

THE EFFECT OF CHLORINE ON PHASE RELATIONS OF A MARTIAN BASALT: IMPLICATIONS FOR MANTLE VOLATILES. J. Filiberto¹ and A. H. Treiman¹, ¹Lunar and Planetary Institute, USRA, 3600 Bay Area Blvd., Houston, TX 77058. Filiberto@lpi.usra.edu

Introduction: High chlorine abundances have been reported in numerous locations on the Martian surface (i.e. GRS global mapping, in situ rock analysis from the Mars exploration rovers, and Cl-rich magmatic and alteration minerals in the SNC meteorites). This data has suggested that Cl may be important during magmatic and degassing processes on Mars. Therefore, we are investigating the effect of Cl on near liquidus crystallization behavior of a Martian basaltic composition.

GRS data: GRS elemental mapping has shown that Cl is not compositionally uniform across the Martian surface but varies from 0.2 to 1 wt% with a mean average of 0.5 wt%. Surface Cl content is correlated positively with H and negatively with Si [1].

MER Rover Data: High Cl contents have been confirmed by the MER rovers. The Adirondack basalts, analyzed by the Spirit rover, have ~0.2 wt% Cl [2] while the soil compositions at Gusev contain up to 1 wt % Cl [2]. The Clovis and Watchtower class rocks of the Columbia hills are also enriched in Cl compared with the Adirondack basalts which may reflect extensive aqueous alteration [2]. The Opportunity rover analyzed rocks at Meridiani Planum that contain 0.5 - 1.5 wt% Cl [3]. The Burns formation at Meridiani Planum represents a mixture of basalt and alteration minerals (i.e. jarosite, Mg-, Ca-sulfates, chlorides, and Fe-, Na- sulfates [4]) all with elevated Cl-contents.

SNC meteorites: The SNC meteorites also contain numerous Cl-bearing alteration products of Martian origin as well as Cl-bearing magmatic minerals. The alteration minerals found in the Nakhilites include siderite, anhydrite, iddingsite, gypsum, carbonate, clay, epsomite, and halite [5-7]. These minerals have been suggested to have been deposited from saline waters near the surface of Mars [6]. The carbonates and iddingsite in the nakhilites contain up to 1.5 wt% Cl [8]. Chassigny contains calcite and gypsum [5] while the shergottites contain gypsum, halite, other chlorides, phyllosilicates, and calcite [5]. Many of the SNC meteorites also contain evidence of magmatic volatiles. Magmatic inclusions within them commonly contain kaersutite, a magmatic Ti-amphibole which can readily accept Cl [9, 10]. The kaersutite in the Chassigny meteorite contains 0.1 wt % Cl [9], and the nakhilite MIL03446 contains abundant Cl-rich amphibole within its melt inclusions (up to 7.0 wt% Cl) [10]. Also, within the melt-inclusions of the Chassigny meteorite is rare Ti-biotite which contains 0.4 wt% Cl [9]. Using a $DCl_{\text{biotite/melt}} \sim 1.5$ [11] suggests that the parent

magma had about 0.3 wt% Cl. Chlor-apatite is also an uncommon but widespread magmatic mineral in the SNC meteorites considered a late stage magmatic product [12-14].

Known Effects of Cl in magmatic systems: While little is known about the effect of Cl in Martian magmatic systems, more is known about the effect of Cl in evolved terrestrial compositions [e.g. 15-17]. However, these relations are melt composition dependent, and all current experimental work is on terrestrial compositions. Therefore, we are conducting high pressure experiments on a synthetic Martian Gusev basaltic composition with Cl added to investigate the effect on liquidus phase relations.

Experimental Strategy: Previous experiments on a synthetic anhydrous [18] and hydrous [19] Gusev basalt composition, Humphrey, are the basis for studying the effects of Cl. The same synthetic powder and experimental technique from the anhydrous experiments [18] are used in this study; however, Cl is added to the starting composition as AgCl, which decomposes at temperature to Ag metal and Cl in the melt. Experiments were conducted in a piston-cylinder apparatus using BaCO₃ sleeves and crushable MgO spacers from 6 kbar to 10 kbar nominal. Pressures and temperatures were corrected with a negative 0.3 pressure correction. 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 1-4 hours (longer times were for lower temperatures). 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.

