WATER IN LUNAR MARE BASALT: CONFIRMATION FROM APATITE IN LUNAR BASALT 14053.

Yang Liu[1], Jeremy W. Boyce [2], George R. Rossman[2], Yunbin Guan[2], John Eiler[2] and Lawrence A. Taylor[1]; Planetary Geosciences Institute, Department of Earth & Planetary Sciences, University of Tennessee, Knoxville TN 37996. (yangl@utk.edu). [2]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena CA 91125.

Introduction: Volatiles play important roles in magma genesis and transport. Recent studies of lunar volcanic glass beads, interpreted to be quenched droplets of ultramafic magmas, detected small but significant concentrations of H (presumably present as OH) [1-2]. Models of melt droplet degassing suggest the water measured in these glasses is residual to much higher magmatic water contents — comparable to terrestrial basalts. Lunar apatite might also preserve a record of pre-eruptive volatiles (in fact, it has been previously shown to have an anion deficiency consistent with the presence of OH [3]) and, importantly, it is less vulnerable to degassing during eruption and so could provide a more direct constraint on pre-eruptive magmatic volatiles. Estimates of OH in lunar apatite, to date, had been conducted by stoichiometric calculation from the electron microprobe analyses of apatite in thin sections [3-5]. The confidence of these estimates is diminished by both the uncertainties in electron microprobe analyses and the possibility that some proportion of anion deficiency reflects vacancies in the apatite structure. We present direct analyses of H (presumably OH) in apatite through ion microprobe measurements of apatite in Apollo 14 basalt 14053, standardized by comparison with terrestrial apatites having independently known OH contents based on manometry and/or spectroscopy. We find lunar apatite in this sample contains approximately 1640 ±180 ppm, 2σ, H as H_2O, by weight. We present these data and the calibration on which it was based, and discuss associated measurement of water contents in lunar apatites reported by [6].

Analytical Methods: To avoid H contamination from epoxy, rock chips of Apollo 14 sample 14053 [7] were polished directly (i.e., without a mounting medium) under methanol. The polished chips were carbon coated for elemental analyses using a Cameca SX100 electron microprobe at the University of Tennessee. One grain in the 7 by 9 mm polished area was found to contain a significantly large surface area for subsequent SIMS analyses.

The sample was then mounted in indium with two synthetic apatites (F- and Cl-apatites with near end-member compositions) and natural apatites from Cerro de Mercado Mine, Durango, Mexico and Mud Tank, NW Territory, Australia. The samples were then gold coated and placed into the Cameca 7f-GEO, at Caltech, under vacuum for >24 hours to drive off surface-absorbed water.
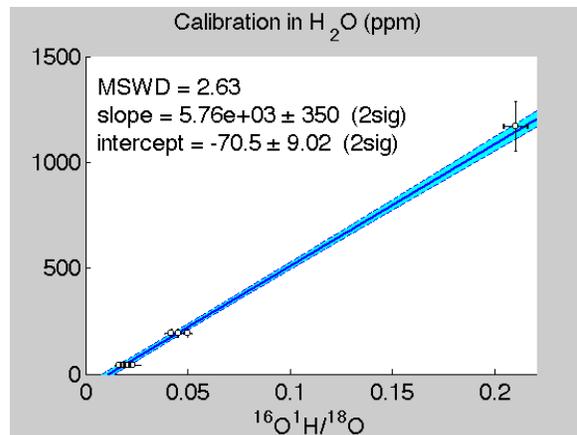

Figure 1. *Calibration curve of ppm wt H_2O vs. the measured $^{16}O^1H/^{18}O$ with a 95% confidence envelope. Note that the slope and intercept depend on the weighting given to each point, which in turn rely on the uncertainties.*

Samples were pre-sputtered for varying times ranging from ~5 to ~25 minutes prior to analyses. The 100 µm field aperture was used to limit the analyses to ions from the central ~10 µm of the beam in order to reduce surface contamination, and the electronic gate was used to further remove the outer 60% of the beam, further reducing contamination.

