

**THE NRL SIMS-SSAMS: A UNIQUE INSTRUMENT FOR COSMO- AND GEOCHEMISTRY.** E. E. Groopman<sup>1</sup>, A. J. Fahey<sup>1</sup>, K. S. Grabowski<sup>1</sup>, and K. C. Fazel<sup>1</sup>, <sup>1</sup>U.S. Naval Research Laboratory, 4555 Overlook Avenue, Washington, DC 20375 (evan.groopman.ctr@nrl.navy.mil)

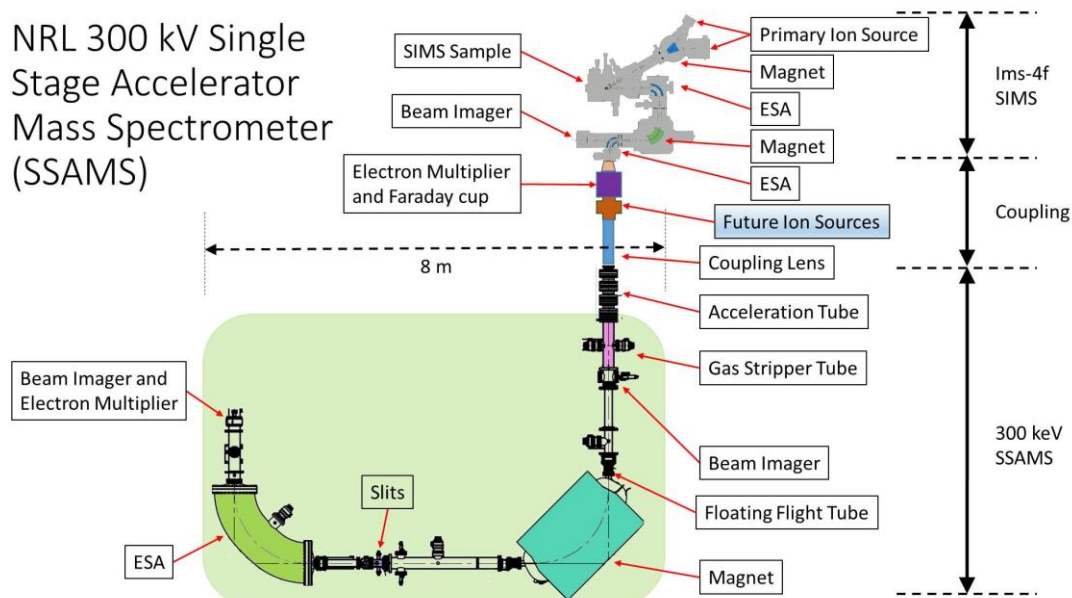
**Introduction:** The U.S. Naval Research Laboratory (NRL) has acquired and built a unique Secondary Ion Mass Spectrometer (SIMS) coupled to a Single Stage Accelerator Mass Spectrometer (SSAMS) designed to address topics in nuclear forensics, geochemistry, cosmochemistry, and materials science. A significant challenge to SIMS analysis of high-mass (>50 u) ions can be the presence of molecular isobaric interferences, especially from complex geological samples, which require ever increasing mass resolution to separate. High mass resolution often comes as a tradeoff with ion transmission. AMS typically utilizes gas stripper cells or thin foils to destroy molecular interferences, though these come at the cost of high beam energies (often MeV), and high losses due to scattering from the stripper and from the production of multiply charge ions, in turn requiring larger sample sizes. The SIMS-SSAMS achieves the benefits of both techniques: the microanalytical capabilities of SIMS and the isotopic specificity of AMS. With a doubly mass-filtered beam and lower accelerating energies (300 keV) than typical AMS, the issues of multiply charged ions and interferences are also minimized.

**Instrument Description:** The NRL SIMS-SSAMS consists of a modified Cameca ims-4f SIMS (4.5 keV extraction voltage) and a custom National Electrostatics Corp. (NEC) SSAMS ( $\mp$ 300 keV) connected by a

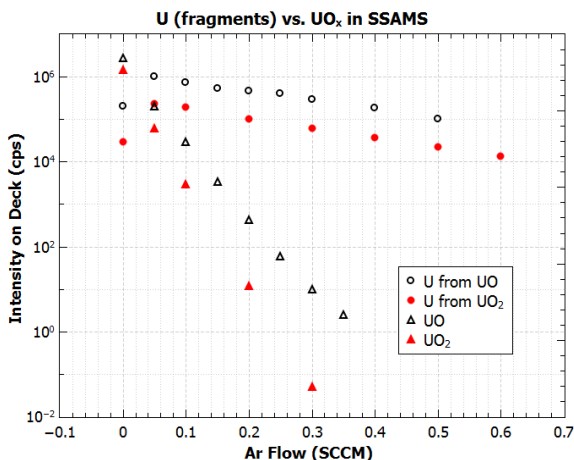
custom coupling section (Figure 1). The SSAMS can accept positive or negative ions, allowing for analysis of nearly the entire periodic table. Following the single-stage accelerator, a gas stripper tube allows for the destruction of molecular ions, both removing unwanted molecular isobaric interferences and allowing for the measurement of atomic ion fragments (e.g.,  $U^+$  from the breakup of  $UO_2^+$ ), also without any molecular isobaric or multiply charged atomic ion interferences. Ar is currently used as the stripping gas, with operational flow rates ranging up to 0.5 standard cubic centimeters per minute (SCCM), although other gases, such as  $N_2$ ,  $O_2$ , and He may be used. The flight tube through the SSAMS magnet is electrically isolated from the rest of the accelerator allowing for electrostatic switching between mass peaks ( $\pm 20$  kV or  $\pm 15.5$  u centered on mass 238 at 300 keV). For nearby masses, this allows for isotope ratio measurements to be made at the SSAMS by only changing the SIMS magnet and the flight tube voltage.