Discussion: A pressure-temperature phase relation diagram for the Cl-added experiments is shown in Figure 1 (red dashed lines), compared with anhydrous [18] (black lines) and hydrous experiments [19] (blue lines) on the same basaltic composition. All experiments below 8 kbar show olivine as the liquidus phase. The experiments conducted at 9.7 kbar have pigeonite on the liquidus, and at approximately 8.5 kbar and 1300°C there is an implied multiple saturation point with both olivine and pigeonite on the liquidus. The

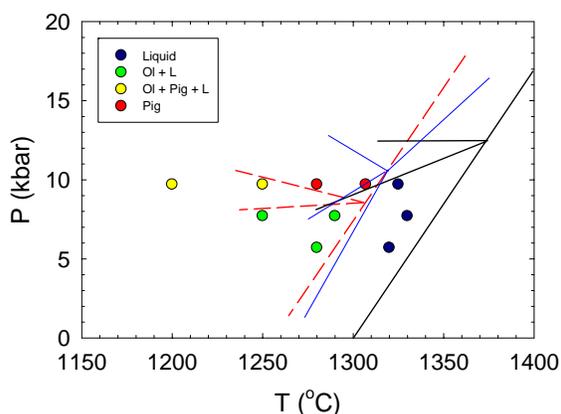


Figure 1. Experimentally determined phase relations for an anhydrous Cl-added synthetic Humphrey basalt. Blue are experiments that contained liquid only, yellow are olivine, pigeonite, and liquid, green are olivine and liquid and red are pigeonite and liquid. Dashed red lines represent phase relations in the Cl-added system. Solid black lines represent phase relations in the anhydrous system [18]. Solid blue lines represent phase relations in the hydrous system [19].

anhydrous experiments have a multiple saturation point at 12.5 and 1370°C, while the hydrous (~0.8 wt% water) have a multiple saturation point at 10.6 and 1320°C. Since experiments were conducted with 0.7 wt% Cl they can be directly compared with hydrous experiments with similar water contents (0.8 wt% water [19]). Cl depresses the liquidus 70°C and 4 kbar compared with 0.8 wt% water which shifts the liquidus 50°C and < 2 kbar, suggesting that Cl has a greater effect on liquidus depression than water. Cl also has a much larger effect on the multiple saturation pressure than water.

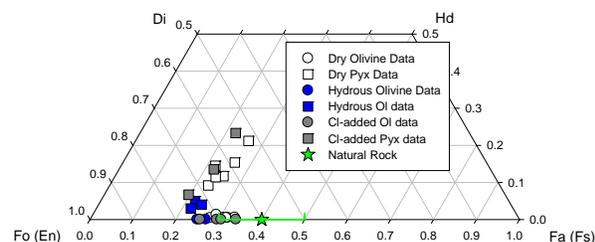


Figure 2. Compositions of experimentally-produced pigeonite (Pig) and olivine (Ol) plotted as QUIF [21] projections for all pressures produced in this study (grey) compared with the anhydrous experiments (white; [18]) and hydrous experiments (blue; [19]). The olivine compositions predicted to be in the rock [20] are shown by a green star with uncertainty in the measurement (\pm Fo10; Morris, personal communication).

Figure 2 shows the pyroxene quadrilateral for the anhydrous experiments (in white; [18]), hydrous experiments (blue; [19]) and Cl-added experiments (gray) compared with the Mössbauer results for the natural rock (green [20]). The anhydrous experiments crystallized pigeonite while the hydrous experiments crystallized orthopyroxene. The Cl-added experiments

crystallized pigeonite but are depleted in Fe and Ca compared with the anhydrous experiments consistent with Cl-complexing with Fe, and perhaps Ca, in the melt.

Since Cl complexes in the melt with Fe and perhaps Ca, it increases Si abundance outside the complexes, and thus promotes silicate polymerization in the melt. Polymerizing the melt increases Si activity stabilizing pigeonite, with respect to olivine, to much lower pressures and depressing the liquidus temperature.

Conclusion: A preliminary study of the effect of Cl on phase relations of a Martian basalt has shown that Cl complexes in the melt depressing the liquidus and multiple saturation pressure to a greater extent than water. By complexing in the melt with Fe, and perhaps Ca, Na and Mg, Cl causes the melt to become polymerized. Polymerizing the melt increases the Si-activity stabilizing pyroxene with respect to olivine. All of this has a large effect on liquidus and multiple saturation point depression. Therefore, small amounts of Cl in the Martian mantle will enable production of basalts at lower temperatures and pressures.

These results are consistent with previous terrestrial work which has shown that Cl affects melt structure by complexing primarily with Fe^{2+} as well as Na, Mg, Ca, and K thereby creating non-bridging O atoms and increasing melt viscosity [17; 22-23]. Since Martian magmas are enriched in Fe and Na compared with terrestrial magmas, Cl solubility will be higher [17], suggesting that Cl may play a larger role in Martian basalt genesis than in typical terrestrial basaltic systems.

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