

### TRACE ELEMENT DETERMINATION IN PRESOLAR GRAINS WITH THE NRL SIMS-SSAMS.

E. E. Groopman<sup>1,2</sup>, A. J. Fahey<sup>2</sup>, K. S. Grabowski<sup>2</sup>. <sup>1</sup>National Research Council Postdoctoral Fellow, 500 Fifth Street NW, Washington, DC 20001 (evan.groopman.ctr@nrl.navy.mil), <sup>2</sup>U.S. Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC 20375.

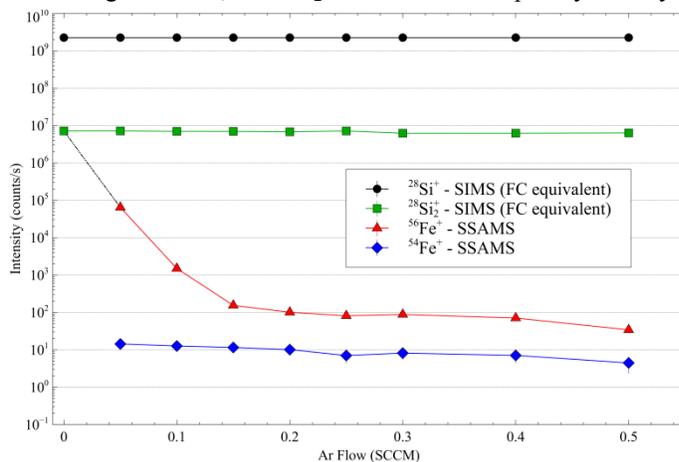
**Introduction:** The U.S. Naval Research Laboratory (NRL) has acquired and built a unique Secondary Ion Mass Spectrometer – Single-Stage Accelerator Mass Spectrometer (SIMS-SSAMS) that combines the high spatial resolution of SIMS with the molecular dissociative capability of AMS and is well suited for topics in cosmo- and geochemistry [1,2]. Unlike traditional tandem AMS, the single stage accelerator allows for the injection of positive or negative ions, which enables the analysis of atomic ions from nearly the entire periodic table. The system consists of a Cameca ims 4f and a National Electrostatics Corporation (NEC) SSAMS joined by a custom coupling section. After the SIMS, the ion beam is accelerated ( $\pm 304.5$  keV) and transmitted through a gas stripper cell filled with Ar where molecular ions are dissociated by collisions with the stripper gas. Transmission in the AMS is nearly 100% without scattering losses in the stripper cell, which can be 50 – 65% under normal operating conditions at flow rates of 0.2 standard cubic centimeters per minute (sccm). In measurements of NIST U<sub>3</sub>O<sub>8</sub> Certified Reference Material particles, we have achieved abundance sensitivity for <sup>239</sup>Pu in the presence of <sup>238</sup>U down to 10 ppb by eliminating hydride interferences (UH<sup>+</sup>/U<sup>+</sup>  $\sim 1.4 \times 10^{-8}$  at 0.2 sccm). This is equivalent to enabling the measurement of 0.1 ppb <sup>236</sup>U in natural U. These measurements are directly applicable to trace element determination, e.g., rare earth elements and actinides, and isotope ratio measurements in presolar grains.

**Methods:** To further test the abundance sensitivity of the SIMS-SSAMS, a  $\sim 350$  nA primary beam of O<sup>-</sup> ions was focused onto an  $\sim 90$   $\mu$ m spot on a Si wafer test sample. <sup>28</sup>Si<sup>+</sup> and <sup>28</sup>Si<sub>2</sub><sup>+</sup> were measured with the SIMS Faraday cup (FC) prior to the SSAMS, while <sup>54</sup>Fe<sup>+</sup> and <sup>56</sup>[Si<sub>2</sub> + Fe]<sup>+</sup> were injected into the SSAMS and counted on the electron multiplier (EM) at the end station. Ordinarily, mass resolving power (MRP)  $m/\Delta m > 2900$  (at 10% peak height) is required to separate <sup>28</sup>Si<sub>2</sub><sup>+</sup> and <sup>56</sup>Fe<sup>+</sup>. However, for abundance sensitivity in the range mentioned above, much higher MRP is required, which would drastically reduce transmission [3] or would be unachievable. To simulate the isolation of unresolvable atomic ions from molecular isobars, the 4f was tuned to its intrinsic MRP of 300. All ion signals were measured for gas stripper flow rates between 0.05 and 0.5 sccm.

**Results:** An Fe concentration of  $\sim 30$  ppb was measured in the Si wafer, including  $< 3$  ppb <sup>54</sup>Fe (Figure 1). With increasing flow rate, the <sup>28</sup>Si<sub>2</sub><sup>+</sup> molecule is completely destroyed, revealing the underlying <sup>56</sup>Fe<sup>+</sup>. With no interfering molecular isobars, the <sup>54</sup>Fe<sup>+</sup> signal decreases with Ar flow rate only due to increased scattering. At an Ar flow rate of 0.2 sccm, the Fe isotope ratio reaches its terrestrial value. Most importantly, we have demonstrated the measurement of an atomic ion species (<sup>56</sup>Fe<sup>+</sup>) that is only 10 ppm of the molecular isobar signal (<sup>28</sup>Si<sub>2</sub><sup>+</sup>) from a single analysis spot in a SIMS instrument!

**Discussion:** Accurate measurements of elemental concentrations and isotope ratios by SIMS, especially for high-mass elements, require the correction for molecular isobars. High mass resolution and energy filtering [4] have been successfully employed, but do reduce sensitivity and transmission. The advantage of the SIMS-SSAMS is remarkable, however, for high-mass elements, where sufficiently high MRP may not be feasible, and/or where ion signals of interest are much smaller than the background, e.g., Figure 1. We plan to apply the capabilities of the SIMS-SSAMS to measurements of trace elements in presolar grains, including the rare earths and actinides. Resonance Ionization Mass Spectrometry (RIMS) is often employed to measure these elements plus Ba, Mo, Zr, etc., due to its high sensitivity and elemental selectivity. The advantages of SIMS include the ability to measure many different elements in an analytical session, higher duty cycles, and fine control over sputtering rates. Having complementary techniques for trace element determination is of utmost importance for informing models of stellar evolution and nucleosynthesis, especially as relatively few grains have been measured individually for such elements.

**References:** [1] Groopman, E.E. et al. (2016) *LPSC XLVII* #2031. [2] Groopman, E.E. et al. (2016) *LPSC XLVII* #2035. [3] Stadermann, F.J. et al. (1999) *LPSC XXX* #1407. [4] Fahey, A.J. (1998) *Int. J. Mass Spectrom.* 176, 63.



**Figure 1:** Ion signal intensity vs. gas stripper flow rate. <sup>56</sup>Fe<sup>+</sup> signal extrapolated to 0 SCCM flow. Error bars often smaller than symbols.