Spot analyses of C, H, F, S, and Cl were made using the Cameca 7f-GEO at California Institute of Technology. A 5 nA Cs^+ primary beam was used with normal-incidence electron gun charge compensation. The following ions were measured: ^{12}C, $^{16}O^1H$, ^{18}O, ^{19}F, ^{31}P, ^{32}S, ^{35}Cl, and $^{19}F^{16}O$. ^{18}O served at the reference element, and $^{19}F^{16}O$ served as an alternative analytical line for ^{19}F which is often present in amounts that (under these conditions) exceed the preferred range of the electron multiplier.

Standardization of Low-OH Apatites for SIMS: The synthetic apatite and Durango apatite were calibrated against Mud Tank apatites, whose absolute OH contents were determined by the manometric measurements of Nadeau *et al.* [8]. Two Mud Tank apatites in [8] contain an average value of 0.83 wt % (or 8300 ppm H_2O) for Mud Tank apatite, and assuming linear absorption coefficients for OH in apatite, water abundances in two synthetic apatites (Cl-Ap = 42 ppm; F-Ap = 192 ppm) and one natural apatite (Durango = 1170 ppm) were determined by absorption spectros-

copy. These three values define a calibration curve for this SIMS session (Figure 1).

Results: The apatite in 14053 is a fluoroapatite containing ~2.2 wt% F and ~0.5 wt% Cl. Seven SIMS spot analyses of this apatite did not appear to be affected by charging or other analytical problems (Fig. 2). (we have neglected an additional five analyses that suffered from analytical artifacts, which we believe stemmed from sample topography and/or poor charge compensation). The range of $^{16}O^1H/^{18}O$ values observed for seven measurements is 0.29 to 0.44. The $^{12}C/^{18}O$ values display a weak but significant positive correlation between $^{12}C/^{18}O$ and $^{16}O^1H/^{18}O$; we interpret this trend as a mixing line between a low-^{12}C, low-$^{16}O^1H$ apatite component and a high-^{12}C, high-$^{16}O^1H$ hydrocarbon (contaminant) component. Because of the potential for contamination in the most H-rich samples, we base our interpretation on the three lowest $^{16}O^1H/^{18}O$ values and a "zero hydrocarbon" intercept ($^{16}O^1H/^{18}O$ = 0.29). Using the calibration in Figure 1, these values correspond to 1600, 1740, 1580, and 1612 ppm H_2O. Considering analytical and calibration uncertainties, we recommend a value for water content in 14053 is 1640 ± 180 ppm (2σ).

Discussion:

The water content we determine for fluor-apatite in sample 14053 is similar to inferred value from [3], but is higher than those determined (500-800 ppm) by [6]. Our determination for lunar apatite is within the range of apatite H_2O contents observed for terrestrial volcanic rocks, and is comparable to measured H_2O contents of apatite (500-4400) from basaltic andesite tephras from Irazu volcano, Costa Rica, which have 1-3 wt% H_2O preserved in coexisting melt inclusions [9, 10].

Apatite in lunar mare basalts occur as a late-stage crystallization product after ~95 to 99% crystallization. They are generally associated with mesostasis rich in Si, K and REEs. The water content of the late-stage melt from which apatite precipitated can be estimated using the partitioning coefficient ($D_{H2O, apat-melt}$ = 0.2-1) between apatite and melt derived from experimental work by Mathez and Webster [10], although we caution that D_{H2O} may vary with melt composition [11]. Nevertheless, these constraints imply a range of water contents for the late stage melt from 1640 to 8200 ppm.

It is difficult to infer the water content in primary (i.e., undifferentiated) melt that is parental to the late-stage liquids from which apatite crystallized because the crystallizing melt may have behaved as an open system. Observation of ubiquitous vesicles in crystalline lunar basalts and a change of intrinsic oxygen fugacity within a given rock ($\Delta\log f_{O2}$ of <0.5 [11-12])

support degassing of water over the course of crystallization. Diffusive loss of water after the crystallization of the sample over the last ~ 4 x 10^9 yrs is also difficult to estimate. In any case, we can infer a lower limit of water in the melt using the estimated value in the late stage melt. Assuming late-stage melt is residual to 95 % crystallization, the minimum water content in the primary melt would be 82-410 ppm. This value is comparable to the range of 260-745 ppm suggested for Apollo 15 green glass melt (very low-Ti, more Mg rich) in [1].

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