

**THE APOLLO 15 VERY LOW-Ti GLASSES, EVIDENCE FOR THE PRESENCE OF INDIGENOUS WATER IN THE MOON'S INTERIOR.** A. E. Saal<sup>1</sup>, E. H. Hauri<sup>2</sup>, M. LoCascio<sup>1</sup>, J. Van Orman<sup>3</sup>, M. J. Rutherford<sup>1</sup> and R. F. Cooper<sup>1</sup>. <sup>1</sup>Department of Geological Sciences, Brown University, 324 Brook St., Box 1846, Providence, RI, 02912. <sup>2</sup>Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road, NW Washington, DC 20015. <sup>3</sup>Department of Geological Sciences Case Western Reserve University, Cleveland, OH 44106.

<sup>12</sup>C, <sup>17</sup>OH, <sup>19</sup>F <sup>32</sup>S and <sup>35</sup>Cl

**Introduction:** The composition and origin of the lunar volatiles has been the subject of considerable interest and one of the most important unsolved questions regarding the formation of the Moon. The general consensus has been that the Moon formed and evolved through a single or series of catastrophic heating events<sup>[1]</sup> in which most of the highly volatile elements were either stripped or evaporated away. Hydrogen being the lightest element is thought to have been completely lost during this period. Most of the geochemical inferences about the deepest section of the moon, including the volatile contents, have been based on studies of the most primitive melts erupted on the Moon's surface, the lunar volcanic glasses<sup>[2]</sup>. The assumption that lunar magmas are anhydrous is based on 1) the accepted model of lunar formation from a giant impact<sup>[1]</sup>, which would cause the depletion in volatiles; and 2) the previously reported analytical techniques either using bulk samples analysis or the in-situ techniques having high detection limits, and therefore were not able to constrain the H<sub>2</sub>O content of the picritic glasses<sup>[3]</sup>. However, during the 38<sup>th</sup> LPSC we reported new volatile contents (CO<sub>2</sub>, H<sub>2</sub>O, F, S, Cl) for the lunar picritic glasses, which by virtue of SIMS analysis provide improved detection limits by almost an order of magnitude<sup>[4]</sup>. The association of the new data, the fire-fountain mechanism of eruption and the condensation and enrichment of volatile elements on the surface of the lunar volcanic glasses suggests the existence of a deep mantle source comparatively enriched in volatiles. The implication that follows this view is that, contrary to prevailing ideas, the bulk Moon is not uniformly depleted in highly volatile elements.

In this abstract, we evaluate the evidence supporting an indigenous origin for the volatiles content, specially H<sub>2</sub>O, and present a diffusive degassing model to estimate the "minimum" primitive volatile content in the lunar volcanic glasses.

**Samples and Analytical Techniques:** We investigated four compositionally distinct glasses from the Apollo 15 very-low-Ti glasses from sample 15427,41. The glassy spherules range in size from 200-400 μm with one outlier at 700 μm for 15427,41. Not all of the glass beads are completely glassy; some of them, usually the larger beads, show crystallization of olivine. The major, and trace-element contents of the lunar volcanic

