TOWARDS THE 1000 ATOM DETECTION LIMIT FOR ^{244}**PU.** R. Trappitsch,[1] M. R. Savina,[1] J. M. Rolison,[1] L. N. Harrison,[1] and N. Dauphas,[2] [1]Lawrence Livermore National Laboratory, Nuclear and Chemical Sciences Division, Livermore, CA 94551, (trappitsch1@llnl.gov) [2]The University of Chicago, Enrico Fermi Institute, and Chicago Center for Cosmochemistry, Chicago, IL 60637

Introduction Plutonium-244 is a radionuclide with a half-life of 80 Ma that can only be produced by the rapid neutron capture (*r*-) process. While the sources of the *r*-process are poorly constrained and heavily discussed [e.g., 1], optical spectroscopy of the neutron star merger associated with the gravitational-wave event GW170817 indicated the presence of freshly nucleosynthesized lanthanides [2], a main product expected from *r*-process nucleosynthesis calculations. Proxy measurements of ^{244}Pu in the early Solar System, measured via ^{244}Pu fission-produced xenon in meteorites [3], show a rather high abundance. If neutrons star mergers are the sole *r*-process source that contributed to the Solar System, the measured early Solar System ^{244}Pu abundance would require that such a merger contributed to the solar neighborhood just prior to Solar System formation (with respect to the half-life of ^{244}Pu). Alternatively, a more frequent *r*-process site that contributes a higher steady state amount of ^{244}Pu to the galaxy must be invoked.

By analyzing the contemporary influx of ^{244}Pu in deep-sea sediments, Wallner et al. [4] concluded that the current steady state ^{244}Pu abundance is around ten times lower than the one in the early Solar System, which would favor that actinides are likely solely formed in neutron star mergers. This conclusion is based on the detection of two counts of ^{244}Pu [4] found in terrestrial crust material and one count found in deep-sea sediment. These authors used accelerator mass spectrometry (AMS) for which they report an overall yield of $\sim 10^{-4}$. Due to the low number of counts the uncertainty on the contemporary ^{244}Pu influx is rather high.

Here we present the first results of the development of a technique for detecting ^{244}Pu in an atom-limited sample by resonance ionization mass spectrometry (RIMS). This technique has a higher yield than AMS and we show a current detection limit of around 1100 atoms of ^{244}Pu at a signal-to-noise ratio of one, which will allow a much more stringent constraint on the influx of interstellar Pu.

Methods To test the current Pu detection limit of the Livermore LION (Laser Ionization Of Neutrals) RIMS instrument [5], we deposited 1μl of a diluted standard CRM136[1] solution on a tantalum stub in a 1.5 mm diameter circular area. The deposited sample was coated with Ti in order to keep the laser-desorbed Pu atoms in a reduced form. Using a 351 nm desorption laser with a spot

size of $\sim 3\%$ of the sample area we slowly desorbed sample material from the surface, subsequently ionized Pu neutrals using a three-color, three-photon resonance ionization scheme, and then analyzed these photoions in a time-of-flight mass spectrometer. By assuming a homogeneous distribution of the sample material over the surface we calculated that 2.6×10^5 ^{239}Pu, 3.7×10^4 ^{240}Pu, and 1.8×10^3 ^{242}Pu atoms were in the analysis spot. Plutonium-238 and ^{241}Pu atoms were also in the analysis spot, however, interferences with non-resonantly ionized ^{238}U and ^{241}Am, respectively, prevent these isotopes from being good indicators of the instrument's sensitivity. We will thus focus our discussion on the Pu isotopes that are free of potential interferences.

Results Figure 1 shows the mass spectrum for the Pu mass region recorded on the CRM136 standard. The ^{238}Pu peak, which has an isotopic abundance in this sample of 0.2%, clearly has a significant contribution from non-resonantly ionized ^{238}U. The ^{242}Pu peak is clearly visible, even though we estimate a total of only 1800 ^{242}Pu in the analysis spot. The green shaded area of the figure shows the selected peak integral around the ^{242}Pu peak. In this peak area we detected a total of 147 ± 12 counts. Using the orange shaded area to determine the background we determined that 56 background counts are expected in the peak area, thus resulting in a total number of 91 ± 13 detected ^{242}Pu counts. Together with the known amount of ^{242}Pu atoms in the analyzed spot we calculate a useful yield for Pu of 5%. The signal-
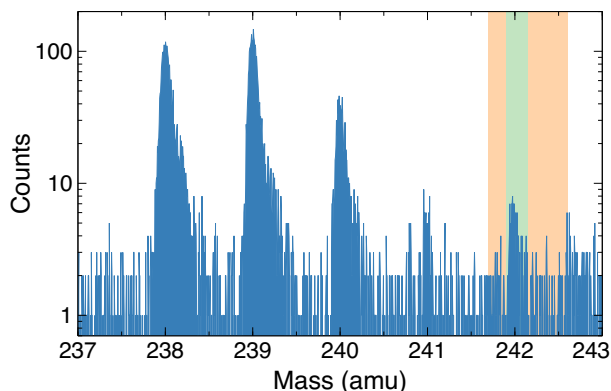

