



ELSEVIER

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

The effect of chlorine on the liquidus of basalt: First results and implications for basalt genesis on Mars and Earth

Justin Filiberto*, Allan H. Treiman

Lunar and Planetary Institute, Universities Space Research Association, 3600 Bay Area Boulevard, Houston, TX 77058, USA

ARTICLE INFO

Article history:

Accepted 22 August 2008

Available online xxxx

Keywords:

Mars
Volatiles
Halogens
Experimental petrology
Phase equilibria
Basalt genesis
Liquidus depression
SNC meteorites
Earth
Subduction zones
Alkalic rocks

ABSTRACT

Chlorine (Cl) is abundant, to percent levels, on Mars, in Mars basalts, and in some Earth basalts. Yet, little is known about the effects of Cl on basalt phase equilibria, which provide crucial constraints on melting temperatures, melt compositions, and melt production. To explore the effects of Cl on basalt equilibria, we located the liquidus (at high P and T) for a Martian basalt composition (the rock Humphrey, Gusev Crater, Mars) with 0.7% Cl-added, and obtained mineral and melt compositions from the experimental charges. Addition of Cl produces an unexpectedly large change in the liquidus—it is shifted to lower temperature by ~ 50 °C, and the field of pigeonite stability is enlarged so that the point of liquidus cosaturation in olivine & pigeonite is shifted down pressure by ~ 4 kbar (from 12.5 kbar and 1355 °C in the Cl-free composition to 8.5 kbar and 1305 °C). This temperature shift is comparable to that produced by addition of $\sim 0.8\%$ H₂O; so, on a molar basis, Cl is twice as effective as H₂O in reducing this basalt's liquidus. Conceptually, the shift in liquidus temperature and enlargement of the field of pigeonite+melt is consistent with formation of complexes between Cl and network-modifying cations (e.g., Mg, Fe, Ca), which would make the latter unavailable to modify (depolymerize) the silicate network. However, the actual effect of Cl is larger than predicted by this simple model, even allowing up to 8 cations complexed per Cl. For Mars, these results suggest that Cl may play a crucial role in its basalts' generation and evolution. While, some aspects of Martian basalt petrogenesis have been consistent with experimental results on water-rich systems (e.g., to $\sim 2\%$ H₂O in basalt magma); the work here suggests that similar experimental results would be obtained for Cl-rich, H₂O-poor systems, and that Martian basalts would contain little water. For Earth, the work here suggests that Cl must be considered explicitly in the petrogenesis of Cl-rich magmas, like those of subduction zones.

© 2008 Published by Elsevier B.V.

1. Introduction

High chlorine abundances 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. These data have suggested that Cl may be important during magmatic and degassing processes as well as surface alteration processes on the Martian surface. Therefore, we have conducted a study investigating the effects of Cl on liquidus and crystallization behavior of a Martian magma composition.

1.1. GRS data

GRS elemental mapping of the Martian surface has shown that Cl is not compositionally uniform but varies from 0.2 to 1 wt.% with a mean average of 0.5 wt.% (Boynton et al., 2007; Keller et al., 2007). 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 (Keller et al., 2007). Models to explain the chlorine distribution on the Martian surface rely on HCl outgassing from volcanic vents (Keller et al., 2007).

1.2. Spirit Rover analyses

High Cl contents have been confirmed by the MER rovers. The Adirondack-class basalts have ~ 0.2 wt.% Cl (Gellert et al., 2006) while the soil compositions at Gusev are enriched in Cl compared with the Adirondack basalts, with up to 1 wt.% Cl (Gellert et al., 2006). The Adirondack-class basalts are fine-grained rocks of basaltic composition with $<20\%$ megacrysts interpreted as olivine ($\sim \text{Fo}_{60} \pm 10$) by Mössbauer spectroscopy (Morris et al., 2004, Morris personal communication), and with irregular vesicles and vugs (Morris et al., 2004; Gellert et al., 2006; McSween et al., 2006). The Adirondack-class rocks are interpreted as fragments of basaltic lava flows that represent basaltic magma compositions (e.g. McSween et al., 2006). The minimal weathering they have experienced (e.g. Hausrath et al.,

* Corresponding author.

E-mail address: Filiberto@lpi.usra.edu (J. Filiberto).

2008) has been abraded away by the rock abrasion tool before the APXS bulk chemical analysis (Squyres et al., 2004). However, the rocks contain vesicles suggesting that they degassed during eruption and the bulk chlorine analysis (0.2 wt.%) may in fact be a lower limit of the magmatic chlorine content.

A pyroclastic sequence, with enriched chlorine contents compared with the Adirondack-class basalts, has recently been discovered at Home Plate in Gusev Crater (Squyres et al., 2007). This sequence is characterized by a coarse granular textured basal unit which progresses to a finer-grained upper unit. Of particular interest in the lower unit is a ~4 cm clast with deformed layers that has been concluded to be a bomb sag (Squyres et al., 2007). The sequence is basaltic in composition with up to 2 wt.% Cl. The combined chemical data and microscopic and Pancam imaging suggests that the sequence represents a pyroclastic deposit that was erupted violently driven by volatile exsolution (Squyres et al., 2007). This suggests that magmatic chlorine is important for basaltic eruptions, and basalt genesis, on Mars.

1.3. Opportunity Rover analysis

Unlike the Spirit Rover, the Opportunity Rover has not encountered extensive basaltic rocks. Instead, Opportunity has analyzed numerous sedimentary sequences which give evidence for Cl-rich waters (e.g. Rieder et al., 2004; Clark et al., 2005; Grotzinger et al., 2005; McLennan et al., 2005). For example, 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, Grotzinger et al., 2005; McLennan et al., 2005) and contains 0.5–2 wt.% Cl (Rieder et al., 2004; Clark et al., 2005). These analyses show the importance of chlorine-rich waters on the Martian surface.

1.4. Martian meteorites

Based on the bulk SNC (Martian) meteorite compositions, Dreibus and Wänke (1986, 1987) suggested that Mars is enriched in chlorine and other volatile elements compared to the Earth. For instances, Mars is inferred to have bulk abundance ratios for Cl/Th near $0.03 \times \text{Cl}$ compared to the Earth's mantle's inferred $\sim 0.01 \times \text{Cl}$ (Dreibus and Wänke, 1985, 1987).

The SNC (Martian) meteorites also contain numerous Cl-bearing alteration products of Martian origin as well as Cl-bearing magmatic minerals. The nakhlites contain many extensively studied Cl-rich alteration products. The alteration minerals found in the nakhlites include siderite, anhydrite, iddingsite, gypsum, carbonate, clay, epsomite, and halite (Treiman et al., 1993; Bridges et al., 2001; Treiman et al., 2002; Treiman, 2005). The carbonates and iddingsite in the nakhlites contain up to 3.0 wt.% Cl (Rao et al., 2008). The Chassigny meteorite contains calcite and gypsum (e.g. Bridges et al., 2001) while the shergottites contain gypsum, halite, other chlorides, phyllosilicates, and calcite (e.g. Bridges et al., 2001). These minerals were deposited from saline waters near the surface of Mars (Treiman, 2005).

