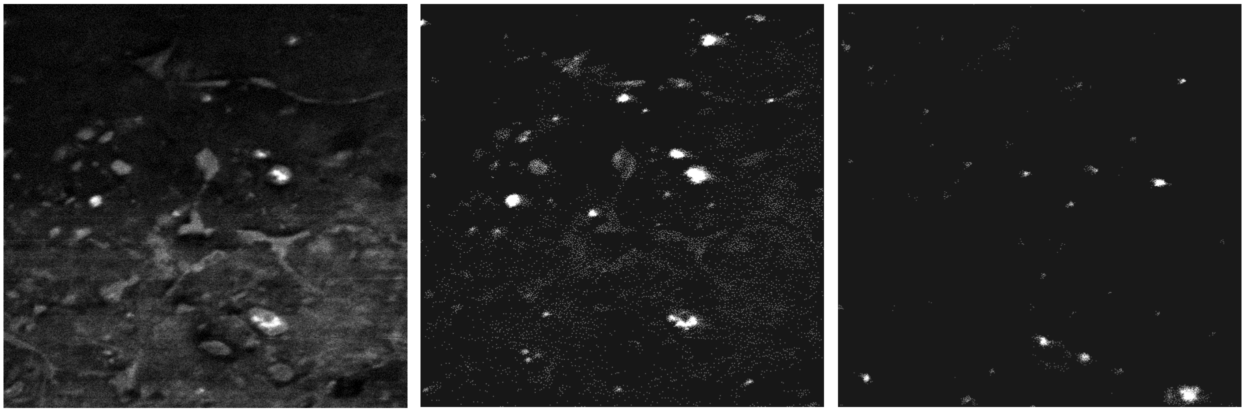


Figure 3- Negative ToF-SIMS spectrum from a sputter cleaned area on the Pu surface

The top row in Figure 4 shows (left to right) the negative ion maps from all negative ions, gallium oxide, and fluorine (brightness proportional to area under selected peaks). The bottom row shows negative ion maps associated with $PuOH_2^-$, the PuH_x^- series, and a positive ion map of Fe^+. The contrast of the maps was optimized to reveal areas of relative high and low intensity for each chemical of interest. Note the distinct, bright features in the PuH_x^- map. These features are mostly anti-correlated with the location of the gallium, hydrocarbons, and fluorine shown in the other maps. The Fe^+ also fails to show a correlation with the PuH_x features. The features, on the order of a few 10's of microns in size, do show a spatial correlation with the hydroxyl peaks ($PuOH_2^-$), suggesting the PuH_x series of peaks are simply fragments from hydroxylated inclusions. Additional work is needed to understand the exact nature of these features. To our knowledge, this SIMS PuH_x map is the first observation of plutonium hydride (or hydroxyl) inclusions in a metal sample revealed from a direct measurement, and not from a topological or chemical inference.



All Negative Ions **$^{71}GaO^-$** **F^-**



$PuOH_2^-$ **PuH_x^-** **Fe^+**

Figure 4 – 500 μm × 500 μm secondary ion maps from the sputter cleaned area on the Pu surface. The contrast for each image was adjusted to reveal areas of relatively high and low intensities.

LOW PRESSURE HYDROGEN REACTIONS

Low pressure deuterium exposures were performed to observe how the aged material reactions with hydrogen, and to possibly map the reactions sites. It was of interest to first expose an oxide surface that was still intact (very briefly sputter cleaned to remove residue from electropolish). Figure 5a and 5b show data from the low mass and high mass ranges, respectively, on an area of the sample that was sputter cleaned for just a few seconds. The low mass regime shows a typical surface state: carbon, O, OH, F, the hydrocarbon group at masses 24, 25, and 26, O_2, ^{35}Cl, ^{37}Cl, and a carbonate at mass 60. The high mass regime shows what could reasonably be considered to be a plutonium oxycarbide, with peaks at PuO, PuC_2, PuO_2, and PuC_2O. The PuH_x series, usually observed after more extensive sputter cleaning (10's of nanometers) is not evident in the spectrum. The sample was exposed to 10 L (10^{-7} Torr for 100 seconds, approximately 10 monolayers) of D_2 gas. Note that the depth resolution of SIMS is only 1-2 monolayers. Figure 6a and 6b show the negative SIMS data from the surface following the D_2 exposure. There is no clear evidence of H/D exchange: the OH, $PuOH_2$, and hydrocarbons remain essentially unchanged. Reaction would have been evident in the shift of the H containing species after scrambling with the deuterium. These results suggest minimal reactions of hydrogen to the native oxide.

