

# Simultaneous Pu and U isotope nuclear forensics on an environmentally recovered hot particle

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## Abstract

An environmentally recovered, mixed Pu-U hot particle from the Thule accident, Greenland has been analyzed by Scanning Electron Microscopy and a large-geometry Secondary Ion Mass Spectrometry based Scanning Ion Imaging (SII) method for simultaneous  $^{235,236,238}\text{U}$  and  $^{239,240}\text{Pu}$  isotope compositions. This SII technique permits the visual assessment of the spatial distribution of the isotopes of U and Pu and can be used to obtain quantitative isotope ratios in any user-defined square region up to a few 100  $\mu\text{m}$  in size. The particle measured here has two, resolvable U isotopic compositions with a single composition of weapons grade Pu. The bulk of the particle has enriched U and weapons grade Pu with  $^{235}\text{U}/^{238}\text{U}$ ,  $^{236}\text{U}/^{238}\text{U}$ , and  $^{240}\text{Pu}/^{239}\text{Pu}$  of  $1.12 \pm 0.04$ ,  $0.006 \pm 0.002$ ,  $0.054 \pm 0.004$ , respectively ( $2\sigma$ ). The Pu isotopic ratio was consistent across the sample but  $^{239}\text{Pu}/^{238}\text{U}_{\text{raw}}$  decreased from  $1.99 \pm 0.07$  to  $0.11 \pm 0.04$  ( $2\sigma$ ) corresponding to the area of the particle with a resolvably different U isotope composition. This portion of the particle has  $^{235}\text{U}/^{238}\text{U}$ ,  $^{236}\text{U}/^{238}\text{U}$ , and  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios of  $0.11 \pm 0.04$ ,  $0.001 \pm 0.002$ , and  $0.05 \pm 0.04$ , respectively ( $2\sigma$ ). The origin of the less enriched U could be environmental that mixed with the particle or heterogeneously enriched U from the weapons. The heterogeneity of hot particles on a micrometer scale highlights the need for spatially resolved techniques to avoid mixing during a bulk or whole particle analysis, as the mixing end-members here would have been lost and the measured ratios would have been inaccurate.

## 1. Introduction

During safety inspections, the interception of unlawful nuclear materials, or an unexpected nuclear detonation, nuclear forensic investigations on particle evidence derived from these scenarios are critical for accurate source attribution. Uranium (U) and plutonium (Pu) isotopic ratios of particles from intercepted materials, forensics materials, or post-detonation samples are, arguably the most valuable evidence in modern nuclear forensics. The critical ratios measured in particles simultaneously provide information regarding the time elapsed since last purification, actinide concentrations, and relevant enrichment values. Consequently, the isotope signatures of particles are invaluable in determining the origin, processing history, and intended purpose of any nuclear material. These particles can be easily obtained via swipes, dust collection, or atmospheric filtering, a process which could also add environmental contamination. Hence, a complication arising from the analysis of mixed actinide particles or those found in nature by traditional bulk solution analysis is mixing or dilution with actinides with a natural or environmental composition<sup>1</sup>. *In situ* techniques, by comparison, can analyze individual particles or areas thereof with high spatial resolution to determine accurately the actinide ratios of interest while avoiding environmental contamination<sup>2-7</sup>.

Secondary Ion Mass Spectrometry (SIMS) is an *in situ* analytical technique highly suited to the analysis of heavy elements (U, Th, Pb) and Pu. However, a complication of SIMS analysis is the effect of both polyatomic species and isobaric interferences on the isotopes of interest. For example, in a mixed U-Pu particle where the isotope ratios of interest are  $^{235}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$ , any hydride interferences (e.g.,  $^{238}\text{U}+^1\text{H} = \text{mass } 239$ ) would produce inaccurate ratios. However, hydride production can also be monitored using mass 236 ( $^{235}\text{U}+^1\text{H}$ ) in the absence of  $^{236}\text{U}$ . Environmental U has no  $^{236}\text{U}$ , due to it being produced in nuclear reactors by the neutron capture

on  $^{235}\text{U}$  or by the decay of  $^{240}\text{Pu}$ . An advantage of using a large geometry, multi-collector equipped SIMS instrument, like the one in this study, is both the ability to collect simultaneously the isotopes of interest, namely  $^{235}\text{U}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{240}\text{Pu}$ , as well as an internal monitor at mass 236 for potential hydride, assuming production of hydrides is consistent across an individual particles. The instrument employed here is equipped for Scanning Ion Imaging (SII). SII is a relatively non-destructive technique, when compared to laser ablation ICP-MS or bulk sample dissolution followed by ICP-MS or TIMS analysis. The multi-collector SII technique used here provides isotopic imaging of e.g.,  $250 \times 250 \mu\text{m}$  areas for U and Pu, after which user-defined regions of interest (ROIs) can be assigned and full U and Pu isotope compositions can be obtained directly from the spatially resolved image data, post analysis. While SIMS has been used in particle analysis for over 10 years and is even capable of automatically searching for enriched particles<sup>9</sup>, there are no examples of a quantitative SII analysis of a mixed U-Pu particle present in the literature. Here we present a novel SII investigation of a mixed U-Pu environmentally recovered hot particle from the Thule nuclear accident, Greenland.

