

CHLORINE-RICH FLUID INTERACTION WITH CHASSIGNITE AND NAKHLITE MAGMAS.

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Introduction: For many years, Mars has been described as a volatile-rich planet in comparison to Earth [i.e., 1]. Understanding the nature of these volatiles is key to understanding many important aspects of martian geology, from igneous and sedimentary processes to the habitability and biologic potential of Mars. Although significant progress has been made regarding martian volatiles from recent orbital and lander missions [2-4], the mineralogy and geochemistry of the martian meteorites has been crucial for identifying chemical signatures of volatiles in the martian interior [5-10]. In fact, recent work on two minerals that have been analyzed in the Nakhlite and Chassignite meteorites from Mars have been of particular importance for understanding volatiles in the martian interior [5-10]. These two minerals include the Ca-phosphate mineral apatite and the silicate mineral amphibole. Both of these minerals contain F, Cl, and OH as essential structural constituents. Although amphibole is relatively uncommon in these meteorites, apatite is nearly ubiquitous (albeit a trace phase). Therefore, it will serve as the primary mineralogic tool in this investigation of volatiles in the martian interior.

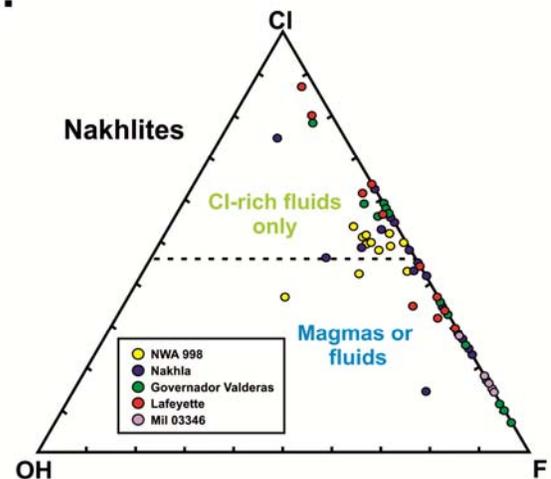
The Nakhlite and Chassignite meteorites are clinopyroxene-rich and olivine-rich cumulus igneous rocks, respectively [i.e., 11]. They have crystallization ages around 1.3 Ga [11], and based on the geochemical similarities among these two rock types, they are typically believed to come from similar magmatic source regions [11-13]. Furthermore, some workers have suggested that at least some of these rocks were comagmatic [13], representing various layers of a thick lava flow or layered intrusion [13].

We focus on volatiles in the Nakhlite and Chassignite meteorites because two earlier studies indicated that one of the meteorites from each of these classes (Chassignite and MIL 03346) contained evidence of having experienced a high-temperature hydrothermal history involving Cl-rich fluids [5-6]. However, the question remains as to whether these fluids were anomalous occurrences in these samples or if Cl-rich fluids were ubiquitous among these meteorites. Therefore, we have attempted to look for similar evidence of Cl-rich fluid interaction in the other samples from the Chassignite and Nakhlite classes.

Analytical Methods: We analyzed apatite in Nakhla, Lafayette, NWA 998, Gobernador Valderas, and MIL 03346 (we anticipate having data for NWA 2737 at the time of presentation). Phosphate grains were identified in thin sections of each meteorite using BSE imaging and verified using energy dispersive spectroscopy (EDS) before EPMA analysis. Electron micro-

probe analyses of individual grains were carried out using procedures that took into account possible F and Cl mobility [14-15]. Analytical conditions were typically 15 kV and 20 nA using a 2-10 μm diameter electron beam depending on grain size.

a.



b.

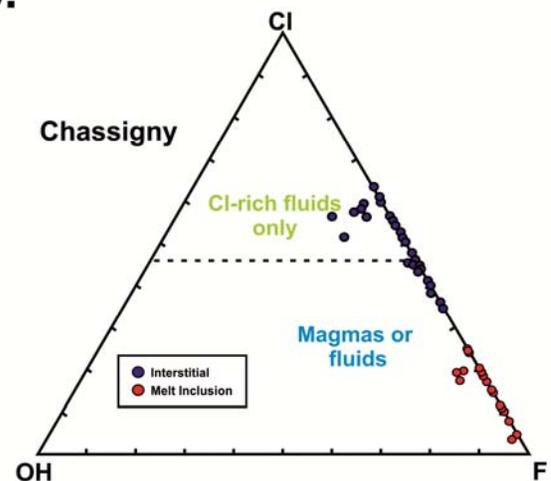


Figure 1: Ternary diagram of apatite volatile contents from EPMA analyses of F and Cl, with OH computed by stoichiometry. The dotted line represents the boundary between magmatic/fluid and fluid only apatite compositions. a) Apatite analyses from the Nakhlites b) Apatite analyses from the Chassignites [5].

