

## SIMS Solutions in Materials and Life Sciences Room Great Lakes C - Session SS-MoA4

### Geosciences

**Moderator: Mostafa Fayek**, University of Manitoba

4:00pm **SS-MoA4-13 Depth Profiling of Solar Wind Helium by Secondary Neutral Mass Spectrometry**, *Hisayoshi Yurimoto*, Hokkaido University, Japan **INVITED**

Our Sun erupts energy plasma from the solar corona. This is called solar wind. The plasma mostly consists of electron, hydrogen, and helium. A coronal mass ejection (CME) is an outburst of significant release of solar wind. As CMEs travel through interplanetary space as interplanetary CMEs (ICMEs), they often cause large geomagnetic storms on Earth when they hit the Earth's magnetosphere. We report the first quantitative measurements in laboratories, depth profiling, of ICME atoms that were collected from "the Halloween solar storms of 2003", which was the largest solar storm during the space age. The solar wind collectors from the NASA Genesis spacecraft provide a unique opportunity to study the speed distribution of ICME plasmas during these events.

We measured solar wind helium from the Genesis collector targets by depth profiling using a secondary neutral mass spectrometer called LIMAS [1, 2]. We used a focused Ga ion beam for the primary ion to sputter the targets. Sputtered neutrals were ionized by strong field using a focused femtosecond laser. The post-ionized ions were introduced into a multi-turn time-of-flight mass spectrometer. We obtained helium depth profiles from 10  $\mu\text{m}$  square with detection limits of  $2 \times 10^{17}$  atoms/cm<sup>2</sup> (4 ppma).

The depth profile of solar wind helium has a shape of Gaussian-like with a peak at  $\sim 20$  nm in depth. The Gaussian-like shape accompany a tail at deeper than  $\sim 100$  nm. We find that the tail corresponds to the ICME plasma of the Halloween solar storms of 2003. The depth profiles are converted to solar wind speed distribution applying SRIM simulation. We find that the ICME plasma speeds of the Halloween solar storms of 2003 reached greater than 2000 km/s and with a total fluence more than 10 times greater than previously reported by any space-based particle instrument. Such extreme fluences mark this event as the most intense recorded measurement of interplanetary plasma during the space age. These new findings and new technique in laboratory add new unique scientific value to investigate solar and geomagnetic activities.

References: [1] Bajo et al. *Surf. Interface Anal.* **51**, 35-39 (2019), [2] Nagata et al. *Applied Physics Express* **12**, 085005 (2019).

4:40pm **SS-MoA4-17 SIMS Measurements of Trace Hydrogen and Fluorine in Nominally Anhydrous Minerals: Implications for Primary and Secondary Processes on the Moon**, *Jed Mosenfelder*, University of Minnesota; *A. von der Handt*, University of British Columbia, Canada; *M. Hirschmann*, University of Minnesota

The advent of ultra-low blank, dynamic SIMS methods for measuring trace light element concentrations in geologic materials has opened up new possibilities for exploring nominally H- and F-free minerals – including plagioclase (Pl), orthopyroxene (Opx), clinopyroxene (Cpx), and olivine (Ol) – as recorders of volatile processing in planetary bodies. The role of volatile elements in the origin and differentiation of the Moon remains controversial [1,2] and amenable to study with this approach. Building on our calibration work and efforts to reduce limits of detection (LOD) [3-6], we have acquired an extensive data set on 19 Apollo samples, including ferroan anorthosite (FAN), Mg-suite, granulitic impactite, and basaltic lithologies. Methods and references are detailed in the PDF attachment.

Our results show that trace amounts of F, up to 1.2  $\mu\text{g/g}$ , are ubiquitous in Pl from FAN. Granulitic impactites contain less F (up to 0.4  $\mu\text{g/g}$ ), while significantly greater amounts are present in some Mg-suite rocks (up to 8.2  $\mu\text{g/g}$  in Opx). Significant F is also present in Cpx from a mare basalt (up to 1  $\mu\text{g/g}$ ). Measurements of H in these samples are more ambiguous. Most analyses reveal no H above the LOD; where present it can be explained in most cases by ionization of sub-mm to mm-sized micropores, identified in and around analysis craters by high-resolution imaging with EPMA (see attachment). Some of these micropores may have contained volatile elements exsolved from crystals during static cooling. In most cases, however, we associate the micropores with shock events. An extreme example is FAN sample 60015, with Pl analyses yielding up to 25  $\mu\text{g/g}$  H<sub>2</sub>O, 60  $\mu\text{g/g}$  F, and 18  $\mu\text{g/g}$  Cl. Cl is highly incompatible in Pl and likely derived from the splash melt that partially coats and infiltrates the sample. H and F

may also have been introduced in this manner – possibly from an extraterrestrial source – or may be redistributed from the Pl crystal structure into micropores by the shock event. This interpretation contrasts with that of Hui et al. [7], who inferred that H in 60015 was structurally bound in Pl and preserved after partitioning with H in the lunar magma ocean (LMO). On one hand, our results call this hypothesis in to question. On the other hand, we can use our robust measurements of F in less shocked FAN to place constraints on F in the LMO (see attachment).

