

**A SURVEY OF LUNAR APATITE VOLATILE CONTENTS FOR DETERMINING BULK LUNAR WATER: HOW DRY IS “BONE DRY”?** F. M. McCubbin<sup>1</sup>, H. Nekvasil<sup>1</sup>, B. L. Jolliff<sup>2</sup>, P. K. Carpenter<sup>2</sup>, R. A. Zeigler<sup>2</sup>.<sup>1</sup>Department of Geosciences, State University of New York, Stony Brook NY 11794-2100. <sup>2</sup>Dept. of Earth and Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, Saint Louis, MO 63130. fmccubbi@ic.sunysb.edu

**Introduction:** On Earth, water affects a variety of physicochemical processes in igneous systems from the thermal stability of melts and crystals, to physical degassing and eruption phenomena. Water also plays a large role in the transport of economically important metal complexes. However, on the Moon, it has been long considered that magmas were essentially devoid of water to influence such properties [1, 2]. The far-reaching implications for our understanding of the structure and evolution of the Moon justify periodic reassessment of this important conclusion.

Because volatile contents of lunar volcanic glasses are so likely affected by degassing processes [3], minerals, specifically those containing hydroxyl as an essential structural constituent, may be more suited for reassessing the lunar magmatic water budget. Because of the paucity of lunar amphibole and the common presence of apatite in lunar samples, apatite is the primary target mineral used here for understanding lunar magmatic water contents.

This work continues the lunar apatite survey of [4], expanding upon the previous set of published electron microprobe data for apatite from lunar samples and obtaining data from additional samples. As was done in [4], all data were assessed crystal chemically in order to enable computation of apatite hydroxyl contents. Although OH<sup>-</sup> was not directly measured in this study, OH<sup>-</sup> values calculated by this method compare favorably with quantitative SIMS analyses [5, 6], thus lending support to the validity of our results. The results provide further insight into potential lithologies that would likely contain “fossilized” lunar magmatic water.

**Apatite in Lunar Rocks:** The nominal OH<sup>-</sup> content of apatite can be calculated from electron microprobe measurements of fluorine and chlorine concentrations. This requires the following assumptions: (i) only F, Cl and OH<sup>-</sup> populate the X-site, (ii) the X-site has no vacancies, and (iii) reliable analyses of F and Cl are available. Assumptions (i) and (ii) are supported by the work of [7], although attempting qualitative detection of CO<sub>2</sub> would be required if conclusions are to be made on computed OH<sup>-</sup> contents alone. Regarding assumption (iii), many published analyses of lunar apatite do not report F<sup>-</sup> and Cl<sup>-</sup> concentrations, and thus the calculation using the above method is not possible. Furthermore, electron-microprobe analysis of apatite is not straightforward because of apparent anisotropic diffusion of F<sup>-</sup> and Cl<sup>-</sup> during excitation by an electron beam when analyses are made parallel to the c-axis [8]. This anisotropic diffusion can cause an over-counting of F<sup>-</sup> and Cl<sup>-</sup> X-ray intensities, and thereby result in a spuriously low derived concentration of OH<sup>-</sup>. Unfortunately, published

apatite analyses cannot be assessed for this potential analytical problem; however, because this problem would only result in *lower* calculated hydroxyl contents, and we are primarily concerned with establishing a lower limit for bulk lunar water contents, all published apatite analyses containing both F<sup>-</sup> and Cl<sup>-</sup> were considered; however, due to the above stated analytical difficulties, conclusions about lunar magmatic water contents will only be made from our own data set.

Apatite grains were analyzed using the JEOL 8200 electron microprobe at Washington University, St. Louis. Probe for Windows<sup>TM</sup> software incorporating a volatile-element correction scheme was used to correct analyzed fluorine concentrations. We analyzed apatite in Apollo samples 12033 and 14161 (2-4 mm rock fragments), and in lunar meteorites LAP 02205, LAP 03632, NWA 2977, and SaU 169. The textures of the apatite grains within these samples varied greatly from large elongate crystals in Apollo samples 14161 and 12-

