

THE VOLATILE CONTENT AND D/H RATIOS OF THE LUNAR PICRITIC GLASSES. A. E. Saal¹, E. H. Hauri², M. J. Rutherford¹, J. Van Orman³. 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: The general consensus is that the Moon formed and evolved through a single or series of catastrophic heating events in which most of the highly volatile elements, especially hydrogen, were evaporated away. That notion has changed with the new reports showing evidence of indigenous water in lunar volcanic glasses [1] and in lunar apatites from mare basalts [2, 3, 4]. These results represent the best evidence for the presence of a deep source within the Moon relatively rich in volatiles. We compiled new and old volatile data (C, H₂O, F, S, Cl) for more than 360 individual Apollo 14, 15 and 17 lunar glasses with composition ranging from very-low to high-Ti contents, and present δD ratios of over 200 single volcanic beads.

Samples and Analytical Techniques: The glassy volcanic spherules range in size from $\sim 100 \mu\text{m}$ to $\sim 1 \text{mm}$. The abundances of volatiles dissolved in the interior of the lunar picritic glasses were measured by SIMS using a Cameca IMS 6F and NanoSIMS at DTM, CIW, employing methods recently developed for the micro-analysis of trace amounts of H, C, F, S, Cl in glasses and nominally anhydrous minerals [5]. Our new SIMS detection limits ($\sim 0.13 \text{ppm C}$; $\sim 0.4 \text{ppm H}_2\text{O}$, $\sim 0.05 \text{ppm F}$, $\sim 0.21 \text{ppm S}$, $\sim 0.04 \text{ppm Cl}$ by weight determined by the repeated analysis of synthetic forsterite located on each sample mount), represent at least 2 orders of magnitude improvement over previous analytical techniques.

Results: After background correction the volatile contents of the lunar volcanic glasses have the following maximum contents: C $\sim 20 \text{ppm}$; H₂O $\sim 160 \text{ppm}$; F $\sim 80 \text{ppm}$; S $\sim 800 \text{ppm}$; Cl $\sim 10 \text{ppm}$ with A14 glasses ranging to the highest volatile contents. Our data 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. Interestingly, a general correlation was found between the volatile enrichment and the incompatible trace elements. This suggests that degassing did not completely erase the initial difference in volatile contents between the distinct compositional groups of volcanic glasses. δD measured in the lunar glasses range from $+179\text{‰}$ to $+5420\text{‰}$, and thus, are undisputably fractionated from terrestrial values. However, the δD is inversely correlated with water contents; some of the D enrichment results from in-situ spallation during interactions with solar and

galactic cosmic rays. The cosmic ray exposure ages of individual lunar volcanic glasses from the same samples examined in this study range from 130 to 300 million years, with a well-defined average of $283 \pm 51 \text{Myr}$ [6]. A notable feature of the highest-H₂O lunar glasses after spallation correction is that they exhibit a much smaller range in δD values than the overall data. The average δD of the five highest-H₂O glasses is $+340\text{‰}$ ($+180\text{‰}/-240\text{‰}$). It is very likely that the original pre-eruptive δD value of these lunar magmas was significantly lower, and that kinetic D/H fractionation has resulted in preferential loss of H during magmatic degassing. A simple kinetic degassing calculation, starting with pre-eruptive magma compositions with H₂O of 250 ppm and 745 ppm [1], and δD identical to the terrestrial mantle (-80‰), defines kinetic degassing trends that reproduce most of our observations within error when hydrogen ions are the diffusing species.

Conclusions: We reported volatile contents (C, H₂O, F, S, Cl) for the lunar picritic glasses, which by virtue of SIMS analysis provide improved detection limits by one to two orders of magnitude. Our results suggest not only a much wetter Moon's interior than previously thought [1], but also suggest that the KREEP component, either through shallow assimilation by the melt or deep hybridization of the LMO cumulate, may influence the volatile composition of the erupted glasses. The δD of the highest-H₂O glasses after corrections for spallation and kinetic degassing suggest a similar isotope ratios to that of the terrestrial MORB.

References: [1] Saal, A. E. et al. (2008) *Nature* 454, 192. [2] McCubbin, F.M. et al. (2010) *PNAS*, 107 (25), 11223. [3] Boyce, J. W. et al. (2010) *Nature* 466, 466. [4] Greenwood, J. P. et al. (2010) *Proc. 41th LPSC* Abs 2439. [5] Hauri, E. H. et al. (2006) *EPSL* 248, 715. [6] Spangler, R. et al. (1984), *J. Geophys. Res.* 89, 487. *Proc. 40th LPSC* Abs 2374.