

SECONDARY ION MASS SPECTROMETRY (SIMS) AT ARIZONA STATE UNIVERSITY. M. Bose¹, R. L. Hervig², L. B. Williams², and P. Williams¹, ¹School of Molecular Sciences, Arizona State University, Tempe AZ 85287-1604, ²School of Earth and Space Exploration, Arizona State University, Tempe AZ 85287-1404.

Introduction to the SIMS facility: SIMS has long been an important component of the cosmochemist's toolbox due to the tiny amount of sample needed to obtain a useful signal. Thus, a standard 30 μm thin section provides so much material that even after extensive SIMS analyses, the section can be returned to a collection with very little apparent damage.

In the secondary ion mass spectrometry (SIMS) facility at ASU we offer analyses on Cameca ims6f and NanoSIMS 50L instruments. The 6f serves users perform a wide range of trace element analyses (from hydrogen to uranium) and isotope ratio measurements (typically H, Li, B, Mg, and selected other systems). The minimum effective lateral resolution achievable on the 6f is around 4 μm . Precise depth profiling with few-nanometer resolution is routine, and detection limits typically range from ppm to ppb. The NanoSIMS allows elemental and isotopic imaging analyses for up to 7 species simultaneously, with ultimate lateral resolution near 200 nm (oxygen primary beam for detection of positive secondary ions) and 25 nm (cesium primary beam for detection of negative secondary ions). Adjacent masses can be detected simultaneously up to m/z 57 and 58; the mass range that can be addressed simultaneously is a factor of 22, e.g. 10–220 u.

Applications with the ims6f: Examples of recent 6f work include: a) depth profiling analyses to support the determination of Cr diffusion in spinel, relevant to the resetting of ⁵³Mn daughter products [1], b) Hydrogen isotope microanalyses of nominally anhydrous minerals in Martian meteorites increasing our understanding of different hydrogen reservoirs on Mars [2], c) partitioning of gold between metal and silicate liquid which revealed strongly decreasing siderophile behavior with depth in a magma ocean [3], and d) zoning of light lithophile elements (Li, Be, B) and lithium isotopes in Martian meteorites suggesting that one sample may have experienced degassing [4].

Our lab has quantified the “useful yields” (ions detected per atom of the species of interest removed from the sample) of many elements [5] allowing calculation of the amount of material that must be consumed to obtain a particular precision. Thus the feasibility of most research projects can be determined prior to damaging a sample. See, for example, *Figure 1* where useful yields for the 4th row elements are presented, obtained under conditions that eliminate most cluster ion interferences. Cobalt, for example, shows a useful yield near 10^{-4} . At a concentration of 1 ppm Co, there are 10^5 Co atoms in each cubic micron. A 20x20x1 μm deep crater would yield 4000 Co⁺ counts, with a statistical

uncertainty of $\sim 1.5\%$ (1σ). Sampling several elements in an analysis can still result in a relatively shallow crater. Elements with lower positive ion useful yield often may be successfully analyzed using negative secondary ions (e.g., As, S).

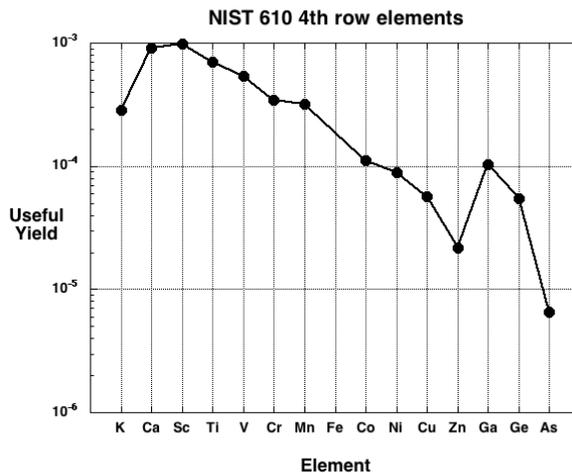


Figure 1. Useful yields for positive ions for 4th row elements determined on NIST 610 glass using the ims6f and applying energy filtering (detecting secondary ions with initial kinetic energy of $\sim 80 \pm 20$ eV). Data from [5].

Applications with the NanoSIMS 50L: Examples of NanoSIMS work partially funded by NASA include: a) *in situ* discovery of presolar grains in pristine, unaltered meteorites [6], b) spatially resolved C and N isotopic measurements to identify isotopically anomalous organics in carbonaceous meteorites [6–8], c) high precision Al-Mg isotopic measurements of micron-sized minerals in the rims of CAIs [9; **Figure 2**], d) trace element zoning (⁷Li, ³⁰Si, ⁴⁸Ti, ⁸⁹Y, ¹⁴⁰Ce, ¹⁴²Nd, ¹⁵²Sm, ¹⁶⁴Dy, and ¹⁸⁰Hf) in mineral phases e.g., zircons and pyroxenes with beam controlled profiles and step-scans [e.g., 10], e) and high-precision ($\sim 2\%$ 1σ) Li isotopic analysis in zircons.