### **1.1 Thule accident and particles**

An American B52 airplane carrying four nuclear weapons crashed onto the sea ice 12 km west of the Thule air base, NW Greenland on the 21<sup>st</sup> of January 1968. Upon impact, traditional explosives within the weapons themselves and the ignition of the jet fuel contributed to the destruction and spread of fissile material. Most of the fissile material was scattered on the sea ice in an area of  $1.6 \times 4.8$  square kilometers<sup>10</sup>. Some of the radioactive material from the warheads accumulated in the benthic marine environment beneath the ice afterwards, as the impact caused the ice to crack, as well as when the ice melted the following summer<sup>11-14</sup>. The particle analyzed

here was recovered from a soil sample in 2003. The sample location was close to the settlement Narssarssuk, situated about 10 km south of the point of impact where some wind-blown contamination from the accident landed. Thule particles have been previously analyzed by several analytical techniques including ICP-MS<sup>1,15-17</sup>,  $\mu$ -pixie<sup>18</sup>, and small geometry SIMS<sup>19</sup>, and have the following range in enriched critical ratios:  $^{235}\text{U}/^{238}\text{U}$  of 0.96 -1.4 and  $^{240}\text{Pu}/^{239}\text{Pu}$  of 0.028 to 0.059<sup>19</sup>.

## **2. Analytical Methods**

The particle was isolated from the sediment using a previously described sample splitting technique<sup>11-14,20</sup>. No hot cell was used or necessary due to very low activities that can be handled without radiological concern. The particle was then pressed into an In metal holder. Gamma radiation originating from the  $^{241}\text{Pu}$  decay daughter  $^{241}\text{Am}$  was measured before and after the SIMS analysis to estimate the amount of material of the particle that was consumed during SIMS analysis. The measurements were carried out at the Swedish Radiation Safety Authority using a calibrated low background, broad energy HPGe<sup>3</sup>. The particle was placed in the same geometry (distance about 10 mm from detector surface) as the calibration source. Due to slightly different size and chemical composition of the calibration source compared to the particle, the resulting activity determination has at most 10 % relative combined uncertainty. Scanning electron microscopy was performed to determine sample morphology and Electron Dispersive Spectroscopy (EDS) maps were made analysis to gain a semi-quantitative understanding of the particle's chemical composition, both of which were performed using an FEI Quanta FEG 650 at the Swedish Museum of Natural History. The SEM was operated with an accelerating voltage of 15 kV at a working distance of 10 mm.

Isotopic analyses presented here were performed using a CAMECA large geometry secondary ion mass spectrometer (IMS1280) at the Swedish Museum of Natural History. A gaussian tuned  $O^+$  primary beam of 100 nA and approximately 20  $\mu\text{m}$  diameter was used to analyze the particle. Following previously reported safeguard analysis protocols<sup>6,8</sup>,  $O^+$  was used for the primary beam. The particle and surrounding area was rastered over a 250  $\mu\text{m}$  x 250  $\mu\text{m}$  square area yielding a 64 x 64 pixel image. Once sputtered from the surface of the particle by the primary ion beam, the secondary ions were processed using the dynamic transfer optical system (DTOS), which is a synchronized raster in the transfer section of the instrument that deflects the ions back onto the ion optic axis of the instrument regardless of their point of origin from the sample, allowing both image acquisition and collection of secondary ions at high mass resolution.

Secondary ions of masses 235, 236, 238, 239, and 240 were measured simultaneously at a mass resolution of 2560  $M/\Delta M$  to resolve any potential polyatomic interferences. Ions were detected using the multi-collector array, which comprises five low-noise (typically  $<0.005$  cps) discrete dynode Hamamatsu R4146-04 electron multipliers (L2, L1, C, H1, and H2, respectively). Since the IMS1280 magnet dispersion and multi-collector array was designed to separate unit masses of Pb (mass 204 to 208) with the detectors closest to each other, an increase in mass dispersion in order to make the peak flats coincident is required, which was achieved using a stigmating octopole device located after the magnet. An NMR field sensor was used in regulation mode to control the stability of the magnetic field during the image analysis. In this configuration, hydride interferences, if present, will be encountered on  $^{235}\text{U}$  ( $^{234}\text{U}_1\text{H}$ ),  $^{236}\text{U}$  ( $^{235}\text{U}_1\text{H}$ ),  $^{239}\text{Pu}$  ( $^{238}\text{U}_1\text{H}$ ) and  $^{240}\text{Pu}$  ( $^{239}\text{Pu}_1\text{H}$ ), which cannot be mass resolved, even using large geometry SIMS instruments like the one employed here. Gain differences between detectors, which are typically  $< 2\%$ , were calibrated by a pre-analysis peak hopping routine. After correction, any residual drift is unlikely

