

APPLICATION OF APATITE HYGROMETRY TO MARTIAN APATITES: WHAT HAS CHANGED IN LIGHT OF NEW APATITE-MELT PARTITIONING MODELS FOR F, Cl, AND OH? F. M. McCubbin¹ and J. W. Boyce¹ ¹Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131. ²Department of Earth, Planetary, and Space Sciences, UCLA Box 951567, Los Angeles, CA 90095-1567. fmccubbi@unm.edu

Introduction: The mineral apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$] 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. Consequently, many have relied on determining empirical partitioning relationships of the volatile components F, Cl, and OH between apatite and silicate melt [i.e., 14, 15, 16-17]; however, a large range in D values was observed.

This large range in values is a direct consequence of F, Cl, and OH being essential structural constituents in apatite, therefore mineral-melt D values for F, Cl, and OH in apatite should not be used to determine the volatile abundances of coexisting silicate melts. However, the ratio of D values (exchange coefficient) for each volatile pair (F-OH, F-Cl, and Cl-OH) displays much less variability [18]. To implement the exchange coefficient to determine the H_2O content of a silicate melt at the time of apatite crystallization, the H_2O abundance of the apatite, an apatite-melt exchange K_d that includes OH (either F-OH or Cl-OH), and the abundance of F or Cl in the apatite and F or Cl in the melt at the time of apatite crystallization are also needed (F if using the F-OH K_d and Cl if using the Cl-OH K_d), which further complicates the implementation of apatite hygrometry. Furthermore, exchange coefficients may vary as a function of temperature, pressure, melt composition, apatite composition, and/or oxygen fugacity, so the effects of each of these parameters must be investigated fully before these exchange coefficients are applied broadly to determine volatile abundances of melt from apatite volatile abundances. Nonetheless, we assess what these exchange K_d values imply about martian magmatic H_2O abundances.

Importance of using an apatite-melt exchange K_d over a D value: The range in D values for OH in

[18] is 0.07-0.24, indicating OH behaves incompatibly with respect to apatite; however, these results do not reflect the entire range in apatite-melt D values for OH that can arise as a consequence of the apatite-melt exchange equilibrium model. Although the abundances of F, Cl, and OH in apatite are fixed based on the stoichiometry of the X site in apatite, which typically sums to one structural formula unit, the F, Cl, and OH abundances in the silicate melt can vary from zero to their respective levels of saturation. As a result, the lower the concentration of F, Cl, and OH in the melt, the higher the required apatite-melt D that results in order to maintain a full X-site in apatite and a constant ratio of D values for F, Cl, and OH. Figure 1 illustrates the possible range of apatite-melt D values for OH as a function of melt F and H_2O abundance. This plot indicates that apatite-melt D values for OH could be much greater than one, and that OH may behave compatibly in apatite under certain conditions. Additional experiments that address the minimum abundance of volatiles in the melt to stabilize apatite are required to assess the true upper limits on the apatite-melt D values for F, Cl, and OH.

Many studies have attempted to estimate a conservatively high apatite-melt D value for OH and use this value to estimate “minimum H_2O abundances” in the melt from which the apatites crystallized, including for Mars [e.g., 19]. The D value that was typically used for this purpose is 0.25, which was calculated by [6] from data in [16]. Based on the apatite-melt partitioning results of [18], and assuming it is appropriate to apply those results, the conservative estimate of an apatite-melt D value for OH of 0.25 is only a valid assumption if the abundance of F in the melt is ≥ 2000 ppm at the time of apatite crystallization (Figure 1). Lower abundances of F in the melt at the time of apatite saturation would require higher apatite-melt D values for OH.

The entire compositional range illustrated in Figure 1 does not necessarily reflect reality because at some point the abundance of volatiles in the melt will be insufficient to stabilize apatite at phosphate saturation and merrillite will form instead. The stability of merrillite is primarily governed by halogen fugacity and the ratio of P to the halogens [8-9, 20]. Interestingly, merrillite stability seems to be largely unaffected by the abundance of H_2O in the melt [21]. Additional ex-

perimental work to determine the phase boundary between merrillite and apatite stability (with respect to halogen and H₂O fugacities) in silicate melts is required to place upper limits on apatite-melt D values for F, Cl, and OH.

