**A SEARCH FOR LIVE $^{244}$Pu IN DEEP-SEA SEDIMENTS: DEVELOPMENT OF AN EFFICIENT DETECTION METHOD.** A. Ofan$^1$, I. Ahmad$^2$, J. P. Greene$^3$, M. Paul$^1$, M. J. Pellin$^3$, and M. R. Savina$^3$; $^1$Racah Institute of Physics, Hebrew University, Jerusalem, Israel 91904, $^2$Physics Division, Argonne National Laboratory, Argonne IL, 60439, $^3$Materials Science Division, Argonne National Laboratory, Argonne IL, 60439

**Introduction:** $^{244}$Pu (t$_{1/2}$ = 81 Ma) is considered extinct in the present Solar System, however it is likely to be present in the Interstellar Medium (ISM) due to ongoing r-process nucleosynthesis [1]. Ongoing nucleosynthesis in the Galaxy is expected to populate a steady-state concentration of long-lived nuclides (t$_{1/2}$ $\geq$ 5-10 Ma) in the ISM, and indeed shorter-lived radioactivities such as $^{26}$Al (0.72 Ma) and $^{60}$Fe (1.5 Ma) have been observed by $\gamma$-ray astronomy [2]. $^{244}$Pu is not detectable at present.

Though now long extinct, live $^{244}$Pu was present in the Early Solar System (ESS), as evidenced by the discovery in meteorites of radiogenic Xe produced by the spontaneous fission of $^{244}$Pu [3]. The ratio of $^{244}$Pu to $^{238}$U in the Early Solar System was $\sim$0.007. The present-day ratio in the ISM is estimated to be $\sim$0.04 [1], though there is considerable uncertainty in this number. The amount of $^{244}$Pu present in the ESS may therefore be representative of its steady-state concentration in the ISM. If ISM material is continuously accreting on Earth, one may be able to find live $^{244}$Pu in a suitable reservoir such as deep-sea sediment.

We consider here two scenarios by which the accretion of ISM material onto Earth could lead to measurable traces of $^{244}$Pu:

(i) Steady-state penetration of ISM grains into the inner Solar System. ISM grains have been detected in the inner solar system by the Galileo [4], Ulysses [5] and Cassini [6] missions, and interstellar dust grains incident on Earth have been detected by the AMOR radar array [7-9]. Based on these data, estimates can be made of the amount of ISM material currently accreting as dust on Earth. Assuming that the ISM has an elemental and isotopic composition similar to that of the Early Solar System, one would expect a flux of $\sim$0.1 $^{244}$Pu atom cm$^{-2}$ yr$^{-1}$ and a $^{244}$Pu concentration on the order of $10^2$-$10^6$ atoms kg$^{-1}$ in deep-sea sediments, owing to their low sedimentation rates of $\sim$0.1 cm yr$^{-1}$.

(ii) The transient influx of direct ejecta from a nearby supernova (SN) explosion. Such an event was recently evidenced by a $^{60}$Fe isotopic anomaly in a deep-sea ferromanganese crust [10]. The time-integrated flux of $^{60}$Fe at Earth from this event was estimated to be $2 \times 10^9$ $^{60}$Fe atoms cm$^{-2}$. From the estimated ratio of SN production yields of $^{60}$Fe and $^{244}$Pu (admittedly very sensitive to the progenitor star mass and type of explosion [11]), one would expect an integrated flux of $10^5$-$10^6$ $^{244}$Pu atoms cm$^{-2}$ in an appropriate sediment layer. An observed correlation between $^{60}$Fe and $^{244}$Pu would give much sought-after evidence for an r-process nucleosynthesis site.