at the low count rates obtained in this study (a few 1000 cps only). SIMS analysis generates negligible mass bias from heavy isotopes<sup>21</sup>, so a mass bias correction was not needed and would in any case be encompassed by the relatively large uncertainties produced in these isotopic measurements, which are in the 0.5 – 1.0 % ( $2\sigma$ ) range. Further, using the same SII method for Pb isotopic measurements (a lower mass number) in post-detonation nuclear glass yielded no detectable mass bias effects<sup>22</sup>. The imaged area was measured for 42 cycles for a total collection time of ca. 6 minutes. With negligible mass bias and gains between detectors accounted for, all isotopic ratios in this study will be accurate. However, the Pu/U will not be accurate due to sputtering efficiency differences between U and Pu. To obtain an accurate Pu/U, future studies will need a matrix matched, known standards with a spectrum of Pu/U. All reported Pu/U ratios are labelled as Pu/U<sub>raw</sub>. Once acquired, the image was processed offline using the CAMECA WinImage2 software package. Regions of interest (ROIs) were selected in each of the images to calculate isotopic compositions of significance.

### **3. Results**

Pre- and post-analysis gamma spectroscopy yielded  $4 \pm 0.4\%$  Bq of <sup>241</sup>Am, indicating no significant consumption of the particle, within the measurement uncertainty of the method, in agreement with conventional SIMS analyses<sup>19</sup>. SEM-EDS analysis illustrates that the soil particle has significant topography (Figure 1), is mostly comprised of clay minerals with a platy morphology, and has an extremely heterogeneous chemical composition (Figure 2). The x-ray spectrum revealed variable abundances of major rock forming elements Na, Mg, Al, Si, K, Ca, Fe, O and minor trace elements, S, Cl, Ti, and U. Pu, U, and Al are coincident in the particle (Figure 2).

Results from the SII analyses for all isotopes measured are presented in Figure 3 and Table 1. The discrepancy of shape of the SII and EDS maps are a result of detection limit and spot size. SIMS has a much higher detection limit for U and Pu than SEM-EDS but the spot size utilized here was 5x larger, so the spatial resolution is not as precise. Isotopic variation maps for critical ratios  $^{235}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  are presented in Figure 4. ROIs for this particle are presented in Figure 5. Isotopic ratios for  $^{235}\text{U}/^{238}\text{U}$ ,  $^{236}\text{U}/^{238}\text{U}$ , and  $^{239}\text{Pu}/^{240}\text{Pu}$  for ROIs determined in Figure 5 are presented in Table 1 and illustrated in Figure 6. From the SII of  $^{238}\text{U}$  (Figure 3), it is apparent that the upper left corner of the particle is of a different U isotope composition than the rest of the particle. This variation in U isotopic composition is also seen in the isotopic variation maps in Figure 3 and is absent in the  $^{240}\text{Pu}/^{239}\text{Pu}$  map. The composition of  $^{235}\text{U}/^{238}\text{U}$  is resolvable across the particle and has a range from the upper left region of the SII to the bulk of the particle of  $0.11 \pm 0.04$  to  $1.12 \pm 0.04$  ( $2\sigma$ ) (Table 1, ROIs determined in Figure 5, Figure 6).  $^{236}\text{U}/^{238}\text{U}$  has a range from  $0.001 \pm 0.002$  to  $0.006 \pm 0.002$  ( $2\sigma$ ) (Table 1), the former being contained in the less  $^{235}\text{U}/^{238}\text{U}$  enriched portion of the particle, the latter being the bulk particle (Table 1, ROIs determined in Figure 5). As stated in the methods, without a matrix matched standard the  $^{239}\text{Pu}/^{238}\text{U}$  ratio cannot be accurately calibrated and is reported here as “raw”. The  $^{239}\text{Pu}/^{238}\text{U}_{\text{raw}}$  ratio decreases from the bulk of the particle to the less enriched  $^{235}\text{U}/^{238}\text{U}$  part from  $1.99 \pm 0.07$  to  $0.11 \pm 0.04$  ( $2\sigma$ ). However, the Pu isotope composition is constant within uncertainty between the two ROIs (Figure 6). Region of Interest 1, which is placed over the bulk particle yields a  $^{240}\text{Pu}/^{239}\text{Pu}$  ratio of  $0.054 \pm 0.004$  ( $2\sigma$ ) and ROI2 placed over the less enriched  $^{235}\text{U}/^{238}\text{U}$  corner yielded a  $^{240}\text{Pu}/^{239}\text{Pu}$  of  $0.05 \pm 0.04$  ( $2\sigma$ , Table 2, Figure 5, Figure 6). The difference in precision is related to the concentration of Pu across the particle, which is variable.

