THE EFFECT OF FLOURINE ON THE LIQUIDUS OF AN ADIRONDACK-CLASS MARTIAN BASALT.

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Introduction: This study presents first experimental results on the effect of fluorine on near-liquidus phase equilibria of an Adirondack-class Martian basalt. The basis of this study is our previous work on anhydrous [1] and chlorine-bearing [2] systems which has already shown that: 1) the Adirondack-class basalts are evolved liquid compositions [1] and 2) that chlorine has a large effect on liquidus depression and is important for basalt genesis on Mars [2]. However, to date there is little experimental work on the effect of fluorine on martian basalts. Yet, fluorine-rich martian basaltic compositions are suggested from the fluorine-rich magmatic minerals in the SNC meteorites [3-6]. Therefore, fluorine may play an important role in Martian basalt genesis and crystallization.

Evidence from martian meteorites: The martian meteorites show evidence for high fluorine concentrations in magmatic and alteration minerals. Magmatic inclusions within the SNC meteorites commonly contain magmatic amphibole which can readily accept F [3, 4]. Kaersutite, a Ti-rich amphibole, in the Chassigny meteorite contains 0.5 wt % F [3], and in NWA 2737 contains ~3 wt % F [4]. Also, within the melt-inclusions of the Chassigny meteorite there is rare Ti-biotite which contains 2.3 wt % F [3]. Using a $D_F^{biotite/melt}$ ~ 5.5 [7], for a biotite with an Mg# ~ 65 [3], suggests that the parental liquid to the amphibole in the Chassigny meteorite had ~ 0.4 wt % F.

Apatite is also a ubiquitous late stage magmatic mineral in the SNC meteorites. It is a significant reservoir of halogens in the SNC meteorites and can be used to compare halogen budgets of different planets [5]. Patiño Douce and Roden [5] compared apatites within the SNC meteorites to apatites from terrestrial basalts. They suggested that martian rocks are water poor compared with terrestrial basalts but contain significant halogen contents.

Others [6] have observed that within the Chassigny meteorite there are two populations of apatite: fluorine-rich, water-poor found in the melt-inclusions and chlorine-rich, water-poor found interstially [6]. They concluded that the F-rich apatite formed in a closed system process within the melt inclusions; while the chlor-fluor-apatite is created via open system fluid migration through the cumulus pile [6]. This implies that fluorine is essential in martian magmatic processes. Thus, we are investigating the effect of fluorine on near liquidus phase relations of a martian Gusev basalt.

Experimental Technique: Previous experiments on a Gusev basalt composition, Humphrey, F-free synthetic anhydrous [1], hydrous [8], and Cl-added [2] are the basis for studying the effects of F. The same synthetic powder and experimental technique from the anhydrous experiments [1] are used in this study; however, F was added to the starting composition as AgF_2, which decomposes at temperature to Ag metal and F in the melt [9]. Experiments were conducted in a piston-cylinder apparatus using $BaCO_3$ sleeves and crushable MgO spacers. Pressure was corrected with a negative 0.3 pressure correction [1]. Temperature was measured using a W5Re/W25Re thermocouple. Experiments were conducted using a piston-out procedure (i.e. pressurized to two kbar above the experimental pressure and then brought down to the final pressure after heating). Samples were melted for 30 minutes above the liquidus temperature and then rapidly cooled to the final crystallization temperature where they remained for 1-2 hours. Experimental run products were analyzed using a Cameca SX-100 electron microprobe at NASA JSC for major element abundances of the residual liquid as well as the crystal phases.

Results: A pressure-temperature phase relation diagram for the F-added experiments is shown in Figure 1 (red lines), compared with anhydrous (black lines; [1]), hydrous experiments (blue lines; [8]) and Cl-added experiments (gray lines; [2]) on the same basaltic composition.