Many of the SNC meteorites also contain evidence of magmatic chlorine. Magmatic inclusions within the SNC meteorites commonly contain magmatic amphibole which can readily accept Cl (Johnson et al., 1991; Sautter et al., 2006). The kaersutite, a Ti-rich amphibole, in the Chassigny meteorite contains 0.1 wt.% Cl (Johnson et al., 1991), and the nakhlite MIL03346 contains abundant Cl-rich amphibole, chloropotassic-hastingsite, within its melt-inclusions (up to 7.0 wt.% Cl) (Sautter et al., 2006). Also, within the melt-inclusions of the Chassigny meteorite there is rare Ti-biotite which contains 0.4 wt.% Cl (Johnson et al., 1991). Using a $D_{\text{biotite/melt}}^{\text{Cl}} \sim 1.5$ (Icnhower and London, 1997) suggests that the parental liquid to the biotite in the Chassigny meteorite 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 interstitially

is considered a late stage magmatic product. The formation history of this chlorapatite is currently debated. Some have argued that the high Cl contents may be due to subsurface processes on Mars (Greenwood, 2005). On the other hand, McCubbin and Nekvasil (2008) have suggested that there are two populations of apatite, at least in the Chassigny meteorite: Cl-rich apatite is present in the mesostasis, and F-rich apatite is present in melt-inclusions. McCubbin and Nekvasil suggest that these two populations reflect closed system processes within the melt-inclusions (allowing formation of fluorapatite), but fluid migration through the cumulate pile causing the formation of chlorapatite. No matter the formation mechanism of the Cl-apatite, a chlorine-rich magmatic fluid is an important constituent for both of these models.

1.5. Modeling chlorine on the surface of Mars

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

- Nelson et al. (2005) 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. (2004) argued for an acid fog model as a mechanism for soil formation. Through short intermittent reactions of synthetic basalt with a synthetic Martian acidic atmosphere, Mg, Fe, Ca, and Al sulfates were experimentally produced.
- Banin et al. (1997) have experimentally shown that Martian soil and dust formed during the last few hundred years by interactions of basaltic rocks with acidic volatiles which release Fe, Al, and Mg. This model relies on volcanic degassing to produce SO_4 and Cl which interacts with surface rocks. These interactions produce salt-rich mineral mixtures which they suggest compose the Martian soil.

The alteration models all rely on Cl from basalt degassing; therefore, understanding the effect of halogens in Martian magmatic regimes is essential to these models.

1.6. Known effects of Cl in magmatic systems

Although 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 ~3 wt.% in basalt to ~1 wt.% in latite (Webster et al., 1999). Chlorine solubility in a magma increases with increasing pressure, decreasing H_2O content, and increasing molar ((Al+Na+Ca+Mg)/Si) (Webster and Rebbert, 1998). 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 (Webster et al., 1999).

In a silicate melt, Cl complexes with Ca, Mg, Fe, Al, and P, forming ion clusters that are distinct from the silicate network (Malinin et al., 1989; Webster and De Vivo, 2002). These complexes affect silicate melts by increasing their viscosity, presumably by enhancing the polymerization of the silicate network (Dingwell and Hess, 1998; Zimova and Webb, 2006). These changes in silicate polymerization and cation activities must affect phase relations in the magma, which are very sensitive to melt composition; all available experiments are on terrestrial compositions. Thus, we are conducting high pressure experiments on the effects of Cl on a Martian basalt composition, that of the Humphrey rock (Adirondack-class) analyzed by the MER Spirit Rover in Gusev crater, Mars. Humphrey was chosen because it is appears to be the least altered of the Adirondack-class basalts (McSween et al., 2006) and our results can be compared with those from earlier Cl-free anhydrous and hydrous liquidus experiments (Monders et al., 2007; Filiberto et al., 2008).

2. Experimental strategy

Previous experiments on a synthetic anhydrous Humphrey composition are the basis for studying the effects of Cl (Filiberto et al., 2008). A synthetic powdered starting material of the Humphrey composition was made from a homogenized mixture of element oxides. The starting composition for this study was made Cr-free to avoid the fO_2 effects on chromite stability (Onuma and Tohara, 1983; Monders et al., 2007). The same synthetic powder from Filiberto et al. (2008) was used for this study; however, Cl was added as AgCl which decomposes at temperature to Ag metal and Cl in the melt (Table 1). Representative experimental charges were probed for Ag in the melt and contain <0.1 wt.%. This shows that Ag does not readily dissolve in the melt and will not effect the phase relations. The powder plus AgCl was stored in a desiccator to ensure that it remained anhydrous.

2.1. High pressure experiments

High pressure experiments were conducted in a QuickPress[®] piston-cylinder apparatus in the laboratories of the ARES division, Johnson Space Center. After loading the powder into a graphite capsule, both were dried at 150 °C for at least 12 hours to ensure that they remained anhydrous. The sample, capsule, and graphite furnace were held in BaCO₃ sleeves and crushable MgO spacers. Temperature was measured using a W5Re/W25Re thermocouple placed in an indentation in the graphite sample capsule and range from above the liquidus to just below the liquidus. Pressures in these experiments ranged from 6 kbar to 12 kbar nominal, as measured on a Heise gauge. Based on the location of the diopside melting curve, pressures were corrected by -0.3 kbar (Filiberto et al., 2008). The oxygen fugacity, fO_2 , of our experiments has not been directly measured. However, the graphite capsules constrain the fO_2 of the assemblage, at elevated pressures, from ~1.5 to 3.5 log units below the FMQ oxygen buffer (Holloway et al., 1992).

Experiments were conducted using a piston-out procedure—the experiment was pressurized cold to 2 kbar above the experimental pressure, brought to melting temperature, and then brought down to the final pressure. Samples were melted for 30 min above the liquidus temperature, rapidly cooled to the final crystallization temperature where they remained for 1–4 h (longer times were for lower temperatures), and finally quenched at pressure. This technique was employed in order to mimic natural magmatic conditions where crystals form directly from a molten liquid, rather than synthesis techniques of going directly to the crystallization temperature where crystals form from the powder. Capsules remained intact during the experiments (no cracks in the capsule walls) and no barium contamination from the pressure sleeve occurred.

Table 1

Starting composition compared with published results (calculated Cr-free and normalized to 100%)

Wt.%	Gellert et al. (2006)	Average Glass Composition
SiO ₂	46.87	46.10
TiO ₂	0.56	0.55
Al ₂ O ₃	10.91	10.48
FeO _T	19.19	19.54
MnO	0.42	0.45
MgO	10.63	10.92
CaO	8.00	8.06
Na ₂ O	2.55	2.51
K ₂ O	0.10	0.10
P ₂ O ₅	0.57	0.59
Cl	0.20	0.71
Total	100.00	100.00

FeO_T = total iron (Fe₂O₃ + FeO).

