PARTITIONING OF F, Cl, AND H_2O BETWEEN APATITE AND A SYNTHETIC SHERGOTTITE LIQUID (QUE 94201) AT 1.0 GPA AND 990-1000 °C.

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Introduction: The mineral apatite $[Ca_5(PO_4)_3(F,Cl,OH)]$ is present in a wide array of planetary materials, and due to the presence of volatiles within its crystal structure, many recent studies have attempted to use apatite to constrain the volatile contents of planetary magmas and mantles [1-9]. In order to use the volatile concentrations of apatite to precisely determine the abundances of volatiles in coexisting silicate melt or fluids, thermodynamic models for the apatite solid solution and for the apatite components in multicomponent silicate melts and fluids are required. Although some thermodynamic models for apatite have been developed [i.e., 10, 11-14], they are incomplete. Furthermore, no mixing model is available for the apatite components in silicate melts or fluids. Several experimental studies have investigated the apatite-melt and apatite-fluid partitioning behavior of F and Cl in terrestrial systems [i.e., 14, 15, 16-17]; however, the partitioning has proved to be compositionally dependent [i.e., 16, 17], and experiments on magmatic systems relevant to extraterrestrial magmas have not been conducted. Moreover, the experimental studies that have been conducted did not determine apatite-melt partition coefficients for OH (hereafter referred to using the oxide component H_2O). In the present study, we conducted apatite-melt partitioning experiments in a Depths of the Earth piston cylinder press at 1.0 GPa and 990-1000 °C on a synthetic martian basalt composition equivalent to the basaltic shergottite Queen Alexandria Range (QUE) 94201.

Experimental Methods: Three powdered mixes were designed based on the QUE 94201 composition with approximately 5 wt.% additional P_2O_5 (to induce early phosphate saturation). Each of the three mixes was either an F, Cl, or H_2O endmember with ~1 wt.% of either F, Cl, or H_2O. The mixes were created by first accurately weighing silicates, oxides, $Ca_2P_2O_7$, $Ca(OH)_2$, CaF_2, and $MgCl_2$ powders in the proportions needed for obtaining the desired compositions. Next, the powders were mechanically mixed sequentially by volume in an automatic agate mortar/pestle grinder for a total of 3.5 hours under ethanol. The $Fe^{3+}/\sum Fe$ value in the mixture was 0.10. Because $MgCl_2$ is soluble in ethanol, the Cl-bearing mix was ground under dry conditions.

Each experiment for the present study was conducted under "wet" conditions, and mixtures of the three powders (each with a different F:Cl: H_2O ratio) were packed into a graphite capsule. Next, the capsule was loaded into a talc-pyrex cell using the same cell assembly reported by Elardo et al. [18]. The assembled cell was then placed within a ½ inch [1.27 cm.] Depths of the Earth piston-cylinder apparatus (using the piston-out method) and pressurized immediately. Next, the temperature was raised to a melting temperature of 1250°C. After melting for 20 minutes, the temperature was dropped to the desired crystallization temperature of 990-1000 °C and left to crystallize for 3.25-8.50 hours. The temperature of each experiment was both controlled and monitored by a W_5Re_{95}-$W_{26}Re_{74}$ thermocouple. At the end of each experiment, the run was rapidly quenched.

Results: Experimental charges were implanted into indium metal within 1" aluminum metal discs and polished for subsequent analysis by SIMS and EPMA. The largest apatites that grew from the silicate melt were approximately 4-5 microns in the shortest dimension, so they could not be analyzed with the 6f ion microprobe. However, glasses from all the experiments were analyzed by SIMS to determine H_2O contents. The apatite in each sample was analyzed by EPMA, and H_2O contents for the apatite were calculated using the F and Cl data assuming the monovalent anion site in apatite summed to one structural formula unit. Glass compositions were also determined by EPMA to obtain F and Cl contents. In all, we conducted 6 succesful experiments. The F, Cl, and H_2O contents of glass and coexisting apatites are presented in Table 1 for all 6 experiments. Values presented are based on the average of approximately 5-10 analyses.

Table 1. F-Cl-H_2O contents of glass and apatite within experimental run products. All values are in wt.%

Exp #	07	12	13	16	17	18
Gl-F	0.08	0.38	0.44	0.17	0.18	0.22
Gl-Cl	0.32	0.45	0.36	0.47	0.93	0.32
Gl-H_2O	2.69	2.70	3.04	2.75	2.96	2.68
Ap-F	1.55	3.09	3.16	2.28	1.95	2.97
Ap-Cl	1.67	0.62	0.50	1.23	1.87	0.68
Ap-H_2O	0.59	0.14	0.16	0.37	0.35	0.18

All of the experiments contained relatively high water contents, which was expected from the use of talc-pyrex cells and an unsealed graphite capsule. From the data in Table 1, we can calculate apatite-melt partition coefficients for F, Cl, and H_2O. Interestingly, the values are not constant within the compositional range we observed. In fact, the partition coefficients are strongly dependent on the fluorine content of the coexisting liquid, as illustrated by Figure 1 a-c. For