glasses are consistent with previously reported data<sup>[2]</sup>. The abundances of volatiles dissolved in the interior of the lunar picritic glasses were measured by SIMS using a Cameca IMS6F and the Nanosims at DTM, CIW, employing methods recently developed for the microanalysis of trace amounts of H<sub>2</sub>O, CO<sub>2</sub>, F, S, Cl in glasses and nominally anhydrous minerals<sup>[4,5]</sup>. For the IMS 6F a typical 10-min SIMS measurement for volatile abundances is made on a singly polished specimen using a Cs<sup>+</sup> primary beam (~14 nA accelerated to 10 kv) with collection of negatively charged secondary ions. We used a 10 μm primary beam rastered at 25 μm, which results in a 35 μm crater. After each beam spot was carefully examined for cracks and dendritic crystals a field aperture was inserted to permit transmission of ions only from the central 10 μm of the 35 μm crater (i.e., always 25 μm away from the crater edge) thus avoiding transmission of ions from the edge of the sputter crater and the surface of the sample. Counting times were 10 s for <sup>12</sup>C and 5 s for <sup>17</sup>OH, <sup>19</sup>F <sup>32</sup>S and <sup>35</sup>Cl. Pressure in the ion probe sample chamber was ~6x10<sup>-10</sup> torr during the analyses. The samples was placed in the ion probe sample chamber for ~12 h before analysis; this approach allowed the best detection limits for H<sub>2</sub>O. Detection limits (~ 6 ppm H<sub>2</sub>O and CO<sub>2</sub>, ~0.09 ppm F, ~0.27 ppm S, ~ 0.03 ppm Cl by weight) were determined by the repeated analysis of synthetic forsterite (0.4 ppm H<sub>2</sub>O as determined by FTIR) located on each sample mount. Calibrations for H<sub>2</sub>O were verified for glasses and nominally anhydrous mineral standards prior to each analytical session; abundances for the other volatile elements (CO<sub>2</sub>, F, S, Cl) were calculated from the calibrations performed on glass standards. For calibration, standard volatile concentrations are plotted against measured volatile/<sup>30</sup>Si ratios. This provides a robust analysis, which is little influenced by primary beam fluctuations or by ionization efficiency changes owing to matrix effects<sup>[5]</sup>. For the Cameca NanoSIMS 50L at DTM we followed the same analytical method used on the 6F, with the exception that crater edge contamination was eliminated by electronic gating rather than a field aperture. A typical 15 minutes measurement used a Cs<sup>+</sup> primary beam (~3 nA accelerated to 8 kv) with collection of negatively charged secondary ions on multiple detectors. We used a 800 nm primary beam

rastered at 12 x 12  $\mu\text{m}$  area and an electronic gating on the central 4.5 x 4.5  $\mu\text{m}$ . We pre-sputter for 6 min prior to analysis and the data was collected on 6 detectors in multi-collection mode:  $^{12}\text{C}$ - $^{16}\text{OH}$ - $^{19}\text{F}$ - $^{30}\text{Si}$ - $^{32}\text{S}$ - $^{35}\text{Cl}$  at MRP of  $\sim 6000$  (sufficient to resolve  $^{16}\text{OH}$  from  $^{17}\text{O}$ ). Counting times were 1 sec. for all masses, and we collected 100 ratios (100 sec. total counting time). Pressure in the ion probe sample chamber was  $\sim 3 \times 10^{-10}$  torr or less during the analyses. Detection limits and precision are similar to the IMS Cameca 6f.

**Results:** After background correction all volcanic glasses have  $\text{CO}_2$  below or within the  $2\sigma$  standard deviation of the detection limit for our runs (6 ppm  $\text{CO}_2$ ) and will not be considered further. The volatile contents have the following ranges: 0-30 ppm for  $\text{H}_2\text{O}$ ; 2-10 ppm for F; 114-270 ppm for S; and 0.03-0.5 ppm for Cl. Two outstanding features of the data is the significant correlation among  $\text{H}_2\text{O}$ , Cl, F and S contents, and the clear relationship between the volatile and the major element contents for the four compositional sub-groups (A, B, C, D) of Delano's very-low-Ti glasses<sup>[6]</sup>. These relationship between volatile and major elements support the hypothesis that there were significant differences in the initial volatile content, and/or the mechanism of degassing and eruption among these glasses was different. Most importantly, the correlations among the volatiles suggest that the measured  $\text{H}_2\text{O}$  content in the volcanic glasses is indigenous. These results suggest that  $\text{H}_2\text{O}$  cannot be produced by solar wind implantation of  $\text{H}^+$  followed by diffusion into the spherule, but rather indicate that all the volatiles represent indigenous contents that were affected by degassing processes subsequently to the fire-fountain style of eruption. To test this hypothesis we determined concentration profiles for the volatiles within a single selected glass bead to evaluate whether or not a concentration gradient exist in a single bead. Our data for the very-low-Ti glass define concentration profiles with decreasing volatile contents from the core to the rim of the glass bead. This is especially significant for  $\text{H}_2\text{O}$ , which decreases from  $\sim 30$  ppm in the center to  $\sim 14$  ppm in the margin of the bead, supporting the hypothesis of the indigenous origin of  $\text{H}_2\text{O}$  subsequently affected by degassing processes during melt decompression and eruption. Moreover, the volatile contents observed on a single glass bead reproduce essentially the same trends in a volatile-volatile plot as those defined by the volatile contents of all the very-low-Ti glasses. All this observation supports the hypothesis that degassing has been the main process affecting the volatile contents of the lunar volcanic glasses.

