

**PARTITIONING OF F AND Cl BETWEEN APATITE AND A SYNTHETIC SHERGOTTITE LIQUID (QUE 94201) AT 4 GPa FROM 1300 TO 1500 °C.** F. M. McCubbin<sup>1</sup>, J. J. Barnes<sup>1</sup>, K. E. Vander Kaaden<sup>2</sup>, and J. W. Boyce<sup>1</sup>, <sup>1</sup>NASA Johnson Space Center 2101 NASA Parkway mail code XI2 Houston, TX 77058 <sup>2</sup>Lunar and Planetary Institute, 3600 Bay Area Blvd, Houston, TX 77058 ([francis.m.mccubbin@nasa.gov](mailto:francis.m.mccubbin@nasa.gov)).

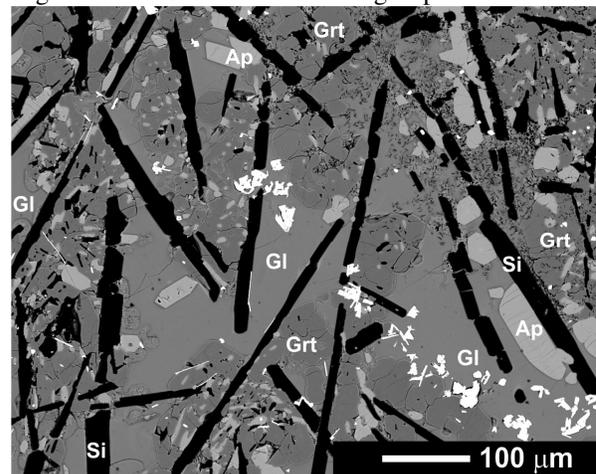
**Introduction:** Apatite [ $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl},\text{OH})$ ] is present in a wide range of planetary materials. Due to the presence of volatiles within its crystal structure (X-site), many recent studies have attempted to use apatite to constrain the volatile contents of planetary magmas and mantle sources [1–3]. In order to use the volatile contents of apatite to accurately 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 [e.g., 4–9], 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 [e.g., 8–13], 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]. However, McCubbin et al., [15] recently reported that the exchange coefficients 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 [5], and McCubbin et al. [15] reported substantial deviations in the Cl-F exchange  $K_d$  along the F-Cl apatite join that could be explained by the preferential incorporation of F into apatite.

In the present study, we assess the effect of apatite crystal chemistry on F-Cl exchange equilibria between apatite and melt at 4 GPa over the temperature range of 1300–1500 °C. The goal of these experiments is to assess the variation in the Ap-melt Cl-F exchange  $K_d$  over a broad range of F:Cl ratios in apatite. The results of these experiments could be used to understand at what composition apatite shifts from a hexagonal unit cell with space group  $P6_3/m$  to a unit cell with monoclinic symmetry within space group  $P2_1/b$ . We anticipate that this transition occurs at >70% chlorapatite based on solution calorimetry data [5].

**Experimental Methods:** The F-only and Cl-only mixes from [12] were used as starting materials for the present study. Each experiment for the present study was conducted under nominally dry conditions, although we did not actively dry the experiments, so we anticipate that water is present in the experiments. For all experiments, mixtures of the two powders (each

with a different F:Cl ratio) were packed into a molybdenum metal capsule.

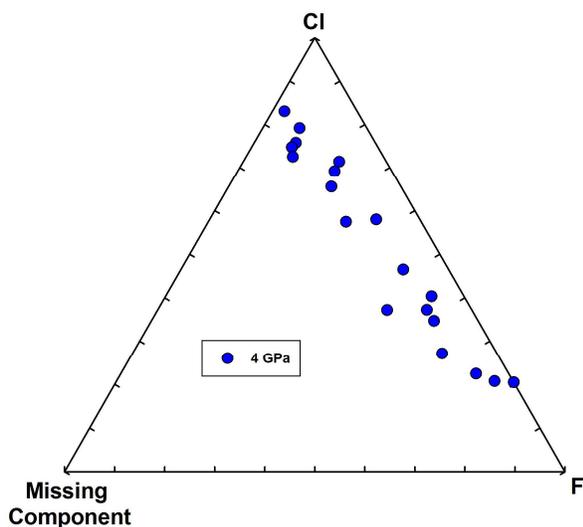
All experiments were conducted in a Walker-style multi-anvil device at the Institute of Meteoritics at the University of New Mexico. Experiments were conducted using the same parts, geometry and cell assembly as [16], although we used molybdenum capsules. Our experiments were run at 4.0 GPa and crystallization temperatures of 1300–1500 °C. Run durations were always 4.0 hours. Each experiment began with a 20–30 minute melting step at 1650 °C.



**Fig. 1** BSE image of the run product of an experiment conducted at 1300 °C and 4 GPa. Phase identification as follows: Gl – glass, Ap – apatite, Grt – garnet, Si – silica.

