DETERMINATION OF HIGH PRECISION ISOTOPE RATIOS IN RETURNED SAMPLES USING MULTI-ION COUNTING.
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The craftsman who wishes to do his work well must first sharpen his tools **–The Analects**

Introduction: Samples have been returned from Stardust, GENESIS, Hayabusa (JAXA) missions. OSIRIS-Rex is being developed to bring a sample from a near-Earth asteroid Bennu (formerly 1999 RQ36), and more will be coming in the future. The amount of extra-terrestrial material returned in these robotic missions is very, very small. The good news is that technology has improved since the manned NASA Apollo mission brought back pounds of lunar samples; the bad news is that the best instrumentation is not yet readily accessible to NASA researchers. Accordingly, I suggest a facility in the US where high-precision measurements of radiogenic isotopes in samples weighing a few micrograms-could be routinely made.

Background: The advent of reliable high-precision isotope ratio measurements for trace elements in returned samples began with the invention of the Lunatic thermal ionization mass spectrometer at Caltech [1]. That instrument gleaned precise isotope data from the Lunar samples (along with other terrestrial and extra-terrestrial samples), paving the way to an unprecedented insight into the origin and evolution of planets, other solar system bodies and, indeed, into the time-scale of formation of the Galaxy and the Universe. Availability of commercial mass spectrometers helped spread this revolution in high-precision isotope analysis globally. This revolution continues to the present-day: innovations in multi-collector mass spectrometry are permitting ultra-high precision isotope ratio measurements that continue to re-shape our understanding of our origins. Instrument development has gone hand-in-hand with innovations in miniaturized low-blank high-yield chemical techniques needed to isolate the relevant trace elements for thermal ionization mass spectrometry. While increasingly sophisticated instruments such as multi-collector ion probes and multi-collector inductively thermal plasma mass spectrometers have allowed us to obtain, respectively, spatially resolved isotope analyses and isotope analyses of difficult to ionize elements, thermal ionization mass spectrometry remains the “gold standard” for obtaining the most reliable isotope measurements for a large number of trace elements.

Thermal ionization mass spectrometry typically requires separating and ionizing $>10^{13}$ atoms of the trace element of choice from a rock. This was possible for returned Lunar samples. However, the new generation of small sample returns could likely provide only $<10^8$ atoms of a trace element. Accordingly, none of these samples returned to date have been amenable isotope ratio measurements, and the science these measurements could provide has remained undiscovered.

So, while NASA and other space agencies have continued to invest in missions for capturing, returning, and curating thousands of small samples from a suite of primitive objects in th**e** solar system (solar wind, interplanetary dust particles, cometary debris, etc.), a rather wide gap remains in our understanding of whether the trace element and isotopic signatures of these objects are commensurate with a rather limited number of primitive meteorites in our collection. Precise measurements from a larger set of return samples are therefore critical. This work requires: (1) the development of a thermal ionization mass spectrometer capable of reliably measuring the isotope composition of elements at an ultra-low level ($<10^8$); and (2), the housing of this instrument in a laboratory dedicated to developing ultra-low blank techniques.

A successful attempt in this direction was made at the Max-Planck-Institut für Chemie in Mainz [2] where an existing Finnigan MAT 262 thermal ionization mass spectrometer was modified to fit five continuous dynode multipliers (= channeltrons), which were mounted on drives so that their positions along the ion-beam focal plane could be changed to measure low to high mass isotopes/molecules. The channeltrons could be cross calibrated and calibrated against a Faraday collector or a secondary electron multiplier (SEM) operating in ion counting mode. Richter et al. [2] demonstrated that depending on the count rate they could obtain isotope ratios for (Sr, Ba, Sm, Nd, Mo, or Os) with an uncertainty as low as about 0.1%. Using this configuration Richter et al. [3] also measured Te isotopes in pre-solar diamonds extracted from carbonaceous chondrites. This mass spectrometer, however, has not been used to measure extraterrestrial returned samples. Moreover, twenty years have elapsed since the development of this mass spectrometer.

