

HALOGEN SYSTEMATICS DURING CRYSTALLIZATION OF THE CHASSIGNITES. P. A. Giesting¹ and J. Filiberto¹, ¹Southern Illinois University, 1259 Lincoln Drive, MC 4324, Carbondale, IL 62901 (giesting@siu.edu, filiberto@siu.edu).

Introduction: Magmatic volatiles are a crucial input to terrestrial planetary atmospheres. The amount and relative proportions of volatile elements, including H, C, F, S, and Cl, in the interiors of the Earth and Mars may have been quite different [1-4]; indeed, a great deal of evidence has been found that shows enrichment of the halogens relative to H₂O in Martian minerals compared to terrestrial equivalents, and therefore most likely also in the magmas that formed them [5-8]. However, just as on Earth, these volatile ratios may vary substantially both spatially and with time. In this study, we use the phases kaersutite (amphibole), apatite (phosphate), and biotite (mica) to examine the changes in halogen ratios during the late-stage cooling history of the chassignites (Chassigny and NWA 2737).

Methods: We surveyed published analyses of halogen and OH contents of hydrous minerals from the chassignites and compared them to analyses of glasses in olivine-hosted melt inclusions [9, 10]. Kaersutite and biotite are found in melt inclusions [10-16], while apatite is found in both melt inclusions and mesostasis [17, 18]. We did not filter any analyses.

Using chemical models [10, 19-24] for volatile partitioning in these minerals from their parental melts, and between melts and (possibly hypothetical) fluids [24, 25], we calculated volatile contents of the melts forming these minerals.

Reliability of models. The models used have not all been calibrated for temperature (T) or pressure (P) [20] or at the likely relevant T and P for late crystallization of the chassignites. In particular, the Cl models for biotite are P -dependent and those results could change significantly when better-calibrated models become available [23-25]. The F models for amphibole are estimates based off of apatite model calculations and require experimental data to improve them [24]. However, we are confident that the relative Cl and F contents of the modeled melts will remain the same in improved model calculations.

Results: Our calculated results for the parental magma in equilibrium with each volatile-bearing phase are presented in Figure 1. These show a similar trend in Cl/F ratios of the melt for both stones (to be expected given their apparently similar initial chemistry and cooling history [10, 16]). The Cl content of the parental melt increases in the order kaersutite, apatite, biotite, while the F content is highest in apatite, with lower F modeled in the melts crystallizing amphibole and biotite.

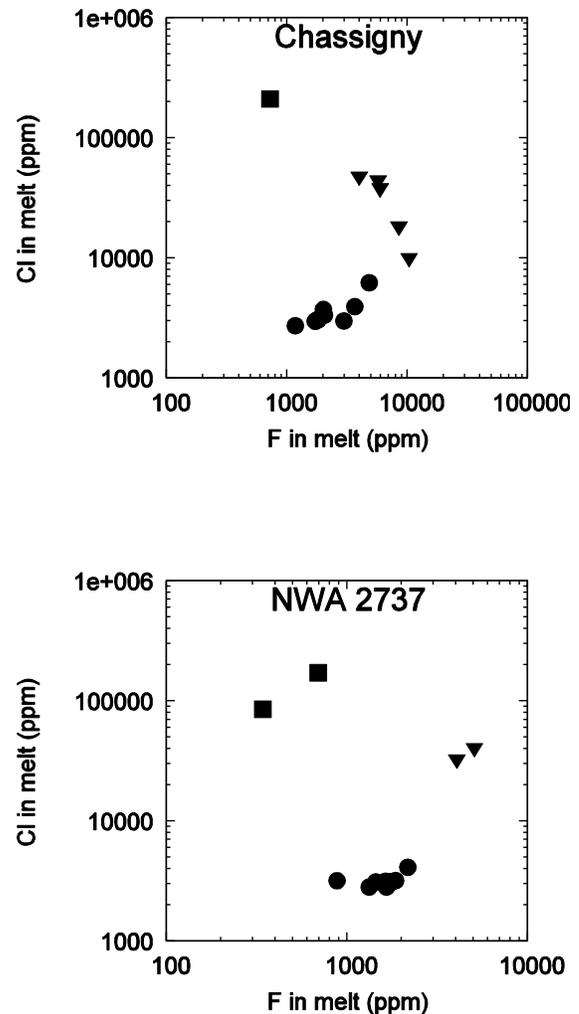


Figure 1. Calculated halogen concentrations of melts crystallizing kaersutite (circles), apatite (triangles), and biotite (squares) in the chassignites.

Discussion

Inferred crystallization history. In the mafic magmatic system(s) where the chassignites crystallized, Cl would have preferentially partitioned into any existing fluid [25], then melt [26], apatite [20], and biotite [19, 27, 28]; Cl fits poorly into the OH site of amphibole [21, 29]. The trends we see suggest that in the chassignites, kaersutite crystallization preceded apatite and biotite crystallization, with the Cl content of the melt and any potential coexisting magmatic fluid increasing throughout crystallization. Mesostasis apatite

from Chassigny has lower Cl content than melt inclusion apatite and could have precipitated from a melt that had degassed Cl [17, 30, 31].

F is relatively compatible in silicate melts and minerals, fits easily in the OH site of the minerals in question [24], and thus F concentrations in the residual melt eventually trended downward as the latter minerals (apatite and biotite) crystallized. The apparent increase in melt F content during amphibole crystallization may mean that F-free phases (pyroxenes, plagioclase) were co-crystallizing with amphibole. In Chassigny, this increase in melt F was accompanied by an increase in melt Cl, while no such trend is apparent in the NWA 2737 data.

The extremely high Cl contents modeled during biotite crystallization exceed the Cl solubility limit of even mafic melts [26] and thus seem to signify the presence of a Cl-rich fluid; such a fluid may have produced the biotite during subsolidus reactions rather than direct precipitation from magma [32]. Presence of a late-stage, halogen-rich fluid is consistent with conclusions drawn earlier for Chassigny [17] and other Martian meteorites [6, 33].

The sequence kaersutite → apatite is the same as previous interpretations of the crystallization order of the chassignites [15]. Biotite, which is rare in both meteorites, was thought to crystallize with or before kaersutite depending on the H₂O content of the individual melt pockets. However, this study did not discuss the effects of halogen concentrations in the melt; halogens may have postponed biotite crystallization via an unknown mechanism. Another possibility is that the biotite-free pathway (Table 3 in ref. [15]) reflects the magmatic history of the chassignites and biotite was formed later by subsolidus processes, probably involving fluid.

Effect on Mg# of ferromagnesian minerals. As noted by Filiberto and coworkers [5, 34], the presence of halogens has a strong effect on the composition of crystallizing olivine and pyroxene and can change the identity of the liquidus phase during cooling of a melt. At the subequal mass concentrations seen during early amphibole crystallization in the chassignites, their effects on Mg# may even out; but as Cl becomes more dominant in the melt, it will favor Fe retention in the melt and Mg incorporation in the crystallizing mineral [5, 34].

Consequences for Martian paleoclimate. The strong increase in Cl concentration in late melts and fluids suggests the expulsion of high Cl vapor into the Martian atmosphere as a result of magmatic degassing [23]. The acidic character of such volatiles would have resulted in acidic precipitation on early Mars and wide-

spread weathering of Martian crustal rocks with the production of kaolin-type clays, evaporites, and other low-temperature minerals, as well as high salinity conditions in Martian surface and groundwater. These same fluids have been implicated as possible sources of ferromagnesian clays during deuteric processes [35], so their mineralogical consequences for Mars' surface are quite complex.

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