2.2. Analyses

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. Analytical conditions were standard for the instrument: 15 kV electron accelerating potential, and focused electron beam of 20 nA current (in a Faraday cup) for minerals and 10 nA current and a defocused beam for glasses. Analytical standards were synthetic oxides and glasses, and raw data were reduced in the Cameca PAP routine. Mass balance calculations were conducted using the least-square computations of the IgPet software (Carr, 2000) in order to determine mineral abundances and ensure that no phase was missed during microprobe analysis. All experiments have sum of the least-square residuals <0.5 showing that no phase was missed during the microprobe analysis. No experiments reported were affected by Cl degassing.

2.2.1. H₂O analysis

Since small amounts of dissolved water can have large effects on liquidus temperatures and phases (e.g. Médard and Grove, 2007), micro-FTIR analysis was conducted to determine water content of the experimental glasses. Samples were analyzed using a Nicolet Contium FTIR at NASA JSC. Total dissolved water contents were determined from the intensity of the broad band at 3570 cm⁻¹ of doubly polished glass wafers. For each sample 512 scans were used to acquire each IR spectrum. Total water concentrations were calculated using the procedures of Dixon et al. (1995) and Mandeville et al. (2002). The experiments contain 0.1 wt.% water which is relatively anhydrous and is the same water content as the previous work enabling a direct comparison (Filiberto et al., 2008).

3. Experimental results

Experimental phase assemblages were determined from 5.7–11.7 kbar. Experimental run products included: glass only; olivine+glass; pigeonite+glass; and olivine+pigeonite+glass. Compositional data for all phases and glasses are given in Table 2.

3.1. Were the experiments at equilibrium?

To assess whether olivine and liquid (glass) in the experiments were at chemical equilibrium, we compared their MgO and FeO contents with literature data believed to represent equilibria. Jones (1984) showed that equilibrium partition coefficients for Mg and Fe between olivine and melt (e.g., $D_{MgO} = [MgO \text{ in olivine}] / [MgO \text{ in melt}]$) are strongly correlated and so can be used to test for equilibrium. Filiberto et al. (submitted for publication) showed that this relationship is slightly compositionally dependent and Martian basalts, with iron contents higher than terrestrial basalts, have slightly higher D_{FeO} / D_{MgO} ratios. D_{MgO} and D_{FeO} from these experiments (Fig. 1) fall close to the equilibrium regression line of Jones (1984, 1995) and Filiberto et al. (submitted for publication).

The $K_{FeO, MgO}^P = [X_{FeO}^{(ol, pig)} X_{MgO}^{(l)}] / [X_{MgO}^{(ol, pig)} X_{FeO}^{(l)}]$ was also calculated to assess equilibrium of the crystallizing phases (Table 2). All olivine and pyroxene fall within the expected range for equilibrium suggesting that they are in equilibrium (Roeder and Emslie, 1970). Thus, the run products from these experiments are consistent with the attainment of olivine-melt equilibria.

3.2. Phase boundaries

Fig. 2 shows the results of these experiments on the Humphrey+Cl composition. At pressures below 8 kbar, olivine is the liquidus phase, and pigeonite pyroxene is the next solid to crystallize at lower temperatures. At pressures above 9 kbar, pigeonite is the liquidus phase, and olivine is the next solid to appear at lower temperature.

Table 2
Average residual liquid compositions, phase assemblages, and phase compositions

