

**EQUILIBRIUM-EXCHANGE APATITE HYGROMETRY AND A SOLUTION TO THE LUNAR APATITE PARADOX.** J. W. Boyce<sup>1</sup>, S. M. Tomlinson<sup>1</sup>, F. M. McCubbin<sup>2</sup>, J. P. Greenwood<sup>3</sup>, and A. H. Treiman<sup>3</sup>,  
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**Introduction:** The prevailing model of Moon formation—the giant impact hypothesis [1]—is constrained in part by the depletion of volatile elements. Recent observations of elevated H [2-5] in lunar materials have implications for the formative conditions of the Earth and Moon [6].

Apatite—Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(F,Cl,OH)—may provide the most global record of lunar volatiles, one that integrates over the widest range of sample ages, localities, and petrogenetic environments. This increased coverage comes at the expense of increased ambiguity: abundances of volatiles in apatite are difficult to interpret. Nevertheless, the contrast between lunar apatites and their host rocks is indisputable: apatites in mare basalts are commonly very rich in H—to the point that they cannot be distinguished from apatites in terrestrial mafic rocks [4]. However, the host rocks of these H-rich lunar apatites are indisputably volatile depleted. These two observations make up what we informally term the “*Lunar Apatite Paradox*”.

**Henrian Partitioning:** The explanation initially offered for high hydrogen abundances in lunar apatite was that crystallization of nominally anhydrous minerals (NAMs) from basaltic magmas had concentrated H into the residual melt [2-4]. This model treats H as a trace element that is incompatible in olivine, pyroxene, and plagioclase, so the abundance of H in the residual melt should increase during crystallization. Apatite is thought to only saturate after >90% crystallization of primitive lunar melts [3, 7], and conventional wisdom would thus suggest that apatite would capture this later stage of magma evolution when the melt would have higher H abundances. Experiments [8-11] combined with measurements of H<sub>2</sub>O<sub>ap</sub> suggest equilibration with very H-rich magmas [ $\leq 3.4$  wt % H<sub>2</sub>O; 12].

Fluorine and Cl are approximately equally incompatible as H in nominally anhydrous minerals [13-17], so crystallization of NAMs should enrich both basalts and their apatites in H, F, and Cl. Simultaneous enrichment of H, F, and Cl in apatite is of course impossible as these elements are constrained by stoichiometry to add up to ~unity in molar occupancy [18].

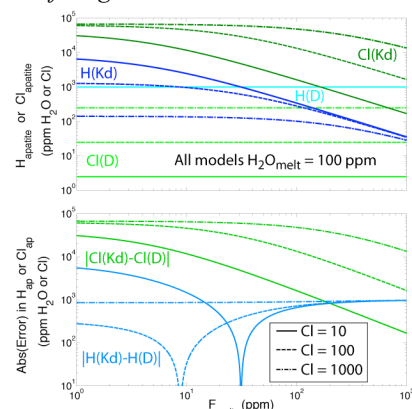
**Non-Henrian Modeling:** It is more appropriate to treat H, F, and Cl in apatite as major elements, comparable to the way one treats partitioning of Mg and Fe between olivine and melt. In the equilibrium exchange

model:  $H_{\text{apatite}} + F_{\text{melt}} \rightleftharpoons F_{\text{apatite}} + H_{\text{melt}}$ , we can write an equation for the equilibrium reaction:

$$K_{\text{ap/m}}^{\text{FH}} = \frac{(F_{\text{ap}})(H_{\text{m}})}{(F_{\text{m}})(H_{\text{ap}})}$$

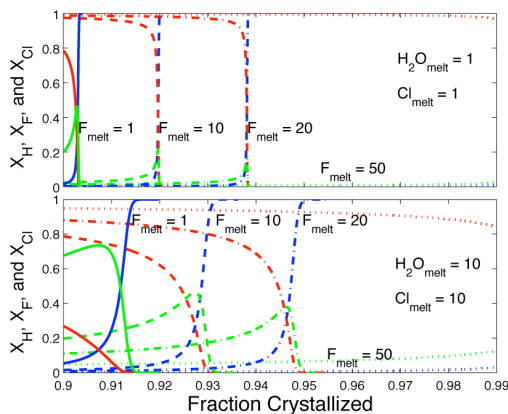
The difference between H<sub>ap</sub> derived from Henrian and equilibrium exchange models is significant, with the two agreeing only for a single value of F<sub>melt</sub>. Note that the hydrogen content of an apatite is a function of Cl<sub>melt</sub> in addition to F<sub>melt</sub>. Increasing Cl<sub>melt</sub> by a factor of 10 decreases H<sub>apatite</sub> by as much as nearly an order of magnitude, especially at low F<sub>melt</sub> (Figure 1).

In this model, the ratios of H, F, and Cl in the melt (not the absolute values) control the H, F, and Cl content of an apatite (Figure 1). These ratios only change by ~1-20% during 90% fractional crystallization of NAMs, depending on the choice of D and assemblage. Thus, the increase in abundance of H in the evolving melt is invisible to apatite, the composition of which is controlled by the ratios of H/(H+F+Cl). *Under these conditions, apatite is quite insensitive to the increasing water content around it, a troubling conclusion for those who wish to use apatite as a monitor of the abundance of magmatic volatiles.*



**Figure 1. Apatite H<sub>2</sub>O and Cl as a function of melt F<sub>melt</sub> and Cl<sub>melt</sub> for H<sub>melt</sub> = 100 ppm H<sub>2</sub>O as predicted by Henrian and non-Henrian models of H and Cl partitioning. A) Models using K<sup>FH</sup> = 50, K<sup>FCl</sup> = 4, and K<sup>ClH</sup> = 50/4 (dark blue and green) compared to Henry's law models (light blue and green) which do not vary as a function of F<sub>melt</sub>. B) Difference between Henrian and non-Henrian models: Note that range of F<sub>melt</sub> where both models yield the same Hap is small and also a function of Cl<sub>melt</sub>.**