Two searches for $^{244}$Pu in different deep-sea materials have been conducted using accelerator mass spectrometry (AMS). Paul et al. [12] analyzed a deep-sea sediment and set an upper limit on the steady-state accretion rate of 0.2 $^{244}$Pu atom cm$^{-2}$ yr$^{-1}$. Wallner et al. [13] analyzed an interior section of a deep-sea crust and obtained one count of $^{244}$Pu, corresponding to a $^{244}$Pu integrated flux of $\sim$3 $\times$ 10$^2$ cm$^{-2}$. These studies used methods with detection efficiencies on the order of 10$^4$ to 10$^6$. We are currently developing methods to improve the detection efficiency (and thereby lower the Pu detection limit) using Resonant Ionization Mass Spectrometry (RIMS).

**Methods:** The RIMS analysis was done on the CHARISMA instrument, which has been described in detail elsewhere [14]. In brief, a sample is mounted in an ultra-high vacuum chamber and material is evaporated with a pulsed UV laser at a power sufficient to release a few thousand atoms per pulse. The gaseous atoms are resonantly ionized with a set of tuned lasers and accelerated into a time-of-flight mass spectrometer. This instrument has demonstrated a useful yield (atoms detected / atoms consumed) of >1%.

Analysis of sediment samples requires a complex chemical procedure to extract and concentrate the Pu onto an area compatible with the desorption laser spot. In our present work, we developed a technique for depositing a chemical analog (Gd) and an isotopic marker for Pu ($^{242}$Pu) in trace quantities onto the end of a 0.5 mm diameter Ta wire for RIMS analysis. Iso-propanol solutions containing various known amounts between $10^7$ and $10^{15}$ atoms of Gd, and between $10^6$ and $10^{12}$ atoms of $^{242}$Pu were prepared and plated [15] onto Ta wires. To determine the deposition efficiency, a solution containing radioactive $^{141}$Ce with a known activity was deposited under the same conditions. The activity was measured with a Ge(Li) detector, establishing a deposition efficiency of 50±10%.

As actinides have a strong tendency to desorb as oxides which are detected with much lower sensitivity in our method, it is necessary to reduce the sample prior to analysis. The electrodeposited wires were coated with a 0.5 μm Ti layer, then heated to 500 °C in high vacuum. This allowed the Pu to diffuse into the
Ti layer (diffusion into Ta is much slower) where it was reduced [16]. This method significantly enhanced the atom/oxide ratio in the laser-desorbed material.

**Results:** Fig. 1 shows the Gd mass spectrum obtained from a wire sample after electrodeposition from a solution containing $10^9$ atoms of Gd. GdO (non-resonant) photoions are detected with a ratio of ~1:10 relative to Gd photoions. While the Gd photoion signal is strongly enhanced at the resonant wavelength, the GdO yield is insensitive to laser tuning. The Gd detection efficiency was measured by repeatedly pulsing the laser on a fixed 60x90 μm spot (~2% of the wire cross section) until the photoion signal was exhausted (approximately 6 hours). From the number of Gd ions counted and the number of Gd atoms in the electrolyte solution used for deposition, an overall detection efficiency of 0.5 ± 0.1% was determined for entire process (deposition, reduction, and detection). This is a significant improvement on the previous AMS methods.

Fig. 2 shows a spectrum similarly obtained for Pu electrodeposited from a solution containing ~$10^{13}$ atoms of $^{242}$Pu. Here the signal is much higher, though this is arbitrary because it depends on the laser fluence. As in the Gd case, the atom/oxide (Pu/PuO) ratio is ~10/1. Fig. 3 shows a spectrum for a sample deposited between $10^6$ and $10^8$ Pu atoms. The exact number of Pu atoms is uncertain due to the behavior of the electrodeposition cell when extremely low levels of Pu are used, however we believe that the number of Pu atoms lying under the laser spot is within an order of magnitude of the number we estimate in sediments. While the signal-to-noise ratio needs to be improved, the method appears to be feasible. We are currently pursuing further improvements in the sample preparation and analysis methods.

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![Figure 1: RIMS spectrum of a portion of a sample containing $10^9$ Gd atoms.](image1)

![Figure 2: RIMS spectrum of a portion of a sample containing $10^{12}$ atoms of $^{242}$Pu.](image2)