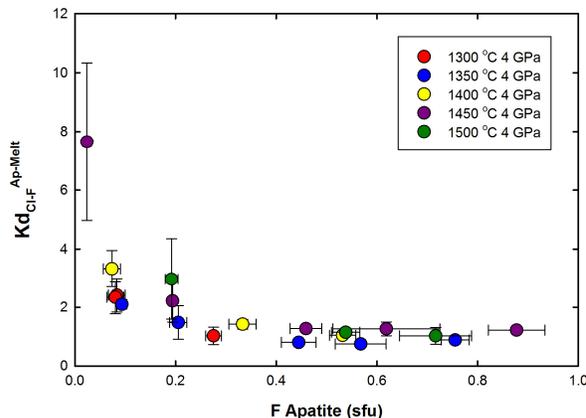
**Results:** Experimental charges were cast in epoxy and subsequently ground and polished for analysis by electron probe microanalysis (EPMA). All of the experiments consisted of several phases, including silicate melt and apatite. Apatite was the only phosphate mineral that crystallized in our experiments. Apatites were up to 40 microns in the shortest dimension (Figure 1), and every experiment had apatite that was in contact with silicate melt. Apatite-melt pairs in each sample were analyzed by EPMA, and a missing structural component in the apatites was calculated using the F and Cl data assuming the monovalent anion site in apatite summed to one structural formula unit. In total, we conducted 19 successful experiments.  $\text{H}_2\text{O}$  contents for our glasses and apatites have not yet been determined. Although  $\text{H}_2\text{O}$  was not added to the experiments, water contamination from a number of sources is possible given that we did not actively attempt to dry the samples. However, we are planning to conduct

analyses of our experimental apatite and glass for H<sub>2</sub>O using the nanoSIMS 50L housed at NASA Johnson Space Center prior to the completion of the present study. Importantly, many of the apatites from our experiments do not have their stoichiometric fill of F and Cl (Figure 2), indicating a missing structural component is present (up to 18 mol% of the apatite X-site). This missing structural component could be attributed to some combination of the anions OH<sup>-</sup>, O<sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, S<sup>2-</sup>, Br<sup>-</sup>, and I<sup>-</sup> and/or structural vacancies and/or structural H<sub>2</sub>O. At this point, we can only rule out S<sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, Br<sup>-</sup>, and I<sup>-</sup>. Although the most likely culprit for this missing component in terrestrial igneous systems is OH<sup>-</sup> [17], assumptions that the X-site is fully occupied by F, Cl, and OH can be erroneous as a possible O<sup>2-</sup> + vacancy substitution has been suggested for some synthetic and naturally occurring Cl-rich apatites [5, 18], like those in the present study. This issue highlights the importance of analyzing our nominally anhydrous experiments for H<sub>2</sub>O.



**Fig. 2** Ternary plot of apatite X-site occupancy for all of the experiments conducted during the present study.

Our EPMA data indicate that the Cl-F exchange coefficient between apatite and melt varies substantially as a function of apatite composition, namely the X-site occupant. In particular, the Cl-F exchange  $K_d$  increases substantially when F occupies less than 25% of the X-site (Figure 3). Furthermore, for the apatites that have >25% F in the apatite X-site, the Cl-F exchange  $K_d$  is relatively constant at a value of  $1.08 \pm 0.21$ . Notably, the Cl-F exchange  $K_d$  determined at 4 GPa and 1300–1500 °C is substantially greater than the Cl-F exchange  $K_d$  of  $0.21 \pm 0.03$  determined at 1.2 GPa and 950–1000 °C [12]. For apatites with less than 25% F in the apatite X site, the Cl-F exchange  $K_d$  increases with decreasing F with a maximum observed value of  $7.6 \pm 2.7$  at an apatite X-site fraction of 0.024 F (Figure 3).



**Fig. 3** Ap-melt, F-Cl exchange  $K_d$  for all of the experiments conducted during the present study as a function of the fraction of F in the apatite X-site.

**Discussion:** The changes we observe in the Cl-F Ap-melt exchange  $K_d$  at low abundances of F in apatite as well as the solution calorimetry data from [7] indicate that the transition from space group  $P6_3/m$  to space group  $P2_1/b$  occurs in apatite when F occupies less than 25% of the X-site. We plan to test this hypothesis by extracting apatites from our run products for analysis by single crystal XRD. In addition to a crystal chemical effect on Cl-F exchange equilibria between F-poor apatite and melt, we also observe an enhancement in the overall Cl-F exchange  $K_d$  value relative to studies at lower pressure and temperature. These results indicate that Cl and F have similar compatibility in apatite at 4 GPa and 1300–1500 °C. This behavior could help explain, in part, the Cl-rich nature of apatite in many terrestrial mantle xenoliths, while typical terrestrial basalts are dominated by F-OH apatites [17, 19–20].

**References:** [1] Boyce et al., (2010) *Nature*, 466, 466–469. [2] McCubbin et al. (2010) *PNAS*, 27, 11223–11228. [3] Patiño Douce and Roden (2006) *GCA*, 70, 3173–3196. [4] Candela (1986) *Geology* 57, 289–301. [5] Hovis and Harlov (2010) *Am Min* 95, 946–952. [6] Tacker and Stormer (1993) *GCA* 57, 4663–4676. [7] Tacker and Stormer, (1989) *Am Min* 74, 877–888. [8] Zhu and Sverjensky (1991) *GCA* 55, 1837–1858. [9] Brenan (1993) *EPSL* 117, 251–263. [10] Mathez and Webster (2005) *GCA* 69, 1275–1286. [11] Webster et al. (2009) *GCA* 73, 559–581. [12] McCubbin et al. (2015) *Am Min* 100, 1790–1802. [13] Boyce et al. (2014) *Science* 344, 400–402. [14] Toplis (2005) *Cont. Min. & Pet.* 149, 22–39. [15] McCubbin et al. (2016) *LPSC #1184* [16] Vander Kaaden et al. (2015) *GCA* 149, 1–20 [17] Piccoli and Candela (2002) *RiMG Phosphates* 255–292 [18] Jones et al. (2014) *GCA* 132, 120–140. [19] Filiberto and Treiman (2009) *Geology* 37, 1087–1090. [20] McCubbin and Jones (2015) *Elements* 11, 183–188.