When we add apatite to the crystallizing assemblage in our model, we now have a mineral into which significant—and variable—quantities of H, F, and Cl will enter. Given that F is significantly more compatible than H or Cl in apatite, adding apatite to the fractionating assemblage initially has a more dramatic effect on the abundance of F than of H or Cl, and as such can cause dramatic changes to the H/(H+F+Cl) and Cl/(H+F+Cl) ratios (Figure 2). With initial  $F \leq 20$  ppm, apatite that grows at  $\geq 94\%$  fractional crystallization evolves to 1.79 wt.%  $H_2O$  (100% OH<sup>-</sup> occupancy), an increase of a factor of  $\sim 1000$  over the initial abundance. Pure OHapatite can be produced during late stage crystallization even in cases where  $H_2O_{melt}$  is very low, provided that apatite is still saturated in the

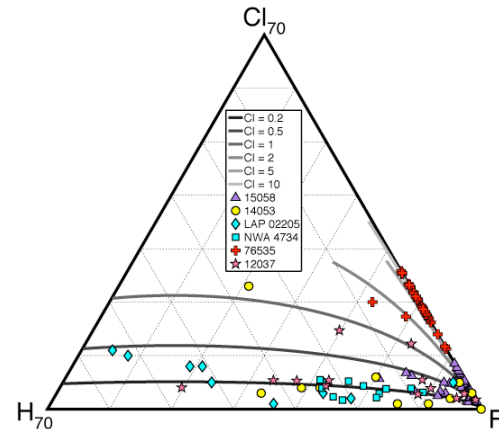


**Figure 2. Mole fraction H, F, and Cl occupancy in apatite derived from equilibrium exchange models of volatile evolution in melt during fractional crystallization of an assemblage containing apatite.**

melt after consuming all the F and Cl.

Previous workers have observed systematic co-variations of Ce, La, SiO<sub>2</sub>, Fe, and S within single crystals [2]. Co-variations in both volatile (H, Cl) and non-volatile (REEs) elements suggests that a common process such as fractional crystallization is operating during the period when the apatite is growing. Very significantly, F is often decreasing relative to H and Cl from core to rim, which is only consistent with a fractionating assemblage that includes apatite.

**Conclusions:** A wide range of magmatic H/F/Cl ratios is not required to explain the entire range of lunar apatite compositions seen in Figure 3: If we vary the degree of crystallization and Cl content of the magma, we can easily reproduce all the features seen in this diverse suite of natural lunar apatites, *even for constant  $H_{melt}$  and  $F_{melt}$* . Variably water-rich and Cl-poor apatite such as those from LAP-paired samples can be generated in this model, provided that Cl contents are less than 0.5 ppm (relative to  $F=10$  ppm and  $H_2O = 1$  ppm). The shorter, Cl-rich trend of 76535 is



**Figure 3. Model curves in truncated H-F-Cl space compared to data from literature. Only Cl content and degree of crystallization need be varied to explain the wide range of lunar apatite compositions observed.**

reproduced—for the same degree of crystallization—in models with  $\geq 5$  ppm Cl, and the same F and  $H_2O$ .

As it is not required that late-stage  $H_2O_{melt}$  contents be elevated in order to explain elevated  $H_2O_{ap}$ , hydrogen-rich apatite cannot be cited as evidence for elevated  $H_2O_{melt}$  *a priori*. This permits reconciliation of H-rich apatites with the high temperatures and associated volatile depletion required by the giant impact hypothesis [1], as well as the <sup>37</sup>Cl-enrichment in lunar materials first noted by [19]. Olivine-hosted melt inclusions in the A17 orange glasses [5] must now stand alone as the only geochemical evidence for any portions of the interior of the Moon being more than damp.

**References.** 1. Hartmann, W.K. and D.R. Davis, 1975, *Icarus*, 24, 504-515. 2. Greenwood, J.P., et al., 2011, *Nat. Geosci.*, 4, 79-82. 3. McCubbin, F.M., et al., 2010, *PNAS*, 107, 11223-11228. 4. Boye, J.W., et al., 2010, *Nature*, 466, 466-469. 5. Hauri, E.H., et al., 2011, *Science*, 10.1126/science.1204626. 6. Pahlevan, K. and D.J. Stevenson, 2007, *EPSL*, 262, 438-449. 7. Sha, L.-K., 2000, *GCA*, 64, 3217-3236. 8. Webster, J.D., C. Tappen, and C. Mandeville, 2009, *GCA*, 73, 559-581. 9. Mathez, E. and J. Webster, 2005, *GCA*, 69, 1275-1286. 10. Huh, M., et al., 2011, *AGU Fall*, 1, 2534. 11. Vander Kaaden, K., et al., 2012, *LPSC*, 43, 1247. 12. Tartese, R. and M. Anand, 2013, *EPSL*, 361, 480-486. 13. Hauri, E.H., G.A. Gaetani, and T.H. Green, 2006, *EPSL*, 248, 715-734. 14. O'Leary, J.A., G.A. Gaetani, and E.H. Hauri, 2010, *EPSL*, 297, 111-120. 15. Hirschmann, M.M., 2006, *Ann. Rev. of Earth and Planetary Sci.*, 34, 629-653. 16. Beyer, C., et al., 2012, *EPSL*, 337-338, 1-9. 17. Fabbriozio, A., et al., 2013, *GCA*, 18. Boyce, J.W., J.M. Eiler, and M.C. Channon, 2012, *AM*, 97, 1116-1128. 19. Sharp, Z.D., et al., 2010, *Science*, 329, 1050-1053.