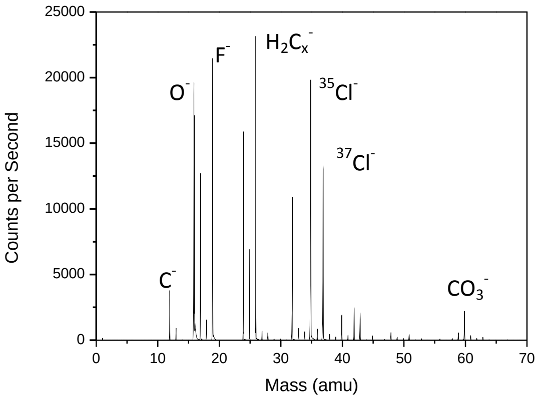


Figure 5a – Low mass SIMS, prior to D_2 dosing

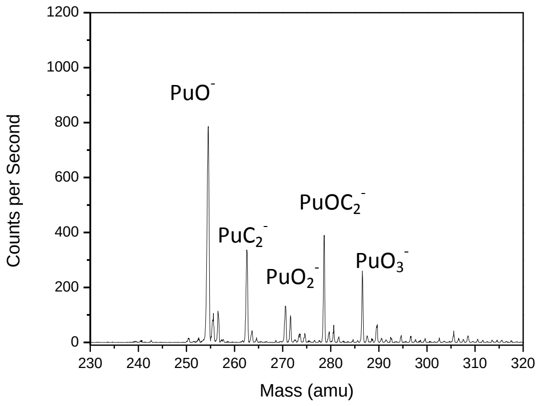


Figure 5b – High mass SIMS, prior to D_2 dosing

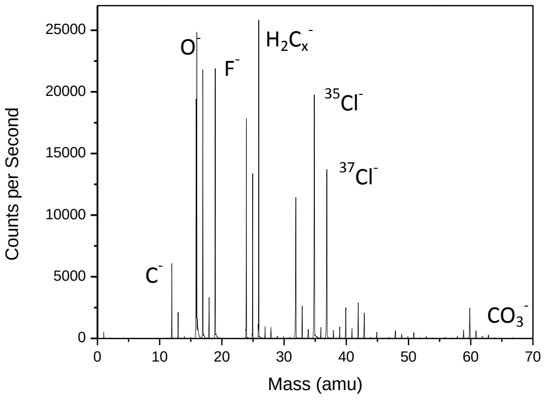


Figure 6a – Low mass SIMS following 10L D_2 dosing

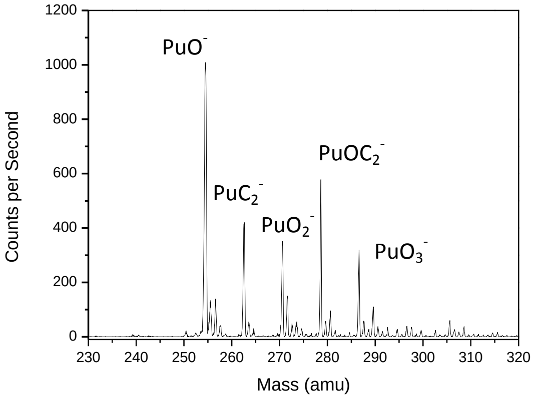


Figure 6b – High mass SIMS following 10L D_2 dosing

SIEVERT'S REACTION CELL

During FY14, the instrument was fitted with a small reaction cell that allows samples to be heated to ~450 °C, and exposed to gases up to an atmosphere in pressure. Figure 7 shows a photograph of this custom designed cell, which includes a very elaborate and highly functional gas handling system, and a downward-facing camera that enables real-time photographs of the samples surface. The intent was to allow higher pressure and temperature exposures than could be obtained in the UHV system while observing the sample surface.