t2.2	Temperature (°C)	1340	1315	1315	1250	1250	1250	1200	1200	1200
t2.3	Pressure (Kb)	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7
t2.4	Run number	HCl-19	HCl-16	HCl-16	HCl-18	HCl-18	HCl-18	HCl-13	HCl-13	HCl-13
t2.5	Phase	Glass	Glass	Pigeonite	Glass	Pigeonite	Olivine	Glass	Pigeonite	Olivine
t2.6	SiO₂	46.09	45.92	53.03	44.52	49.01	35.51	44.52	47.67	34.98
t2.7	TiO₂	0.52	0.58	0.09	0.72	0.24	0.04	0.73	0.39	0.02
t2.8	Al₂O₃	10.17	11.30	2.99	12.93	5.19	0.11	14.24	6.83	0.08
t2.9	FeO_T	18.73	19.16	15.56	18.69	16.15	31.21	18.03	16.90	36.67
t2.10	MnO	0.43	0.42	0.43	0.38	0.51	0.56	0.35	0.46	0.57
t2.11	MgO	10.89	8.64	24.04	5.86	18.91	33.27	4.27	16.22	27.91
t2.12	CaO	7.96	8.54	3.13	9.00	9.22	0.40	7.86	9.35	0.31
t2.13	Na₂O	2.52	2.75	0.21	4.01	0.46	0.07	5.22	0.66	0.04
t2.14	K₂O	0.11	0.14	0.06	0.14	0.00	0.00	0.22	0.01	0.01
t2.15	P₂O₅	0.59	0.64	0.02	0.80	0.03	0.17	1.05	0.11	0.06
t2.16	Cl	0.74	0.89	0.02	0.80	0.00	0.00	1.47	0.07	0.01
t2.17	Total	98.77	98.96	99.58	97.84	99.73	101.34	97.95	98.68	100.65
t2.18	Water (wt.%)									
t2.19	$K_D^{FeO-MgO}$			0.29		0.27	0.29		0.25	0.31
t2.20	Phase Abun. (wt.%)	100	89	11	70	21	9	52	40	8
t2.21	Phase Comp.			En ₆₇ Wo ₉ Fs ₂₄		En ₅₈ Wo ₂₄ Fs ₁₈	Fo ₆₆ Fa ₃₄		En ₅₀ Wo ₂₇ Fs ₂₃	Fo ₅₇ Fa ₄₃
t2.22	Temperature (°C)	1325	1307	1307	1280	1280	1280	1250	1250	1250
t2.23	Pressure (Kb)	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7
t2.24	Run number	HCl-1	HCl-2	HCl-2	HCl-11	HCl-11	HCl-11	HCl-20	HCl-20	HCl-20
t2.25	Phase	Glass	Glass	Pigeonite	Glass	Pigeonite	Olivine	Glass	Pigeonite	Olivine
t2.26	SiO₂	45.91	43.32	51.53	44.92	52.49	36.48	44.67	50.61	35.55
t2.27	TiO₂	0.57	0.55	0.11	0.56	0.12	0.01	0.62	0.17	0.02
t2.28	Al₂O₃	10.68	11.00	2.51	11.03	3.13	0.53	11.00	3.33	0.19
t2.29	FeO_T	19.74	19.97	15.27	19.76	14.98	25.39	19.31	16.71	29.32
t2.30	MnO	0.42	0.42	0.42	0.44	0.42	0.44	0.41	0.53	0.52
t2.31	MgO	10.60	10.51	25.55	10.55	26.37	37.15	7.69	23.07	35.14
t2.32	CaO	7.85	8.25	2.50	8.05	2.37	0.32	9.20	4.97	0.34
t2.33	Na₂O	2.30	2.49	0.09	2.80	0.12	0.03	3.20	0.18	0.03
t2.34	K₂O	0.10	0.11	0.01	0.09	0.01	0.00	0.13	0.00	0.01
t2.35	P₂O₅	0.58	0.60	0.03	0.57	0.05	0.24	0.65	0.01	0.43
t2.36	Cl	0.80	0.68	0.01	0.61	0.01	0.01	0.76	0.01	0.00
t2.37	Total	99.56	97.21	98.01	99.39	100.70	100.62	97.62	99.59	101.55
t2.38	Water (wt.%)	0.1	0.12							
t2.39	$K_D^{FeO-MgO}$			0.31		0.30	0.36		0.29	0.33
t2.40	Phase Abun. (wt.%)	100	97	3	96	4	tr	82	15	3
t2.41	Phase Comp.			En ₇₄ Wo ₇ Fs ₁₉		En ₇₄ Wo ₇ Fs ₁₉	Fo ₇₂ Fa ₂₈		En ₆₈ Wo ₁₃ Fs ₁₉	Fo ₆₈ Fa ₃₂
t2.42	Temperature (°C)	1200	1200	1200	1310	1290	1290	1250	1250	1200
t2.43	Pressure (Kb)	9.7	9.7	9.7	7.7	7.7	7.7	7.7	7.7	7.7
t2.44	Run number	HCl-4	HCl-4	HCl-4	HCl-17	HCl-21	HCl-21	HCl-6	HCl-6	HCl-12
t2.45	Phase	Glass	Pigeonite	Olivine	Glass	Glass	Olivine	Glass	Olivine	Glass
t2.46	SiO₂	46.78	47.96	35.64	45.22	45.20	37.58	47.33	37.96	48.39
t2.47	TiO₂	0.72	0.35	0.03	0.53	0.57	0.01	0.63	0.01	0.74
t2.48	Al₂O₃	13.79	6.42	0.12	10.57	10.32	0.12	12.23	0.07	13.97
t2.49	FeO_T	16.95	16.31	30.26	19.28	19.21	24.20	19.08	27.37	16.53
t2.50	MnO	0.39	0.47	0.53	0.47	0.42	0.44	0.42	0.48	0.36
t2.51	MgO	4.82	17.51	32.43	10.83	10.25	39.09	6.26	34.89	5.20
t2.52	CaO	9.39	9.03	0.34	7.92	8.43	0.26	9.49	0.33	9.68
t2.53	Na₂O	3.10	0.35	0.03	2.47	2.95	0.03	2.99	0.02	3.28
t2.54	K₂O	0.15	0.00	0.00	0.09	0.09	0.01	0.11	0.01	0.13
t2.55	P₂O₅	0.72	0.15	0.22	0.55	0.61	0.22	0.67	0.21	0.76
t2.56	Cl	0.89	0.00	0.01	0.67	0.72	0.01	0.71	0.00	0.79
t2.57	Total	97.71	98.57	99.62	98.61	98.77	101.97	99.93	101.37	99.82
t2.58	Water (wt.%)	0.13			0.09					
t2.59	$K_D^{FeO-MgO}$		0.26	0.27			0.33		0.26	
t2.60	Phase Abun. (wt.%)	73	17	10	100	98	2	85	15	74
t2.61	Phase Comp.		En ₅₅ Wo ₂₃ Fs ₂₂	Fo ₆₅ Fa ₃₅			Fo ₇₄ Fa ₂₆		Fo ₆₉ Fa ₃₁	
t2.62	Temperature (°C)	1200	1200	1300	1280	1280	1280	1200	1200	1200
t2.63	Pressure (Kb)	7.7	7.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
t2.64	Run number	HCl-12	HCl-12	HCl-22	HCl-9	HCl-9	HCl-9	HCl-14	HCl-14	HCl-14
t2.65	Phase	Olivine	Pigeonite	Glass	Glass	Olivine	Olivine	Glass	Olivine	Olivine
t2.66	SiO₂	38.80	52.31	45.20	46.87	37.56	47.07	47.07	36.73	36.73
t2.67	TiO₂	0.03	0.19	0.57	0.58	0.02	0.70	0.70	0.07	0.07
t2.68	Al₂O₃	0.18	3.58	10.06	11.73	0.21	13.06	13.06	0.29	0.29
t2.69	FeO_T	31.57	17.99	19.57	18.48	26.27	16.84	16.84	28.85	28.85
t2.70	MnO	0.58	0.51	0.45	0.41	0.47	0.41	0.41	0.52	0.52

Table 2 (continued)

t2.1	Temperature (°C)	1200	1200	1300	1280	1280	1200	1200
t2.2	Pressure (Kb)	7.7	7.7	5.7	5.7	5.7	5.7	5.7
t2.3	Run number	HCl-12	HCl-12	HCl-22	HCl-9	HCl-9	HCl-14	HCl-14
t2.4	Phase	Olivine	Pigeonite	Glass	Glass	Olivine	Glass	Olivine
t2.75	MgO	28.64	20.18	10.89	7.61	35.65	4.99	31.40
t2.76	CaO	0.40	5.15	8.16	8.65	0.31	10.42	0.35
t2.77	Na ₂ O	0.05	0.20	2.64	2.66	0.02	3.03	0.02
t2.78	K ₂ O	0.01	0.01	0.09	0.11	0.00	0.12	0.01
t2.79	P ₂ O ₅	0.02	0.07	0.60	0.63	0.28	0.70	0.27
t2.80	Cl	0.01	0.02	0.59	0.63	0.00	0.57	0.04
t2.81	Total	100.29	100.20	98.82	98.34	100.78	97.92	98.55
t2.82	Water (wt.%)			0.11				
t2.83	K _p ^{FeO-MgO}	0.35	0.28			0.30		
t2.84	Phase Abun. (wt.%)	20	6	100	89	11	78	22
t2.85	Phase Comp.	Fo61Fa38	En58Wo13Fs29			Fo70Fa30		Fo66Fa34

These results are consistent with a liquidus point multiply saturated with pigeonite + olivine at 8.5 ± 0.5 kbar and 1305 ± 10 °C.

The experiments have Fo₇₄ on the liquidus and range through Fo₅₇. The pyroxenes range from En₇₄Wo₇Fs₁₉ to En₅₀Wo₂₇Fs₂₃, CaO content increases as temperature decreases (Fig. 3). The pyroxene crystallizing from the melt is pigeonite with CaO contents ranging from 2.5 to 9 wt.%. The olivines crystallizing from Humphrey after 10–20% crystallization fall in the compositional uncertainty range predicted by the Mössbauer results for the olivine in the natural rock (Morris et al., 2006, Morris, personal communication), consistent with previous notions that this rock represents a basaltic liquid composition and does not contain cumulate olivine (Monders et al., 2007; Filiberto et al., 2008).

