REDOX STATES, OXYGEN FUGACITY, AND HYDROGEN DISTRIBUTION IN LUNAR VOLCANIC GLASS BEADS: RESULTS FROM THE SPECTROSCOPY CONSORTIUM ADDRESSING REDOX ACQUIRED BY BEADS (SCARAB) TEAM. M. D. Dyar1,2, A. Lanzirotti1, M. C. McCanta4, E. Recchuiti4, E. C. Sklute1, and S. Sutton3, 1Planetary Science Institute, 1700 East Fort Lowell Rd., Suite 106, Tucson, AZ 85719 (mdyar@psi.edu), 2Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, 3Center for Advanced Radiation Sources, The University of Chicago, Argonne, IL, 60439 4Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN, 37996.

Introduction: This group is measuring oxidation state and H gradients in pristine and previously studied lunar volcanic glass beads using x-ray absorption spectroscopy (XAS) to measure Fe, Ti, Cr, V, and Eu valence states and quantify intrinsic oxygen fugacity (\(f_{O_2}\)). Results are correlated with attenuated total reflection (ATR) H maps on the same beads. Results are being used to assess lunar eruptive mechanisms recorded in glass beads, help interpret lunar interior oxygen fugacity, and inform our understanding of both pre-and post-eruptive mechanisms in lunar igneous materials and the lunar interior.

FTIR Mapping of H: Using the Vertex 70 reflectance FTIR at the Univ. of Massachusetts in Amherst, we have mapped more than two dozen glass beads from the Apollo Next Generation Sample Analysis (ANGSA) core 73002. Hydrogen maps were made by applying a peak area integration (OPUS B class integration) of the broad hydration feature from ~3800-3000 cm\(^{-1}\), which has been shown to be due to OH in mineral structures [1], and to correlate to hydrogen concentrations [2,3]. The unscaled integration areas provided a qualitative assessment of hydrogen distribution across a sample.

FTIR data were used to create hydrogen maps for lunar beads 2 and 4 from sample 15427,83 (Figure 1). While the absolute value in the color scale has no specific meaning, the qualitative distribution of hydrogen in the sample can be visualized. Depletion of H within the beads differs between beads 2 and 4. Lunar bead 2 shows a depletion pattern that, compared with the backscatter electron image (BSE) of the bead, appears to coincide with the fractures in the bead (Fig. 1, top). It is inferred the fracture created a pathway by which H could readily exit the glass, though the enrichment near the fracture indicates that the degassing was not complete. In bead 4, there is no fracture to provide a pathway for degassing, so hydrogen diffuses in a front from core to rim (Fig. 1, bottom). The observed medium to high pattern of hydrogen enrichment in the center grades into a steady depleted rim on the bead.

Tomography of ANGSA Lunar Samples: Tomographic XRF-XRD-XAFS methodologies were used to examine unsectioned lunar beads from the 73002 ANGSA cores to search for gradients in the most pristine lunar materials, allowing for chemistry, crystalline structure and oxidation state to be studied in as close to an “as-sampled” state as possible, in separated lunar beads. We collect coupled X-ray fluorescence and diffraction tomographic datasets with a 1-2 \(\mu\)m beam that translates and rotates through the focused beam to create the sinogram for reconstruction. In samples from 73002, we collected tomographic XRF-XRD at \(\sim\)18 keV incident beam energy, which allowed for reconstruction of major and trace element distributions within the unsectioned bead, as well as diffraction intensities. We also repeatedly collected tomographic datasets at 80 incident beam energies scanned across the Fe K edge, which allowed for reconstruction of the Fe XANES.

Figure 2 shows XRF tomographic reconstructions of Sr, Zn and Fe through the bead, showing complex compositional heterogeneity, with Sr and Fe depleted in the bead core, possible enrichment of Fe at the bead surface, and very clear enrichment in Zn at the bead surface with possible enrichment in Zn at the bead core.
The strong enrichment in Zn at the bead surface are consistent with observations made by [4] regarding the discovery of a Zn-rich mineral on the pristine surface of orange pyroclastic beads from Apollo sample 74220. The XRF and XRD results both show evidence that this glass bead has undergone recrystallization.

Lunar agglutinates from 73002,357 were also analyzed and provide key insights in to how best to interpret Fe XAS spectra collected from soil material. Micro-XRD data from this sample shows they are mineralogically heterogenous, with a consistent presence throughout of diffraction by metallic Fe, likely nanoscale. Modeling XAS data as mixtures of a small amount of np-Fe plus silicate glass leads to a better understanding of potential redox signatures.

**XAS Oxybarometry of ANGSA Lunar Samples:**
To evaluate \( f_{\text{O}_2} \) of lunar volcanic glass beads, we utilized Cr, V, Ti, and Fe XAFS following methods by [5]. Samples 73002-344A and B show little evidence of recrystallization, and are thus excellent candidates for XAS mapping of flat surfaces. We collected a series of spectroscopic transects on each bead. For both beads, Ti and Fe XAFS look fairly homogeneous, with Ti oxidized and largely as Ti\(^{4+}\), V as all V\(^{3+}\), and Fe very reduced and dominated by Fe\(^{2+}\). Interestingly, both beads show clear heterogeneity in Cr valence, with more reduced Cr at the bead rims. Bead 344A (Figure 3) shows a rim with reduced Cr (down to an average valence of 2.3) and a more oxidized interior (2.7 to 2.9) based on the approach described in [6]. This rim feature may suggest that the melts reacted with the lunar atmosphere before quenching. In other beads, the gradient is reversed, with oxidized rims.

These results also show the relative insensitivity of Fe and V oxybarometers at redox conditions near the iron-wüstite buffer as compared to Cr when studying redox conditions of lunar samples. This highlights the need to use Cr XAFS data of lunar glasses to most accurately constrain recorded redox conditions.

Converting our calculated Cr valence state results to \( f_{\text{O}_2} \) [6] shows that the majority of beads analyzed so far appear more oxidized (~IW+1). A possibility to explain this is that the bead-producing fountains are more oxidized that typical mare basalts [7].

**Ongoing Work:** Our results on multiple samples from ANGSA cores show that oxidation states recorded in pyroclastic beads can be highly heterogeneous, probably reflecting mixing of beads from multiple sources. As we complete our analyses, we expect to integrate H and oxidation state measurements to make comparisons among redox ratios, gradients, and derived \( f_{\text{O}_2} \) to analogous gradients for hydrogen to constrain the effects of eruptive processes on volatile behavior.

**Acknowledgments:** Supported by NASA ANGSA award #80NSSC19K0802, and by RISE2 node of the NASA SSERVI, award #80NSSC19M0215.

**References:**

![Figure 2. Tomographic reconstruction of the Sr, Zn and Fe Kα emission intensity through bead 73002,357-a. Bead diameter 200 μm.](image)

![Figure 3. Cr XRF map of bead 73002,344A (~200 μm) with incident beam energy on the Cr\(^{2+}\) peak at 5995 eV. This map shows high Cr\(^{2+}\) associated with the rim and more oxidized Cr in the interior, with some variability.](image)