

IS THERE EVIDENCE FOR WATER IN LUNAR MAGMATIC MINERALS? A CRYSTAL CHEMICAL INVESTIGATION. F. M. McCubbin¹, H. Nekvasil, and ¹D. H. Lindsley¹ Department of Geosciences, Stony Brook University, Stony Brook NY 11794-2100, fmccubbi@ic.sunysb.edu.

Introduction: Water is widely responsible for many of the geologic processes that take place on Earth. For example, it has been shown to greatly affect various physical properties of magmas, thermal stabilities of minerals and melts, and magma eruptive processes. Although, it is widely accepted that lunar magmas never contained sufficient H₂O 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. This work serves as a reassessment by summarizing evidence suggesting a “wetter” moon.

Although detectable amounts of H₂O have yet to be measured in lunar rocks, there are largely unexplored mineralogical reservoirs that hold significant potential for providing insight into the possible presence of structurally bound OH⁻ at some stage of lunar magmatic history. The most suitable candidates are apatite and amphibole because both minerals contain OH⁻ as an essential structural constituent. While amphibole is extremely rare in lunar rocks, apatite is a more commonly found accessory phase.

Lunar Phosphates: Phosphates are found in a wide range of lunar rocks, from the mare basalts to the highland anorthosites, and are also found as grains within lunar soils. Apatite, Ca₅[PO₄]₃X (X = F, Cl, and OH⁻) and merillite (ideally Na₂Mg₂Ca₁₈P₁₄O₅₆) are the two common mineralogical reservoirs for phosphorus in lunar rocks [3]; although, merillite is an anhydrous phosphate, OH⁻ is an essential structural constituent of apatite. Therefore, apatite holds most promise among the phosphates for quantitative assessment of magmatic water contents of lunar minerals.

The nominal OH⁻ content of apatite can be calculated from fluorine and chlorine concentrations. This requires the following assumptions: (i) only F, Cl and OH substitute into the X-site, (ii) the X-site has no vacancies, and (iii) reliable analyses of F⁻ and Cl⁻ are available. Regrettably, many published analyses of lunar apatite do not report F⁻ and Cl⁻ concentrations, and thus the calculation using the above method is not possible. Furthermore, electron-microprobe analysis of apatites is not straightforward because of an apparent anisotropic diffusion of F⁻ and Cl⁻ during excitation by an electron beam when analyses are made parallel to the c-axis [4]. This anisotropic diffusion can cause an over-counting of F⁻ and Cl⁻ X-ray intensities, and thereby result in an apparent decrease in the amount of OH⁻. In fact, this over-counting of halogens, coupled

with the absence of direct measurements for OH⁻ in lunar apatite, may have reinforced the conclusion that lunar magmas are water-free [i.e. 1,5]. A closer look at available data shows that lunar apatite contains a significant amount of “missing” component in spite of the likelihood of over-counting of F⁻ and Cl⁻ (Fig. 1). This apparent missing component indicates the strong need

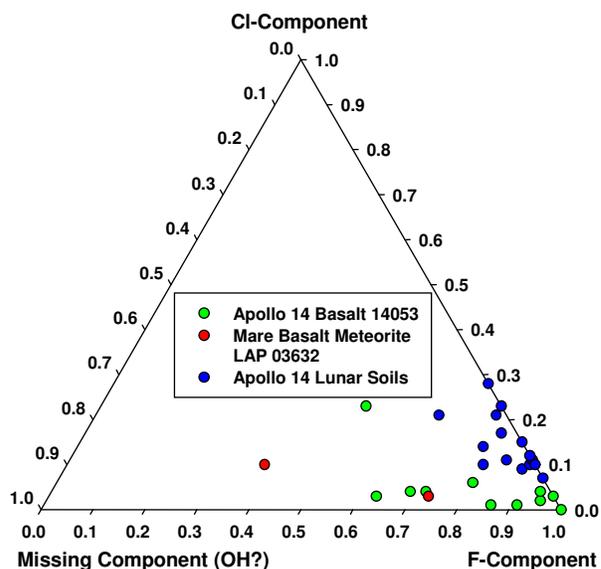


Figure 1. Ternary plot of lunar apatite X-site with F⁻, Cl⁻, and missing component (usually attributed to OH⁻). Compositions are from Apollo 14 Basalts [6], a Mare Basalt meteorite [7], and Apollo 14 soils [5]. Data for which (F + Cl) > 1 atom were plotted as F-Cl apatite with F:Cl ratio matching the analysis.

for additional analysis of the volatile contents of apatite within lunar materials.