4. Discussion

4.1. The effect of chlorine on phase equilibrium

Fig. 4 compares the pressure–temperature phase relations for the Cl-added experiments and the anhydrous experiments on the Humphrey composition (Filiberto et al., 2008). Both sets of experiments have olivine on the liquidus at low pressure and pigeonite on the liquidus at high pressure. Chlorine has a significant and large effect on the liquidus position—addition of 0.7% Cl moves the olivine–pigeonite liquidus point down 4 kbar and 50 °C (from 12.5 kbar and 1355 °C to 8.5 kbar and 1305 °C). Addition of Cl also, enlarges the stability field of pigeonite greatly compared to the dry experiments (thus accounting for the decreased P of the multiple saturation points).

Addition of Cl does affect the compositions of the solid phases, although not to a great extent. Olivine grown from Cl-bearing melt is

slightly more magnesian than olivine from anhydrous Cl-free melt (Fo₇₄ versus Fo₇₂), even though the former grows at lower temperature. This shift in olivine compositions appears as a change in Fe partitioning between olivine and melt (Fig. 1), where addition of Cl decreases the equilibrium $D_{\text{Fe}}^{\text{ol-melt}}$. Pigeonite shows a similar shift in composition, being more magnesian in the Cl-bearing charges. Also, pigeonites in Cl-bearing charges are less calcic than those in the anhydrous Cl-free experiments (Fig. 5).

The shift in mineral compositions and liquidus temperatures suggests that Cl in the silicate magma forms complexes with its network-modifying cations (Mg, Fe, Ca, Na; see Stebbins and Du, 2002; Webster and De Vivo, 2002). Since the nature of the Cl-cation complexes is compositionally dependent (e.g. Malinin et al., 1989; Stebbins and Du, 2002; Webster and De Vivo, 2002; Bureau and Metrich, 2003), and Martian basalts are high in iron and magnesium it seems likely that, in our experiments, Cl complexes mostly with Fe, Mg, and Ca. This Cl-complexation would decrease the FeO- and MgO- (and other cation) activity in the melt and increase the overall SiO₂ activity of the melt. Increasing the silica activity of the melt will cause the melt to become more polymerized, which should shift the liquidus temperature down and stabilize pigeonite with respect to olivine.

Although this model for complexation between Cl and network-modifying cations seems reasonable, it cannot be verified. To test the model, we performed several ‘thought experiments’ using the computer code PMELTS (Ghiorso et al., 2002) to predict the location of the liquidus of the silicate melt, assuming Cl and its complexed cations were effectively unavailable to the surrounding silicate melt. To model this in PMELTS, we thus ignored Cl, removed proportions of

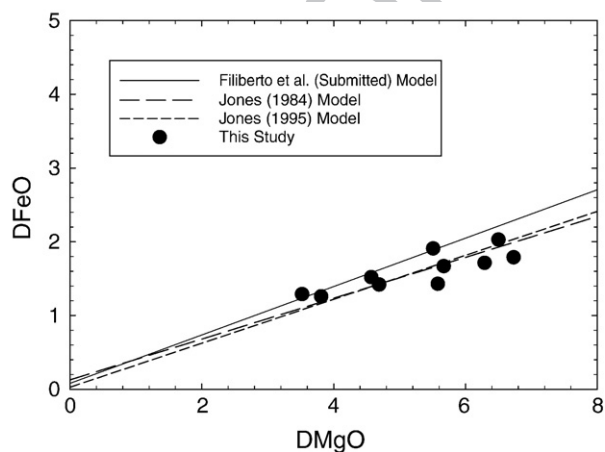


Fig. 1. Cation fraction crystal/melt partition coefficients for Mg (D_{MgO}) and Fe (D_{FeO}) for experimentally-produced olivine from this study compared with the partitioning models (Filiberto et al., submitted for publication; Jones, 1984, 1995).

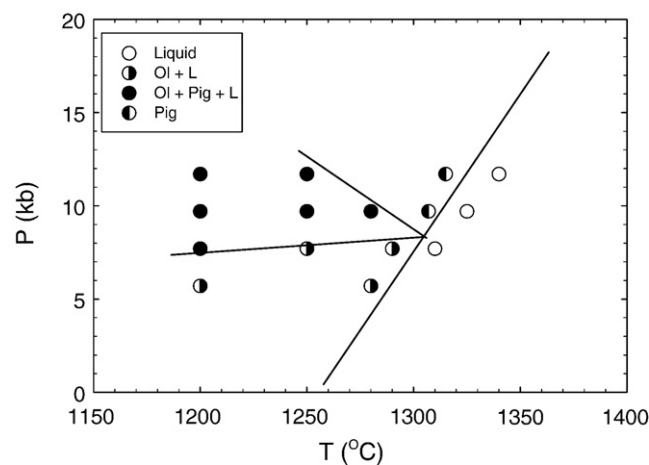


Fig. 2. Experimental determined phase relations for synthetic Cl-added Humphrey basalt. Open circles are experiments that contained liquid only, right half filled circles are olivine and liquid, filled circles are olivine, pigeonite, and liquid, and left half filled circles are pigeonite and liquid.

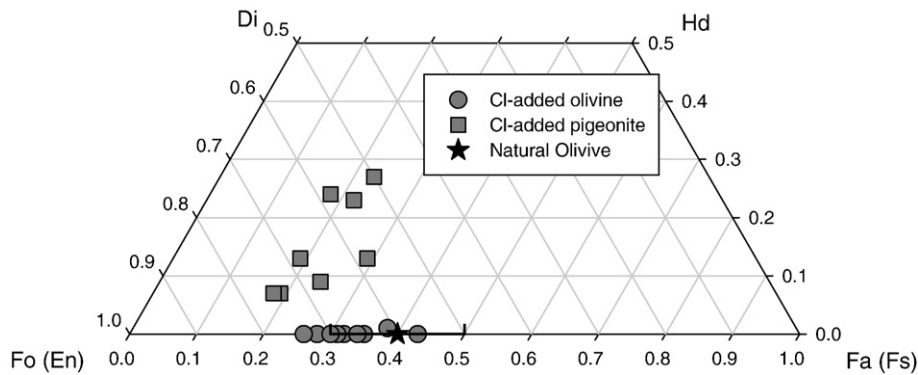


Fig. 3. Compositions of experimentally-produced pigeonite (gray squares) and olivine (gray circles) plotted as QUILF (Andersen et al., 1993) projections for all pressures produced in this study. The olivine compositions predicted to be in the rock (Morris et al., 2004) are shown by a black star with uncertainty in the measurement (\pm Fo₁₀ Morris, personal communication).

network-modifying cations from the silicate melt, and calculated the liquidus location for the remaining silicate composition. However, it was not possible to reproduce the experimental results on the Cl-added Humphrey composition with this model and PMELTS calculations (although it is not clear that the program is properly calibrated for these compositions). PMELTS shows that complexing Cl with Fe, up to 8 Fe per Cl, will not produce the observed 50 °C reduction in the liquidus because the melt becomes more magnesian (as does the observed olivine, see above). Complexing Cl with 8 Mg per Cl should reduce the liquidus temperatures by ~40 °C, but should yield more ferroan olivine than the Cl-absent case, rather than the more magnesian olivine that is observed. So, this simple mechanistic model cannot be correct, and additional study and modeling are clearly needed.

