RECORD OF WATER DEGASSING DURING MAGMA ASCENT. M. C. McCanta[1], M. D. Dyar[2], and E. Sklute[2], [1]Dept. of Earth & Planetary Sciences, University of Tennessee, 1621 Cumberland Ave, Knoxville, TN 37996 (mmccanta@utk.edu), [2]Planetary Science Institute, 1700 East Fort Lowell, Tucson, AZ 85719.

Introduction: Saal et al. [1] measured H_2O in lunar picritic glass beads using SIMS at levels of ca. 10-50 ppm H_2O. These were the first direct measurements of volatiles in lunar glasses and diffusional modelling allowed for back-calculations that estimated 745 ppm H_2O (minimum 260 ppm) in their source region, suggesting a potentially "wet" lunar interior. These modelled levels of H_2O (and all other volatile species) are significantly higher than those in the as-erupted samples because volatile species are not stable in the melt phase under low pressure conditions [e.g., 2] and are therefore expected to have been lost during magma ascent and eruption (Fig. 1).

Moreover, there are differences in measured volatile concentrations (not corrected for diffusive loss during ascent and eruption) among very-low-Ti green glasses (>30 ppm H_2O), low-Ti green glasses (up to 46 ppm H_2O), and high-Ti orange glasses (>15 ppm H_2O) [1]. These results and analyses of melt inclusions in lunar olivine grains [3] suggest that volatiles may be heterogeneously distributed in the lunar interior.

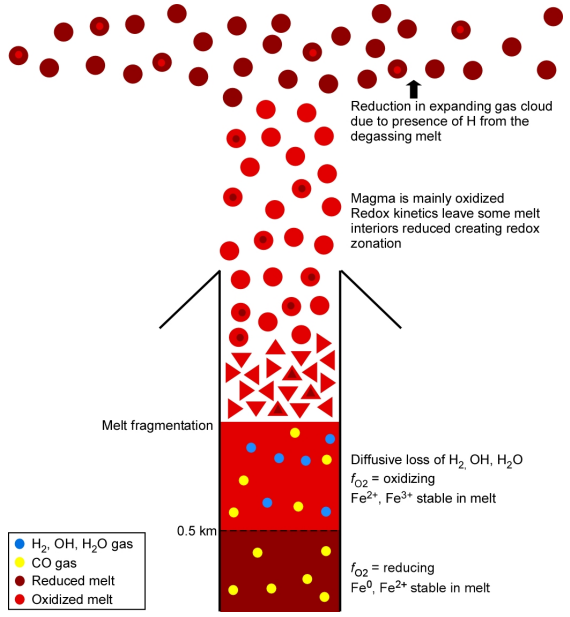

Figure 1. Oxidation/reduction environments in a melt column during ascent and eruption. From [4].

Background: Remote sensing provides macroscale observations of the lunar surface. Data from the Moon Mineralogy Mapper (M^3) instrument on the Chandrayaan-1 spacecraft [5-6] have been used to identify "hydrous" surface deposits. These analyses required the additional step of attempting to isolate endogeneous from exogeneous water resulting from solar wind implantation. Multiple potential candidate sites were identified across the lunar surface with estimated H_2O contents of up to 150 ppm for pyroclastic deposits and localized values of 300-400 ppm at some potential volcanic vent regions [5]. The heterogeneity of these H_2O concentrations is similar to that observed in the analytical works of [1,3]. However, *the total H_2O concentrations are significantly higher than those directly measured in the lunar glasses thought to be representative of the pyroclastic deposits* [1]. Additionally, high-Ti deposits have been observed [5] to be higher in H_2O than low-Ti, which was suggested to relate to faster cooling rates (i.e., less degassing) experienced by the high-Ti magmas. This conclusion is in direct contrast to the results of [1], where the high-Ti orange glasses contained almost no H_2O (>15 ppm) while the low-Ti green glasses had the most (up to 46 ppm). All glasses [1] contained significantly less H_2O than that estimated using M^3 data. The high H_2O concentrations measured by [5-6] in ostensibly degassed deposits would imply significantly higher amounts of H_2O in the lunar interior. These remote measurements must be reconciled with high-resolution, Earth-based sample analysis.

Additional insight into melt (glass) H_2O concentration is provided by the oxidation state (recorded as oxygen fugacity: f_{O2}) of the sample, as H and f_{O2} are often correlated [e.g., 7]. For example, as water is diffusively lost (primarily as H_2 or OH) during magmatic degassing, the remaining system becomes more oxidizing [e.g., 8]. Therefore, quantifying the $Fe^{3+}/\Sigma Fe$ of volcanic glasses may also provide important information regarding volatile degassing processes [e.g., 9].

Ideal terrestrial analogues for the lunar fire fountain eruptions are those observed at Kilauea volcano, Hawaii. Although magmatic and surface pressures and volatile contents and concentrations are quite different on Earth than the Moon, the basic geologic processes are similar (Fig. 1). Here we detail analytical work to constrain the H_2O diffusion and Fe^{3+} oxidation profiles in basaltic beads from Hawaiian fire fountain deposits to better constrain the changes that take place during ascent and eruption terrestrially. We then apply the results to lunar glass beads erupted under lunar conditions to determine the range of H_2O concentrations possible in pyroclastic deposits and compare that to remotely sensed values.

