

## Supplementary Information for

Discovery of Fissionogenic Cs & Ba Capture Five Years After Oklo Reactor Shutdown

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## Methods

The NAUTILUS combines a standalone Cameca ims 4f secondary ion mass spectrometer (SIMS), containing conventional electron multiplier (EM), Faraday cup (FC), and micro-channel plate (MCP) detectors, with a National Electrostatics Corporation single-stage accelerator mass spectrometer (SSAMS), which acts as a large molecule-filtering detector with a suite of MCPs, FCs, and an EM at different locations (1-3). The NRL SSAMS was designed to accommodate ions of mass-to-charge ratio ( $m/z$ ) up to  $\pm 300$ , and unlike traditional tandem AMS systems can accept positive or negative ions. This allows for orders of magnitude increases sensitivity for electropositive elements, which comprise most of the periodic table. Our ability to measure electropositive elements with higher sensitivity is important when high spatial resolution is required using SIMS and when the consumed sample is relatively small. Electrostatic deflectors are used to switch between SIMS and SSAMS detectors during instrument tuning and analyses. When using the SSAMS, ions of a single  $m/z$  are injected from the SIMS (4.5 keV) and accelerated by 300 kV and focused to a waist in the center of a gas stripping cell filled with Ar, where collisions between the ion beam and the room-temperature Ar efficiently dissociate molecules. The SSAMS magnet then filters the resulting atomic and molecular ion fragments before detection. Simultaneous electrostatic peak switching (EPS) is used to peak jump between isotopes differing up to  $\pm 6.5\%$  of each magnet's central  $m/z$  field on the SIMS and the SSAMS (3). One interesting feature of EPS is that it removes the necessity of locally cycling through isotopes in mass order, since peak jumping does not affect each magnet's hysteresis. As such, more intense isotopes may be selected first for centering during each measurement cycle. Using the SSAMS to remove molecular isobars allows us to run the SIMS with low mass resolving power, between 300 – 500 ( $M/\Delta M$ , 10% peak height), to maximize transmission. It also improves instrument stability, and we do not observe any mass fractionation while using EPS on the SIMS, unlike when operating with high mass resolving power. The gas thickness in the stripping cell may be calibrated for the unique molecular background in a sample. Typically, an Ar gas thickness of  $7 \times 10^{15}$  atoms/cm<sup>2</sup> results in a  $10^5$  to  $10^6$  reduction in molecular transmission at the expense of 50 to 70% reduction in atomic ion transmission (3). Of particular note is that direct, molecule-free spot and imaging measurements are enabled by the combination of SIMS and SSAMS capabilities, allowing us to measure fission products and isotope depletions due to n-capture. SIMS typically relies on energy filtering and molecular oxide ion deconvolution to measure REEs since there are abundant molecular isobars in this mass range (4-6). However, the deconvolution relies on the assumption of normal isotope abundances and so is incompatible with analyses of isotopically perturbed systems, such as from the Oklo natural reactors. NAUTILUS does not resolve nuclear isobars since we use a low accelerating energy, analyze charge +1 ions, and do not employ an energy-sensitive detector. This makes it an excellent complement for element-specific techniques, such as resonance ionization mass spectrometry (RIMS), especially for the elements Mo and Zr.

Two acquisition “modes” may be used interchangeably on the NAUTILUS: molecular filtering, and molecular fragment analysis. In both modes the SIMS secondary ion beam for a single  $m/z$  is deflected into the SSAMS for analysis. In filtering mode, the SSAMS spectrometer is tuned to analyze ions of the injected  $m/z$ , so the gas stripping cell acts as a molecule filter, dissociating molecules so that only incident atomic ions reach the end station. In fragment mode, the SIMS and SSAMS are tuned to different  $m/z$  settings.

We inject molecular ions, e.g.,  $\text{UO}^+$ , from the SIMS, dissociate the molecules in the gas cell, and tune the SSAMS to analyze the  $\text{U}^+$  fragments. Ba and Cs were measured in filtering mode in this paper while both methods were used for U and the REEs. Fragment mode is particularly useful for when molecular ion signals of a given element are more intense than their atomic counterpart, e.g., it is often the case in SIMS that the secondary intensity of  $\text{UO}^+$  is more than  $10\times$  that of  $\text{U}^+$  from  $\text{UO}_2$ . Instead of a transmission loss of  $\sim 50\%$  of the atomic ions to remove an intense molecular background with a gas thickness of  $7\times 10^{15}$  atoms/cm<sup>2</sup> (see (3)),  $>95\%$  of molecules can be dissociated using comparatively little gas. This results in less scattering loss for fragment mode. Whereas 95% molecule reduction may not be adequate for trace element measurements under an intense background in filtering mode, it is highly preferable if the SIMS molecule signal of interest provides higher sensitivity.

