NANOANALYSIS OF SUBLIMATES ON PRISTINE LUNAR ORANGE GLASS BEADS

T.A. Williams[1], S.W. Parman[1], A.E. Saal[1], R.C. Ogliore[2], M. Iskakova[2], and A.J. Akey[3], [1]Department of Earth, Environmental and Planetary Sciences, Brown University, 324 Brook St., Providence, RI, 02912, [2]Department of Physics, Washington University in St. Louis, St. Louis, MO 63130, [3]Center for Nanoscale Systems, Harvard Univ., Cambridge, MA 02138. Email: thomas_williams@brown.edu

Introduction: Constraining the volatile contents of the Moon's interior is one of the most important research areas in lunar science with implications for how the Moon formed, how it evolved, and what resources are available for use in future human exploration. Analyses of lunar glass beads demonstrate that at least part of the lunar mantle retains significant volatile contents [1,2]. Much of the beads' original volatiles were lost during the volcanic eruptions that formed them, but some of the volatiles desublimated out of the volcanic gas cloud and onto the surfaces of the glass beads, and are now present as 20-50 nm thick coatings [3].

Thermodynamic modeling of sublimate formation [4] and ATEM imaging [5] indicates that the compositions of the sublimates evolved throughout desublimation. The petrology and geochemistry of the coatings therefore provides a unique opportunity to constrain the pressure-temperature-composition (PTX) evolution of the gas cloud, and individual beads might record different paths through the cloud. Here we use a range of nanoanalytical tools to measure the compositional variation in the sublimates, with the ultimate goal of further constraining the volatile content of the magmas and the lunar interior.

Samples: We examined sublimates on pristine Apollo 17 orange glass beads that were extracted from sample 74001. This sample was collected in a double drive tube at the south rim of Shorty Crater and transported from the moon sealed in the drive tubes. They were opened and stored in nitrogen at JSC.

Airless Sample Handling: The sublimates react with air [6] and so our sample handling minimized air exposure. Our ultimate goal is completely airless handling from beginning to end. The samples were shipped under nitrogen and opened in a nitrogen glove box, where they were mounted on SEM stubs. The samples were transferred to the SEM in an airless transfer device, and coated with a conductive gold layer after SEM analyses. After this, they were exposed to air, with the idea that the coating would largely protect them from reaction with air, and that the trace element and isotope analyses by NanoSIMS would be minimally affected.

Methods: The beads were imaged using the FEI Helios NanoLab 660 DualBeam scanning electron microscope at the Centre for Nanoscale Systems at Harvard University. Compositional information was obtained with an EDAX X-ray Energy Dispersive Spectrometer (EDS) system. S-rich areas were targeted for trace element and isotope depth profiling.

Trace element abundances (^{19}F, ^{37}Cl, ^{63}Cu, ^{79}Br, and ^{127}I) were measured using the CAMECA NanoSIMS 50 at Washington University in St Louis. A Cs+ primary beam of ~507 pA (D1 aperture) was rastered over a 15 x 15 μm^2 area for ~3 minutes to pre-sputter through the gold coat. We then switched to ~8 pA and rastered over a 10 x 10 μm^2 area for analysis. All elements were measured simultaneously, with most parameters tuned for ^{63}Cu. A similar procedure was used to measure ^{34}S/^{32}S ratios, for which we used a Cu_2S standard.
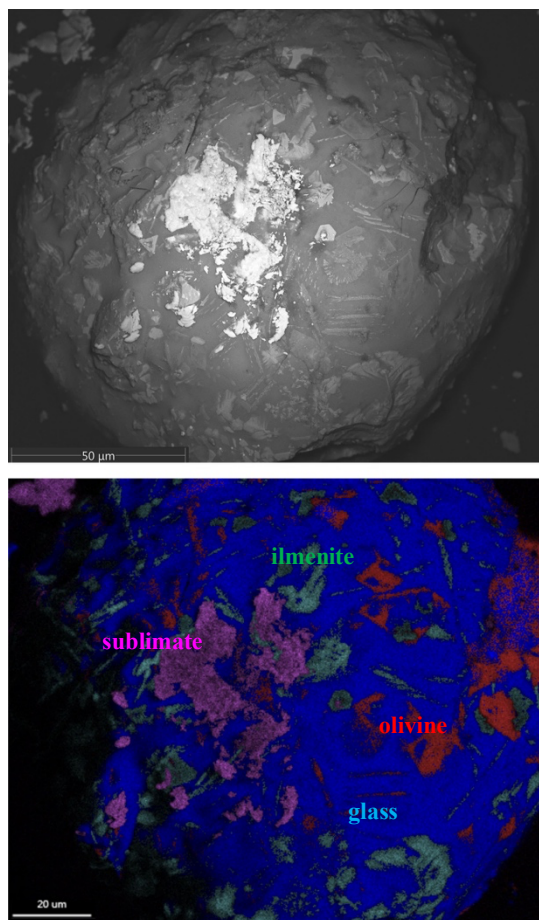

Fig. 1: Top: A bead from 74001. The lighter patch on the smooth surface is the layer with vapor condensates. Bottom: EDS map of the same bead. S (pink), Si (blue), Mg (red), Ti (green).

Results:

Preliminary results of 74001 glass beads. The thickness and areal extent of the surface coating is highly variable from bead to bead. Because the condensates are so thin, the majority of the excitation volume in EDS analysis is within the glass, even at low voltage. However, the condensates are distinguishable via their higher sulfur concentrations (Fig. 1). Possible ilmenite and olivine crystals on the surface of the beads are identifiable as areas of high Ti and Mg, and the uncoated glass surface is rich in Si.

