

**THE VOLATILE CONTENT OF THE APOLLO 15 PICRITIC GLASSES.** B. Friedman<sup>1</sup>, A. E. Saal<sup>1</sup>, E. H. Hauri<sup>2</sup>, J. Van Orman<sup>3</sup>, M. J. Rutherford<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.

**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. 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>. We previously reported new volatile contents (CO<sub>2</sub>, H<sub>2</sub>O, F, S, Cl) for the lunar picritic glasses<sup>[4]</sup>, which by virtue of SIMS analysis provide improved detection limits by one order to two order of magnitude<sup>[5]</sup>. The association of the these 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 report new volatile data for over 200 individual Apollo 15 picritic glasses with composition ranging from very-low to low Ti contents (sample 15427,41; 15426,138; 15426,32).

**Samples and Analytical Techniques:** The glassy spherules range in size from 100-200  $\mu\text{m}$ . Not all of the glass beads are completely glassy; some of them, usually the larger beads, show crystallization of olivine. The abundances of volatiles dissolved in the interior of the lunar picritic glasses were measured by SIMS using a Cameca IMS 6F 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>[5]</sup>. A typical 10-min SIMS measurement for volatile abundances is made on a singly polished specimen using a Cs+ primary beam (~14 nA accelerated to 10 kv) with collection of nega-

tively charged secondary ions. We used a 10  $\mu\text{m}$  primary beam rastered at 25  $\mu\text{m}$ , which results in a 35  $\mu\text{m}$  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  $\mu\text{m}$  of the 35  $\mu\text{m}$  crater (i.e., always 25  $\mu\text{m}$  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  $<5 \times 10^{-10}$  torr during the analyses. The samples was placed in the ion probe sample chamber for ~24 h before analysis; this approach allowed the best detection limits for H<sub>2</sub>O. Detection limits (~0.58 ppm C; ~ 2.5 ppm H<sub>2</sub>O, ~0.05 ppm F, ~0.21 ppm S, ~ 0.04 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>[6]</sup>.

**Results:** After background correction the volatile contents have the following ranges: C is within background;  $0-70 \pm 0.4$  ppm for H<sub>2</sub>O;  $1.6-60 \pm 0.1$  ppm for F;  $58-885 \pm 1.3$  ppm for S; and  $0-3 \pm 0.02$  ppm for Cl. Our new values represent an increase in the volatile concentrations by approximately a factor of 2 from previously reported volatile data<sup>[4]</sup> and a significant decrease in the detection limits for H<sub>2</sub>O and C by a factor of three. Two outstanding features of the data is the significant correlation among H<sub>2</sub>O, Cl, F and S contents, and the clear relationship between the volatile and the major element contents of the 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 H<sub>2</sub>O content in the volcanic glasses is indigenous. These results confirm that H<sub>2</sub>O cannot be produced by

solar wind implantation of H<sup>+</sup> 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.

**Conclusions:** We reported volatile contents (H<sub>2</sub>O, F, S, Cl) for the lunar picritic glasses, which by virtue of SIMS analysis provide improved detection limits by one to two order of magnitude. 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. Cosmochim. Acta* 59, 201–215. [4] Saal et al. (2008) *Nature* 454, 192-195. [5] Hauri E. H. et al. (2006) *EPSL* 248, 715-734. [6] Delano, J. W., (1979) *Proc. 10th LPSC* Vol. 1. 275-300.