The critical distinction is that molecular fragments, e.g.,  $\text{U}^+$  and  $\text{O}^+$  from the dissociation of  $\text{UO}^+$ , have their resulting energies partitioned according to the mass fraction of their parent molecule, e.g., an injected molecule of  $^{238}\text{U}^{16}\text{O}^+$  at 304.5 keV will yield a molecular fragment of  $^{238}\text{U}^+$  with an energy of  $(238/254) \times 304.5 \text{ keV} \approx 285.3 \text{ keV}$ . Since the trajectory of an ion through a magnetic sector is governed by the product of its mass and energy (charge = +1), an ion with mass 238 u and energy 285.3 keV will have the same trajectory as an ion with mass  $\sim 223$  u and energy 304.5 keV. By setting the SSAMS magnet to a field around, e.g.,  $m/z = 214$ , the  $\pm 6.5\%$  EPS range spans a mass range of 200 to 227, which fully encompasses  $\text{Pb}^+$  ions injected from the SIMS and  $\text{U}^+$  molecular fragments from  $\text{UO}^+$  injected from the SIMS. This is also useful for U-Th-Pb dating since the SSAMS magnet can be kept at a single field setting and allow through injected  $\text{Pb}^+$  ions and  $\text{U}^+$ ,  $\text{Th}^+$  fragments. Since ion beam-gas collisions are stochastic, it is always possible that some small molecular background survives the stripping interaction so one must be careful with respect to the given sample and its unique background. This illustrates one of the other benefits of fragment mode, as any other molecular or atomic ion (sans nuclear isobars) that is injected at a chosen  $m/z$  from the SIMS will have its energy partitioned differently, so it will not make it through the SSAMS magnet. The most challenging scenario would be a hydride addition onto a molecule, e.g.,  $^{235}\text{U}^{16}\text{O}^1\text{H}^+$  overtop of  $^{236}\text{U}^{16}\text{O}^+$ . In this case, however, the energy partitioning for  $^{235}\text{U}^+$  would give it an effective mass of 219.15 u while  $^{236}\text{U}^+$  would have an effective mass of 221.02 u, fully 2 u different! We have also not observed any partial molecule fragmentation, e.g.,  $\text{UO}_2^+$  into  $\text{UO}$  and  $\text{O}$  fragments, which could complicate some analyses. An additional benefit of fragment mode is that it allows us to investigate the composition of incident molecules by tuning the SSAMS to the different fragments. We can further verify each fragment component by searching for the isotope in several charge states. In most cases this would allow us to rule out complex and unlikely interferences.

Individual spot and imaging analyses were performed using 100 pA to 1 nA  $\text{O}^-$  and  $\text{O}_2^-$  primary beams. Both filtering and fragment modes were used for spot measurements of U, Ba, Sm, Eu, Gd, and Eu. Isotope images were acquired in filtering mode on  $^{132,134-138}\text{Ba}^+$  and  $^{133}\text{Cs}^+$  over  $250 \mu\text{m} \times 250 \mu\text{m}$  regions counting for 200 to 300 s on each isotope per frame ( $256 \text{ px} \times 256 \text{ px}$ ). In-house analysis software was used to post-process isotope images. Following the discovery of fissionogenic Ba and Cs in Ru grains, scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDXS) maps were used in conjunction with SIMS  $^{99}\text{Ru}^+$  imaging to locate new Ru aggregates. Earlier work on this

sample had characterized the aluminous hydroxy phosphate by transmission electron microscopy (TEM), SEM, and SIMS (7) and by noble gas mass spectrometry via laser ablation (8, 9). The sample had been previously cut, polished, and ultrasonically washed in methanol.

Molecule-free isotope ratio imaging with micrometer-scale resolution was developed as part of this work. In-house software and hardware were developed to control the ion optical deflector plates on the Cameca ims 4f primary and secondary columns giving us complete control over beam patterning, dwell times, and timing. The ims 4f series and its cousin large-geometry machines are stigmatic ion microscopes, so the individual ion trajectories of the secondary ion beam are preserved throughout the mass spectrometer, allowing for stigmatic images to be captured on a two-dimensional detector. This is impossible in the SSAMS since it is achromatic, the gas stripping cell causes ion scattering, and since the beam divergence entering the accelerator would lead to unacceptable transmission loss. Using the dynamic transfer optical system of the ims 4f, which is a set of deflector plates following the immersion lens, the trajectories of ions at each pixel may be negated so that all ions regardless of origin enter the mass spectrometer at the same location (10). By knowing the location of the primary beam at each pixel, quantitative images may be reconstructed by gating a counter on the EM for the dwell time at each pixel. The ions therefore also enter the accelerator at the same location for each pixel. We use Python and National Instruments LabVIEW® to generate raster patterns for the primary and secondary beam deflectors, with a tunable delay for proper synchronization, and a TTL pulse train, which we send over a fiber optic line to the accelerator (since fiber can withstand the 300 kV accelerator bias) to trigger the Keysight 53220A counter/timer connected to our custom EM electronics. In this way, molecular filtering is achieved on raster ion images without any loss of spatial resolution, which one might naively expect would occur due to gas cell scattering, since the filtering occurs pixel-by-pixel. SIMS and SSAMS ion images on the same isotopes were interleaved during some analyses to compare the molecule-free and molecule-full images. To our knowledge, the NAUTILUS has the only micrometer-scale imaging capability on an AMS system and certainly the only AMS imaging capability with the sensitivity to detect trace quantities of electropositive elements such as U and the REE.