To explore the capability for high precision measurements while maintaining high spatial resolution using the O⁻ primary beam, we did preliminary measurements of lithium isotopes on NIST 612 and a zircon standard M257 with lithium concentrations of ~ 40 ppm and ~ 0.86 ppm, respectively. Analyses were performed by rastering an O⁻ primary ion beam over a $3 \times 3 \mu\text{m}^2$ square area, with measurements taken from the inner 25% of that area, i.e., $1.5 \times 1.5 \mu\text{m}^2$. Four consecutive measurements (~ 1 hour each) yielded preliminary data

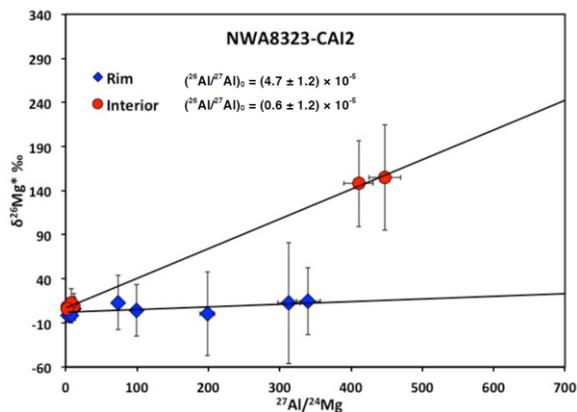


Figure 2: Al-Mg isochron for a CAI in NWA 8323 and its Wark-Lovering rim that constrains the minimum time difference between CAI and rim formation to ~690k years. Data from [9]. For these measurements San Carlos olivine and augite, Lake County plagioclase and NIST 610 synthetic glass were used as terrestrial standards. The 2σ reproducibilities on the external standards were 3.2 ‰, 2.6 ‰, 11.9 ‰ and 2.6 ‰, respectively.

showing ~2‰ (1σ) precision for ${}^7\text{Li}/{}^6\text{Li}$ ratios for NIST 612, and ~1.5‰ precision in zircon M257, with a beam size of $<1\mu\text{m}$. Given that the expected variations in $\delta^7\text{Li}$ in cases of Li diffusion are ~10 to 50‰, and the Li concentrations of target natural zircons range from ~1 to 15 ppm, the precision obtained by the NanoSIMS will be adequate to document kinetic isotopic effects. Such measurements can be also done in extraterrestrial materials.

Another novel NanoSIMS application has been to characterize nanopores in black shale, and use specific elemental ratios (H/C and O/C as used on Van Krevelen plots) as a measure of organic type and thermal maturity of the organics, which can be useful to study macromolecular C in extraterrestrial materials. Li and B isotopes were also investigated as a function of thermal maturity. In order to quantify these volatile elements and their isotopic fractionation, relative sensitivity factors in kerogen samples of different maturities were calculated [11] by measuring Li and B depth profiles in implanted glassy C on both the instruments. Based on the preliminary data, it appears that the B/C ratios in the same C-rich matrix, are similar for both instruments, as are Li/C ratios. These new calibrations allow quantitative analysis of B and Li in C-rich matrices for comparison with silicates using the NanoSIMS, which is a subject of ongoing research.

Fundamental research and quantification: We constantly explore mechanisms of ion formation [e.g., 12]. The more we understand in this arena, the better

we can design protocols to support novel analyses of rare materials. Because of the potential for matrix effects, we also make extensive use of ion implantation into the phase of interest to provide matrix-matched quantification of the secondary ion signals [e.g. 13, 14]

Instrumentation: Instrumentation developments include exploration of analog electron multiplier operation for precise isotope ratio determination over a very wide dynamic range [15] and development of a new cesium ion source for the NanoSIMS producing a 25 nm diameter Cs^+ beam with a factor of 4 greater current than the factory source allowing higher throughput and potentially lower user costs [16; Figure 3].

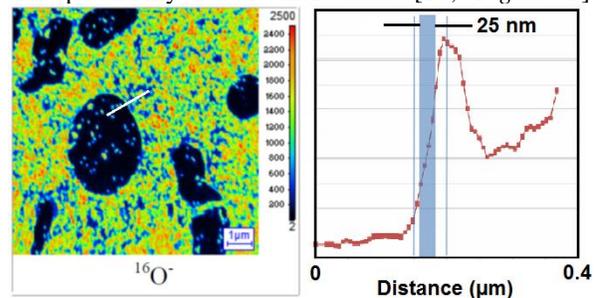


Figure 3. O^- ion image ($10 \times 10 \mu\text{m}$) of a beam size test sample using the new ASU Cs^+ primary ion source showing ~25 nm beam diameter for a line scan over a sharp feature image.

Our facility, current applications and instrumental developments will be presented at the meeting.

References: [1] Posner E. S. et al (2016) *Geochim. Cosmochim. Acta*, 175, 20–35. [2] Mane P. et al. (2016) *Meteorit. Planet. Sci.*, in revision. [3] Righter K. et al (2015) *Meteorit. Planet. Sci.*, 50, 604–631. [4] Udry A. et al. (2016) *Meteorit. Planet. Sci.*, DOI:10.1111/maps.12582 [5] Hervig R. L. et al. (2006) *Chem. Geol.*, 227, 83–99. [6] Bose M. et al. (2014) *Earth Planet. Sci. Lett.*, 399, 128–138. [7] Pizzarello S. and Bose M. (2015) *Astrophys. J.*, 814, 107–114. [8] Bose M. and Zega T. (2016) 47th LPSc (this conf.) [9] Mane P., et al. (2015) 46th LPSc, Abstract #2898. [10] Brugman K. K. et al. (2015) AGU meeting, Abstract #8269. [11] Williams L. and Bose M. Euroclay Conf., 2015. [12] Franzreb K. et al. (2004) *Surf. Sci.*, 573, 291–309. [13] Williams P. et al (1983) *Nucl. Instru. Methods*, 218, 299–302. [14] Hervig R. L. et al (2003) *Dev. in Volcanology*, 5, 83. [15] Williams P. et al. (2013) *Surf. Interface Anal.*, 45, 549–552. [16] Williams P. et al. US Patent Application, October 2015.

Acknowledgements: We thank NSF (EAR-1352996; PI R. Hervig). MB thanks the EOS NExSS grant for travel support (NNX15AD94G).