INHOMOGENEOUS DISTRIBUTION OF MAGMATIC VOLATILES IN THE LUNAR INTERIOR: CLUES FROM THE MINERAL APATITE.
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Introduction: The magmatic volatiles water, fluorine, and chlorine play critical roles in the physicochemical processes that control thermal stabilities of minerals and melts, magma eruptive processes, and transport of economically important metals. While these volatiles are significant constituents in many terrestrial and martian magmas, lunar magmas are generally depleted in these three volatiles (i.e., 1, 2-5). Nevertheless, Cl, F and H_2O likely became concentrated in late stage lunar melts because of their incompatible behavior with respect to high-temperature mineral phases. Importantly, the concentration of these volatiles in the hypothesized urKREEP residual melt could have played a significant role in all post-differentiation magmatism (e.g., mare basalts and magnesian suite rocks) that was generated by "urKREEP-heating" (due to the solidus-depressing abilities of the volatiles); however, little is currently known about the relative abundances of volatiles in late-stage lunar melts. Although these late-stage melts have not yet been found as quenched glasses and therefore, their volatile content cannot be studied directly, the volatiles in these liquids ought to have been incorporated into F-, Cl-, and OH-bearing mineral phases. As such, these minerals can be used to assess the relative amounts of dissolved volatiles in their parent magmas. Because lunar phosphates contain elevated amounts of both phosphorus and rare earth elements (REE), components that are generally enriched in late-stage liquids due to their incompatible nature (they are also two of the main constituents in the hypothesized ur-KREEP liquid), they would be a potentially useful mineral group for understanding magmatic volatiles, which also typically behave incompatibly.

Apatite [$Ca_5(PO_4)_3(F,Cl,OH)$] and RE-merrillite [$(Mg,Fe)_2REE_2Ca_{16}P_{14}O_{56}$] are the two main P-bearing minerals on the Moon (6) and they are found in a wide range of lunar rock types. Although merrillite is a volatile-free phosphate, fluorine, chlorine, and hydroxyl are essential structural constituents of apatite, making it the ideal phase for our study. Electron probe microanalysis (EPMA) of lunar apatite can be used to estimate the relative amounts of fluorine, chlorine, and potentially water in coexisting melt using known partitioning data between the apatite volatile site (X-site) and silicate melt and/or fluid (i.e., 7, 8-10). Importantly, partitioning studies show that Cl, F, and OH⁻ have melt/apatite partition coefficients that not only deviate from unity but also vary with anion. Relative to melt, F partitions strongly into apatite whereas Cl and OH⁻ are less com-

patible in apatite under a range of P-T conditions (i.e., ≤ 10 kbar & ≤ 1150 °C) . Complicating the issue further, apatite/melt partition coefficients are highly dependant upon melt composition (i.e., 8, 10); therefore, understanding the composition of the liquids from which apatite has crystallized is a crucial step in understanding the magmatic volatile content of that liquid.

Hydroxyl cannot be measured directly by EPMA; however, it can be calculated from electron microprobe measurements of fluorine and chlorine if direct hydrogen analysis is not available. This requires the following assumptions: (i) only F, Cl, and OH⁻ populate the X-site, (ii) the X-site has minimal vacancies, and (iii) reliable analyses of F and Cl are available. Unfortunately, electron-microprobe analysis of fluorine in apatite is not straightforward because of apparent anisotropic diffusion of this anion during excitation by an electron beam when analyses are made parallel to the c-axis (11). This anisotropic diffusion can cause over-counting of F⁻ X-ray intensities, thereby resulting in spuriously high concentrations. If any OH were present, it would be masked in such analyses. Moreover, because this analytical problem directly affects the fluorine concentrations, use of partition coefficients is rendered useless if analyses are not monitored for such over-counting.

Previous studies of this type did not take into account the potential analytical problems discussed above; however, we have devised a reliable method for testing the quality of apatite data collected by EPMA (Our analytical methods are identical to those described in the following abstracts: 12, 13; A plot illustrating count acceleration is presented in Figure 1.) and have employed this method to investigate the fluorine and chlorine contents of apatite in a variety of Apollo samples and lunar meteorites: 14161,7111, 14161,7233 14161,7269 14161,7264 14161,7110 14161,7062, 12033,634-25, 79195, 12037,224, 74246, 12023,147,1, 10084, LAP 02205, LAP 03632, SaU 169 and NWA 2977. Discriminating between "good" and "bad" analyses following this approach, we then compared the volatile contents of apatite based on their respective lithologic group (i.e., mare basalt vs. magnesian- and alkali-suite rocks). From our analyses, we are also able to speculate as to the possible presence of magmatic water in these liquids, although direct OH⁻ analysis of lunar apatite by secondary ion mass spectrometry (SIMS) is required before we can definitively verify the presence of OH⁻.
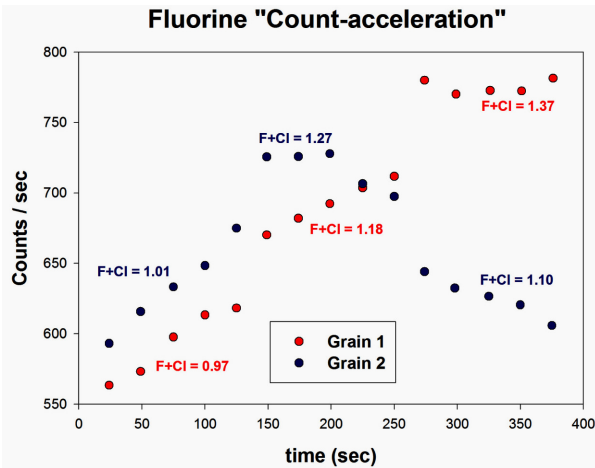
Figure 1. Example plot of two different apatite grains that exhibit fluorine count acceleration.

