

A Search for live ^{244}Pu in Deep-Sea Sediments: Preliminary Results of Method Development. M. R. Savina¹, M. Paul², A. Ofan², J. G. Barzyk¹ and M. J. Pellin¹, ¹ Materials Science Division, Argonne National Laboratory, Argonne IL, 60439 (msavina@anl.gov), ²Racah Institute of Physics, Hebrew University, Jerusalem, Israel 91904.

Introduction: We report on the initial stages of a search for live ^{244}Pu from interstellar grains in deep-sea sediments using Resonant Ionization Mass Spectrometry (RIMS). The study of interstellar grains has attracted considerable attention in recent years with the detection of ISM grains in the inner solar system by the Galileo [1] and Ulysses [2, 3] missions. Interstellar dust grains incident on Earth have been detected by the AMOR radar array [4-6]. Based on these data, estimates can be made of the amount of ISM material accreting as dust on Earth.

The grains themselves ablate away on entry into the atmosphere so that direct study is not possible; however it may be possible to detect short-lived (i.e. $t_{1/2} < \sim 10^8$ yr) radioisotopes delivered to Earth by the grains. Indeed, the recent detection of a spike of live ^{60}Fe ($t_{1/2} = 1.5$ My) in a deep-sea nodule [7] is direct evidence of contemporary interstellar material being deposited on Earth.

That the ^{60}Fe is concentrated in sediments ~ 2.8 My old is evidence that its deposition was the result of a discrete event, probably a supernova explosion. In this work, we seek to detect short-lived radioisotopes that are continuously deposited. Many isotopes with half-lives greater than about 5-10 My should attain a steady state concentration in the ISM due to their continuous creation in supernovae, etc [8]. Among these ^{244}Pu is interesting. It has a long half life of 81 My. It is a pure r -process isotope, and is unlikely to be produced by cosmogenic nuclear reactions. Its presence in the early solar system has been inferred from Xe isotopic anomalies in meteorites [9, 10].

The ratio of ^{244}Pu to ^{238}U in the early solar system was ~ 0.007 [11]; the present-day ratio in the ISM has been estimated at ~ 0.04 [8], though there is considerable uncertainty in this number. Combining these numbers with the measurements of the ISM dust flux on Earth allows us to estimate the accretion rate of ^{244}Pu on Earth, and thus the amount one might expect to find in repositories such as deep-sea sediments. Using the estimate for the present-day ratio of $^{244}\text{Pu}/^{238}\text{U}$, we calculate an accretion rate of ~ 7 atoms of ^{244}Pu $\text{cm}^{-2} \text{yr}^{-1}$. If we assume that the early solar system ratio still exists in the ISM, we calculate an accretion rate of ~ 1 atom of ^{244}Pu $\text{cm}^{-2} \text{yr}^{-1}$.

Two searches for ^{244}Pu in two different deep-sea materials have been conducted using accelerator mass spectrometry (AMS). Paul et al. [12, 13] analyzed deep-sea sediments and found one count of ^{244}Pu ,

which was the amount expected from nuclear bomb test fallout. They used the data to put an upper limit on the ^{244}Pu accretion rate of 0.2 atoms $\text{cm}^{-2} \text{yr}^{-1}$. Wallner et al. [14] detected one count of ^{244}Pu in an interior portion of a deep-sea nodule (thus excluding ^{244}Pu from fallout), from which we derive an upper limit of 2×10^{-3} atom $\text{cm}^{-2} \text{yr}^{-1}$.

Both of these results are far below the expected value. There may be several reasons for this: 1) the residence time of dust in ISM may be much greater than the half-life of ^{244}Pu , 2) the dust flux may be overestimated, 3) not all of the dust arriving at Earth may contain ^{244}Pu , and 4) the production of ^{244}Pu in supernovae may be less than estimated. Whatever the case may be, the previous work points to the need for a more sensitive detection method. In this work, we seek to extend the search using RIMS, which should be able to detect ^{244}Pu down to an accretion rate of about 10^{-4} to 10^{-5} $\text{cm}^{-2} \text{yr}^{-1}$ using a deep-sea sediment as the sample.

Methods: The CHARISMA instrument has been described in detail elsewhere [15, 16]. In brief, a sample is mounted in an ultra-high vacuum chamber and irradiated with a pulsed UV laser at a power sufficient to evaporate several thousand atoms per pulse. The cloud of liberated atoms is intercepted by two lasers, one of which excites the element of interest to an electronically excited state, while the other ionizes the resonantly excited atoms, leaving the other elements as neutrals. The ions are then accelerated into a time-of-flight mass spectrometer for analysis. This instrument has been shown to have a useful yield (atoms detected / atoms consumed) of $> 1\%$ [17], compared to 10^{-4} to 10^{-6} for the AMS methods discussed above.

The collection and processing of deep-sea sediments is described in detail elsewhere [12, 13]. The sample was dredged from the Pacific Ocean near Hawaii from a water depth of 5,800 meters. One kg of the dry sediment is available for RIMS analysis. The Pu is extracted from the material and electrodeposited on Ti wires.

To avoid handling significant quantities of Pu in the laboratory, La was used in place of Pu for initial method development. A modification of a resonance ionization scheme developed by Worden et al. [18] was developed for Pu detection, and La can be detected via a slight re-tuning of the laser frequencies.

Preliminary Results: In order to obtain the highest sensitivity in RIMS, one must ensure that the spe-

cies of interest desorbs from the sample in the form of atoms rather than being incorporated into molecules. Given that Pu rapidly forms a stable oxide that persists after laser desorption, this is a paramount consideration for the present investigation. Our initial work has concentrated on sample preparation techniques designed to minimize the amount of oxide present.

The sample was a solution of La electrodeposited on a Ti wire. Figure one shows the results for a sample analyzed as-deposited and another that was reduced in H₂ prior to analysis. The reduced sample shows a much more La and a much higher La/LaO ratio, indicating that H₂ reduction enhances the sensitivity of the method. The La/LaO ratio cannot be directly assessed by this method however, since LaO is not resonantly ionized by the laser and its useful yield is not known. In general one expects the useful yield for LaO to be at least two orders of magnitude lower than La, which would correspond to roughly equal quantities of La and LaO in the spectrum of the reduced sample. We are currently improving the sample preparation method to obtain a higher useful yield for La.

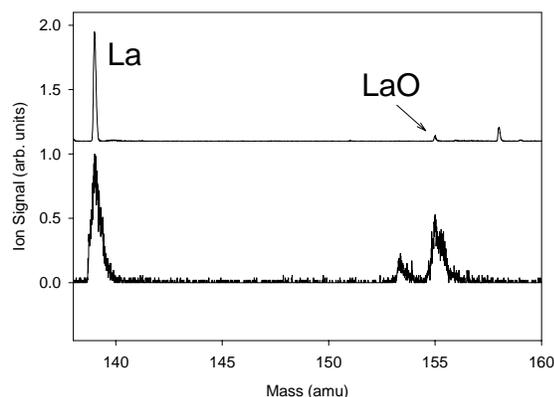


Figure 1: RIMS spectra of reduced (upper trace) and as-deposited samples of La on Ti. The units are arbitrary, however one can see from the signal-to-noise ratio that the upper trace contains much more La than the lower one.

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