APATITE-MELT PARTITIONING AT 1 BAR: AN ASSESSMENT OF APATITE-MELT EXCHANGE EQUILIBRIA RESULTING FROM NON-IDEAL MIXING OF F AND Cl IN APATITE.

F. M. McCubbin[1], G. Ustunisik[2], and K. E. Vander Kaaden[1,3] [1]NASA Johnson Space Center, mailcode XI2, 2101 NASA Parkway, Houston, TX 77058. [2]Department of Earth and Planetary Sciences, American Museum of Natural History, New York, NY, 10024. [3]Institute of Meteoritics, 1 University of New Mexico, MSC03-2050, Albuquerque, NM 87131 (francis.m.mccubbin@nasa.gov).

Introduction: The mineral apatite [$Ca_5(PO_4)_3(F,Cl,OH)$] is present in a wide range of planetary materials. Due to the presence of volatiles within its crystal structure (X-site), many recent studies have attempted to use apatite to constrain the volatile contents of planetary magmas and mantle sources [1-5]. In order to use the volatile contents 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 multi-component silicate melts and fluids are required. Although some thermodynamic models for apatite have been developed [i.e., 6, 7-10], they are incomplete. Furthermore, no mixing model is available for all of the apatite components in silicate melts or fluids, especially for F and Cl components. Several experimental studies have investigated the apatite-melt and apatite-fluid partitioning behavior of F, Cl, and OH in terrestrial and planetary systems [i.e., 10, 11, 12-14], which have determined that apatite-melt partitioning of volatiles are best described as exchange equilibria similar to Fe-Mg partitioning between olivine and silicate melt [14-18]. However, McCubbin et al., [14] recently reported that the exchange coefficients may vary in portions of apatite compositional space where F, Cl, and OH do not mix ideally in apatite. In particular, solution calorimetry data of apatite compositions along the F-Cl join exhibit substantial excess enthalpies of mixing [7]. In the present study, we conducted apatite-melt partitioning experiments in evacuated, sealed silica-glass tubes at ~1 bar and 950-1050 °C on a synthetic martian basalt composition equivalent to the basaltic shergottite Queen Alexandria Range (QUE) 94201. These experiments were conducted dry, at low pressure, to assess the effects of temperature and apatite composition on the partitioning behavior of F and Cl between apatite and basaltic melt along the F-Cl apatite binary join, where there is non-ideal mixing of F and Cl in apatite.

Experimental Methods: Two powdered mixes were synthesized based on the QUE 94201 composition with approximately 5 wt.% additional P_2O_5 (to induce early phosphate saturation). The two mixes were either an F or Cl endmember with ~1 wt.% of F and Cl, respectively. The mixes were prepared by first weighing silicates, oxides, $Ca_2P_2O_7$, CaF_2, and $MgCl_2$ powders in the proportions needed for obtaining the target 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.

Experiments were conducted in a Deltech vertical quench furnace at LDEO of Columbia University. The mixes were packed into high purity Mo capsules. Weighed capsules were then placed into a silica tube sealed at one end. 0.5″ and 1″ glass spacers were placed just above the capsule to minimize the volume inside the tube. After evacuating for 15 mins, the tube was stretched to form a capillary, sealed, and suspended on a thin Pt-wire. The assembly was gradually lowered into the hot spot where the horizontal temperature differences were within 1°C. Each sample was first held at 1150°C for 30 mins then lowered to the temperature of interest ranging between 1050°C to 950°C where it stayed for 8 hr. The temperature of each experiment was controlled by a type S thermocouple. Each experiment was drop-quenched in cold water.

Analytical Methods/Results: Experimental charges were mounted in epoxy and polished for subsequent analysis by EPMA. The apatite and quenched glass in each sample was analyzed by EPMA using the procedures outlined by McCubbin et al., [14]. The F and Cl contents of glass and coexisting apatites are presented in Table 1 for all 11 experiments based on the average of approximately 5-20 analyses.

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

Exp #	T (°C)	F_{Gl}	Cl_{Gl}	F_{Ap}	Cl_{Ap}
Q1b.001	1050	0.66	0.21	3.64	0.24
Q1b.002	1000	0.62	0.31	3.56	0.32
Q1b.003	950	1.16	0.58	3.47	0.34
Q1b.004	1050	0.46	0.81	3.20	1.06
Q1b.005	1000	0.33	0.68	3.33	0.87
Q1b.006	950	0.57	1.17	3.22	0.93
Q1b.007	1050	0.27	1.24	2.60	2.02
Q1b.008	1000	0.10	1.03	2.41	2.25
Q1b.009	950	0.23	2.13	2.39	2.39
Q1b.010	1050	0.07	1.79	1.19	3.91
Q1b.012	950	0.14	4.05	1.52	3.49

Although we did not measure the H_2O content of the apatite or melt, the experiments were dried and conducted in evacuated, sealed silica-glass tubes, so the pH_2O in the system was necessarily low given the extremely low solubility of H_2O in silicate melts at low pressure [19, 20]. Moreover, substantial overpressure of H_2O would have caused the silica tubes to rupture. From the data in Table 1, we can calculate apatite-melt partition coefficients for F (3-25) and Cl (0.58-2.2).