Lunar Amphibole: Amphibole, A₀₋₁M(4)₂M(1-3)₅T₈O₂₂O(3)₂, is very rare in lunar rocks, and has only been reported in the following lunar samples: Apollo 11 sample 10058 [8], Apollo 12 sample 12021 [9], and in 2 Russian lunar samples. On Earth, amphibole is commonly considered an indicator of hydrous magmatic conditions; however, F⁻ and Cl⁻ can also stabilize amphibole in relatively dry magmas. Similar to apatite, amphibole also incorporates F⁻, Cl⁻, and OH⁻ into a distinct crystallographic site (O(3) site); however, amphibole is more complex because it can also readily incorporate O²⁻ into the O(3) site as a primary magmatic feature [10,11], making quantification of structurally bound OH⁻ more difficult without direct OH⁻

analysis. Nonetheless, there are permissive lines of evidence that can be used to assess the possible presence of OH. Of the amphibole analyses presented in the above publications, only [9] reports F⁻ and Cl⁻ analyses (Table 1).

Table 1. Lunar amphibole composition of Apollo 12 sample 12021 from Dence et al. [9] with two crystal chemical models showing site occupancies assuming all Fe is ferrous and all space in O(3) not filled with Cl and F is filled with (I) OH⁻ and (II) O²⁻ respectively. Cations are normalized to 24 anions.

Oxide	Wt%	Atomic Sites	OH Model	O ²⁻ Model
SiO ₂	42.1	Si ^T	6.24	6.48
TiO ₂	0.1	Al ^T	1.76	1.52
Al ₂ O ₃	16.7	Total ^T	8.00	8.00
FeO	14.2	Al ^{M1-3}	1.15	1.51
MgO	9.9	Ti ^{M1-3}	0.01	0.01
CaO	12	Fe ^{M1-3}	1.62	1.18
Na ₂ O	1.3	Mg ^{M1-3}	2.19	2.27
K ₂ O	0.6	Mn ^{M1-3}	0.03	0.03
MnO	0.2	Total ^{M1-3}	5.00	5.00
F	0.4	Fe ^{M4}	0.14	0.65
Cl	0.2	Ca ^{M4}	1.86	1.35
Total	97.7	Total ^{M4}	2.00	2.00
T, M1-3, M4, A, and O(3) superscripts refer to the crystallographic site in which the atom sits for each model.		Ca ^A	0.05	0.63
		Na ^A	0.37	0.39
		K ^A	0.11	0.12
		Total ^A	0.53	1.14
		F ^{O(3)}	0.19	0.19
		Cl ^{O(3)}	0.05	0.05
		OH, O ^{O(3)}	1.76	1.76
	Total ^{O(3)}	2.00	2.00	

The structural formula for this amphibole can be assessed for two possibilities: (a.) Consistency with a fully hydroxylated amphibole in which all Fe is present as Fe²⁺. In this case, as shown in Table 1, there is good correlation between Na⁺ + K⁺ and the A-site occupancy of the amphibole [0.37 (Na) + 0.11 (K) = 0.48 ~ 0.53 (A-site occupancy)], which is a constraint that must be met for stoichiometric amphibole [12]. Additionally, the cation assignments for the M(1-4) sites match well for typical calcic amphiboles [12], and (b.) consistency with a significant oxy-component in the amphibole. The low F⁻ + Cl⁻ values (F + Cl = 0.24) would require

in this case that 1.76 atoms of oxygen were present in the O(3) site of the amphibole (Table 1), which is more than twice the highest amount of primary magmatic oxy-component experimentally determined for kaersutite [11], which is a Ti-rich amphibole with abundant oxy-component because of a Ti-substitution mechanism. Low-Ti amphiboles such as the lunar amphibole of Table 1 should have even lower amounts of oxy-component. Furthermore, a completely oxy-substituted lunar amphibole would require at least 21% Fe³⁺ to reduce the number of cations to ≤16 (a structural requirement for amphibole), and a considerable amount of Ca²⁺ in the amphibole A-site, which is not a common atomic arrangement for most amphiboles [12]. For amphibole oxy-component to be as high as 1.76 apfu (atoms per formula unit), it would be more reasonable to call upon post-magmatic processes that reduced the original hydroxyl content of the amphibole, such as post-crystallization dehydrogenation [13,14]. Hence, this case also requires water to have been present in the structure at the time of crystallization.

Summary: Although there has been extensive evidence reported in the literature supporting completely dry lunar magmas, we have summarized evidence from volatile-bearing minerals that suggests some water may have been present in the hosting magma. More work is clearly needed that attempts a direct analysis of OH in lunar materials. Lastly, the presence of water in lunar magmatic minerals would not necessarily indicate that lunar magmas were water-rich, but would imply that lunar magmas were not anhydrous and may have had water contents similar to relatively dry intraplate magmas found on Earth.

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