

THE VOLATILE CONTENTS (CO₂, H₂O, F, S, Cl) OF THE LUNAR PICRITIC GLASSES. A. E. Saal¹, E. H. Hauri², M. LoCascio¹, J. Van Orman³, M. J. Rutherford¹ and R. F. Cooper¹. ¹Department of Geological Sciences, Brown University, 324 Brook St., Box 1846, Providence, RI, 02912. ²Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road, NW Washington, DC 20015. ³Department of Geological Sciences Case Western Reserve University, Cleveland, OH 44106.

Introduction: Studies of volatile elements in magmatic systems have particular importance, because volatiles influence mantle melting, magma crystallization and volcanic eruption, and their abundances and spatial distribution provide important constraints on models for the thermal and chemical evolution of the Moon's interior. 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 today is that the Moon formed and evolved through a single or series of catastrophic heating events[1] 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[2]. Most of the geochemical inferences about the deepest section of the moon have been based on studies of the most primitive melts erupted on the Moon's surface, the lunar volcanic glasses[3]. The assumption that lunar magmas are anhydrous is based on 1) the accepted model of lunar formation from a giant impact[1], which would cause the depletion in volatiles; and 2) the previously applied analytical techniques having high detection limits, which were not able to constrain the volatile contents (e.g. H₂O) of the picritic glasses[4]. However, there exists indirect evidence that volatile elements might have played a role in the generation of the lunar volcanic glasses. The association of a fire-fountain mechanism of eruption with 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, using state-of-the-art analytical techniques, we report the magmatic volatile contents of individual lunar picritic glasses from the Apollo 15 and 17 landing sites.

Samples and Analytical Techniques: We investigated three compositionally distinct glasses from two lunar samples: very-low-Ti and low-Ti glasses in sample 15427,41, and high-Ti glasses in sample 74220,864 from Apollo 15 and 17 landing sites respectively. The glassy spherules range in size from 100-300 μm for 74220,864 and 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 either olivine (15427,41) or olivine and ilmenite (74220,864). The major, and average trace-element contents of the lunar volcanic glasses are consistent with previously reported data[3]. 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 H₂O, CO₂, F, S, Cl in glasses and nominally anhydrous minerals[5]. For the IMS 6F 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 negatively charged secondary ions. We used a 10 μm primary beam rastered at 25 μm , which results in a 35 μm crater. We pre-sputter for 3-5 min prior to analysis, during this time, we monitored secondary ion images of ¹²C, ¹⁷OH, ¹⁹F, ³²S and ³⁵Cl projected on the channel plate. This procedure helped avoid inclusions and cracks, which appear as bright features on the projected image (especially ¹²C image), and dendritic crystals (dark shapes on ³²S image). After each beam spot was carefully examined 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 ¹²C and 5 s for all other elements. Pressure in the ion probe sample chamber was $\sim 6 \times 10^{-10}$ 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 H₂O. Detection limits (~ 6 ppm H₂O and CO₂, ~ 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 H₂O as determined by FTIR) located on each sample mount. Calibrations for H₂O were verified for glasses and nominally anhydrous mineral standards prior to each analytical session; abundances for the other volatile elements (CO₂, F, S, Cl) were calculated from the calibrations performed on glass standards. SIMS calibrations are regressions of ion probe signals compared to known concentrations. The ion probe

signal is normally taken as the intensity ratio of two elements, one being the element of interest and the other a matrix element common to many phases. In this study, standard volatile concentrations are plotted against measured volatile/ ^{30}Si ratios. This provides a robust analysis, which is little influenced by primary beam fluctuations or by ionization efficiency changes owing to matrix effects[5]. The techniques for the Nanosim will be reported by Hauri in this abstract volume.

Results: All volcanic picritic glasses have CO_2 below or within the 2σ standard deviation of the detection limit for our runs (6 ppm CO_2) and will not be considered further. The volatile contents after background correction have the following ranges: 4-46 ppm (± 2 ppm 2σ) for H_2O ; 4-40 ppm (± 0.2 ppm 2σ) for F; 115-576 ppm (± 3 ppm 2σ) for S; and 0.06-2 ppm (± 0.03 ppm 2σ) for Cl. Two outstanding features of the data is the significant correlation among H_2O , Cl, F and S contents shown in Table 1, and the clear relationship between the volatile and the major and trace element contents for the four compositional subgroups (A, B, C, D) of Delano's very-low-Ti glasses[6]. These relationship between volatile, major and trace 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_2O content in the volcanic glasses is indigenous. These results suggest that H_2O cannot be produced by solar wind implantation of 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 H_2O , which decreases from ~ 30 ppm in the center to ~ 14 ppm in the margin of the bead, supporting the hypothesis of the indigenous origin of H_2O 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. this observation supports the hypothesis that degassing has been the main process affecting the volatile contents of the lunar volcanic glasses. Finally, there seems to be a clear

distinction between the S and F contents of the different groups of picritic glasses, consistent with their distinctive major and trace element compositions[3]. The very-low-Ti glasses range to the lowest F and S values, the high-Ti group is intermediate and the low-Ti glasses have the highest contents of these elements. Thus, the data suggests significant differences in either the volatile content of their mantle source material, and/or their mechanism of degassing and eruption.

Lunar magmas are generally believed to have been produced by melting of cumulates at depth [3]; however the source of the heat required for the generation of the primitive melts is not clear. The presence of volatiles in the lunar glasses, suggesting a non-trivial volatile content in their melt-source region, may provide a possible solution to this problem, as the presence of water in lowering the melting temperature of silicate rocks is well known. The possible origin of the volatiles will be discussed.

Conclusions: We reported new volatile contents (CO_2 , H_2O , 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" H_2O 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.

Table 1: Correlation matrix for volatiles contents in green glasses from Apollo 15 landing site.

	H_2O ppm	F ppm	S ppm	Cl ppm
H_2O ppm	1.0000			
F ppm	0.9333	1.0000		
S ppm	0.8845	0.8683	1.0000	
Cl ppm	0.9560	0.9797	0.8897	1.0000

References:

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