## 4. Discussion

### 4.1 Particle morphology and elemental composition

The particle morphology and EDS composition is characteristic of a largely geological material (Figure 1,2). The bulk particle composition is clearly a mixture between environmental materials from the soil at sampling site, the ice sheet (e.g., silicate dust), and materials from the nuclear weapons. This is indicated by the presence of major rock forming elements (Si, Mg, O) and high concentrations of U, Pu, and Al in a discrete area (Figure 2).

### 4.2 Evaluating the potential influence of hydrides

It is impossible to mass resolve  $^{238}\text{U}+\text{H}$  from  $^{239}\text{Pu}$  and thus, critical Pu ratios can be affected by the presence of hydride ( $^{238}\text{U}+\text{H}$ ,  $^{239}\text{Pu}+\text{H}$ )<sup>19</sup>. Since hydride formation affects each species in a similar way, a baseline calculation can be made using  $^{236}\text{U}$  to understand the hydride formation and possible interferences during the measurements of the particle here. Thus, two end-member possibilities are calculated for determining  $^{239}\text{Pu}/^{238}\text{U}_{\text{raw}}$  here: 1) all  $^{236}\text{U}$  is  $^{235}\text{U}$  hydride and when  $^{239}\text{Pu}/^{238}\text{U}_{\text{raw}}$  is calculated the % of  $^{238}\text{U}+\text{H}$  is subtracted from the  $^{239}\text{Pu}$  measurement and 2) all  $^{236}\text{U}$  is real and calculate the  $^{239}\text{Pu}/^{238}\text{U}_{\text{raw}}$  without a correction. Assuming that  $^{236}\text{U}$  is all hydride yielded a  $^{239}\text{Pu}/^{238}\text{U}_{\text{raw}}$  ratio of 2.01 and assuming  $^{236}\text{U}$  has no hydride interference yielded a  $^{239}\text{Pu}/^{238}\text{U}_{\text{raw}}$  ratio of 1.99. Thus the actual value is this somewhere between 2.01 and 1.99, which is unresolvable with the analytical precision achieved with the SII technique. Furthermore, the Pu isotopic ratio measured across the particle does not vary, despite a large, order of magnitude variation in Pu concentration,  $^{239}\text{Pu}/^{238}\text{U}_{\text{raw}}$ , and highly variable  $^{236}\text{U}/^{238}\text{U}$  (Table 1, Figure 7). If these ratios were strongly affected by hydride interferences, there would be a negative

correlation between  $^{236}\text{U}/^{238}\text{U}$  v.  $^{240}\text{Pu}/^{239}\text{Pu}$  but the Pu isotopic ratio is invariant within analytical uncertainty. Thus, hydrides are considered minimal and are excluded from any further discussion.

### 4.3 Particle isotopic variability

The area that is less enriched in  $^{235}\text{U}/^{238}\text{U}$  is easily seen in the ion image of the particle (Figures 4, 5) and in the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio map (Figure 5). The compositions of each of the particle's isotopic end-members can be calculated using the ROIs presented in Figure 5, are given in Table 1, and illustrated in Figure 6. Within the particle there is clearly a heterogeneity in Pu/U and in the  $^{235}\text{U}/^{238}\text{U}$  composition of the material, while  $^{240}\text{Pu}/^{239}\text{Pu}$  remains constant (Figure 6, Table 1). The values for the bulk of the particle are generally in agreement with small geometry SIMS analysis (Grey fields in Figures 6, 19). The origin of the less enriched U, however, remains ambiguous. There are two unresolvable hypotheses that account for the composition of the less enriched U: 1) the less enriched U is from the accident and the U used for the Thule fissile material was impure or 2) the less enriched U is a mixture of enriched U from the accident and from environmental U. Regardless, if this particle were to be dissolved and analyzed with bulk methods or non-spatially resolved techniques, the less enriched U would have been mixed with the bulk of the particle, resulting in a U-isotope composition somewhere between the two end-members presented as the dotted line in Figure 6. The analytical approach was successful in this study because the heterogeneous part of the particle did not have  $^{236}\text{U}/^{238}\text{U}$  significantly above 0, within analytical uncertainty. If a more complex particle or a  $^{236}\text{U}$ -enriched particle were to be analyzed, a series of standards containing  $^{236}\text{U}$  would need to be prepared and analyzed to monitor any potential interferences. Nonetheless, the SII presented here is an excellent demonstration of the

benefits to spatially resolved imaging techniques for the analysis of environmentally recovered, mixed U-Pu particles that are heterogeneous on the micrometer scale.