All F-bearing experiments below 9 kbar have olivine as the liquidus phase and above 12 kbar have pigeonite on the liquidus. At 9.7 kbar and 1270 °C there is a multiple saturation point with both olivine and pigeonite on the liquidus. The anhydrous experiments have a multiple saturation point at 12.5 kbar and 1370 °C, the hydrous experiments (~0.8 wt% water) have a multiple saturation point at 10.6 kbar and 1320 °C, and chlorine-bearing experiments (0.7 wt% Cl) have a multiple saturation point at 8.5 kbar and

1305°C. 0.5 wt% F depresses the liquidus 80 °C compared with 0.8 wt% water which shifts the liquidus 50 °C and 0.7 wt% chlorine which shifts the liquidus 50 °C.
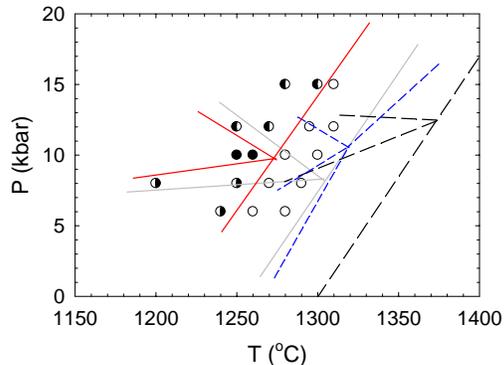

Figure 1. Experimentally determined phase relations for an anhydrous F-added synthetic Humphrey basalt (shown in red lines). White circles represent experiments that contained liquid only, black circles are for olivine, pigeonite, and liquid, right filled circles are for are olivine and liquid and left filled are pigeonite and liquid. Solid gray lines represent phase relations in the Cl-added system [2]. Dashed black lines represent phase relations in the anhydrous system [1]. Dashed blue lines represent phase relations in the hydrous system [8].

Figure 2 shows the pyroxene quadrilateral for the anhydrous experiments (white; [1]), hydrous experiments (blue; [8]), Cl-added experiments (gray; [2]), and F-added experiments (red) compared with the Mössbauer results for the natural rock (green; [10]). The anhydrous and chlorine-added experiments crystallized pigeonite while the hydrous experiments crystallized orthopyroxene. The F-added experiments crystallized pigeonite, which are more ferroan than those in the anhydrous experiments, consistent with the fluorine's depression of the liquidus temperature.
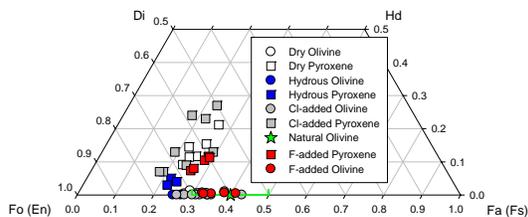

Figure 2. Compositions of experimentally-produced pyroxene and olivine plotted as QUIIF [11] projections for all pressures produced in this study (red) compared with the anhydrous experiments (white; [1]), hydrous experiments (blue; [8]), and chlorine-added experiments (grey; [2]). The olivine compositions predicted to be in the rock [10] are shown by a green star with uncertainty in the measurement (± Fo10; Morris, personal communication).

Discussion: The results here show that F has a greater effect on liquidus depression than comparable mass or molar proportions of water or Cl. The results also show that added F has a small or moderate effect on stability of pyroxene versus olivine near the liquidus, as does water [12]. On the other hand, Cl stabilizes pyroxene with respect to olivine and depresses the multiple saturation pressure [2]. These behaviors are consistent with the known effects of F, Cl, and water on melt structure. Fluorine breaks Si-O bonds by forming Al-F and Si-F bonds whereas water breaks bridging oxygen forming Si-OH bonds [13-16]. Chlorine, on the other hand, complexes with Na, Fe, and other divalent cations in the melt [17]. This has fewer consequences on melt structure but does have a large effect on Fe, Na, and other cation-activity.

Conclusion: As a preliminary study on the effect of F on phase equilibria, we have shown that F depresses the liquidus to a greater extent than water. Therefore, small amounts of dissolved fluorine will enable basalts to be produced at lower temperatures. The results suggest that fluorine is important during basalt genesis and needs to be included in models of partial melting and fractionation.

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