**Diffusive Degassing Model:** To evaluate diffusive volatile loss from the lunar volcanic glasses during

eruption we applied a model of diffusion from a sphere with concomitant surface evaporation to the measured volatile concentration profiles within a single glass bead<sup>[3]</sup>. The crucial input parameters of the diffusion model are 1) the sphere radius, 2) the temperature of the melt during eruption, 3) the cooling rate, 4) the initial volatile concentrations in the glass beads, 5) the diffusion coefficients of the volatiles within the melt, 6) the time available for diffusion and 7) the rates of evaporation at the surface of the melt sphere. We considered a range in cooling rates (1-100  $^\circ\text{C}/\text{sec}$ ) and time for the melt to quench (30-600 sec), and for each pair of cooling rate and time to quench we allow the initial concentrations and evaporation rate constant of each volatile species to vary to achieve the best fit (minimum  $\chi^2$  value) to the concentration profiles measured in the glass bead. We selected the model outputs that minimized the sum of  $\chi^2$  for all of volatiles together, using the optimum values of initial concentration and evaporation constant determined for each volatile at the cooling rate and cooling time of interest. We found that: 1) the cooling rates had to be quite low, slower than 5  $^\circ\text{C}/\text{sec}$ , consistent with the cooling rates obtained independently for the very-low-Ti glasses<sup>[7]</sup>; 2) the rates of evaporation had to be quite low, within the range  $10^{-6}$  to  $10^{-8}$  m/sec; and 3) the best fit to all the volatile concentration profiles occur at cooling rates of 3  $^\circ\text{C}/\text{sec}$  and time to quench of 120 sec. suggesting an initial concentration for water unexpectedly high,  $\sim 750$  ppm with a minimum of 260 ppm at the 95% confidence.

**Conclusions:** We reported volatile contents ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , F, S, Cl) for the lunar picritic glasses, which by virtue of SIMS analysis provide improved detection limits by almost an order of magnitude. To our knowledge this is the first definitive confirmation of the presence of "magmatic"  $\text{H}_2\text{O}$  in primitive lunar basalts. Our results suggest that, contrary to the prevailing ideas, the bulk Moon is not uniformly depleted in highly volatile elements, and the presence of water in particular must be included to constrain models for the thermal and chemical evolution of the Moon's interior.

**References:** [1] Canup R. M. (2004) *Annu. Rev. Astron. Astrophys.* 42, 441-475. [2] Shearer C.K. et al. (2006), *In Rev. in Min. & Geochem.* Vol. 60. [3] Fogel R. A. and Rutherford M. J. (1995) *Geochem. Cosmochem. Acta* 59, 201-215. [4] Saal et al., (2007) *Proc. 38th LPSC* Abs. 2148. [5] Hauri E. H. et al. (2006) *EPSL* 248, 715-734. [6] Delano, J. W., (1979) *Proc. 10th LPSC* Vol. 1. 275-300. [7] Arndt et al. (1984) *Proc. 15th LPSC* Vol. 1. 275-300 vol 89, C2325-C232.