Samples and Methods: Volcanic glass beads from Kilauea volcano, Hawaii were provided by the

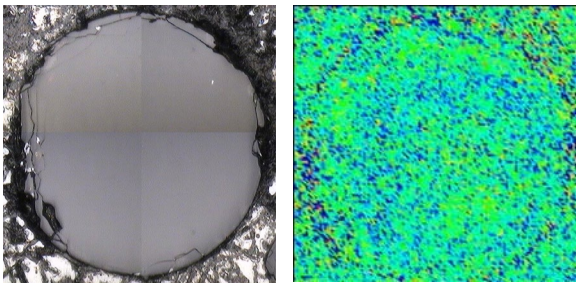

Figure 2. ATR micro-FTIR H map of glass bead (right, with photo at left) from Apollo 17 sample 74220, showing H gradients at the edge and interior.

Smithsonian Museum of Natural History. Beads were halved, placed in epoxy discs, and polished resulting in complete rim to rim cross sections. Additionally, several green glass beads from Apollo 15 and orange glass beads from Apollo 17 were analyzed.

Reflectance IR (ATR) determinations of H. Volcanic glass H concentrations were mapped *in situ* using reflectance FTIR at the University of Massachusetts on a Bruker Vertex 70 with a Hyperion 3000 microscope and an MCT focal plane array detector. H maps were created in OPUS using the area under the 3200-3500 cm^{-1} peak and known molar absorptivity coefficients. The ATR micro-FTIR technique, while less quantitative than transmission FTIR, allows the same polished surface to be used for 2D correlation maps and XAS redox studies. Both H and Fe^{3+} concentrations can thus be coregistered. FTIR was performed first to minimize the potential for beam damage.

X-ray absorption spectroscopy (XAS) determination of $Fe^{3+}/\Sigma Fe$. Redox ratios of glasses were analyzed *in situ* using spot sizes of ca. 1×1 µm at the GSECARS X-ray Microprobe (13-ID-E) at the Advanced Photon Source at Argonne National Lab. Multivariate analytical methods [12] were used to predict the Fe^{3+} concentrations.

Results and Implications: Zonation in H concentration (Fig. 2) and $Fe^{3+}/\Sigma Fe$ (Fig. 3) was observed in multiple glass beads studied. This geochemical evidence of degassing is apparently retained in glass beads erupted under surface pressure conditions. The gradient from high H cores to low H rims is negatively correlated with the Fe^{3+}, which show low Fe^{3+} cores and high Fe^{3+} rims. This zonation is due to diffusional loss of H or OH, which would lead to more oxidizing environment. Because redox re-equilibration takes place rapidly [e.g., 9], melt redox could reset prior to cooling through the glass transition temperature.

Prior Hawaiian research indicates that melt inclusions and glasses from submarine eruptions (i.e., quenched at higher pressure) retain the most H_2O (up to 1 wt.%), while those from fire fountains erupted under atmospheric pressure exhibit near-total degassing of H_2O, with maximum H_2O concentrations at the 1-bar solubility limit in basaltic melts [2]. This solubility limit would be significantly less on the Moon, where current atmospheric pressure is ~3×10^{-15} bars. Although models [10] suggest a short-lived atmospheric pressure of ~9×10^{-3} bars may have been sustained at 3.5 byr, this would only result in a maximum basaltic melt H_2O solubility of ~100 ppm using the data of [11]. This pressure-related solubility limit has critical implications for how much H_2O could reasonably be retained in basaltic melts erupted on the lunar surface for the majority of lunar history, regardless of the rapidity of cooling. *While the lowest remotely detected H_2O estimations may be feasible, H_2O values of hundreds of ppm are not possible.*

ATR micro-FTIR mapping of Hawaiian glass beads is ongoing to constrain degassing behavior. In addition, a new source of pristine lunar glass beads from unopened Apollo drill cores sampled as part of the ANGSA program, will provide new information on glass volatile concentrations at the lunar surface.

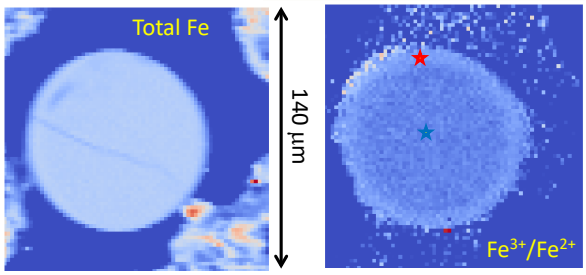

Figure 3. Apollo 11 lunar glass bead. XRF map of Fe Kα (left) showing total Fe distribution in the bead and a map of calculated Fe^{3+}/Fe^{2+} (right). For the total Fe map, dark blue areas show low Fe while white and red areas show high Fe. In the Fe^{3+}/Fe^{2+} map, dark blue shows areas of low Fe^{3+}, with lighter shades of blue showing where Fe^{3+} contents are higher.

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References: [1] Saal et al. (2008) *Nature* 454, 192-196. [2] Wallace P. and Anderson A. T. (2000) in *Encyclopedia of Volcanoes*, 149-170. [3] Hauri et al. (2011) *Science* 333, 213-215. [4] McCanta M. C. et al. (2019) *Amer. Mineral.* 453-458. [5] Milliken R. E. and Li S. (2017) *Nature Geosci.* 10, 561-565. [6] Li S. and Milliken R. E. (2017) *Science Adv.* 3, e1701471. [7] Mysen B. et al. (2011) *GCA* 75, 6183-6199. [8] Christie D. M. (1986) *EPSL* 79, 397-411. [9] McCanta M. C. et al. (2017) *Icarus* 285, 95-102. [10] Needham D. H. and Kring D. A. (2017) *EPSL* 478, 175-178. [11] Newcombe M. E. (2017) *GCA* 200, 330-352. [12] Dyar et al. (2016) *Amer. Mineral.* 101, 744-748.