4.2. Comparing the effects of volatiles: Cl vs water

Fig. 6 compares the effect of water and Cl on the liquidus relations of the Humphrey composition. As shown above, the anhydrous liquidus has a multiple saturation point at 12.5 kbar and 1365 °C, while the Cl-added liquidus (0.7 wt.% Cl) has a multiple saturation point at 8.5 kbar and 1305 °C. The hydrous (~0.8 wt.% water) liquidus has a multiple saturation point at 10.6 kbar and 1320 °C (Monders et al., 2007). Thus 0.7 wt.% Cl depresses the liquidus temperature of the Humphrey composition as much as does 0.8 wt.% water. So, on a molar basis, Cl is twice as effective as water at depressing the liquidus temperature of the Humphrey composition. As shown above, Cl also

has a much larger effect on the multiple saturation pressure and pyroxene/olivine stability than water.

Water attacks bridging oxygens in the melt structure, which depolymerizes the melt and depresses its liquidus (e.g. Zeng et al., 1999). However, this change appears to have little (if any) effect on olivine–pyroxene–melt phase equilibria and multiple saturation pressure. Chlorine, by forming complexes in the melt, affects cation activity, viscosity, as well as polymerization of the melt and thereby causes the liquidus depression, increased pigeonite stability, and multiple saturation point depression. This is seen in the phases crystallizing from the melts. The pyroxenes show a difference in composition between the chlorine added and the hydrous and anhydrous experiments. The hydrous and anhydrous experiments form a linear array with the hydrous experiments being less calcic than the anhydrous experiments due to the lower crystallization temperatures. The chlorine added experiments do not plot on this linear array and have more magnesium than the pyroxene in the hydrous and anhydrous experiments (Fig. 7). This suggests that by forming Fe–Cl and perhaps Mg–Cl or other cation–Cl complexes in the melt, chlorine decreases the activities of Fe and Mg silicates (and oxides) in the melt. The olivine crystallizing from the hydrous experiments is Fo₇₅ while the chlorine added experiments have Fo₇₄ on the liquidus and the anhydrous experiments have Fo₇₂, this discrepancy can be accounted for by the slight difference in compositions between the hydrous experiments and the Cl-added and hydrous experiments (Table 3). (See Filiberto et al., 2008 for a full description of the differences between the hydrous and anhydrous experiments).

4.3. Implications for basalt genesis

4.3.1. Mars: water or not?

One of the current, critical unknowns about Mars is its water cycle—sources, sinks, abundances, and history of its H₂O (e.g. Carr, 1996). And, one of the more contentious aspects of its water cycle is the abundance of water transferred from the Martian mantle to its surface in basalts. Experimental studies of dry and volatile-bearing compositions have been central to this discussion.

On one hand, several experimental studies have concluded that Martian basaltic magmas contained significant water, from 0.5 to 2% H₂O by weight. Johnson et al. (1991) inferred that the parent magma of the Chassigny martian meteorite, a dunite, contained 1.5 wt.% H₂O; this inference is in accord with the work of Nekvasil et al. (2007), who concluded that Chassigny's parent magma contained >0.5 wt.% dissolved water during its crystallization at 7–11 kbar. Dann et al. (2001) inferred that the parent magmas of the shergottite basalts contained ~2.0 wt.% dissolved water at shallow pressures. And Dalton et al. (2007) and Draper (2007) inferred that the Martian basalt Yamato 980459 originally contained 0.5–2.0 wt.% H₂O as a magma in Mars' mantle. Mineral chemical zoning patterns were interpreted to

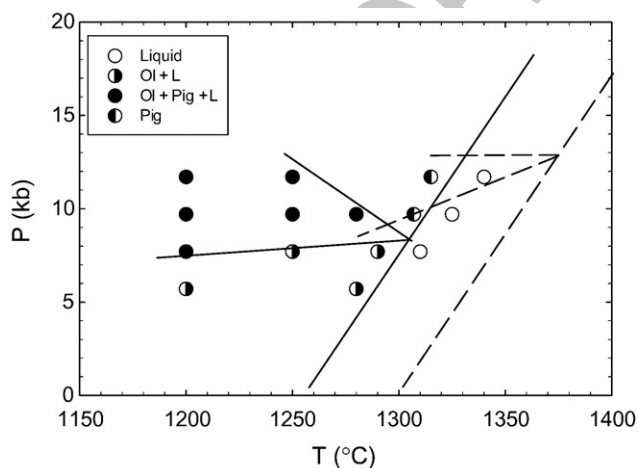


Fig. 4. Experimentally determined phase relations from this study (solid lines) compared with previously anhydrous published experimental work (dashed lines; Filiberto et al., 2008).

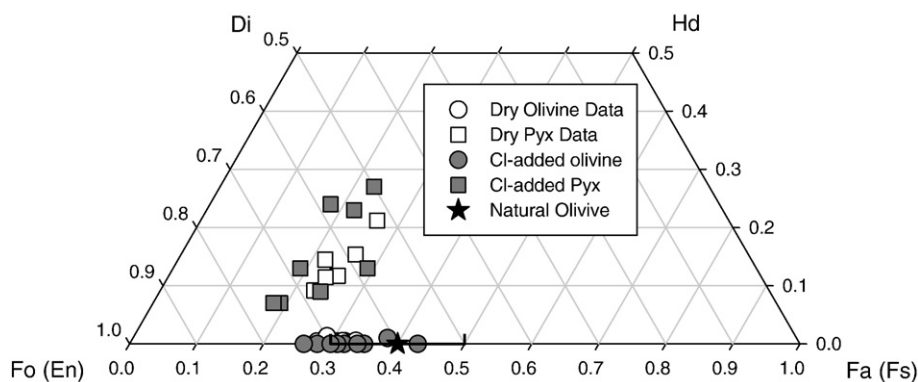


Fig. 5. Compositions of experimentally-produced pigeonite (squares) and olivine (circles) plotted as QUILF (Andersen et al., 1993) projections for all pressures produced in this study (gray symbols) compared with the anhydrous experiments (white symbols; Filiberto et al., 2008). The olivine compositions predicted to be in the rock (Morris et al., 2004) are shown by a black star with uncertainty in the measurement ($\pm Fo_{10}$ Morris, personal communication).

417 be consistent with such large water contents (Lentz et al., 2001;
418 McSween et al., 2001).

419 On the other hand, several experimental and petrographic studies
420 concluded that parent magmas of the Martian meteorite basalts
421 contained nearly no H₂O. Foremost among these is Stolper and
422 McSween (1979), who found that phase relations and mineral

423 compositions of the shergottite Martian meteorites were consistent
424 with anhydrous magma. In addition, the Martian meteorites now
425 contain nearly no H₂O, and show very limited direct evidence that
426 they ever did (e.g. Carr and Wänke, 1992; Karlsson et al., 1992; Watson
427 et al., 1994; Leshin et al., 1996; Leshin, 2000; Dyar et al., 2004; Jones,
428 2004, 2007).

