

MAPPING HYDROGEN VARIATIONS IN SILICATE GLASSES: ERUPTIVE LUNAR DEGASSING.

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Introduction: The Apollo program returned a multitude of lunar samples, many of which contained picritic glass beads interpreted to result from explosive volcanism [1]. These primitive glass beads provide a unique opportunity to analyze the volatile contents of lunar melts, as well as evaluate the amount of volatiles lost during degassing [2]. Point analyses of volatile species such as H₂O [e.g., 3] suggest that glass beads degassed during the ascent and eruption of the melt. High resolution measurements of the amount of H₂O in these glasses are needed to constrain lunar evolution because the beads represent the only direct samples of internal lunar H₂O available for analysis.

The oxidation state (f_{O_2}) of a system can be correlated with the H content and therefore facilitate additional evaluation of melt H₂O concentration [4]. In-situ analysis of both the H₂O and f_{O_2} of volcanic glasses allows for evaluation of the processes and degree of volatile degassing. Terrestrial analogues, which are more readily available, can be used to better understand lunar glass H₂O content and subsequent diffusive loss during eruption. An understanding of the processes and rates of volatile loss can then be utilized to constrain the initial H₂O content of the lunar interior, providing a more detailed geochemical understanding of original lunar H₂O contents.

Measurements by the ANGSA-funded SCARAB (Spectroscopy Consortium Addressing Redox Acquired by Beads) team seek to constrain the initial H₂O content of the lunar interior and H₂O loss during eruption, in combination with measurements of Fe³⁺. This abstract focuses on H mapping.

Samples: Glasses analyzed in this study include an East Pacific Rise (EPR) pillow basalt, Hawaiian fire fountain beads, and lunar glass beads from Apollo 17 (74220,266). The EPR pillow basalt and Hawaiian bead are both polished thick sections. The lunar glass beads are from a standard thin section.

Methods: Fourier transform infrared (FTIR) analyses were performed using both a Bruker Vertex 70 with a Hyperion 3000 microscope (Umass, Amherst) equipped with an MCT point detector and a 64×64 pixel focal plane array (FPA) detector, as well as using the Bruker Lumos II equipped with a 64×64 pixel PFA detector at (Bruker Demo Laboratory, Billerica, MA). All samples were lightly polished directly prior to analysis to remove possible surface H₂O. Coarse MCT

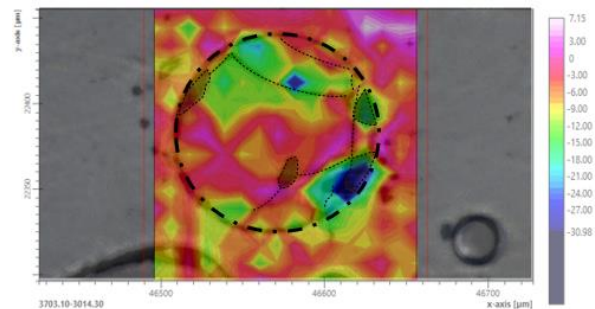


Figure 1. Hydrogen abundance map with 2×2 binning and 3703-3014 integration overlain the BSE image of Lunar Bead 4 from sample 74220,226.

maps at higher spectral (4 cm⁻¹) but lower spatial resolution were made to guide FPA image acquisition. Once obtained, each group of spectra was offset-normalized to the baseline value between 4000-3990 cm⁻¹. Noisy pixels were manually removed in each FPA image prior to binning. Binning was used to increase the signal to noise ratio (SNR); 2×2, 4×4, and 8×8 bins were compared to find the maximum possible spatial resolution that provided an adequate SNR. 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 [5], and to correlate to hydrogen concentrations [6,7]. End-points of integration were chosen to avoid the epoxy-associated feature near 2990 cm⁻¹ and appropriately average out thin-sample sinusoidal interference. The unscaled integration areas provide a qualitative assessment of hydrogen distribution across a sample.

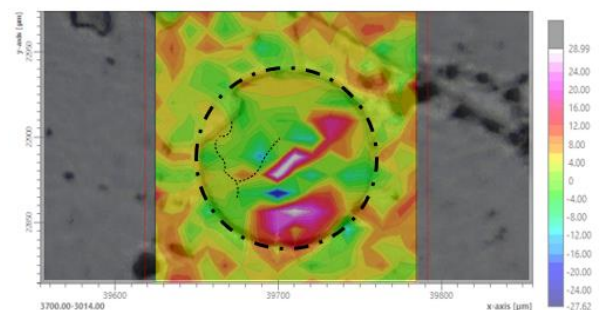


Figure 2. Hydrogen abundance map with 2×2 binning and 3700-3014 integration overlain the BSE image of Lunar Bead 5 from sample 74220,226.

X-ray absorption spectra (XAS) for the EPR pillow basalt were collected in situ at the GSECARS X-Ray Microprobe (13-ID-E) at Advanced Photon Source at Argonne National lab [8]. XAS analyses of the lunar and Hawaiian glass beads are ongoing.