## 5. Conclusions

The method presented here is a relatively non-destructive, spatially resolved technique to both visually and quantitatively understand the variations in U and Pu isotope ratios in environmentally recovered particles. The presence of hydride interferences was monitored using  $^{236}\text{U}/^{238}\text{U}$  and shown to be minimal for this particle, not affecting the critical ratios beyond analytical uncertainty. The region of the particle that contains less enriched U was easily detected and avoided during the image processing. The critical ratios  $^{235}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  calculated here for the bulk particle are  $1.12 \pm 0.04$  and  $0.054 \pm 0.004$  (all  $2\sigma$ ), respectively, confirming the presence of highly enriched U and weapons grade Pu at the Thule site. Furthermore, these ratios are within uncertainty of those previously produced by traditional SIMS for the Thule particles with no measurable mass loss to the particle. Consequently, use of relatively non-destructive techniques, such as this, preserve the possibility for analyzing at a future time to verify the compositions measured here or to analyze for further isotopic (e.g.,  $\text{Pb}^{22-23}$ ) or trace element systematics, which could contribute corroborating evidence for a forensic investigation.

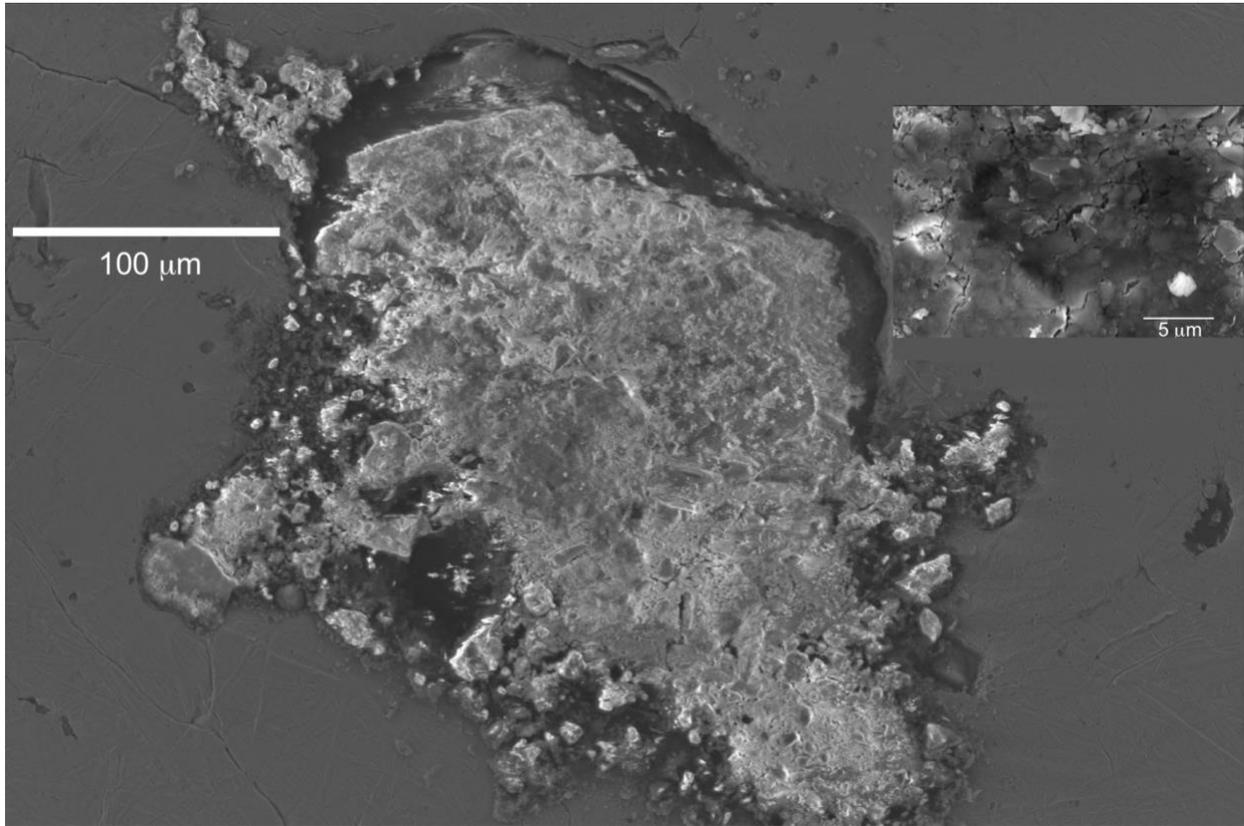
## 6. Acknowledgements

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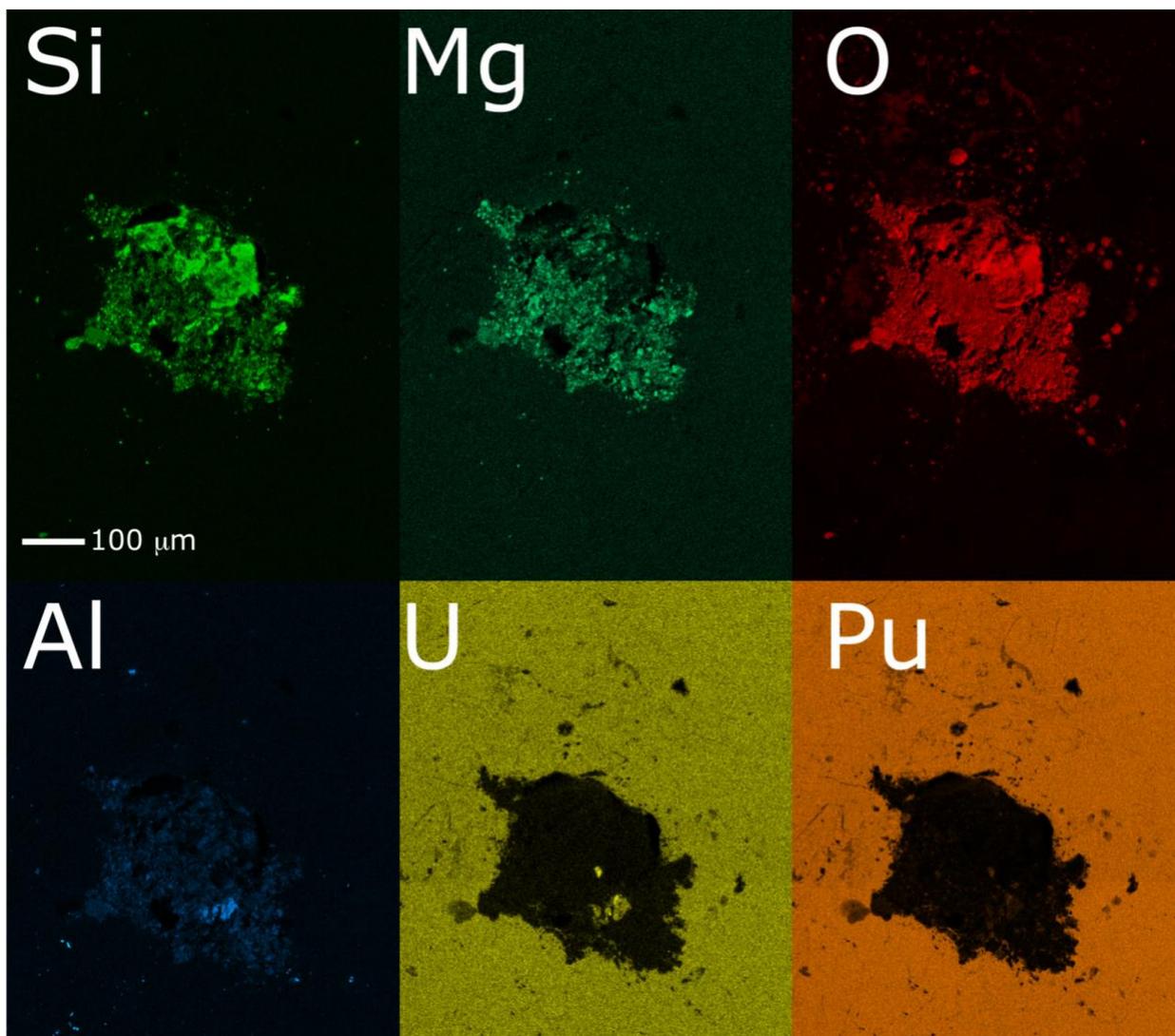
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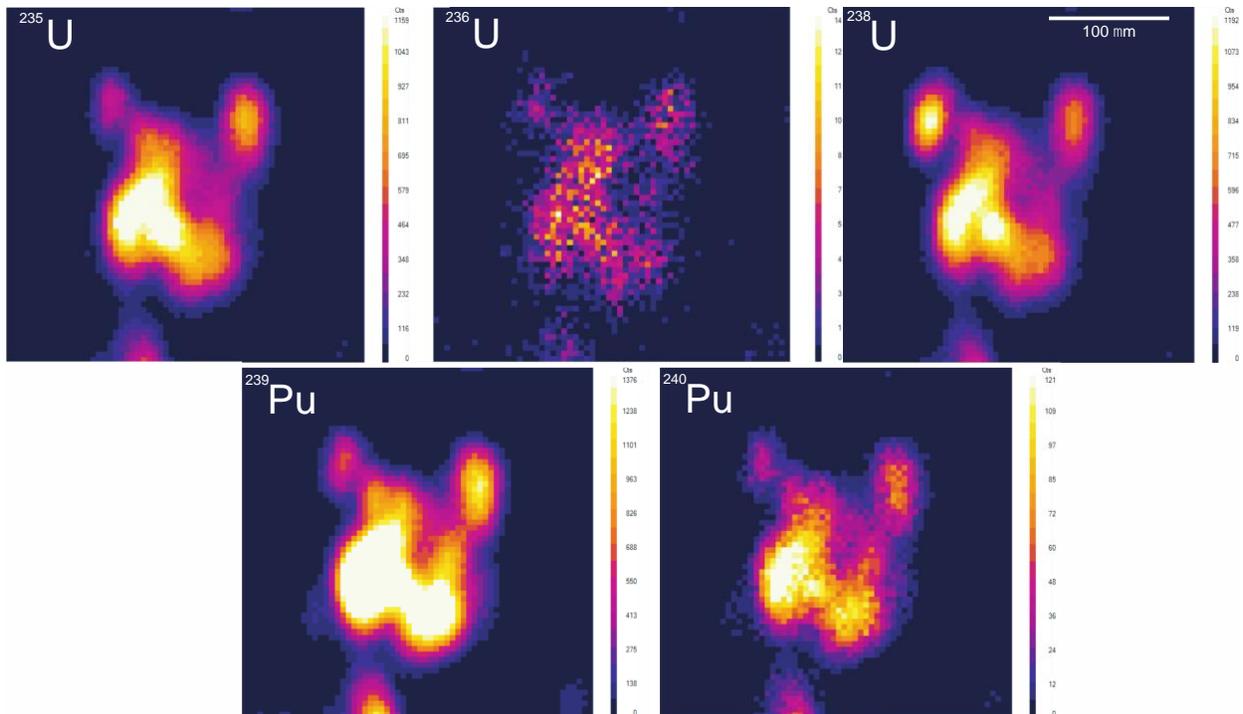
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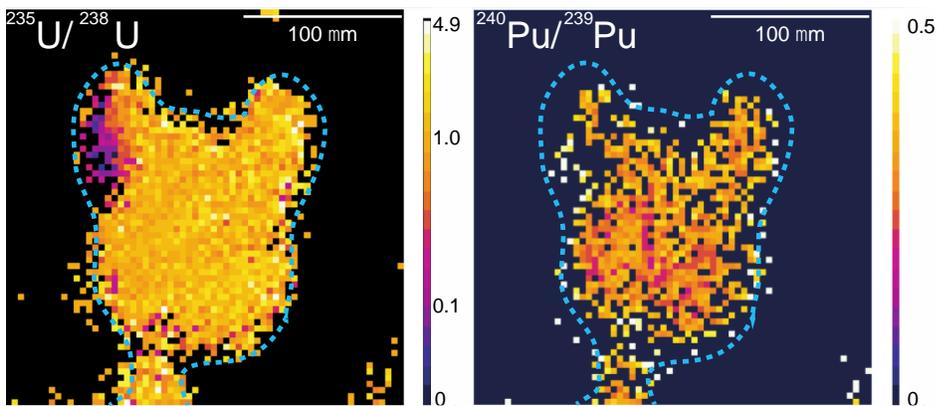
**Figure 1. Scanning electron image of the mixed Pu-U Thule environmentally recovered hot particle embedded in In. Inset is a closeup of the particle's surface, dominated by minerals with a platy morphology.**