429 These conflicting results, water-rich versus water-poor, may be
430 reconcilable through the experimental results here, where we have
431 shown that chlorine affects mineral-basalt phase relations in the same
432 way and to similar extent as does water (at least for liquidus relations).
433 As shown in Fig. 6, similar weight proportions of H₂O and Cl have
434 similar effects on the liquidus temperatures of the Humphrey basalt. If
435 these effects can be extrapolated to other Martian magma composi-
436 tions, then Cl-rich Martian magmas compositions would reasonably
437 have similar mineral-melt phase equilibria as do water-rich magmas.

438 So, did the parent magmas of Martian meteorite basalts contain
439 significant chlorine? There is strong evidence that they did. All of the
440 Martian meteorites contain apatite, which is chlorapatite or fluor-
441 chlorapatite, with limited or minimal hydroxyl component (e.g.
442 Treiman et al., 1993; Sautter et al., 2006; McCubbin and Nekvasil,
443 2008). Many of the Martian meteorites also contain kaersutitic
444 amphibole in magmatic inclusions, and those amphiboles are not
445 hydroxy-kaersutites, but chlor-, chlor-fluor- or oxy-kaersutites (Tre-
446 iman et al., 1993; Watson et al., 1994; Sautter et al., 2006). Because
447 apatite and amphibole accept OH from basaltic magma more readily
448 than Cl (Stormer and Carmichael, 1971; Mathez and Webster, 2005;
449 Patino Douce and Roden, 2006), it seems likely that the parent
450 magmas of the Martian meteorites were richer in Cl than OH. If so, the
451 experiments here, on a Cl-rich anhydrous composition, are relevant.

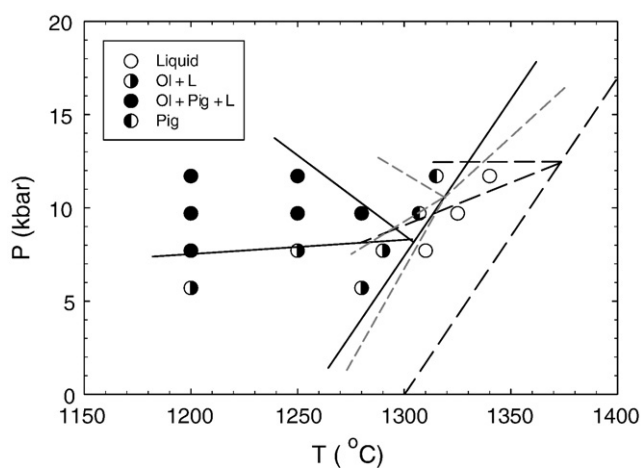


Fig. 6. Experimentally determined phase relations from this study (solid lines) compared with previously anhydrous published experimental work (black dashed lines; Filiberto et al., 2008) and hydrous experimental work (gray dashed lines; Monders et al., 2007).

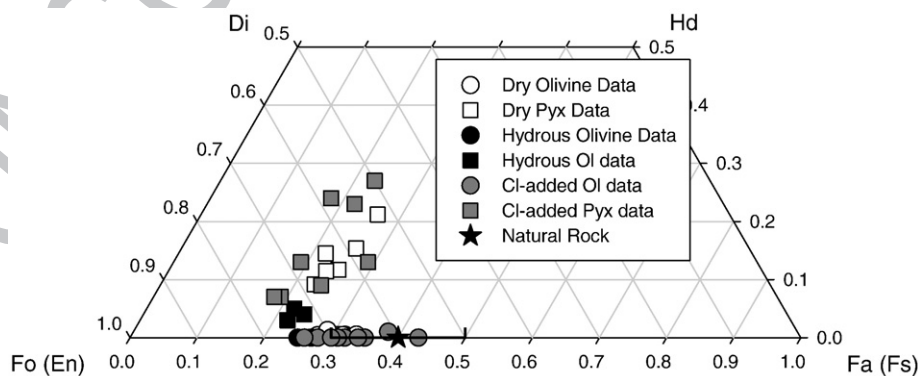


Fig. 7. Compositions of experimentally-produced pigeonite (squares) and olivine (circles) plotted as QUILF (Andersen et al., 1993) projections for all pressures produced in this study (gray symbols) compared with the anhydrous experiments (white symbols; Filiberto et al., 2008) and hydrous experiments (black symbols; Monders et al., 2007). The olivine compositions predicted to be in the rock (Morris et al., 2004) are shown by a black star with uncertainty in the measurement ($\pm Fo_{10}$ Morris, personal communication).

Table 3

Starting composition compared with starting composition of previous work (normalized to 100%)

Wt.%	Experimental Glass Composition	Monders et al. (2007) ^a	Filiberto et al. (2008)
SiO ₂	46.10	46.85	45.99
TiO ₂	0.55	0.48	0.56
Al ₂ O ₃	10.48	10.69	10.89
Cr ₂ O ₃	0.00	0.79	0.00
FeO _T	19.54	18.91	20.01
MnO	0.45	0.43	0.42
MgO	10.92	11.46	10.89
CaO	8.06	8.02	8.12
Na ₂ O	2.51	1.77	2.44
K ₂ O	0.10	0.06	0.10
P ₂ O ₅	0.59	0.56	0.58
Cl	0.71	0.00	0.00
Total	100.00	100.00	100.00

FeO_T = total iron (Fe₂O₃ + FeO).^a = Ave estimated composition.

In fact, this Cl-enrichment of Martian basalts is consistent with the inferred composition of Mars and its mantle. Based on the Martian meteorite compositions, Mars is enriched in cosmochemically volatile elements compared to the Earth (e.g. Dreibus and Wänke, 1986, 1987). For instance, Mars is inferred to have bulk abundance ratios for Na/Th and K/Th of $\sim 0.3 \times \text{Cl}$, compared to the Earth's values of ~ 0.2 and $\sim 0.1 \times \text{Cl}$. Mars' enrichment in chlorine is similar—Cl/Th near $0.03 \times \text{Cl}$ compared to the Earth's mantle's inferred $\sim 0.01 \times \text{Cl}$ (Dreibus and Wänke, 1985, 1987). This general Cl-enrichment is consistent with the presence of Cl-rich apatite and amphibole in the Martian meteorites (e.g. Sautter et al., 2006; McCubbin and Nekvasil, 2008), and with *in situ* analyses on Mars surface (see Introduction). For Mars, then, chlorine may take the place of water as the principal volatile element in igneous petrogenesis.

4.3.2. Earth: water- and chlorine-rich systems

Unlike the Martian meteorites, which show little evidence for magmatic water, terrestrial basalts contain up to a few wt.% water. However, terrestrial basalts also contain up to 0.7 wt.% chlorine as well (Johnston, 1980; Webster and Rebbert, 2001). If the effects of chlorine on the Humphrey basalt from this study can be extrapolated to terrestrial basaltic compositions, then Cl-rich systems would have similar mineral-melt phase equilibria to water-rich magmas. This must be considered in the petrogenesis of Cl- water-rich magmas, like those of subduction zones and evolved intra-plate suites.

