

FIRST U-TH-PB MEASUREMENTS WITH THE NEW NRL SIMS-SSAMS. E. E. Groopman¹, A. J. Fahey¹, K. S. Grabowski¹, and K. C. Fazel¹, ¹U.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. The SSAMS can accept positive or negative ions, allowing for analysis of nearly the entire periodic table. Following the acceleration lenses, 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^+), without any molecular isobaric or multiply charged atomic ion interferences. Additionally, 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 on the SSAMS by only changing the SIMS magnet and the flight tube voltage. The instrument is more fully described in [1].

Measurement Description: Grenville Skarn (GS) titanite has been suggested as a reference material for SIMS U-Th-Pb analyses based upon its high U and Th concentrations (100 – 1000 ppm), high $^{206}Pb/^{204}Pb$ (500 – 2500) and $^{208}Pb/^{204}Pb$ (200 – 1200) ratios, and

low isotopic heterogeneity [2]. We randomly selected 13 spots on 3 chips of GS crystal OLT-1 for analysis. A 10keV 50 – 100 nA O^- primary beam was defocused over a 75 μ m diameter area for Köhler (uniform) illumination of each spot.

Secondary ions of $^{204,6-8}Pb^+$, $^{248}[ThO]^+$, and $^{267,270}[UO_2]^+$ were extracted with the SIMS and sent into the SSAMS where $^{204,6,7,8}Pb^+$, $^{232}Th^+$, and $^{235,8}U^+$ were measured at the end station electron multiplier (Th^+ and U^+ were measured as fragments from the breakups of their oxide molecules). Counting times of 1 – 4 s were used for each ion per cycle. The benefits of such a scheme are that the oxide ion signals from Th and U are often $>10\times$ more intense than their atomic ion signals, increasing sensitivity, and that Pb^+ , Th^+ , and U^+ ions can be measured at the SSAMS end station by keeping the SSAMS magnet at only one magnetic field! Following acceleration, ions entering the gas stripper cell have kinetic energies of 304.5 keV. Atomic ions have their energies reduced by a few 100s of eV due to electronic interactions with the Ar stripper gas, a small fraction of their total kinetic energy. The stripper cell was filled with Ar gas at a flow rate of 0.2 standard cubic centimeters per minute (SCCM) and differentially pumped out of the cell. Atomic ion fragments have their energies reduced by the proportion of mass that they lose due to molecular breakup, e.g., U^+ fragments leave the gas stripper cell with $\sim 88\%$ of UO_2^+ 's initial kinetic energy, the same proportion of mass remaining from the molecule breakup, $(238\text{ u})/(270\text{ u}) = 0.8815$, thus traveling through the SSAMS magnet flight tube along the same path as an ion of mass $238\text{ u} \times 0.8815 = 209.78\text{ u}$ with a kinetic energy of 304.5 keV. Therefore the atomic ions and molecular fragments of Pb^+ , ThO^+ , and UO_2^+ can all easily pass through the SSAMS magnet set to mass $\sim 210\text{ u}$ by simply adjusting the electrostatic offset ($\pm 13.5\text{ u}$ at this mass and kinetic energy). This setup significantly reduces the complexity of synchronizing two magnets over a large mass range ($\sim 70\text{ u}$) and improves the instrument's duty cycle. The ultimate benefit of these measurements is the elimination of molecular isobaric interferences for all masses. By utilizing a double mass-filtered beam, multiply charged ion or otherwise interfering molecules cannot reach the end station, as molecular fragments or otherwise.

Results: While the excellent isotopic and compositional properties of GS reported by [2] make this sample an attractive reference material, the mass spectrum (Figure 1) remains quite complex, with significant

