

THE SECOND CONFERENCE ON THE LUNAR HIGHLANDS CRUST AND NEW DIRECTIONS

**Degassing pathways of Cl-, F-, H-, and S-bearing magmas near the lunar surface:
Implications for the composition and Cl isotopic values of lunar apatite†**

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ABSTRACT

Experimental degassing of H-, F-, Cl-, C-, and S-bearing species from volatile-bearing magma of lunar composition at low pressure and f_{O_2} close to the quartz-iron-fayalite buffer (QIF) indicates that the composition of the fluid/vapor phase that is lost changes over time. A highly H-rich vapor phase is exsolved within the first 10 min of degassing leaving behind a melt that is effectively dehydrated. Some Cl, F, and S is also lost during this time, presumably as HCl, HF, and H₂S gaseous species; however much of the original inventory of Cl, F, and S components are retained in the melt. After 10 min, the exsolved vapor is dry and dominated by S- and halogen-bearing phases, presumably consisting of metal halides and sulfides, which evolves over time toward F enrichment. This vapor evolution provides important constraints on the geochemistry of volatile-bearing lunar phases that form subsequent to or during degassing. The rapidity of H loss suggests that little if any OH-bearing apatite will crystallize from surface or near surface (~7m) melts and that degassing of lunar magmas will cause the compositions of apatites to evolve first toward the F-Cl apatite binary and eventually toward end-member fluorapatite during crystallization. During the stage of loss of primarily H component from the melt, Cl would have been lost primarily as HCl, which is reported not to fractionate Cl isotopes at magmatic temperatures (Sharp et al. 2010). After the loss of H-bearing species, continued loss of Cl would result in the degassing of metal chlorides, which have been proposed as a mechanism to fractionate Cl isotopes (Sharp et al. 2010). After the onset of metal chloride degassing, the $\delta^{37}\text{Cl}$ of the melt would necessarily increase to +6 (82% Cl loss), +8 (85% Cl loss), and +20‰ (95% Cl loss) at 1, 4, and 6 h, respectively, which was approximated using a computed trajectory of $\delta^{37}\text{Cl}$ values in basalt during degassing of FeCl₂. This strong enrichment of ^{37}Cl in the melt after metal chloride volatilization is fully consistent with values measured for the non-leachates of a variety of lunar samples and would be reflected in apatites crystallized from a degassing melt. Our results suggest that a range in $\delta^{37}\text{Cl}$ from 0 to >20‰ is expected in lunar apatite, with heavy enrichment being the norm. While 95% loss in the initial Cl content of the melt (280 ppm Cl left in the melt) would cause an increase to +20‰ in $\delta^{37}\text{Cl}$, the ability to measure this increase in a lunar sample is ultimately dependent upon the starting Cl abundances and whether or not a mechanism exists to concentrate the remaining Cl such that it can be subsequently analyzed with sufficient accuracy. Therefore, the higher the starting Cl abundances in the initial melts, the heavier $\delta^{37}\text{Cl}$ values that can be measurably preserved. Importantly, such enrichments can occur in spite of high initial hydrogen contents, and therefore, our experiments demonstrate that elevated values of $\delta^{37}\text{Cl}$ cannot be used as supporting evidence for an anhydrous Moon. Furthermore, if the H-bearing vapor has a significant H₂ component, this process should also result in strong enrichment of δD in the residual magmas that reach the lunar surface or near-surface environment. Apatites within some mare basalts exhibit elevated δD of 1000 ‰ depending on the initial value (Tartese and Anand 2013) in addition to the $\delta^{37}\text{Cl}$ values, but elevated $\delta^{37}\text{Cl}$ values are accompanied by only modest enrichments in δD in apatites from samples of the highlands crust (McCubbin et al. 2015a).

Keywords: Experimental degassing, lunar magmas, magmatic volatiles, apatite, chlorine isotopes, hydrogen isotopes