Typical terrestrial oceanic island tholeiitic basalts and mid-ocean ridge basalts contain little chlorine (e.g. Johnston, 1980; Jambon et al., 1995), but magmas associated with subduction zones (and some intra-plate alkali magmas) can contain up to 0.7 wt.% Cl (e.g. Johnston, 1980; Webster and Rebbert, 2001). As shown above, small proportions of Cl in magma can affect its liquidus temperature, permitting it to evolve to lower temperatures before solidifying. Chlorine will increase pyroxene stability to lower pressures and therefore change the residual liquids produced by fractionation and partial melting. Previous fractionation and partial melting experimental investigations have inferred that water-rich systems are required to produce intra-plate alkali-rich compositions as well as andesites associated with subduction zones (e.g. Grove et al., 2002; Nekvasil et al., 2004; Whitaker et al., 2008), but chlorine-rich systems might reasonably yield the same products. Therefore, fractionational crystallization and partial melting models of chlorine-rich magmas should explicitly account for the effects of Cl.

5. 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 Mg, and Ca, Cl causes an increase in 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 dissolved chlorine will enable basalts on Mars and Earth to be produced at lower pressures and temperatures. These results suggest that chlorine is important during basalt genesis and needs to be included in models of partial melting and fractionation on Mars and Earth.

Acknowledgements

We thank J. Webster, D. Baker, and A. Aiuppa for organizing the Halogens workshop. We are grateful to L. Le and A. Peslier for assistance with microprobe analyses. We are appreciative of J. Longhi and an anonymous reviewer for helpful reviews of this manuscript. This work was supported by NASA MFR grant # NNG06GH29G to A.H. Treiman, and by the Lunar and Planetary Institute. LPI contribution # 1425.

References

- Andersen, D.J., Lindsley, D.H., Davidson, P.M., 1993. QUIF: A Pascal Program to assess equilibria among Fe–Mg–Mn–Ti oxides, pyroxenes, olivine, and quartz. *Computers and Geosciences* 19 (9), 1333–1350.
- Banin, A., Han, F.X., Kan, I., Cicelsky, A., 1997. Acidic volatiles and the Mars soil. *Journal of Geophysical Research* 102 (E6), 13341–13356.
- Boynton, W.V., et al., 2007. Concentration of H, Si, Cl, K, Fe, and thin the low- and mid-latitude regions of Mars. *Journal of Geophysical Research* 112 (E12S99). doi:10.1029/2007JE002887.
- Bridges, J.C., et al., 2001. Alteration assemblages in Martian meteorites: implications for near-surface processes. *Chronology and Evolution of Mars* 365–392.
- Bureau, H.e., Metrich, N., 2003. An experimental study of bromine behaviour in water-saturated silicic melts. *Geochimica et Cosmochimica Acta* 67 (9), 1689–1697.
- Carr, M.H., 1996. Accretion and evolution of water. *Water on Mars*. Oxford University Press, New York, pp. 146–169.
- Carr, M.J., 2000. Iqpet for Windows. Terra Softa Inc., Somerset, N.J.
- Carr, M.H., Wänke, H., 1992. Earth and Mars: water inventories as clues to accretional histories. *Icarus* 98 (1), 61–71.
- Clark, B.C., et al., 2005. Chemistry and mineralogy of outcrops at Meridiani Planum. *Earth and Planetary Science Letters* 240, 73–94.
- Dalton, H.A., Sharp, T.G., Holloway, J.R., 2007. Investigation of the effects of water on a Martian mantle composition. *Lunar and Planetary Science, XXXVII: Abstract # 2102*.
- Dann, J.C., Holzheid, A.H., Grove, T.L., McSween, H.Y., 2001. Phase equilibria of the Shergotty meteorite: constraints on pre-eruptive water contents of martian magmas and fractional crystallization under hydrous conditions. *Meteoritics & Planetary Science* 36 (6), 793–806.
- Dingwell, D.B., Hess, K.U., 1998. Melt viscosities in the system Na–Fe–Si–OF–Cl: contrasting effects of F and Cl in alkaline melts. *American Mineralogist* 83 (9–10), 1016–1021.
- Dixon, J.E., Stolper, E.M., Holloway, J.R., 1995. An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. *Journal of Petrology* 36 (6), 1607–1631.
- Draper, D.S., 2007. Water-undersaturated near-liquidus phase relations of Yamato 980459. *Lunar and Planetary Science, XXXVII: Abstract # 1447*.
- Dreibus, G., Wänke, H., 1985. Mars, a volatile-rich planet. *Meteoritics* 20 (2), 367–381.
- Dreibus, G., Wänke, H., 1986. Comparison of Cl/Br and Br/I ratios in terrestrial samples and SNC meteorites. *MECA Workshop on the Evolution of the Martian Atmosphere: 13–14*.
- Dreibus, G., Wänke, H., 1987. Volatiles on Earth and Mars—a comparison. *Icarus* 71 (2), 225–240.
- Dyar, M.D., Mackwell, S.J., Seaman, S.J., Marchand, G.J., 2004. Evidence for a wet, reduced Martian interior. *Lunar and Planetary Science, XXXV: Abstract # 1348*.
- Filiberto, J., Treiman, A.H., Le, L., 2008. Crystallization experiments on a Gusev Adirondack basalt composition. *Meteoritics & Planetary Science*.
- Filiberto, J., Jackson, C., Treiman, A.H., Jones, J.H., Le, L. submitted for publication. Partitioning of Ni between Olivine and an Iron-Rich Basalt: Experiments, Partition Models, and Planetary Implications *American Mineralogist*.
- Gellert, R., et al., 2006. Alpha particle X-ray spectrometer (APXS): Results from Gusev crater and calibration report. *Journal of Geophysical Research-Planets* 111 (E2), E02S05. doi:10.1029/2005JE002555.
- Ghiorso, M.S., Hirschmann, M.M., Reiners, P.W., Kress, V.C., 2002. The pMELTS: a revision of MELTS for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa. *Geochemistry Geophysics Geosystems* 3, 1030. doi:10.1029/2001GC000217.
- Greenwood, J.P., 2005. Chlorine-rich apatites in SNCs: evidence for magma-brine interactions on Mars? *Meteoritics & Planetary Science, 40 Supplement, Proceedings of 68th Annual Meeting of the Meteoritical Society: Abstract #5312*.
- Grotzinger, G., et al., 2005. Stratigraphy and sedimentology of a dry to wet eolian depositional system, Burns formation, Meridiani Planum, Mars. *Earth and Planetary Science Letters* 240, 11–72.

- Grove, et al., 2002. The role of an H₂O-rich fluid component in the generation of primitive basaltic andesites and andesites from the Mt. Shasta region, N. California. *Contributions to Mineralogy and Petrology* 142 (4), 375–396.
- Hausrath, E.M., Navarre-Sitchler, A.K., Sak, P.B., Steefel, C.I., Brantley, S.L., 2008. Basalt weathering rates on Earth and the duration of liquid water on the plains of Gusev Crater, Mars. *Geology* 36 (1), 67–70.
- Holloway, J.R., Pan, V., