EXPERIMENTAL INVESTIGATION INTO THE EFFECT OF CHLORINE IN A MARTIAN BASALTIC SYSTEM.

J. Filiberto[1], and A.H. Treiman[1] [1]Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston, TX 77058. Filiberto@lpi.usra.edu.

Introduction: High chlorine abundance have been reported in numerous locations on the Martian surface from GRS global mapping, to in situ rock analysis from the Mars exploration rovers to Cl-rich magmatic and alteration minerals in the SNC meteorites. This data has suggested that Cl may be important during magmatic and degassing processes as well as surface alteration processes on the Martian surface. Therefore, we are initiating a study investigating the effects of Cl on liquidus and crystallization behavior of a Martian magma 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 shows a positive correlation with H and a negative correlation with Si [1]. The high concentrations in the Medusae Fossae Formation have been suggested to be related to volcanic degassing while in other areas the Cl enrichment may be due to ground water transportation and evaporation [1].

Spirit Analysis: High Cl contents have been confirmed by the MER rovers. The Adirondack basalts have ~0.2 wt% Cl [2] while the soil compositions at Gusev are enriched in Cl compared with the Adirondack basalts, with up to 1 wt % Cl [2]. The Clovis class rocks of the Columbia hills are also enriched in Cl, as well as S, P, K, Ti, Ni, and Br, compared with the Adirondack basalts. These enrichments may be caused by aqueous alteration [2]. The Watchtower class rocks are Cl-enriched compared with the Clovis class which may reflect more extensive aqueous alteration [2].

Opportunity Analysis: 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]).

SNC meteorites: The SNC meteorites also contain numerous Cl-bearing alteration products of Martian origin as well as Cl-bearing magmatic minerals.

The Nakhlites contain many extensively studied alteration products. The alteration minerals found in the Nakhlites 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 nakhlites 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 nakhlite 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 there is rare Ti-biotite which contains 0.4 wt% Cl [9]. Using a $D_{Cl}^{biotite/melt}$ ~1.5 [11] suggests that the liquid had about 0.3 wt% Cl.

Apatite is also an uncommon but widespread Cl-bearing magmatic mineral in the SNC meteorites. Apatite in melt-inclusions and interstially is considered a late stage magmatic product. The formation history of the chlorapatite is currently debated. Some have argued that the high Cl contents may be due to subsurface processes on Mars [12]. While others [13, 14] have suggested that there are actually two populations of apatite one being Cl-rich apatite which is found interstially in Chassigny, and the other population being F-rich apatite found in the melt-inclusions. They suggest that this is due to closed system processes within the melt-inclusions causing formation of flourapatite but fluid migration through the cumulate pile causing the formation of chlorapatite [13, 14]. No matter the formation mechanism of the Cl-apatite, a chlorine fluid is an important constituent for both of these models.

Modeling Chlorine on the surface of Mars: As chlorine has been shown to be abundant on the surface of Mars thus it may play an important role during magmatic and alteration processes. There are currently many models that rely on Cl for weathering and soil production on the Martian surface, for example:

- Nelson et al [15] suggest that Martian soils were formed in low temperature, low water/rock ratio environments and can be a sink for mobile elements such as the halogens (i.e. S and Cl).
- Tosca et al. [16] have argued for an acid fog model as a mechanism for soil formation. Through short intermittent reactions of a synthetic basalt with a synthetic Martian acidic at-

mosphere, Mg, Fe, Ca, and Al sulfates were experimental produced.

- The formation of the Burns formation is currently debated but may be derived by evaporation of ground water [4, 17].

Known Effects of Cl in magmatic systems: While little is known about the effect of Cl in Martian magmatic systems, much is known about the effect of Cl in evolved terrestrial compositions.

Chlorine is relatively soluble in magmas, with a maximum solubility from 2.9 wt% in molten basalts to 1 wt% in latites [18]. Chlorine solubility in a melt increases with increasing pressure, decreasing H_2O content, and increasing molar ((Al + Na +Ca + Mg)/Si) [19]. Since Cl solubility decreases with increasing H_2O and SiO_2 content, increasing the Cl content of a melt by fractionation can cause exsolution of a Cl-rich vapor from the magma and potentially drive an eruption [18].

In a silicate melt, Cl complexes with Ca, Mg, Fe, Al, and P [20], and thus can affect phase relations. However, these relations depend sensitively on melt composition, and all current experimental work is on terrestrial compositions. Since no experimental work has been done to investigate the effect of Cl on Martian magmatic compositions, we are conducting high pressure experiments on a synthetic Gusev basaltic composition with Cl added to investigate liquidus phase relations and degassing behavior.

