

COMPARING THE EFFECTS OF H₂O, F, AND Cl ON NEAR-LIQUIDUS PHASE EQUILIBRIA OF A MODEL HIGH-Fe BASALT: IMPLICATIONS FOR VOLATILE INDUCED MANTLE MELTING.

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Introduction: Volatile species, such as H₂O, CO₂, F, and Cl, are important in the generation and differentiation of basaltic melts. On the Earth, dissolved H₂O (or in certain circumstances CO₂) is thought to be the dominant volatile in most basaltic magmas. Therefore, significant effort has been placed on understanding how water and CO₂ affect basalt genesis and crystallization of terrestrial magmas [e.g., 1, 2]. However, water may not be the dominant volatile species in magmas on other planetary bodies [3-6]. Martian basalts are thought to be enriched in halogens (up to 0.2 wt% Cl and F) and depleted in water compared to terrestrial magmas [3-4, 6]. Lunar basalts contain small amounts of dissolved H₂O but much less than terrestrial or Martian basalts [5, 7-9]. They also contain F and Cl but the exact amount is highly debated and is likely less than terrestrial or Martian magmas. Venusian magmas are thought to be water poor and CO₂ rich, but the exact compositions (especially in terms of volatile contents) of these magmas are poorly constrained [10].

In order to understand how F and Cl affect liquidus depression, near liquidus basalt crystallization, and mantle melting, we compare experimental results of a high-Fe basalt composition with fluorine, and chlorine added independently. We also compare these results to experiments on the effect of water on olivine liquidus depression of basalts with varying bulk compositions. Finally, we perform preliminary calculations for the changes in basalt liquidus temperatures and Fe-Mg partitioning relevant for planetary magmas.

Experimental technique: An Fe-rich model basalt (Martian Adirondack-class basalt Humphrey) was used as the starting composition. Experiments have been conducted nominally volatile free [11], with 0.7 wt% Cl [12], and with 1.75 wt% F [13] in graphite capsules at 0.5 - 2 GPa. Fluorine was added to the starting mix as AgF₂ and Cl was added to the starting mix as AgCl. Hydrous (0.8 wt% bulk H₂O) experiments [14] have been conducted on a similar bulk composition, which can be compared with the F and Cl experimental results.

Results: Figure 1 shows the *P-T* results for the volatile-free, fluorine bearing, chlorine bearing and water bearing experiments. From these experimental results we can calculate the change in temperature (ΔT) from the anhydrous liquidus to the experimental temperature of the volatile bearing runs.

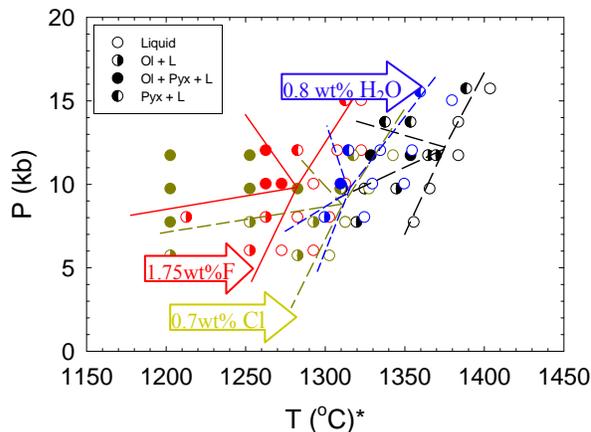


Figure 1. Experimentally determined near-liquidus phase relations for synthetic Humphrey composition nominally volatile free (black) [11], and with 0.7 wt% Cl (yellow) [12], 0.8 wt% H₂O (blue) [14], and 1.75 wt% F (red) [13].

Liquidus Depression: Figure 2 shows the effect of F and Cl on liquidus temperature compared with models for the effect of water on liquidus depression. On a weight percent basis F and Cl have, within error, the same effect on liquidus depression. However, based on atomic fraction F and Cl are actually twice as effective as H on liquidus depression.

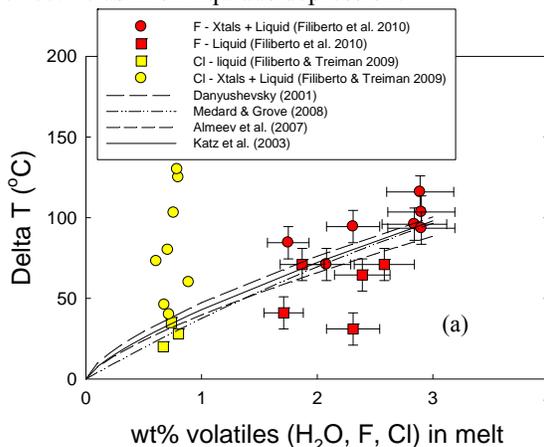
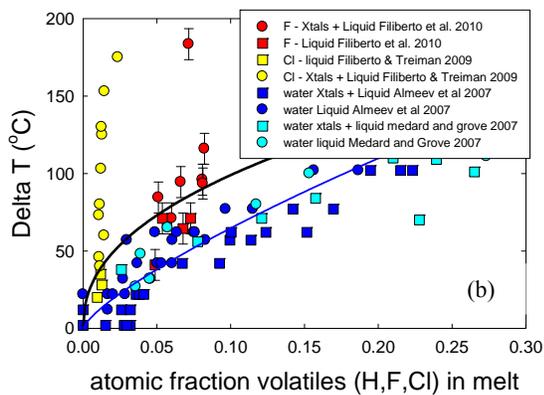