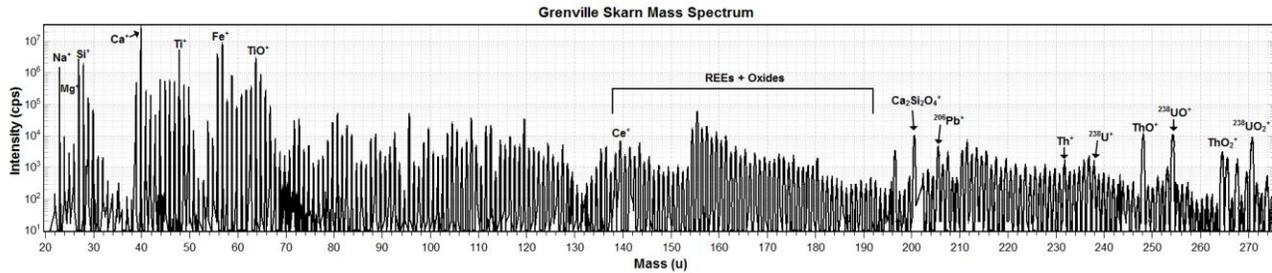


Figure 1: SIMS mass spectrum of Grenville Skarn OLT-1 from 20 u to 275 u (gap between 201 – 202 u). Large molecular ion isobaric interferences are present throughout the mass range, including around $^{232}\text{Th}^+$ and $^{238}\text{U}^+$. The majority of peaks cannot easily be identified and likely have multiple constituents. With the SIMS-SSAMS, molecular isobaric interferences are eliminated. (REE = Rare Earth Element)

peaks at nearly every mass, limiting the potential analytical accuracy of SIMS measurements. Our measurements find reasonable agreement with those in [2], though our analytical uncertainties remain large (Figure 2). A faulty power supply for the SIMS magnet has been identified as a contributor to the scatter in our current measurements, restricting our measurement reproducibility. The gains in precision and accuracy through the reduction of molecular interferences are much smaller than the current analytical uncertainties. Despite analytical scatter, our average measurement lies off of the growth curve in Figure 2 in part due to transmission differences between U^+ molecular fragments and Pb^+ atomic ions in the SSAMS. For SIMS-SSAMS measurements, both the relative sensitivity factors (RSFs) of atomic and molecular ions and the transmission losses of atomic and molecular ions (fragments) in the accelerator due to scatter must be accounted for. The RSFs for the SIMS-SSAMS are not currently well known, so the points in Figure 2 will be shifted when these values are updated.

Discussion: These measurements detail the first attempt to perform U-Th-Pb analyses with a SIMS-SSAMS instrument where molecular isobaric interferences are eliminated. Isobaric interferences otherwise reduce the accuracy of measurements of geological standards and samples. While these measurements are in fair agreement with those reported in [2], improvements in the current instrumental setup, the replacement of faulty electronics, and the exploration of the instrument's operating parameters will greatly increase our precision. In the near future we intend to switch the SIMS to a 10 kV extraction voltage, which will increase the sensitivity. We will also upgrade the SIMS sample chamber to allow for O_2 flooding, which along with an O_2^- primary beam should greatly increase our ionization yields [4]. We plan to replace the SIMS magnet flight tube with one that is electrically isolated, mirroring the electrostatic peak switching capabilities of the accelerator magnet. This upgrade will improve our instrument's duty cycle, since electrostatic switching is much faster than magnetic switching, and will

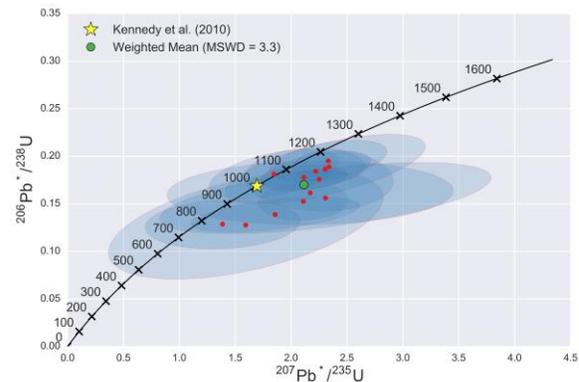


Figure 2: Wetherill concordia diagram [3] for $^{206}\text{Pb}^+ / ^{238}\text{U}$ vs. $^{206}\text{Pb}^* / ^{238}\text{U}$ (* indicates radiogenic component) for 13 measurement spots. Growth curve ticks in My. While in general agreement with the results in [2], our analytical uncertainties remain large, but will be improved with hardware upgrades.

allow for more reliable synchronization between the two magnets. Further characterization of the transmission of the SSAMS, especially with respect to atomic ions vis-à-vis molecular fragments, is necessary to properly calibrate isotope ratios. Once the SIMS-SSAMS operating parameters have been fully characterized, the instrument should provide the ability to perform rapid *in-situ* U-Th-Pb (and other isotopic system) measurements, free of molecular isobaric interferences, of complex geological materials.

References: [1] Groopman, E.E. et al. (this conference). [2] Kennedy, A.K. et al. (2011) *Can. Mineral.*, 48, 1423-1443 [3] Wetherill, G.W. (1956) *Trans. Am. Geophys. Union*, 37, 321-326 [4] Schmitt, A.K. et al. (2010) *Chem. Geo.* 269, 386-395

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