**Figure 2. EDS maps of the mixed Pu-U Thule environmentally recovered hot particle embedded in In, which has an interference in the EDS energy peaks with U and Pu outside of the particle. The brightness of EDS maps are relative in scale.**



**Figure 3. Scanning ion images of  $^{235}\text{U}$ ,  $^{236}\text{U}$ ,  $^{238}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{240}\text{Pu}$  for a Thule mixed U-Pu environmentally recovered hot particle.**



**Figure 4. Scanning ion image isotope ratio map of  $^{235}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  for a Thule mixed U-Pu environmentally recovered hot particle. The blue outline was obtained using the intensity maps for  $^{238}\text{U}$  presented in Figure 3.**

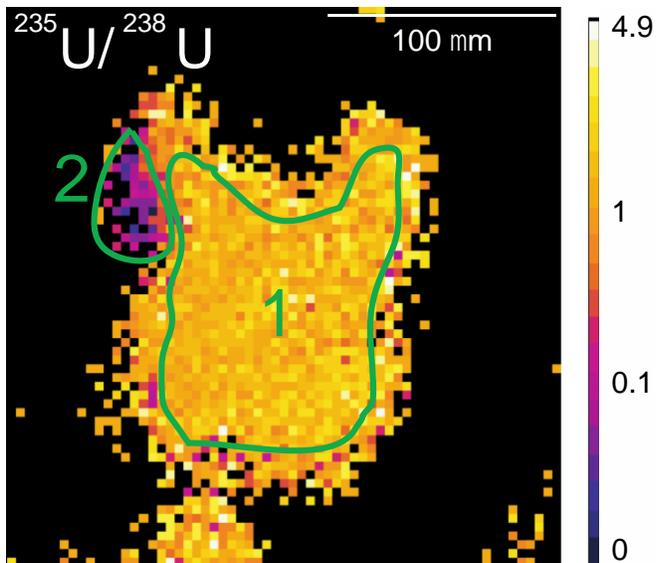


Figure 5. ROIs used for the assessment of the Pu and U isotopic composition of the bulk particle and the U of unknown origin.

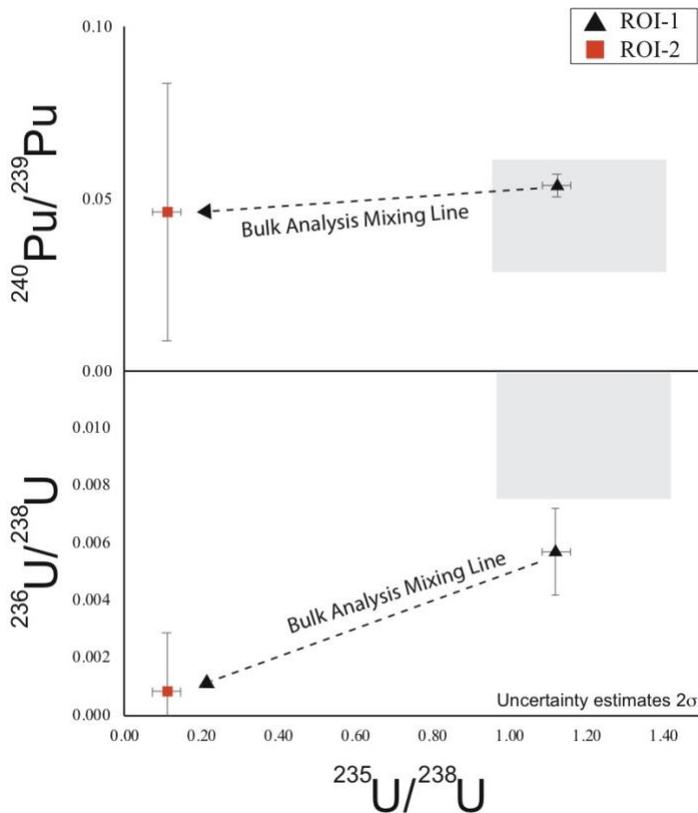


Figure 6. Determination of critical ratios  $^{235}\text{U}/^{238}\text{U}$ ,  $^{236}\text{U}/^{238}\text{U}$ , and  $^{240}\text{Pu}/^{239}\text{Pu}$  in the low enriched U portion of the particle (ROI2, Figure 5) and the bulk portion of the particle

(ROI1, Figure 5). The grey field represent previously determined values for several Thule particles by traditional SIMS<sub>19</sub>. Dotted line represents what a mixture between the two end-members, which is the predicted composition if the particle was measured by a bulk or larger-beam method.

**Table 1. U and Pu isotopic ratios determined by ROIs in Figure 5.**

	$^{235}\text{U}/^{238}\text{U}$	2s	$((^{235}\text{U}+^1\text{H})/^{238}\text{U})$	2s	$((^{238}\text{U}+^1\text{H})+^{239}\text{Pu})/^{238}\text{U}$	2s	$((^{239}\text{Pu}+^1\text{H})+^{240}\text{Pu})/((^{238}\text{U}+^1\text{H})+^{239}\text{Pu})$	2s
ROI-1	1.12	0.04	0.006	0.002	1.99	0.07	0.054	0.004
ROI-2	0.11	0.04	0.001	0.002	0.11	0.04	0.05	0.04

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