Data: Preliminary FTIR hydrogen maps for select beads in thin section 74220,226 are shown in Figs. 1 and 2. While the absolute value in the color scale has no specific meaning for these plots, the qualitative distribution of hydrogen in the sample can be analyzed. The depletion of H within the beads appears to be patchy with no apparent radial zoning. Lunar Bead 4 has two primary patches of considerable depletion and when the map is compared with a back-scatter electron (BSE) image of the bead, the depleted areas appear to coincide with the fractures in the bead (Fig. 1). It can be inferred that the fracture created a pathway by which H could readily exit the glass. In lunar bead 5, there is a similar observed trend of H depletion in

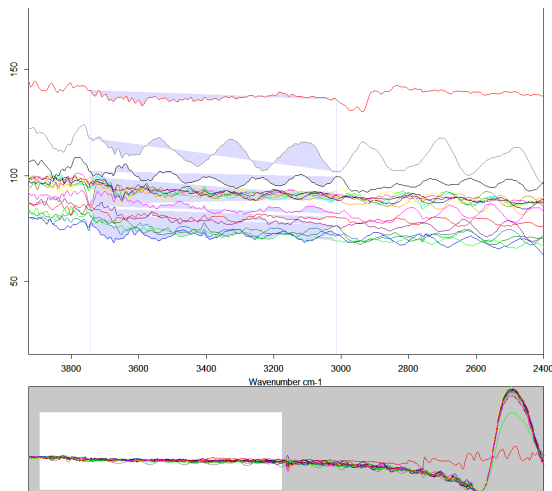


Figure 3. Sample spectral data. The red line offset at the top is from an epoxy-rich pixel. The blue shaded area indicates bounds of integration for H-abundance.

proximity to fractures in the bead (Fig. 2).

FTIR data show contamination from the mounting epoxy (Fig. 3); its interference is observed as the blue and red lines that diverge from the clear Si reflectance feature that spans from ~ 1200 cm^{-1} to the end of the spectral range. Epoxy can be mapped using a clear organic feature ~ 2950 cm^{-1} . Generally, epoxy maps are inversely correlated with Si maps, indicating that admixing of the two spectral components occurs at the edges of the sample where the bead thickness is decreasing. Thus, any zoning seen at the edges is interpreted to be due to thickness effects. Future sample preparation will attempt to minimize the epoxy inter-

ference and the thin-sample sinusoidal interference by using thicker sections when possible.

Summary and Future Work: Understanding the amount of H lost during degassing and eruptive processes can aid in allowing for estimation of primary volatile content in a melt. Preliminary data indicate that H loss is associated with fractures on the beads from sample 74220,226. Those data do not show epoxy contributions in the center of the bead where the sample is the thickest, though the thinner edges suggest some interference (Fig. 4).

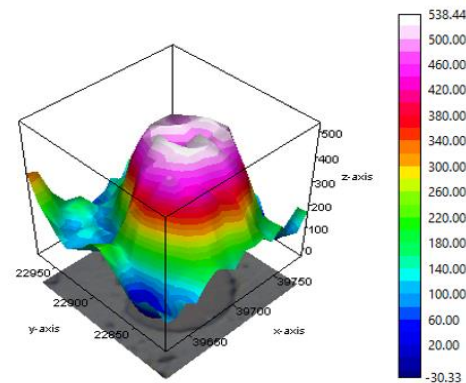


Figure 4. Si abundances for Lunar Bead 5 with integration ($1155\text{-}751$ cm^{-1}) and 2×2 binning to indicate the boundaries of epoxy contamination on the sample.

Because the thin sections cause double reflection during FTIR analysis, thick sections will be utilized for these studies where feasible. Future data acquisition will be focused on obtaining valid and uncontaminated values for H content in the Hawaiian glass beads, lunar glass beads, and EPR pillow basalt. Comparisons can then be made among different samples to infer the degree of degassing that occurred in each of the three eruptive environments. This will allow for constraints to be placed on the similarities and disparities between lunar and terrestrial explosive basaltic volcanism and its subsequent volatile loss, as well as allowing for primary abundances to be estimated.

References: [1] Heiken et al. (1991) *Lunar Sourcebook*, Cambridge Univ. Press. [2] Hauri et al. (2015) *Earth & Planet. Sci. Let.* 409, 252-264. [3] Saal et al. (2008) *Nature* 454, 192-196. [4] Hauri et al. (2011) *Science* 333, 213-215. [5] Bell & Rossman (1992) *Science* 255, 1391-1397. [6] Johnson & Rossman (2003) *Am. Min.* 88, 901-911. [7] Seaman et al. (2006) *Am. Min.* 91, 12-20. [8] Lanzirotti et al. (2018) *Am. Min.* 103, 1282-1297.