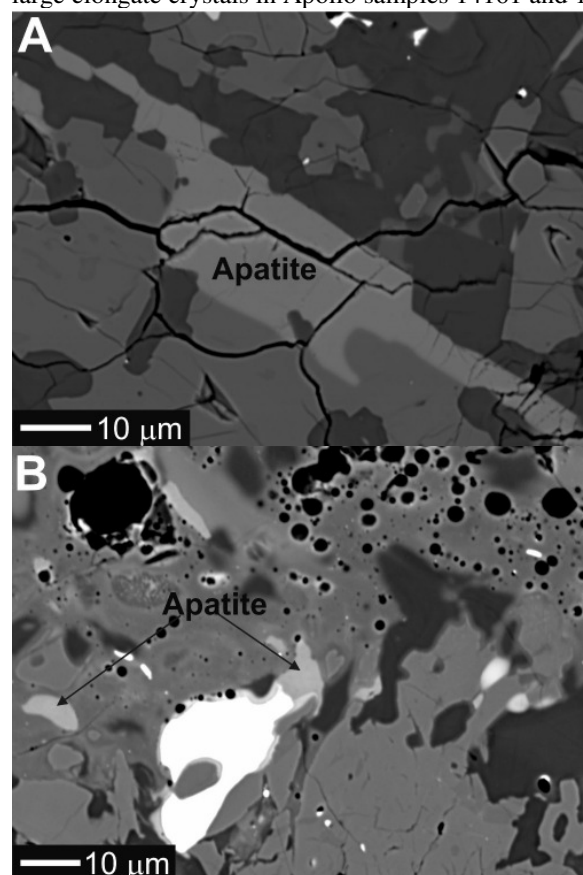
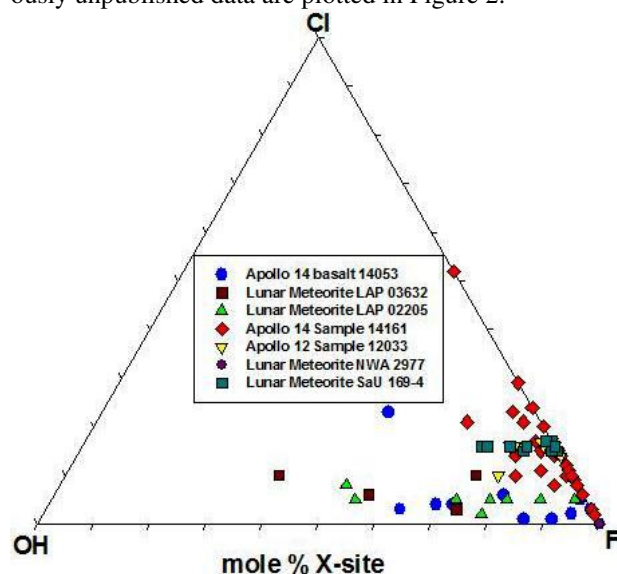


Figure 1. (A) BSE image of elongate subhedral apatite in Apollo 14 sample 14161. (B) BSE image of anhedral apatite patches in Lunar Meteorite SaU 169.

033, and lunar meteorite NWA 2977, to small anhedral apatite patches in LAP 02205 and LAP 03632. Figure 1 (A & B) illustrates the range in apatite textures observed during our investigation. The volatile components of published electron microprobe analyses based on stoichiometric constraints along with our own previously unpublished data are plotted in Figure 2.



**Figure 2.** Ternary plot of lunar apatite X-site occupancy (mol% X-site). Previously published apatite analyses from [9-12]. Data for which  $(F + Cl) > 1$  atom were plotted along the OH free join with a F:Cl ratio matching that of the analysis. For the analyses completed with the JEOL 8200 electron microprobe at Washington University, analytical uncertainty was  $\pm \sim 0.06$  apfu in the X-site along an F-OH tie-line.

The volatile contents of lunar apatite vary substantially. Moreover, much of the data do not plot along the F-Cl join, indicating that hydroxyl appears to represent a substantial constituent of many lunar apatite grains. However, the apatite grains with the highest apparent OH<sup>-</sup> contents are lunar meteorites (both LAP meteorites), and these two meteorites also show large ranges in calculated OH<sup>-</sup> suggesting that terrestrial alteration may play a role for these samples. For this reason, apatite from Apollo samples would be the most dependable grains for quantifying lunar magmatic water contents.

The Apollo samples analyzed for this study primarily focused on “KREEPy” samples associated with impact melt breccias because these samples were available, and they were known to have measurable apatite grains. The average F+Cl sums for each of these samples ranged from 0.97-1.04 apfu in the X-site when the analyses were assessed for volatile element corrections. This range is within the analytical uncertainty for determining the presence of a missing component within the X-site attributable to the presence of OH<sup>-</sup>. This is not surprising considering the high-temperature histories associated with these impact-melt lithologies. Samples associated with alkali-suite lithologies also have

high F+Cl sums, likely because these are second-generation melts. For these samples, a more sensitive technique such as SIMS or nanoSIMS is required for detecting measurable OH<sup>-</sup>. Moreover, these techniques would directly quantify OH<sup>-</sup> versus calculating OH<sup>-</sup> indirectly based on crystal chemical relationships.

The Apollo 14 sample 14053 (Aluminous basalt), analyzed by [8], has computed OH<sup>-</sup> contents that extend to around 30 mol % OH<sup>-</sup> in the X-site, which is well above the analytical uncertainty for detection of a missing component in this site. Coupled with possible abundances of OH<sup>-</sup> in apatite grains from the LAP meteorites (mare basalts), apatite grains from lunar basalts may be the best samples for finding preserved lunar magmatic water. Therefore, Apollo basalts will be included in the next set of samples to be analyzed using our specialized apatite analytical procedure.

**Need for Reassessment of bulk lunar water:** The most recent estimate for the bulk water content of the Moon is  $< 1$  ppb, reported by Taylor et al. [2]. This value was predominantly based on the fact that primary magmatic water had never been discovered in lunar materials. However, subsequent to the publication of this value, Saal et al. [13] reported measuring upwards of 50 ppm water in green, red, and orange fire fountain glasses from Apollo 15 and 17 landing sites. At the same time, McCubbin et al. [4] surveyed published lunar apatite analyses, finding strong crystal chemical evidence for structurally bound OH<sup>-</sup> in apatite from lunar rocks. These two studies have produced a need for reassessing the bulk water content of the Moon. However at this time, insufficient data is available for doing such calculations. Analyses of lunar apatites are ongoing, and computational investigations of bulk lunar water will be completed once sufficient data is collected.

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