APATITE FROM APOLLO SAMPLES 14161 AND 12033: ANALYTICAL HURDLES AND IMPLICATIONS FOR RELATIVE FLUORINE AND CHLORINE CONTENTS IN LATE-STAGE LUNAR MAGMAS AND MELTS. F. M. McCubbin1, H. Nekvasil1, B. L. Jolliff2, P. K. Carpenter2, R. A. Zeigler2, and D. H. Lindsley1.1Department of Geosciences, State University of New York, Stony Brook NY 11794-2100. 2Dept. of Earth and Planetary Sciences and the McDonnell Center for the Space Sciences, Washington University, Saint Louis, MO 63130. fmccubbi@ic.sunysb.edu

Introduction: Magma volatiles such as 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 such volatiles (and typically found in only trace amounts in quenched lunar glasses [1-5]). Nevertheless, these volatiles likely became concentrated in late stage lunar melts because of their incompatible behavior with respect to high-temperature mineral phases. Importantly, these volatiles in the hypothesized urKREEP residual melt could have played a significant role in all post-differentiation magmatism that was generated by “urKREEP-heating” (due to the solids-depressing abilities of the volatiles). However, little is known about the relative abundances of these volatiles in late-stage lunar melts. Although late-stage residual melts are not likely to have been preserved as quenched glass and therefore, cannot be interrogated directly about their volatile content, the volatiles in the late-stage liquids were eventually incorporated into F- and Cl-bearing apatite, which can be used as a gauge for assessing the relative amounts of fluorine and chlorine in these types of liquids.

Apatite \([\text{Ca}_3(\text{PO}_4)_2(\text{F},\text{Cl},\text{OH})]\) can be used to estimate the relative amounts of fluorine and chlorine in coexisting melt using known partitioning data between apatite and silicate melt or fluid [i.e., 6-8]. Importantly, however, the partitioning studies show that Cl, F, and OH do not partition equally into the apatite volatile site (X-site), thus the volatile contents of the apatite do not equal those of the melt. In fact, [6] and [7] have shown that fluorine partitions very strongly into apatite, and chlorine and hydroxyl are less compatible in apatite under a range of geologically relevant conditions. Use of such partition coefficients, however, is complicated by problems inherent to analysis of anions in ternary apatite, and special measures must be used to obtain “high-quality” electron-microprobe data from apatite [e.g., 9-10] in order to back out information about melt volatile contents.

We have devised a reliable method for testing the quality of apatite data collected by electron microprobe and have employed this method to investigate the fluorine and chlorine contents of apatite in Apollo samples 14161 and 12033. We then used known partitioning data to estimate the relative abundances of fluorine and chlorine in the late stage liquids that crystallized these apatites.

Analytical Procedure and Results: Apatite grains were analyzed using the JEOL 8200 electron microprobe at Washington University, St. Louis, using Probe for WindowsTM software. Because [9] had previously reported that fluorine and chlorine X-ray intensities change with time during electron microprobe analyses in which the electron beam is parallel or near parallel to the c-crystallographic axis, we monitored our apatite analyses for “count-acceleration” [rate change for (counts/second)/second]. We found that count-acceleration primarily occurs for fluorine and appears to be independent of crystallographic orientation (contrary to the results of [9]), although further work is needed to systematically determine what factors do control the occurrence of F-count acceleration. Figure 1A shows two grains in which F-count acceleration occurs, and Fig 1B shows two grains in which F-count acceleration is minimal. By monitoring these count rates, we can determine the reliability of the fluorine analyses. This is of particular importance when OH abundance is significant and is obtained by calculation.

For apatite with low OH-abundances, over-counted F-analyses are not as much of a problem as long as the Cl-contents are accurate. We have previously concluded that the apatite in the samples analyzed here contain insignificant amounts of hydroxyl [e.g., 10] (< 10 mol% of X-site). Therefore, while many of our analyses experienced F-count acceleration (analogous to Fig. 1A), and are therefore less reliable than analyses without such acceleration, the reliability of our Cl-analyses in these nearly binary apatites allows such data to be used to assess melt F/Cl ratios.

The apatite grains analyzed during this study are plotted in Figure 2. All apatite from sample 12033 appear to have similar F/Cl ratios. In contrast to this, apatite within some individual lithologic fragments in sample 14161 show ranges in F/Cl ratios. This is most pronounced in sample 14161, 7062.

Discussion: Recently, Mathez and Webster [6] reported the partitioning of fluorine and chlorine between apatite and basaltic melt. They reported that \(D_{\text{Cl}}\text{Ap/Melt}^{\text{Ap}}\)
is 0.8 and that $D_F^{\text{Ap-Melt}}$ is ~3.4, indicating that high fluorine contents in apatite do not necessarily correlate to a high melt F/Cl ratio.

Apatite grains in Apollo sample 12033 have a fairly constant F/Cl ratio. If the partitioning data of [6] are applicable to this system, the late-stage (impact) melt that crystallized the apatite in 12033 had a range in F/Cl wt. ratio from ~0.60 to ~0.78, indicating that chlorine was more abundant in the late-stage melts than fluorine in spite of the higher fluorine abundance of the apatite. This conclusion holds also for all samples in Figure 2 except 14161, 7062 & 7264. This conclusion differs from previous general conclusions concerning F/Cl ratios in lunar melts [i.e., 11]) in which lunar magmas are considered to be dominated by fluorine relative to chlorine.

The F/Cl ratios of apatite within rock fragment 14161, 7062 vary tremendously (Fig. 2). Based on the same partitioning coefficients as above, the F/Cl wt. ratio for the melts that produced the apatite in 14161, 7062 ranged from ~0.12 to ~5.57. This variability may indicate that the late-stage liquids associated with the magmas that produced this fragment had dramatically variable fluorine and chlorine contents over minute distances (over the range of apatite thermal stability) due to liquid immiscibility or disequilibrium processes. Alternatively, the variability may reflect a miscibility gap in the low-OH apatite system. (In this latter case, the simple partition coefficients are not applicable.) While the F/Cl ratio of the late stage melts responsible for crystallizing apatite in sample 14161, 7062 cannot be determined, at least some of the apatite indicates low F/Cl ratios of the magma.

The results of this study point to the potential volumetric significance of chlorine relative to fluorine in late-stage lunar magmas and impact melts


Figure 1. Plots showing fluorine count rates with time. Each grain was analyzed in the same spot two to three times for a duration of 125 seconds per each analysis. (A) Strong F-count acceleration. (B) Minimal F-count acceleration.

Figure 2. 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 OH, and <0.01 apfu for Cl.