Experimental Strategy: Previous experiments [21] on a synthetic anhydrous Humphrey composition are the basis for studying the effects of Cl. Figure 1 shows the experimentally derived liquidus relations for the synthetic Humphrey composition, Cl-free and nearly anhydrous (0.1 wt% H_2O). The same synthetic powder is used for this study; however, Cl is added as AgCl, which decomposes at temperature to Ag metal and Cl in the melt.

Liquidus and near-liquidus experiments are being conducted in a piston-cylinder apparatus at the Johnson Space Center using graphite capsules, $BaCO_3$ sleeves, and crushable MgO spacers at pressures from 4 to 16 kilobars. Temperature is measured using a W5Re/W25Re thermocouple. Experiments are conducted piston-out (i.e. pressurized to two kbar above the experimental pressure, brought to temperature, and then brought down to the final pressure). 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 and finally quenched. Experiments are conducted using unlined graphite capsules

The few experiments complete at this writing contain only glass and confirm that 0.8 wt% Cl has been successfully added to the starting composition. 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. Mass balance calculations were conducted using the least square computations of IgPet [22] in order to determine mineral abundances and ensure that no phase was missed during microprobe analysis. The least squares results also allow for the assessment of whether or not a chloride brine complex has degassed from the experiment, the extent of degassing, and composition of the brine.

The ongoing experiments will elucidate the effect of Cl in Martian magmatic systems and place constraints on the availability of Cl for acidic atmospheric soil formation models.

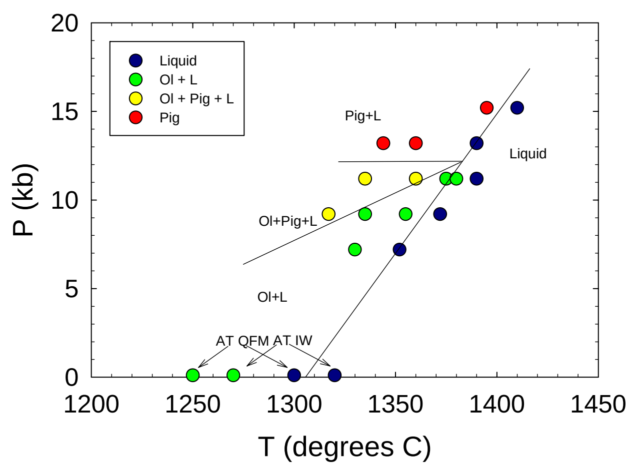

Figure 1: Experimental determined phase relations from [21] for an anhydrous, Cl-free, synthetic Humphrey basalt. Blue circles are experiments that contained liquid only, green are olivine and liquid, yellow are olivine, pigeonite, and liquid, and red are pigeonite and liquid.

References: [1] Keller J.M., et al. (2007) *JGR,. 111* E03S08. [2] Gellert, R. et al. (2006) *JGR 111*. [3] Rieder R. et al. (2004) *Science 306,* 1746-1749. [4] McLennan S. et al. (2006) *Earth and Planet. Sci. Letters, 240,* 95-121. [5] Bridges J.C. et al. (2001) *Chron. and Evol. of Mars,* 365-392. [6] Treiman A.H. (2005) *Chemie Der Erde-Geochemistry, 65,* 203-270. [7] Treiman A.H. et al. (2002) *Earth and Planet Sci Letters, 204,* 323-332. [8] Rao M.N. et al. (2006) *LPS XXXVII,* Abstract # 1969. [9] Johnson M.C. et al. (1991) *Geochim et Cosmo Acta, 55,* 349-366. [10] Sautter V. et al. (2006) *Earth and Planet Sci Letters, 252,* 45-55. [11] Icenhower J.P. and D. London (1997) *Contribs to Min and Pet, 127,* 17-29. [12] Greenwood J.P. (2005) *Meteoritics & Planet Sci, 40S,* Abstract #5312. [13] McCubbin et al.

(2007) *LPS XXXVIII*, Abstract # 1347. [14] McCubbin et al. (2006) *LPS XXXVII*, Abstract # 1098. [15] Nelson M.J. et al. (2005) *Geochim et Cosmo Acta*, *69*, 2701-2711. [16] Tosca N.J. et al. (2004) *JGR, 109*, (E05003). [17] Grotzinger G. et al. (2005) *Earth and Planet Sci Letters*, *240,* 11-72. [18] Webster J.D. et al. (1999) *Geochim et Cosmo Acta, 63*, 729-738. [19] Webster J.D. and Rebbert C.R. (1998) *Contrib to Min and Petr*, *132*, 198-207. [20] Webster J.D. and De Vivo B. (2002), *American Miner, 87*, 1046-1061. [21] Filiberto J. and Treiman A.H. *LPS XXXVIII*, Abstract #1341. [22] Carr, M.J. (2000), *Igpet for Windows*.