$D_{H2O}^{apatite/melt}$, the value is always $\ll 1$, with an upper limit approximating about 0.3, which is consistent with the "conservative" value used in previous studies to estimate magmatic water contents from apatite in lunar rocks [6].
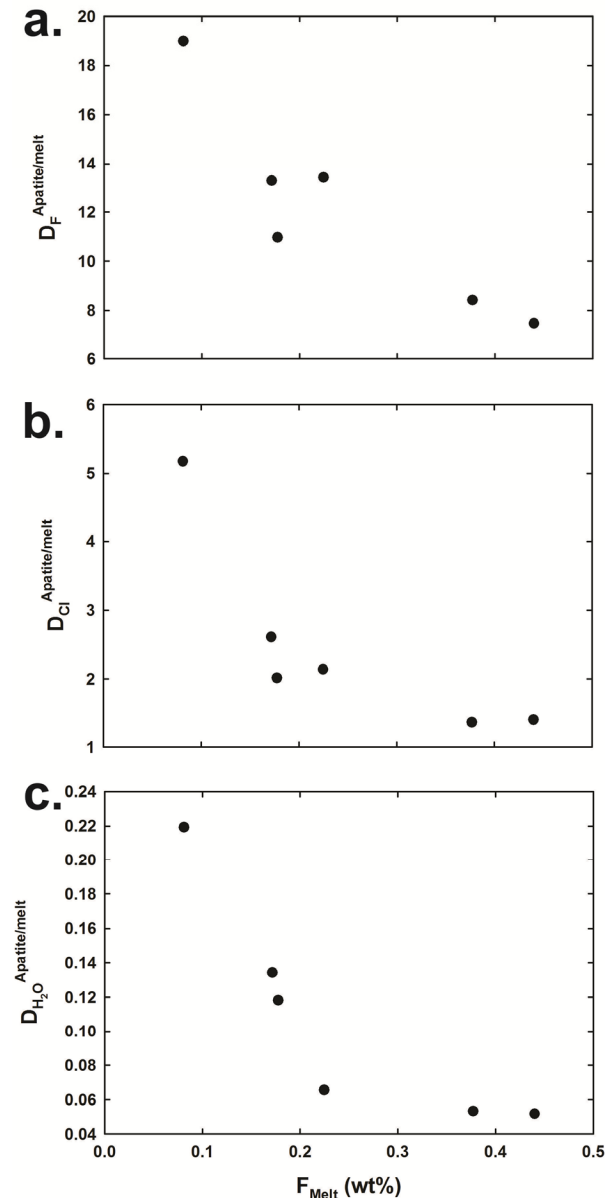

Figure 1. Apatite-melt partition coefficients for **a.** fluorine, **b.** chlorine, and **c.** H_2O, as a function of melt fluorine value.

Discussion: The apatite-melt partition coefficient behavior from Figure 1 illustrates the dangers in using a single apatite-melt partition coefficient to determine melt volatile concentrations from apatite in planetary materials. To illustrate this point further, we have plotted the experimental apatite compositions on an F-Cl-OH ternary (Figure 2), along with the experimental run numbers and apatite-melt partition coefficients for H_2O. Although much more data are needed before knowing precisely which partition coefficient is appropriate for a given system, this diagram provides a first order guide on how to select appropriate apatite-melt partition coefficients. We attribute the observed partitioning behavior of F, Cl, and H_2O in this system to the fact that F, Cl, and H_2O are essential structural constituents in apatite with a strong preference order of $F>Cl\gg H_2O$. Interestingly, our apatite-melt partitioning values for F and Cl deviate significantly from those reported for terrestrial basalt [16]. Consequently, the "fluid only" field in the apatite ternary discussed by [2] will likely be more limited as one moves off the F-Cl binary. Additional work is needed to determine the presence of a fluid-only compositional field within the apatite F-Cl-OH ternary system.
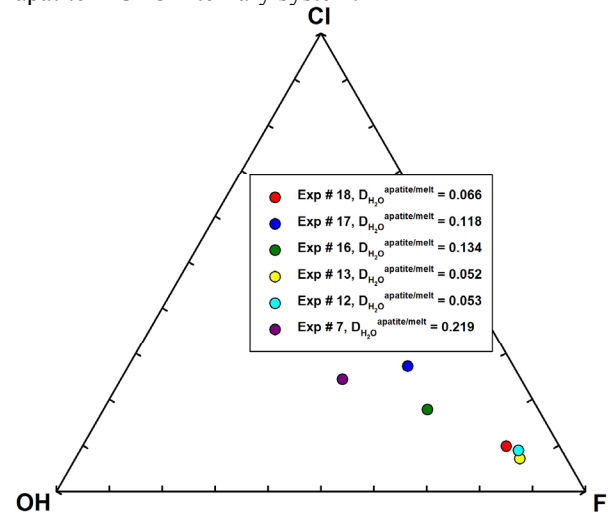

Figure 2. F-Cl-OH ternary diagram with average apatite compositions from each of the 6 successful experiments plotted. $D_{H2O}^{apatite/melt}$ is indicated for each experiment.

Future Work: Experiments are ongoing to determine the behavior of F-Cl-H_2O partitioning in this system. Many of the experiments run thus far were of a relatively short duration (3.25-8.5 hrs). Future experiments will be run for longer periods of time (48-96 hours) to see if there are any problems with equilibration. Crystallization experiments on each of the end-member compositions, as well as along the F-OH and Cl-OH joins, are ongoing.

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