

APATITE-MELT PARTITIONING IN BASALTIC MAGMAS: THE IMPORTANCE OF EXCHANGE EQUILIBRIA AND THE INCOMPATIBILITY OF THE OH COMPONENT IN HALOGEN-RICH APATITE. F. M. McCubbin¹, K. E. Vander Kaaden¹, R. Tartèse², E. S. Whitson¹, M. Anand^{2,3}, I. A. Franchi², S. Mikhail⁴, G. Ustunisik⁵, E. H. Hauri⁶, J. Wang⁶, and J. W. Boyce⁷ ¹Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131. ²Planetary and Space Sciences, The Open University, Milton Keynes, MK7 6AA, UK. ³Department of Earth Sciences, The Natural History Museum, London, SW7 5BD, UK. ⁴Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., N.W, Washington, DC 20015 ⁵Department of Earth and Planetary Sciences, American Museum of Natural History, New York, NY, U.S.A. ⁶Department for Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd., N.W, Washington, DC 20015 ⁷Department of Earth and Space Sciences, University of California, Los Angeles, CA, USA. (fmccubbi@unm.edu).

Introduction: The mineral 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, many recent studies have attempted to use apatite to constrain the volatile contents of planetary magmas and mantle sources [1-9]. 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., 10-14], 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 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. In the present study, we conducted apatite-melt partitioning experiments in a piston cylinder press at 1.0 GPa and 950-1000 °C on a synthetic martian basalt composition equivalent to the basaltic shergottite Queen Alexandria Range (QUE) 94201. These experiments were conducted to assess the effects of apatite composition on the partitioning behavior of F, OH, and Cl between apatite and basaltic melt.

Experimental Methods: Three powdered mixes were synthesized 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 prepared by first weighing silicates, oxides, $\text{Ca}_2\text{P}_2\text{O}_7$, $\text{Ca}(\text{OH})_2$, 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 $\text{Fe}^{3+}/\Sigma\text{Fe}$ 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 (undried starting materials and a talc cell), and mixtures of the three powders (each with a different F:Cl: H_2O ratio) were packed into a graphite or Mo 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 1.27 cm (diameter) 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 950-1000 °C and left to crystallize for 3.25-8.50 hours. The temperature of each experiment was controlled by a $\text{W}_3\text{Re}_{95}\text{-W}_{26}\text{Re}_{74}$ (Type C) thermocouple. At the end of each experiment, the run was rapidly quenched by shutting off the power to the system.

Methods/Results: Experimental charges were pressed into indium metal within 1” aluminum metal discs and polished for subsequent analysis by SIMS (6f and NanoSIMS) 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 the 6f to determine H_2O contents. NanoSIMS was subsequently used to analyze both melt and apatite in each of the experimental charges. The apatite in each sample was also analyzed by EPMA, in order to compare the F and Cl data (along with computed OH) to the nanoSIMS results. Glass compositions were also determined by EPMA to obtain F and Cl contents. The F, Cl, and H_2O contents of glass and coexisting apatites are presented in Table 1 for all 12 experiments based on the average of approximately 5-15 analyses. F and Cl analyses of all glasses are from EPMA unless noted with an asterisk, in which case they are from NanoSIMS. All H_2O abundances are from SIMS unless noted with an asterisk, in which case the amount of H_2O was computed by stoichiometry. F values for NanoSIMS and EPMA in apatite were very similar and within 2σ standard deviations, so the F value presented is an average value from both techniques with the exception of experiment Q1.010 for which only nanoSIMS data was

acquired. Chlorine data for apatite are from EPMA unless noted with an octothorp, in which case they are from NanoSIMS.

Table 1. F-Cl-H₂O contents of glass and apatite within experimental run products. All values are in wt.%

Exp #	F _{Gl}	Cl _{Gl}	H ₂ O _{Gl}	F _{Ap}	Cl _{Ap}	H ₂ O _{Ap}
Q1.007	0.08	0.32	2.57	1.51	1.66	0.62*
Q1.010	0.15 [#]	1.18 [#]	3.56	1.56	2.69 [#]	0.44
Q1.012	0.38	0.45	2.72	2.97	0.62	0.34
Q1.013	0.44	0.36	2.86	3.16	0.53	0.32
Q1.016	0.17	0.47	2.92	2.10	1.23	0.56
Q1.017	0.18	0.93	3.05	1.83	1.87	0.51
Q1.018	0.23	0.32	2.81	2.69	0.68	0.49
Q1.020	b.d.	1.37	3.26	b.d.	5.52	0.24
Q1.024	0.81	0.02	3.12	3.63	0.02	0.07*
Q1.057	0.30	2.14	3.01	1.61	2.86	0.26*
Q1.061	0.02	2.43	3.41	0.24	4.40	0.26
Q1.062	0.12	3.23	3.33	0.74	4.27	0.32*