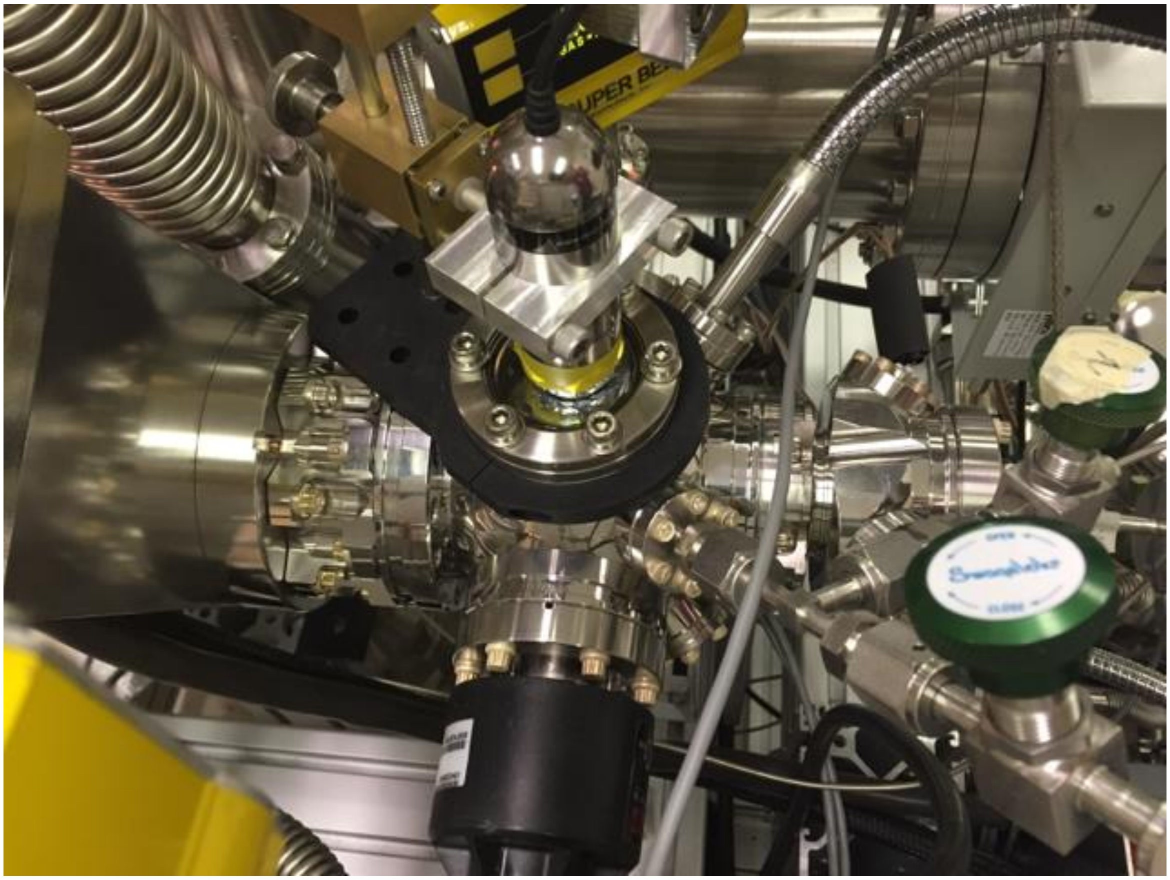


Figure 7 – ToF-SIMS reaction cell.

During the 2nd quarter of FY15, the aged sample was taken to over 375 °C for a total of six hours in order to "prove-in" the cell, which was designed and constructed in-house. During the heating, the pressure rose from a base pressure of 3×10^{-9} Torr to approximately 2×10^{-7} Torr. The outgassing species were monitored by the quadrupole mass spectrometer and revealed typical components (e.g. H_2O, CO). Some fraction of the gas evolution was certainly from the sample stub, mounting hardware, and cell walls.