The State of the Art and what it means for Sample Return Analysis and Science: The next generation of thermal ionization mass spectrometers (e.g., Triton Plus) has better ion optics, which gives an ion transmission efficiency of about 35% for a double-filament geometry. Fitted with an array of new (low noise and highly stable) compact discrete dynode multipliers, along with an SEM and Faradays connected to low noise high gain (10^{13} Ω) amplifiers, the sample-size needed for high-precision analyses of low-abundance isotopes is greatly reduced. This sensitivity is sufficient for the community to obtain reliable isotope ratios in single, small objects. Below are examples of the current feasibility of such measurements:

1. *Osmium isotope composition of Solar Wind using Genesis sample*s. Due to crash landing of the Genesis capsule available collector material is rather limited requiring measurement of Os isotopes in a 1 fg sample (= 3.2 million atoms). Poisson counting statistics calculation shows that a 1% uncertainty in the measurement of 1 fg of Os is feasible using multi-ion counting. To make such measurement requires a background noise of << 1 cps. The compact discrete dynode multipliers have a dark current of <0.1 cps and therefore an array of these multipliers can be used to precisely measure Os isotope ratios of a 1 fg sample. At Dartmouth we are developing clean reagents and procedures that would permit such measurements to be made in silicon collectors.

2. *Osmium isotopes in Wild 2 comet samples*. Samples of Wild 2 comet collected during Stardust are likely to have an Os concentration of about 1000 ng/g. If so, a 10 µm sized olivine grain (Figure) would yield about 1.6 fg of Os, suitable for analysis using the multi-ion counting, provided of course that it can be cleanly separated from the aerogel.

3. Rb-*Sr, Sm-Nd and Os isotopes in dust from the Itokawa \interplanetary dust particles*. Much larger dust samples collected by Hayabusa on 25143 Itokawa asteroid could be analyzed for not only Os but also for Sr, Sm, Nd and other elements. For example, an 80 µm sized grain from Itokawa could contain about 0.7 pg (2.8×10^9 atoms) of Nd. For an effective ionization efficiency of about 20% (as NdO^+, e.g., [4]) multi-ion counting would yield a $^{143}Nd/^{144}Nd$ ratio with a counting precision of about 1.5 epsilon units (1-sigma; 1 epsilon unit = 1 part in 10,000).

The Nd isotopes could be measured with an array of Faraday cups connected to 10^{13} Ω feedback resistors. The noise level for 660 s integration on 10^{13} Ω feedback resistors is 0.3 µV and recent studies [5-6] have used static multi-collection to obtain precise measurements of 10 pg Sr and Nd standards and samples. So, with the availability of a mass spectrometer with these new capabilities, much smaller samples could be used to analyze trace elements and isotopic ratios of minor elements. This capability could help guide discussion toward the size of the samples to be collected on the future sample return missions.

In addition to analyzing return samples, such a mass spectrometer would allow the community to investigate the provenance of pre-solar grains [2-3] and evaluate how they impact the isotope composition of CAIs, chondrules and bulk meteorites. There are other areas of extraterrestrial-materials research which could benefit from access to this type of facility; for example, isotope composition of difficult to ionize elements such as Sn (e.g., [7]) could be precisely measured. Availability of a mass spectrometer fitted with an array of new (low noise and highly stable) compact discrete dynode multipliers, along with an SEM and Faradays connected to low noise high gain amplifiers would allow significantly more precise measurements and could open up new areas of research.

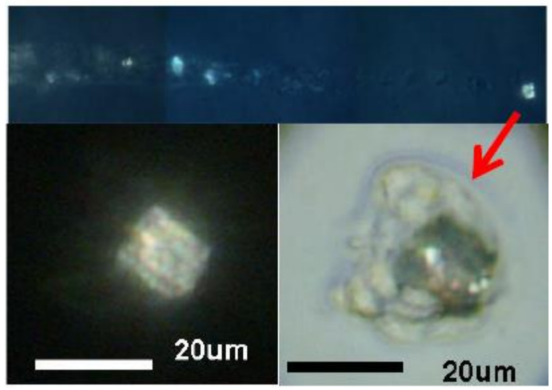

Figure. A JSC Curatorial picture from [7] of Stardust track #48, with inserts showing the terminal particle in dark and bright field. This 10 micron particle could be suited to the measurement of isotopic ratios.

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