As discussed previously by Boyce et al., [15] and McCubbin et al., [14], F and Cl are essential structural constituents in the mineral apatite, so their partitioning behavior should deviate substantially from Henrian behavior of trace elements. Similar to the partitioning behavior of Fe and Mg between olivine and silicate liquids, the partitioning behavior of F and Cl between apatite and silicate melt are best described by an exchange coefficient (Equation 1):

$$K_{D_{Ap-Liq}}^{Cl-} = \frac{X_{Liq}^{F} \div X_{Ap}^{F}}{X_{Liq}^{Cl} \div X_{Ap}^{Cl}} \quad (1)$$

where X_{Liq}^{F} is the wt.% F in the melt, X_{Ap}^{F} is the wt.% F in the apatite, X_{Liq}^{Cl} is the wt.% Cl in the melt, and X_{Ap}^{Cl} is the wt.% Cl in apatite. These exchange coefficients can change as a function of melt composition, pressure, temperature, apatite composition, and oxygen fugacity; however, McCubbin et al., [14] reported that $K_{D_{Ap-Liq}}^{Cl-F} = 0.21 \pm 0.03$ (Figure 1) over a wide range of ternary (F-Cl-OH) apatite compositions at 1.0 GPa and 950-1000 °C. In the present study of apatite along the F-Cl join, $K_{D_{Ap-Li}}^{Cl-F}$ varies from 0.21 ± 0.02 at F-rich compositions to 0.07 ± 0.01 at Cl-rich compositions at ~1 bar and 950-1050 °C (Figure 1). In addition to variable $K_{D_{Ap-Liq}}^{Cl-F}$ values along the F-Cl apatite join, the Cl-F K_D values consistently decrease with decreasing F in the apatite structure, indicating that F becomes proportionally more compatible in apatite compared to Cl as apatite becomes more Cl-rich. This observation holds true until at least 70% chlorapatite, however without additional data, we cannot assess the range 70-100% chlorapatite.

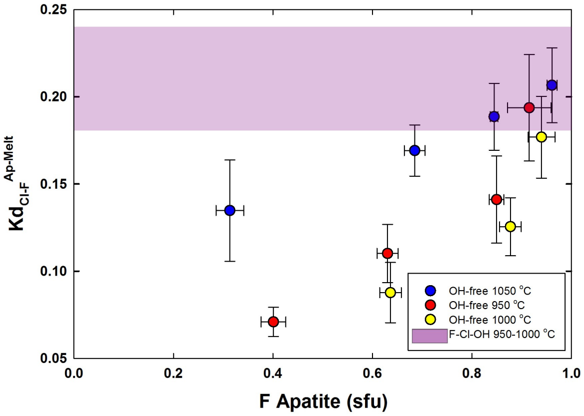

Figure 1. Plot of $K_{D_{Ap-Liq}}^{Cl-F}$ values vs. F structural formula units (sfu) in apatite. Error bars on the exchange K_D were derived from propagating the standard deviation of the mean from each average analysis through the K_D value. The shaded purple region represents the Cl-F exchange K_D determined by McCubbin et al., [14] for the F-Cl-OH system at 1 GPa.

In addition to apatite composition, temperature also appears to play a role in the partitioning behavior, where the highest T (1050 °C) displays the slowest rate of change in the K_D value, which is expected, although 950 °C and 1000 °C seem to display identical behavior within error.

Discussion: The results of this study indicate that apatite-melt partitioning behavior is affected by the mixing behavior of F, Cl, and OH in the apatite structure, as predicted by McCubbin et al., [14]. Furthermore, the exchange equilibria, which appeared to remain relatively constant over a wide range of apatite compositions at a fixed P, T, X_{melt}, and fO_2, are not immune to variability when F, Cl, and OH mix nonideally on the apatite X-site.

In addition, the results herein indicate that F becomes proportionally more compatible in apatite relative to Cl as apatite compositions become more Cl-rich. This behavior is likely due to the structural accommodation mechanism that allows for mixing of F and Cl in OH-free F-Cl apatite, which involves the establishment of an off-mirror F site within the X-site channels. This new site allows apatite to maintain hexagonal symmetry in space group $P6_3/m$ and minimize electron density by increasing F-Cl atomic distances in the channels [21]. Fluorine is crucial to this accommodation, so it is not surprising that F compatibility relative to Cl increases. At some point along the F-Cl join, the hexagonal symmetry breaks down and the b-axis doubles, resulting in monoclinic symmetry within space group $P2_1/b$. We anticipate that this transition occurs at >70% chlorapatite based on existing solution calorimetry data [7]. We anticipate this structural change to affect the exchange K_D value as well.

This work illustrates the importance of understanding the thermodynamic mixing properties of F, Cl, and OH in apatite before employing exchange K_D values for apatite-based melt hygrometry even when various intensive parameters (e.g., P, T, X_{melt}) are constrained.

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