With the system functioning as planned, experiments were performed to attempt to initiate hydrides on the surface of the sample. Figure 8a shows the negative secondary ion spectrum (high mass region) from an area that had been sputter cleaned before the heating step. The area shows a typical oxide surface with the presence of Pu-O and Pu-C fragments, plus a very small set of PuH_x peaks from mass 240-243. The secondary ion fragments shown are very typical of patterns observed, on the aged sample, from an area sputter cleaned to a depth of a few 10's of nanometers, at which point the PuH_x^- peaks become evident. Figure 8b shows fragments from the same mass range following the temperature excursion to 450 ^oC for several hours. Note the relative increase in the mass 263 peak, which is assigned to PuC_2^-, and other peaks containing a combination of Pu, carbon, and oxygen. From XPS experiments performed previously in MST-16, it is known that heating Pu in vacuum will drive bulk carbon to the surface. The hydrogen containing peaks from 240-243 amu are absent from the spectrum. The sample was placed back into the reaction cell; the temperature raised back up to 450 ^oC, and hydrogen gas was introduced into the chamber to a pressure of about 10 mTorr. The pressure in the chamber was monitored as the gas slowly adsorbed into the metal over the course of several hours. This process was repeated three times to obtain an approximate hydrogen concentration of 1 percent. Figure 8c shows the sample surface following the hydrogen loading. The surface is rich with PuO_xH_y fragments, indicating extensive hydroxylation. The sample surface was sputtered in an attempt to locate the PuH_x fragments, which had hopefully formed to a great extent, under the carbonaceous oxide layer. Figure 8d shows a spectrum after sputtering for 90 seconds. The oxide layer is still heavily contaminated with carbon. Sputtering for nearly two hours (an approximate depth of 500 nm) resulted in a nearly identical spectrum. The PuH_x peaks were not observed, even to this depth. It should also be noted that the low mass spectra showed an absence of iron and gallium peaks from the oxide layer.

During the heating and hydrogen loading of the sample, the image of the sample surface taken from the cell camera was monitored. As the experiments progressed, the image contrast and brightness began to fade. Inspection of the viewport window revealed a semi-reflective coating had formed on the inside surface of the viewport, obscuring the sample image. The nature of this coating is unknown.

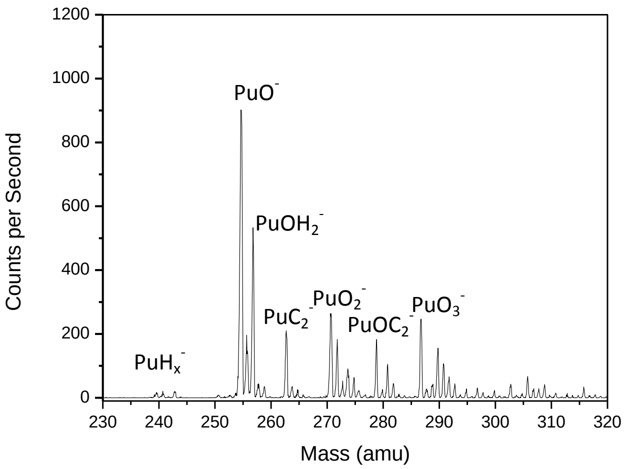


Figure 8a – Sputtered area prior to heating

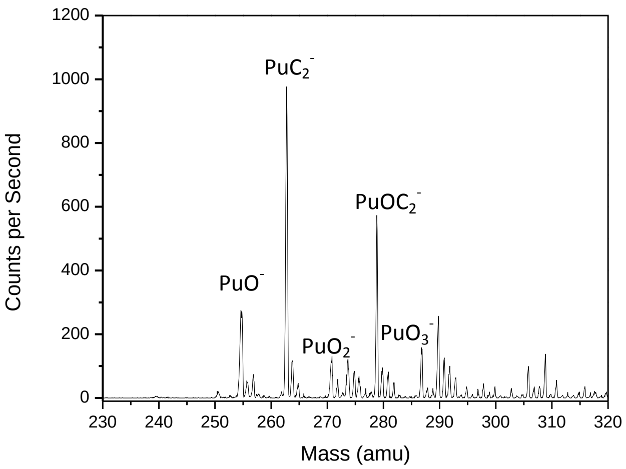


Figure 8b - Surface following heating to 450 °C.

