

MAGMATIC DEGASSING IN PLANETARY BODIES: WHAT APATITE CAN TELL US H. Nekvasil¹, F. M. McCubbin² and G. Ustunisik¹, ¹Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100 Hanna.Nekvasil@sunysb.edu, ² Institute of Meteoritics, 1 University of New Mexico, MSC03-2050 Albuquerque, NM 87131 fmccubbi@unm.edu

Introduction: The use of apatite to assess magmatic contents of halogens and water is becoming increasingly feasible through refined SIMS and electron microprobe analysis. The recent successes of a variety of workers [1-4] in detecting measurable amounts of OH in lunar apatite has opened the door to investigating magmatic volatile abundances in planetary materials devoid of the typical volatile-rich minerals of terrestrial igneous assemblages. An important goal of such studies is to assess the bulk volatile content of the planetary body; however, even the extrapolation of apatite volatile abundances to those of the primary magma is complicated by the fact that apatite is commonly a late-crystallizing mineral. By the stage of apatite saturation, the residual melt compositions may have been strongly affected by crystallization and some extent of open- or closed-system degassing. Not only is volatile partitioning between apatite and melt affected by volatile concentration, e.g., [5] for the case of Cl, but the fluid composition (particularly relative halogen concentrations) may also be affected because of changes in Cl solubility as the melt evolves compositionally due to crystallization [6]. These problems complicate retrieval of reliable instantaneous magmatic volatile contents, to say nothing of parental magma volatile contents.

In the simplest case of crystallization without degassing, quantification of parental magma concentrations requires a reasonable estimate of degree of crystallization from careful petrography. This will be more uncertain if fractionation took place at some stage of the magmatic history and material was left behind. Further complicating back-calculation of parental magma volatile content is the possibility of fluid loss. Fluid saturation either at or above the solidus temperature is inevitable in volatile-bearing melts that undergo extensive crystallization. Because apatite is commonly a late-stage mineral it may have crystallized from melt that suffered extensive loss of volatiles. Furthermore, magmas that ascend to shallow levels slowly enough to nucleate bubbles may degas through first boiling, without extensive crystallization. In planetary bodies without plate margin tectonics or extensive meteorite bombardment, crustal mixing will be limited and the preponderance of surface rocks will have had at least a late-stage low-pressure history, thereby increasing the probability that the magma from which they formed underwent some extent of degassing.

As a first stage towards understanding the effects of crystallization and degassing history on apatite compositions, we are looking at what the apatites themselves have recorded about degassing history. Ideally, this would involve studies of zoned apatite coupled with careful petrogenetic analysis to assess the crystallization stages of the apatite. However, few coupled studies of this nature exist. Nonetheless, the multiple SIMS analyses of apatite in three lunar samples of [1] provide invaluable information for assessing whether lunar apatite can preserve information on its degassing history.

Variation in volatile contents in lunar apatite:

SIMS analysis of apatites from high-Al mare basalt 14053, from an alkali suite clast from 15404, and from an olivine gabbro cumulate lunar meteorite (NWA 2977) show significant compositional variability within the same sample and sometimes within the same apatite grain that extends beyond the published analytical uncertainties [1]. The variations are not random, but show a systematic path. The data on apatite in 14053, 16 and 15404, 51 indicate a path of first strongly decreasing water content at nearly constant Cl content, followed by a major drop in Cl content. The F content rises throughout both segments of the Cl path. Such a path is permissive, albeit not definitive, in the variation of the two available data points for NWA 2977 apatite. These paths cannot be explained by simple closed-system fluid-undersaturated crystallization, but rather are strongly suggestive of degassing.

Implications for magmatic degassing:

The instantaneous magmatic volatile content can be approximated for each apatite analysis using published volatile partition coefficients for water, F, and Cl between apatite and basaltic melt ([5], [1]). Using these simple partition coefficients, the changes in magmatic volatile contents reflect the changes observed in the apatites. If the OH loss at constant Cl is accepted at face value, this would suggest loss of almost pure water. However, if this loss is a result of second boiling, then two opposing processes would have taken place. Crystallization of nominally volatile-free minerals would increase the Cl content of the residual melt, while fluid loss would decrease the Cl content. The relative role of these opposing processes would dictate the actual change observed. The increase in absolute F content in the melt confirms the process of second boiling as having played a role in modifying the volatile contents of the magmas from which the apatite crystallized in both