All of the experiments contained relatively high water contents, which was expected from the use of talc-pyrex cells, undried starting materials, and unsealed capsules. From the data in Table 1, we can calculate apatite-melt partition coefficients for F (4.5-19), Cl (1-5), and H₂O (0.02-0.24). Although these are the first apatite-melt partitioning data reported for H₂O that were derived from the direct analysis of H₂O in both melt and apatite, previous studies have reported partitioning data for F and Cl (and H₂O estimated stoichiometrically). Previous studies reported apatite-melt partition coefficients as follows: F (3.4-40), Cl (0.8-4.5) [16-17].

It is important to note that F, Cl, and OH are essential structural constituents in the mineral apatite, so the partitioning behavior of the volatiles should deviate substantially from Henrian behavior of trace elements. Similar to the partitioning behavior of Fe and Mg between olivine and silicate liquids [19-20], the partitioning behavior of F, Cl, and OH between apatite and silicate melt are best described by an exchange coefficient (Equation 1) [21-22]:

$$K_{D_{Ap-Liq}^{F-H_2O}} = \frac{X_{Liq}^F \div X_{Ap}^F}{X_{Liq}^{H_2O} \div X_{Ap}^{H_2O}} \quad (1)$$

where X_{Liq}^F is the wt.% F in the melt, X_{Ap}^F is the wt.% F in the apatite, $X_{Liq}^{H_2O}$ is the wt.% H₂O in the melt, and $X_{Ap}^{H_2O}$ is the wt.% H₂O in apatite. These exchange coefficients can change as a function of melt composition, pressure, temperature, apatite composition, and oxygen fugacity. Therefore, the available data on apatite-melt partitioning should be considered very limited from this study at 1.0 GPa and 950-1000 °C.

It is also important to note that H₂O is highly incompatible in apatite compared to F and Cl under these conditions ($K_{D_{Ap-Liq}^{F-H_2O}} = 0.011 - 0.016$; $K_{D_{Ap-Liq}^{Cl-H_2O}} = 0.02 - 0.08$).

Discussion: Many have tried to use apatite as a tool for quantifying volatile abundances in parental magmatic liquids (X) and magmatic source regions (Y) from apatite compositions; however these models typically require that volatile partitioning in apatite is similar to trace elements using the following equations, which are all derived from the general batch melting equation and assume equilibrium crystallization:

$$X_{H_2O}^{PM} = \frac{(1-F_P^{Saturation}) \times X_{H_2O}^{Ap}}{D_{H_2O}^{Ap-Melt}} \quad (2)$$

$$Y_{H_2O}^{MS} = \frac{(1-F_P^{Saturation}) \times F_{Source}^{Partial Melting} \times X_{H_2O}^{Ap}}{D_{H_2O}^{Ap-Melt}} \quad (3)$$

Where $X_{H_2O}^{PM}$ is the H₂O content of the parental melt, $Y_{H_2O}^{MS}$ is the H₂O content of the mantle source, $F_P^{Saturation}$ is the degree of crystallization before apatite saturation, $X_{H_2O}^{Ap}$ is the amount of H₂O in apatite (wt.%), $D_{H_2O}^{Ap-Melt}$ is the apatite-melt partition coefficient for H₂O, and $F_{Source}^{Partial Melting}$ is the degree of partial melting that occurred to produce the parental melt.

However, as discussed herein, the partitioning data between apatite and silicate melt should be treated as exchange equilibria because they are essential structural constituents in apatite. Consequently, equations (2) and (3) above require slight modification before quantification of water contents. Specifically, either the F or Cl abundances of the melt at the time of apatite crystallization is needed, which adds a degree of complexity to quantification of melt volatile abundances from apatite alone.

In place of the term $\frac{X_{H_2O}^{Ap}}{D_{H_2O}^{Ap-Melt}}$ in (2) and (3) above, which equals $X_{Liq}^{H_2O}$ from (1), (4) should be used instead to estimate the water contents of a parental liquid or magmatic source region from apatite:

$$\frac{X_{Liq}^F \times X_{Ap}^{H_2O}}{K_{D_{Ap-Liq}^{F-H_2O}} \times X_{Ap}^F} = X_{Liq}^{H_2O} \quad (4)$$

Cl could be used in place of F in equation (4).

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