The SIMS-SSAMS runs in-house LabVIEW software and is therefore fully extensible to handle any type of data acquisition or sample feasible with the hardware.

**Discussion:** One of the most significant benefits of the SIMS-SSAMS is its ability to separate atomic ions from molecular ion isobaric interferences. Examples of



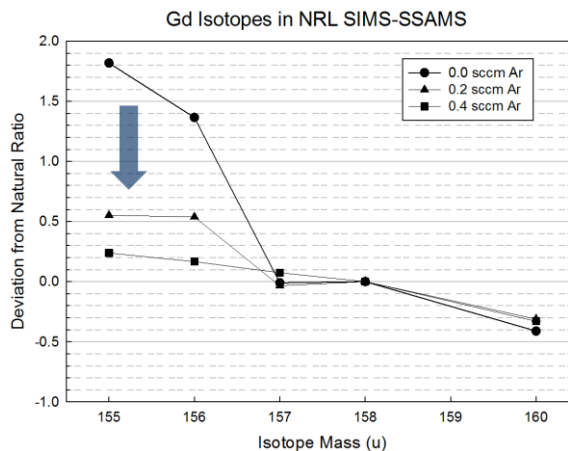
**Figure 1:** Schematic of the NRL SIMS-SSAMS consisting of a modified Cameca ims-4f, coupling section, and NEC  $\pm$ 300 keV SSAMS. The 1 m radius accelerator magnet has focal points at the center of the gas stripper cell and the exit slits.



**Figure 3:** Measurements of  $U^+$  fragment transmission from  $UO^+$  (open circles) and  $UO_2^+$  (filled circles) vs. Ar flow rate from a sample canary glass. Also shown are the molecular destruction rates of  $UO^+$  (open triangles) and  $UO_2^+$  (filled triangles) vs. Ar flow rate. For a reduction in  $U^+$  transmission of 65% at a flow rate of 0.2 SCCM, comparable molecular destruction (of a potential molecular isobaric interference) is 4 – 5 orders of magnitude.

the exponential losses ( $e^{-\lambda x}$ ) due to scattering (from molecular breakup) and molecular destruction in the gas stripper cell are shown in Figure 2, where  $x$  is the Ar flow rate and  $\lambda$  is the scale parameter.  $\lambda$  for molecular destruction is more than  $11\times$  that of losses due to fragment scattering, indicating that for every atomic (fragment) ion lost due to scattering in the gas stripper, nearly 60,000 interfering molecules are destroyed, yielding an efficient means to remove unwanted molecular isobaric interferences. This also implies that even atomic ion signals that are orders of magnitude less intense than a molecular interference can be effectively isolated and counted with the SSAMS. For example, Figure 3 illustrates the destruction of oxide interferences from the light Rare Earth Elements (REEs) on  $Gd^+$  ions from a sample of N. Korean monazite (National Museum of Natural History #147239), with complete destruction of the interfering ion signal at a flow rate of 0.4 SCCM (though this more generally depends upon the beam intensity and the specific molecule). Separation of the  $Gd^+$  peaks from light REE oxides would otherwise require mass resolving power (MRP;  $\Delta m/m$ )  $> 7000$  or the use of energy filtering [2,3], both of which greatly reduce the total ion counts of the species of interest. Even higher MRP would be required to separate interfering C-bearing molecules. The NRL SIMS-SSAMS greatly eases the complexity and difficulty of such measurements, able to be run with lower MRP (and higher transmission) than would otherwise be required and with greater atomic ion specificity.

**Future Upgrades:** Our ims-4f instrument also contains a floating flight tube, which with an offset voltage



**Figure 2:** Example of the measurement of  $Gd^+$  isotopes in N. Korean monazite NMNH 147239 following the destruction of interfering  $CeO^+$  and  $LaO^+$  molecules. With increasing flow rate the isotope ratios more closely match the true composition. Separating any of the isotopes of Gd from molecular oxide interferences from the light REE would otherwise require MRP ( $\Delta m/m$ )  $> 7000$ .

of  $\pm 600$  V (at SIMS kinetic energy of 4.5 keV), will provide the same electrostatic mass range as the accelerator magnet and flight tube. In the near future we plan to implement electrostatic peak switching on the SIMS, which will improve the duty cycle of all measurements, allow for faster mass-spectral acquisitions, and provide a faster and more reliable way to synchronize peak switching between the two magnets.

We plan to replace the ims-4f sample chamber with the sample chamber from an ims-6f, which will yield a number of important benefits including stage height control, ports for  $O_2$  flooding, and windows for laser post-ionization, the latter two of which will increase ion yields. Optical spectra of atoms sputtered from sample surfaces indicate that the atoms are ejecta in various excited states [4], some of which might be ionized by a focused laser above the sample surface. Since only  $\sim 1\%$  of sputtered atoms are typically ionized under normal SIMS operating conditions, there remain large potential improvements in sensitivity. We have also added the ability to use an  $F^-$  (or  $SF_5^-$  cluster) primary beam, which enhances beam brightness by  $5\times$  relative to  $O^-$ , resulting in increased ion yields and/or higher lateral resolution (lower beam current) [5].

**References:** [1] E.E. Groopman (this conference). [2] Zinner, E. & Crozaz, G. (1986) *Int. J. Mass Spectrom. Ion Processes*, 69, 17-38 [3] Fahey, A.J. (1998) *Int. J. Mass Spectrom.* 176, 63-76 [4] Suchanska, M. (1997) *Prog. Surf. Sci.*, 54, 265-209 [5] Pillatsch, L. et al. (2010) *Surf. Interface Anal.* 42, 645-648

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