Results: Apatite compositions from the Nakhlites analyzed in the present study, as well as apatite from the Chassignite apatite analyzed in a previous study [5] are presented in Fig. 1a and Fig. 1b respectively. Apatite grain sizes in the Nakhlite meteorites ranged from sub micron to about 20-30 μm in the largest dimen-

sion. The apatite compositions in the Nakhilites span a wide range of F-Cl compositions within a single sample. Furthermore, the apatite compositions in the Nakhilites, which are all from regions interstitial to the cumulus clinopyroxene grains, span a much wider range than was observed for the texturally equivalent apatite in Chassigny.

Although OH contents of the apatite have not been measured in the present study, they can be estimated by stoichiometry. Consistent with computed OH components in apatite from Chassigny (which have been verified by SIMS [8]), the computed OH component in apatite from the Nakhilites is within the detection of a missing component using the EPMA technique [15].

Apatite as a tool for determining magmatic volatile abundances: In order to use the volatile concentrations of apatite to precisely determine the abundances of volatiles in coexisting silicate melt and/or fluid, 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., 16-17], they are incomplete. However, several experimental studies have determined the apatite-melt partitioning behavior of F and Cl in terrestrial systems [18-19]. Although these are likely to be compositionally dependent, they can be used to give a first order approximation of the F and Cl content of the melt or fluid that co-existed with the apatite. For basaltic liquids, which are the most realistic for martian compositions, $D_F^{\text{apat/basalt}} = 3.4$ and $D_{Cl}^{\text{apat/basalt}} = 0.8$ [18], although the partition coefficient for chlorine is only applicable to basaltic liquids that are fluid-undersaturated. Although the $D_{H_2O}^{\text{apat/basalt}}$ was not directly determined in the study by Mathez and Webster [18], it was computed by McCubbin et al. [20] using the calculated hydroxyl components and the minimum-melt water contents from each of the experiments. This yielded an apatite-basaltic melt partition coefficient for water ranging from about 0.1-0.25 H_2O (i.e., $0.1 \leq D_{H_2O}^{\text{apat/basalt}} \leq 0.25$). These partition coefficients indicate that fluorine is strongly preferred over chlorine in apatite, and chlorine is strongly preferred over hydroxyl.

Apatite as an indicator of Cl-rich fluids: Owing to the $D_{Cl}^{\text{apat/basalt}}$ (0.8) [18] and the upper solubility limit of about 4.5 wt% chloride in basaltic melts [25-26], the upper limit of chlorine that can be incorporated into an apatite from a fluid-undersaturated basaltic melt is approximately 3.6 wt% Cl. However, end-member chlorapatite contains upwards of 6.8 wt% Cl. Therefore, a significant portion of apatite compositions are only accessible by Cl-rich fluids or chloride-saturated basaltic melts. Consequently, apatites with chlorine abundances significantly larger than 3.6 wt% likely formed from either Cl-rich fluids or chloride-

saturated basaltic melts. Fields indicating the maximum amount of chlorine that can be incorporated into igneous apatite in the absence of fluids are shown in Fig. 1a,b.

Volatile history of the Nakhilite and Chassignite meteorites: Although the computed hydroxyl contents of the apatite from all of the Nakhilites and Chassignites analyzed to date are low (typically <0.15 structural formula units of missing component), it does not require formation from a very water-poor system as the apatite/melt and apatite/fluid partition coefficients for H_2O are quite low [18,20,23]. Furthermore, recent analysis of water contents of kaersutite and Ti-biotite in the Chassigny meteorite have indicated that parent magmas likely had several thousands of ppm H_2O [7].

With the exception of MIL 03346, all of the Nakhilites have some apatite compositions that require equilibration with a Cl-rich fluid or chloride-saturated basaltic melt. Importantly, the interaction of MIL 03346 magma with Cl-rich fluids was demonstrated by [6] using the sealed melt-inclusion assemblage that included potassic chlorohastingsite. Therefore, all of the samples from the Chassignite and Nakhilite classes that we have investigated record strong evidence for having interacted with Cl-rich fluids at some stage of their petrogenetic history.

Future Work: Textural and chemical analysis of apatite in the Nakhilite and Chassignite meteorites is ongoing to determine the source of the Cl-rich fluid(s). Specifically, we are attempting to determine whether the fluids were exogenous or endogenous to the magmatic systems. Additionally, we are investigating the possible reason(s) behind the compositional variability within each Nakhilite sample; although, based on the compositional variability, it likely involves either degassing or fluid mixing [5].

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