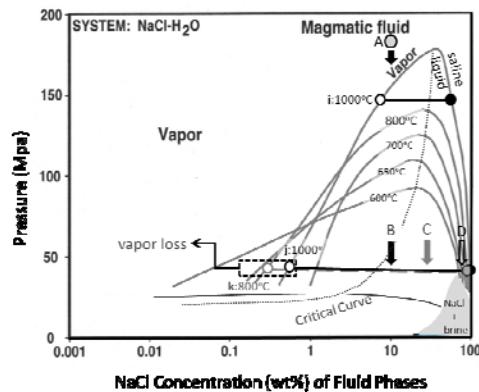
14053 and 15404. This increase is consistent with crystallization, and hence, crystallization-induced second boiling, since first boiling would result only in a decrease of the abundance of F.

Mass balance constraints: In their study of diffusion profiles in lunar glass beads, [7] approximated a loss of 45 wt% F during low-pressure degassing. [10] noted a loss of 59% F to a fluid during low pressure degassing experiments of a synthetic 14053 lunar melt composition. Mass balance calculations were conducted using this latter value and the assumption that apatite is the only volatile-bearing mineral and has a maximum abundance of 2 wt% of the system. The percentage loss of a volatile from the melt (to a fluid) is based on the decrease relative to the concentration if the volatile were to increase incompatibly in the melt during crystallization of anhydrous phases (minus the amount tied up in apatite). In this way, the net increase in F content of the melt from 7300 to 8700 ppm is obtained by a combination of 67.7% crystallization and 59% loss of F to a fluid. (Note: The percentage of crystallization computed is based on the interval given; there may have been more crystallization earlier to get to the 7300 ppm concentration of F.) Over this same crystallization interval, the net decrease in Cl is calculated to result from an 88 wt% loss of Cl to the fluid (coupled with the 67.7% crystallization). This is remarkable agreement with the 89.1 ± 2.4 obtained during experimental degassing [10].

The Cl loss from the melt is not linear, however. Much of this crystallization (to 66.3% crystallinity) occurs with little net change in Cl content but strongly decreasing water content in the melt. The loss of Cl during this dehydration stage is computed to be 66.8% (of the Cl content that would arise from this crystallization minus the amount tied up in apatite at this stage). The strong decrease in Cl content of the melt from 5640 to 2120 ppm during the second stage takes place during the remaining 1.4% crystallization and involves 24% loss of the overall Cl content that would arise from an incompatible increase during 67.7% crystallization using the final apatite compositions.)

Constraints on the degassing process: Magmas with low water contents or those undergoing rapid ascent may retain their water and halogens to low pressures. Upon crystallizing, either a single fluid or a vapor + saline liquid assemblage will exsolve. Model systems such as NaCl-H₂O, e.g., [8], provide invaluable insights into the compositions of such phases as well as degassing pathways. Based on the extensive OH loss with little change in Cl content recorded in the lunar apatite discussed, it is likely that this single fluid or vapor is very water-rich, in keeping with the width of the two-phase region at low pressures (Fig. 1).

Figure 1. Modified from [8] showing the water-rich nature of low pressure fluids and the increase in salinity upon loss of the water-rich vapor phase (B-D). Once the bulk fluid composition reaches D, only a brine exsolves.



The two-phase region makes it possible for a degassing path to involve early production and loss of water-rich vapor, the production of saline liquid in increasing abundance from the Cl lost to the fluid during the dehydration phase, retention of saline liquid/brine followed by loss of a brine once the bulk H₂O:Cl ratio shifts to the brine limb of the solvus. It is this loss of a brine that would be reflected by the sharp decrease in Cl content observed in the apatite.

Implications for Cl isotopes: [9] noted that lunar samples show a large range of $\delta^{37}\text{Cl}$ values from -1 to $+24\text{\textperthousand}$. They indicated that the enrichment in $\delta^{37}\text{Cl}$ is inconsistent with loss of HCl and more consistent with loss of metal chlorides and concluded that lunar magmas could not have had much water. However, the degassing pathways evidenced by the apatites studied here would produce a range of chlorine isotopic compositions, from little fractionation during the primary stage of dehydration when presumably HCl is produced in addition to water vapor, to the late-stage heavy enrichment upon loss of highly saline brine under very low water conditions. We therefore maintain that the heavy enrichment does not imply an anhydrous Moon but rather a solvus controlled degassing path involving late-stage loss of brine; however future work on mixed volatile fluid compositions at very low oxygen fugacity, consistent with lunar magmatism (i.e., IW -1 to -2), is needed to assess this further.

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