Future work is in progress to measure H, F, and Cl in additional Mg-suite samples and basalts (including high-Al, high-Ti, and KREEP varieties), including a sample recently released after 50 years of cold storage as part of the Apollo Next Generation Sample Analysis program.

5:00pm **SS-MoA4-19 Multi-Collector Configuration Considerations for Age-Dating Measurements of Particles by Large Geometry Secondary Ion Mass Spectrometry**, *Todd Williamson*, *E. Groopman*, *D. Simons*, National Institute of Standards and Technology (NIST)

Large geometry secondary ion mass spectrometry (LG-SIMS) has been widely used for isotopic measurements of uranium particles for many years. Recently, it has been demonstrated it is possible to perform chronometry (a.k.a age-dating) measurements of single uranium-containing, micrometer-sized particles using LG-SIMS. For this chronometry measurement, the analytes measured are the <sup>234</sup>U – <sup>230</sup>Th mother-daughter chronometry pair. This measurement protocol was developed using the single, mono-collector electron multiplier (EM) configuration on a LG-SIMS instrument with the preponderance of the counting time of an analysis cycle being on the <sup>230</sup>Th to maximize measurement precision. Most LG-SIMS instruments have a multi-collector system configured with five EM detectors, which allows for simultaneous measurement of up to five isotopes, improving measurement precision and detection limits over single, mono-collector protocols. We will present results of our work adapting the mono-collector chronometry measurement protocol to the multi-collector configuration of an LG-SIMS with a focus on uranium particle measurements. The multi-collector configuration allows the simultaneous counting of both <sup>230</sup>Th and <sup>234</sup>U, with the added advantage of allowing the collection of <sup>231</sup>Pa and <sup>232</sup>Th isotopes, too. Simultaneously counting all isotopes should improve the overall measurement precision, as well as eliminate transient artifacts during the analysis that could result in inaccurate data. We will present results focusing on three aspects of this work. The first topic will discuss comparison of the multi-collector configuration to the mono-collector configuration with an emphasis on measurement precision and variability. Results for both age-dating and more conventional uranium isotopic measurements will be discussed. The second topic will discuss how increased background from peak tailing – often referred to as abundance sensitivity – can negatively impact measurement detection limits for the multi-collector configuration. The reason for abundance sensitivity potentially having negative consequences for age-dating measurements is the design constraints of multi-collector systems for LG-SIMS. The final topic will discuss the viability of <sup>231</sup>Pa measurements using the multi-collector configuration in regard to precision and detection limits which could be expected for age dating measurements using the <sup>235</sup>U – <sup>231</sup>Pa chronometer pair.

5:20pm **SS-MoA4-21 Construction of New Biomolecular Architectures Using Large Argon Clusters**, *Benjamin Tomasetti*, Université Catholique de Louvain, Belgium; *V. Delmez*, université catholique de Louvain, Belgium; *C. Lauzin*, université Catholique de Louvain, Belgium; *A. Delcorte*, Université Catholique de Louvain, Belgium

The ability to biofunctionalize surfaces with proteins is a major challenge in many fields such as biocatalysis, tissue engineering or biomedical devices. We established a new variant of soft-landing using the argon cluster source available on a time-of-flight secondary ion spectrometer (ToF-SIMS) to transfer intact biomolecules from a pure sample target onto a collector in the vacuum. Lysozyme (MW=14 kDa) was soft-landed in this way onto a Si collector and the integrity and bioactivity of the transferred molecules were demonstrated by gel electrophoresis and bioassays [1].

After establishing the successful buildup of films of different non-volatile molecules with a good thickness control, more complex architectures could be prepared. First, we demonstrated the great flexibility of the method toward the nature of the substrate. Multilayers of bradykinin were deposited on a paper surface, knowing that this type of deposition is not possible with a solution-based method (Fig.1). Second, we investigated the construction of mixed multilayers, composed of various species. A bilayer of bradykinin and Irganox 1010, built by successive transfer with 10 keV Ar<sub>3000</sub><sup>+</sup>, was studied by dual-beam depth profile analysis. It revealed that

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the molecular layers are well-separated and that the new material is stable in time (Fig.2). The mechanical stability against external stresses was also checked with basic tests (tape test, ect.). The ability to construct such bilayers paves the way to new applications which could not be considered previously. Indeed, we are able to build alternate multilayers of proteins with comparable solubility that can neither be adsorbed from solution without mixing on the surface nor sublimated without degradation.

In order to increase the flexibility of the method in terms of geometry, choice of clusters and possible ion selection after desorption, a home-built transfer instrument using a pulsed valve for the production of large ionic clusters is currently being home-built in our laboratory.

[1] V. Delmez et al., J. Phys. Chem. Letters, 2021, 12, 952-957.

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