Depth profiles with NanoSIMS: We obtained 11 successful trace element depth profiles on 4 beads, after
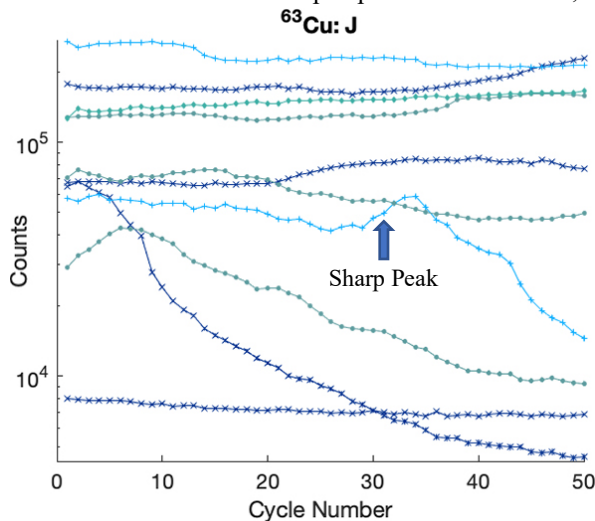

Fig. 2: Counts of ^{63}Cu against cycle number (log scale). The surface of the condensate is at cycle number one. Desublimation proceeded from right (initial coating) to left (last coating). The error bars are smaller than the individual analysis markers (circles). Each bead is displayed with a different colour and marker.
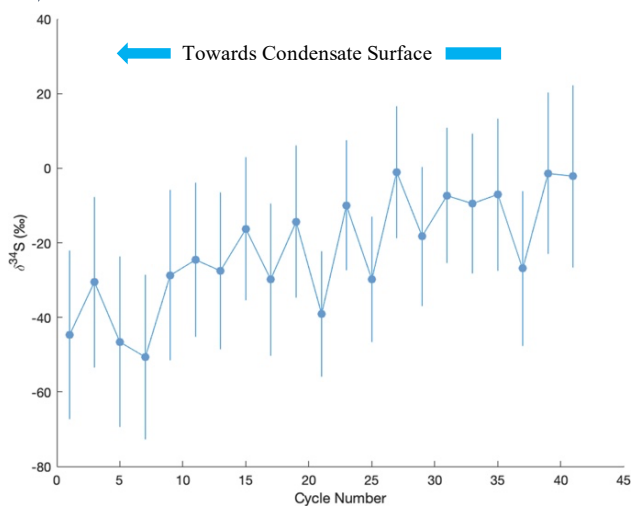

Fig. 3: $\delta^{34}S$ in a vertical profile down from the exterior of a coating (cycle zero). Vertical lines are 1σ error bars.

selection based on EDS analysis of 16 beads. Overall, concentrations vary by a factor of 10 between coatings. On some beads the relative concentrations of the elements remains fairly constant, or show slight decreases towards the surface. However, on others there are large increases in concentration towards the bead surface. Some display sharp peaks in their profiles (e.g. Fig. 2). In most profiles, ^{63}Cu and ^{79}Br covary closely, as do ^{37}Cl and ^{127}I.

In our sulfur isotope depth profiles on two beads the $\delta^{34}S$ values of the condensates may become lighter towards the surface of the coating (e.g. Fig. 3). The exact identity of sublimate phases was not determined, so it is unclear what standard to use to correct for matrix effects. Therefore, the absolute $\delta^{34}S$ values are uncertain and should not be overinterpreted, but their relative values and variation in the profiles should be accurate.

Discussion: Our results show that we can resolve trace element and isotope variations in the condensates on a nm scale. The diversity of volatile abundances throughout the condensate layer on different beads supports the idea that the beads record different paths through the volcanic gas cloud. The increase in concentrations seen in some sublimates is consistent with the thermodynamic models [4] suggesting they are recording decreasing temperatures as the cloud evolved. Peaks within the profiles imply heterogeneity and mixing within the gas cloud [5].

The greater the degree of kinetic fractionation during condensation, the more negative the δ^{34}S of the sublimate should be [7]. The possible trend in our sulfur data could therefore be interpreted as increasing disequilibrium through time in the gas cloud. It could also be due to a change in the composition of the gas cloud and condensate during deposition, or a changing isotopic fractionation factor. These processes will need to be considered during our modelling of de-sublimation.

Further NanoSIMS and Atom Probe Tomography analysis aims to image condensate layers on a greater number of beads. The PTX evolution of each bead will be modelled thermodynamically, with the ultimate goal of further constraining the volatile content of the magmas and the lunar interior.

References: [1] Hauri, E. H., et al. (2011) *Science, 333, 213–215.* [2] Saal, A. E., et al. (2008) *Nature, 454, 192–195.* [3] Meyer C. et al. (1975) *LPSC Proc., 10, 1673-1699.* [4] Renggli, C. J. et al. (2017) *Geochimica et Cosmochimica Acta, 206, 296–311.* [5] Ross D. K., et al. (2011) *LPS XLII, Abstract #2203* [6] Ma, C., & Liu, Y. (2019) *American Mineralogist, 104, 447–45.* [7] Saal, A. E., Hauri, E. H. (2021) *Science Advances, 7, 4641-4665.*