Figure 2. (a) temperature depression (ΔT) vs. wt % dissolved F and Cl compared with models for the effect of water [2, 15-17] (b) temperature depression (ΔT) vs. atomic fraction of volatiles. Black curve is a regression line through the F and Cl data combined. ΔT = Volatile-free liquidus *T* – experimental run temperature in °C.



Fe-Mg Partitioning: In order to understand how F, Cl, and water are incorporated into the melt structure and how they will affect basalt genesis, we compare how each volatile affects Fe-Mg partitioning between minerals and coexisting melts. $K_{D_{\min-melt}^{Fe-Mg}}$ increases with increasing F concentration in the melt, i.e., the minerals are more ferroan than what they would have been without added F. This result suggests that F in the melt complexes with Mg (leaving less Mg free to enter silicate minerals). Conversely, addition of Cl causes a decrease in $K_{D_{\min-melt}^{Fe-Mg}}$, which suggests that Cl in the melt forms stronger complexes with Fe than Mg. Addition of water, on the other hand, appears to have no significant effect on $K_{D_{\min-melt}^{Fe-Mg}}$ compared to volatile-free systems.

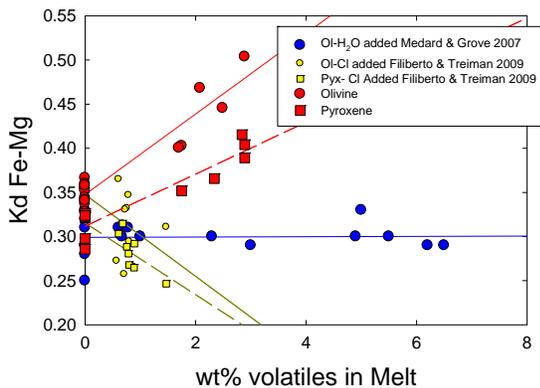


Figure 1. $K_{D_{\min-melt}^{Fe-Mg}}$ vs. dissolved volatiles (H_2O , blue, [2]; Cl, yellow, [12], and F, red, [13]) in the melt for olivine (circle) and pyroxene (square).

$$K_{D_{\min-melt}^{Fe-Mg}} = \frac{[X_{FeO}(Ol/pyx)X_{MgO}melt]}{[X_{MgO}(Ol/pyx)X_{FeO}melt]}$$

Implications: In order to evaluate the effects of volatile species on basalt genesis, we can use the experimental results, along with actual volatile abundances in planetary magmas, to calculate the amount of temperature depression and change in $K_{D_{\min-melt}^{Fe-Mg}}$ and therefore mineralogy. To do this we need to assume that the

effect of each species on liquidus depression and $K_{D_{\min-melt}^{Fe-Mg}}$ is additive.

Martian basalts may contain up to 0.2 wt% F, 0.3 wt% Cl and 0.2 wt% H_2O [3, 18]. From this we would expect a 30°C shift in the liquidus temperature and a shift in $K_{D_{\min-melt}^{Fe-Mg}}$ of ~ -0.01 for both pyroxene and olivine. Therefore, during partial melting, magmas produced will be slightly more Fe-rich than they would have been in a volatile-free system, and the residuum after partial melting will be slightly richer in Mg.

Lunar magmas are thought to contain < 850 ppm H_2O , similar amounts of Cl, and ~ 10 ppm F [5, 7, 9]. These proportions suggest a shift of less than 10°C in liquidus temperatures and a shift of -0.005 in K_D . Thus, the lunar volatiles will have only a minor effect in mineral compositions, shifting them to slightly higher Fe/Mg than in a volatile-free system. However, in order to fully understand lunar basalt genesis actual concentrations of H_2O , Cl, and F are needed.

Conclusions: Dissolved volatiles have a large effect on not only liquidus/solidus depression but the minerals crystallizing from a magma and left behind during partial melting in the mantle. Large proportions of dissolved chlorine (such as found in Martian magmas and terrestrial subduction zones) will decrease the liquidus depression similar to water but will also enrich the magmas in Fe. F has the opposite effect as Cl – it depresses the liquidus but will cause the magmas to become more Mg-rich. Water, while having large effects on liquidus depression, does not have a dramatic effect on Fe/Mg of a magma.

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