**Table S1. Isotopic composition of Oklo RZ 13 minerals. Errors are (2 $\sigma$ ) on the last significant digit. "--" indicates no measurement.**

Sample	$^{235}\text{U}/^{238}\text{U}$ (%)	$^{149}\text{Sm}/^{147}\text{Sm}$	$^{151}\text{Eu}/^{153}\text{Eu}$	$^{161}\text{Dy}/^{163}\text{Dy}$	$^{162}\text{Dy}/^{163}\text{Dy}$	$^{164}\text{Dy}/^{163}\text{Dy}$
Uraninite	0.3655(7)	0.00485(5)	0.261(2)	0.454(11)	0.798(17)	0.265(7)
Alum. Phosphate	--	0.0054(2)	0.292(6)	0.50(4)	0.87(6)	0.37(4)
Terrestrial	0.7254	0.9219	0.9161	0.759	1.023	1.135
	$^{155}\text{Gd}/^{156}\text{Gd}^\dagger$	$^{157}\text{Gd}/^{158}\text{Gd}^\dagger$	$^{155}\text{Gd}/^{160}\text{Gd}^\dagger$	$^{156}\text{Gd}/^{160}\text{Gd}$	$^{157}\text{Gd}/^{160}\text{Gd}^\dagger$	$^{158}\text{Gd}/^{160}\text{Gd}$
Uraninite	0.0190(4)	0.0198(9)	0.132(3)	6.96(8)	0.067(3)	3.40(4)
Alum. Phosphate	0.049(3)	0.072(9)	0.34(2)	7.1(4)	0.26(3)	3.63(20)
Terrestrial	0.7230	0.6300	0.6770	0.9364	0.7159	1.1363
	$^{132}\text{Ba}/^{136}\text{Ba}$	$^{134}\text{Ba}/^{136}\text{Ba}$	$^{135}\text{Ba}/^{136}\text{Ba}$	$^{137}\text{Ba}/^{136}\text{Ba}$	$^{138}\text{Ba}/^{136}\text{Ba}$	$^{133}\text{Cs}/^{136}\text{Ba}$
Uraninite	0.0127(5)	0.310(3)	0.836(5)	1.455(8)	9.25(4)	0.0290(8)
Alum. Phosphate	0.01282(6)	0.3079(4)	0.8374(9)	1.443(1)	9.103(7)	0.0723(3)
Ru inclusion $^\ddagger$	0.0118(11)	0.306(5)	1.77(3)	2.47(3)	11.30(13)	1.00(2)
Ru-1	0.0122(6)	0.345(5)	1.63(2)	2.19(2)	9.80(8)	1.247(15)
Ru-2	0.0126(2)	0.319(1)	1.082(4)	1.6765	9.39(2)	0.427(3)
Ru-3	0.0123(2)	0.319(2)	1.103(5)	1.687(6)	9.39(3)	0.410(4)
Ru-4	--	0.304(2)	0.938(6)	1.542(8)	9.28(4)	0.154(2)
Ru-5	--	0.307(2)	0.888(4)	1.483(6)	9.18(3)	0.085(3)
Ru-6	--	0.404(7)	2.38(3)	2.88(3)	10.39(9)	2.52(3)
Ru-7	--	0.387(6)	2.14(3)	2.64(3)	10.25(10)	2.09(3)
Ru-8	--	0.343(6)	1.39(3)	1.94(4)	9.46(18)	0.77(2)
Terrestrial	0.0127	0.308	0.839	1.431	9.13	--

$^\dagger$  Gd-155 and Gd-157 were completely depleted. Their current abundance is equivalent to a 4‰ addition of terrestrial Gd, which is outside of the measurement error on  $^{160}\text{Gd}$ . n-capture and  $^{155,157}\text{Gd}$  depletion may be judged by the  $^{156}\text{Gd}/^{160}\text{Gd}$  and  $^{158}\text{Gd}/^{160}\text{Gd}$  ratios.

$^\ddagger$  Ru metal and sulfide aggregate completely entrained in  $\text{UO}_2$  crystal. All other Ru aggregates located in between  $\text{UO}_2$  grains.

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