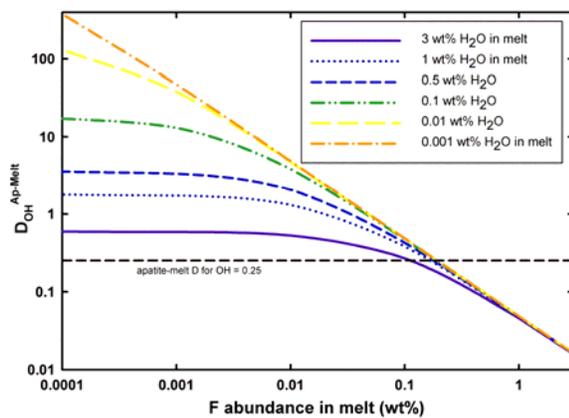


Figure 1. Model illustrating how the D value for OH can vary greatly as a function of F and H₂O abundance in the melt. This model was constructed using the F-OH exchange K_d value and the following two assumptions 1) the apatite that forms from the melt is stoichiometric with no X-site vacancies and 2) apatite is the stable phosphate mineral that would form from the melt. The commonly used apatite-melt D value for OH of 0.25 is plotted for reference.

Previous estimates of magmatic H₂O in martian magmas from apatite-melt D values: McCubbin et al., 2012 [19] used an apatite-melt D value of 0.25 to determine the H₂O abundances of parental magmas for the enriched (represented by Shergotty) and depleted (represented by QUE94201) shergottites. That study determined that parental melts contained approximately 730-2870 ppm H₂O and the source regions contained approximately 73-290 ppm H₂O.

New Estimates of magmatic H₂O in martian magmas from apatite: As discussed earlier, in order to determine the parental magmatic abundances of H₂O from apatite, one must know F, Cl, and OH contents of the apatite, the appropriate exchange K_d values, as well as the amount of F or Cl in the bulk rock. Because Cl is more susceptible to degassing than F [22], it is more robust to conduct these estimates with F. There is limited data available for halogen abundances of martian meteorites, but data is available for both Shergotty (52 ppm F) and QUE94201 (40 ppm F), two samples for which we have reliable apatite compositions [i.e., 19].

For Shergotty (52 ppm F), the apatite contained 1.3 wt.% F, 2.1 wt.% Cl, and 0.62 wt.% H₂O. Using the F-OH exchange K_d of 0.01 (i.e., $D_{OH/DF}$) [18], the parental melt of Shergotty has approximately 2500 ppm H₂O, with an approximated source region that has 250

ppm H₂O. These values fortuitously match those reported by [19] for Shergotty.

For QUE94201 (40 ppm F), the apatite contained 2.3 wt.% F, 0.9 wt.% Cl, and 0.43 wt.% H₂O. Using the F-OH exchange K_d of 0.01 (i.e., $D_{OH/DF}$) [18], the undegassed QUE94201 bulk rock would have had approximately 800 ppm H₂O, which is consistent with the lower range reported by [19]. Importantly, QUE94201 is not a primary melt composition, so estimating the amount of water in its parental melt and source is not possible; however it can be estimated using a primary primitive depleted shergottite melt Yamato980459. SIMS analysis of an olivine-hosted melt inclusion revealed that it has 10 ppm F [23], which is a factor of 4 lower than the bulk rock F content of QUE94201. If this dilution factor is applied here, it would imply that a parental melt for QUE94201 would be approximately 200 ppm H₂O, which is similar to SIMS analyses for H₂O in the Yamato980459 melt inclusions (146 ppm H₂O [23]). Assuming 20-40% partial melting to produce Yamato980459 [23], it would imply that the depleted shergottite source region has approximately 40-80 ppm H₂O, which is up to 45% lower than what was estimated by [19] and at the upper range of what was reported by [23]. These results indicate that the depleted source region for the shergottites may in fact be drier than the enriched shergottite source region, which could explain some of the other observed differences between the two geochemical groups (e.g., elevated oxygen fugacity for the enriched shergottites [24]). Nonetheless, the martian interior seems to have on the order of mid-high 10²'s to low 100³'s of ppm H₂O, which is similar to portions of Earth's interior.

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