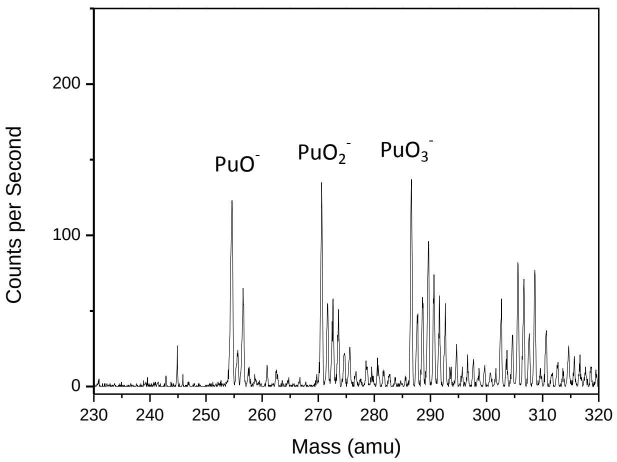


Figure 8c – Surface following hydrogen loading

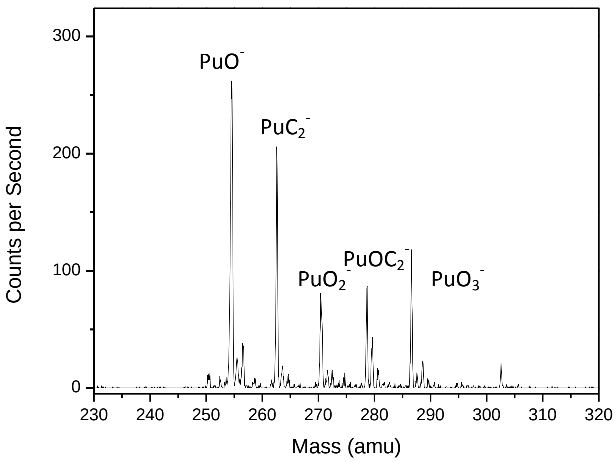


Figure 8d – Surface sputtered for 90 seconds

CONCLUSION

Fiscal year 2015 resulted in an extensive data set from the aged Pu sample. The first known maps of PuH^- species, found below the top surface oxide layer, were created. Several attempts were made to correlate the location of the PuH^- peaks with certain impurities in the lattice, but no clear evidence was observed. Indeed, the heating excursions alone created a thick oxycarbide layer void of impurities of interest such as iron and gallium. Other notable results include:

- Deuterium exposures on plutonium showed that the native oxide does not participate, in any detectible level, with hydrogen reactions. The ToF-SIMS spectrum of the native oxide remains mostly unchanged following doses of several Langmuir of deuterium (1 Langmuir = 10^{-6} Torr sec).
- The heating resulted in massive carbon loading of the oxide layer. Impurities of interest such as gallium and iron were not measured within this thick surface layer.
- After loading the aged sample with hydrogen at elevated temperatures, no hydride formations were observed
- The aged sample was returned to PF-4 for possible microprobe and metallography
- The ToF-SIMS work was presented as a poster at the Materials Capability Review, May 3-6.
- An abstract was been submitted to the 20 International Conference on Secondary Ion Mass Spectrometry (September 13th-18th, Seattles WA) highlighting this work as the first systematic study of the plutonium surface with ToF-SIMS. The abstract has been accepted for a presentation.

Future work will involve small dosing of the surface with moderate pressure hydrogen at room temperature. This must be done carefully, as extensive hydriding may can material to spall and introduce a Pu hydride particulate hazard in the system. Future work will also take advantage of the system’s new capability for depth profiling. This will add yet another dimension to the data.