Figure 1: RIMS spectrum of CRM136. The green shaded area shows the integration region for the ^{242}Pu peak while the orange shaded areas show the integration regions for the background correction.
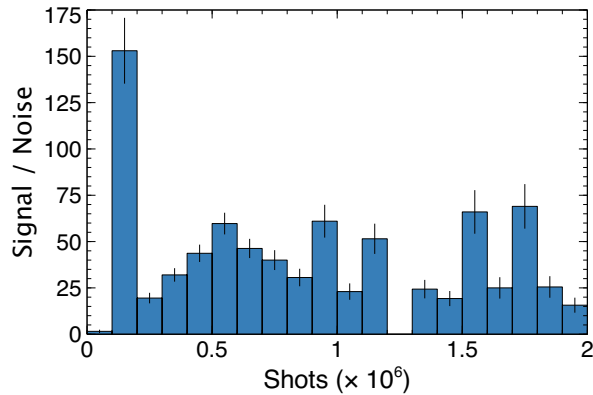
Figure 2: Signal-to-noise over time when binning 10^5 shots together. The figure clearly shows that the sample is not yet depleted and thus that a higher useful yield can still be achieved when measuring longer.

to-noise ratio for this detection is ~ 1.6. We can thus estimate that at a signal-to-noise level of 1 we would still be able to detect 1100 atoms of ^{242}Pu in the sample.

Discussion In comparison with a U useful yield of 38% measured on reduced U-metal [6], our measurement of a 5% useful yield for Pu seems rather low especially since the Ti coating is expected to reduce the sample such that Pu should come off the surface in its atomic form. In the mass spectrum in Figure 1, we collected a total of 2×10^6 individual time-of-flight mass spectra. Figure 2 shows a time sequence of the signal-to-noise ratio for ^{239}Pu in bins of 5% laser shots (i.e., 100 seconds of collection time per bin). The figure clearly shows that the sample under the desorption spot had not yet been depleted when we terminated the measurement since the signal-to-noise in the last bin is still significantly larger than one. The calculated useful yield is thus only a lower limit and is limited by an early termination of the measurement. Note that even at this lower limit we already show a sensitivity increase of a factor of 500 in comparison with the AMS measurements by Wallner et al. [4]. Furthermore the RIMS detection limit is about a factor of ten better than the AMS detection limit. AMS is generally background free but has a low yield of only $\sim 10^{-4}$ [4] for Pu, thus around 10^4 atoms need to be present in a given sample for detection. In contrast, RIMS can detect as little as 1100 atoms at a signal-to-noise ratio of one, which makes RIMS the preferred technique for determining the contemporary interstellar influx of Pu via measurements of ^{244}Pu.

Outlook A better sample than terrestrial deep-sea sediments and crust material to study the influx of interstellar ^{244}Pu would be lunar top soil. Apollo 17 returned samples skimmed from the top centimeter of lunar soil with exposure ages > 100 Ma [7]. Using an average in-

flux value determined from the early Solar System value [3], we expect $\sim 1.5 \times 10^6$ ^{244}Pu atoms in 10 g of lunar top soil. Using the lower limit set by Wallner et al. [4], $\sim 1.5 \times 10^5$ atoms of ^{244}Pu would be expected in the same sample. Even this lower number could easily be measured by RIMS, and would be similar in magnitude to the ^{239}Pu peak shown in Figure 1.

Furthermore, a lunar sample is not prone to contamination with anthropogenic Pu and any potential anthropogenic contamination is easily detected. A lunar sample is only expected to contain live ^{244}Pu, so any other Pu isotope however would be the result of anthropogenic contamination. Anthropogenic ^{244}Pu without other Pu isotopes is extremely rare; very few ^{244}Pu isotopic spike standards exist.

We plan to dissolve a 10 g lunar sample, spike the sample with a known amount of ^{242}Pu, and then purify Pu. Subsequent RIMS analysis of Pu will then determine the ^{242}Pu/^{244}Pu isotopic ratio to calculate the concentration of lunar ^{244}Pu. Analog to previous work [4], we will then be able to constrain the source of *r*-process nucleosynthesis with significantly smaller uncertainties due to the > 500 times higher sensitivity of RIMS over AMS.

References

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