Results: The samples studied here lie within the following lithologic groups: (1) magnesian- and alkali-suite rocks (14161,7111, 14161,7269 and 14161,7264) (2) KREEPy impact melt rocks associated with magnesian- and alkali-suite rocks (14161,7233, 14161,7110, 14161,7062, 12033,634-25 and SaU 169-4) and (3) mare basalts (79195, 12037,224, 74246, 12023,147,1, 10084, LAP 02205, LAP 03632 and NWA 2977). We analyzed apatite from each of these samples, and their volatile components are plotted in Figure 2. We have grouped the magnesian- and alkali-suite rocks with the KREEPy impact melt rocks.
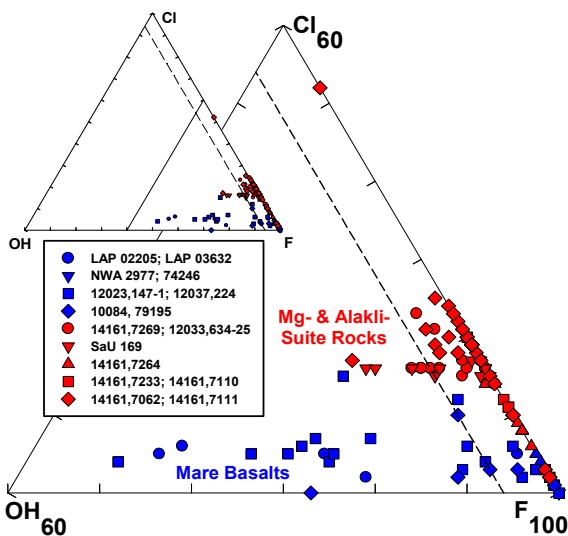

Figure 1. Ternary plot of lunar apatite X-site occupancy (mol% X-site). Data for which (F + Cl) > 1 atom were plotted along the OH$^-$ free join with a F:Cl ratio dictated assuming the Cl value is correct. Analytical uncertainty was ± ~0.06 apfu for F and <0.01 apfu for Cl. The dotted line represents our analytical ability to detect a missing component that can be attributed to OH. Mare basalts are plotted in blue, and magnesian- and alkali-suite rocks (including impact melt rocks) are plotted in red.

Discussion: Figure 2 illustrates the contrast in volatile contents of apatite in mare basalts vs. those within magnesian- and alkali-suite rocks. Mare basalt apatites have a higher average F:Cl ratio than those in magnesian- and alkali-suite rocks. Moreover, the mare basalt apatites have a substantially larger missing component (on average) than apatite in the magnesian- and alkali-suite rocks, although quantitative OH$^-$ analysis by SIMS is needed to verify this result.

The apatite data for the magnesian- and alkali-suite rocks have been discussed in (12 &, 13), therefore we focus here on the crystal chemistry of the mare basalt apatite. The computed average missing component in the mare basalt apatite is ~10% (excluding bad analyses) of X-site occupancy, which corresponds to an apatite water content of ~1800 ppm if this missing component is OH. One of the analyses from Apollo sample 12037,224 shows an apatite with 46% missing component in the X-site corresponding to an apatite water content of ~8200 ppm (if the missing component is OH). Since $D_{H2O}^{apat/melt \; or \; fluid} << 1$ (8-10), the (residual late-stage) melt from which this apatite crystallized may have had a magmatic water content of over 1 wt% at the time of apatite crystallization. However, further experimental work is needed to precisely determine the partitioning behavior.

Mare basalts and rocks associated with the magnesian suite are believed to have distinctly different petrogenetic histories (See 14 for an extensive review); however, both are post magma-ocean lithologies that were derived from melting of the lunar interior. The systematic differences between apatite volatile contents of these two lithologic types indicates that their source regions had different magmatic volatile budgets. This, in turn, indicates that magmatic volatiles in the lunar interior are likely inhomogenously distributed, and understanding the volatile budget of the planetary body as a whole will require study of a variety of rocktypes.

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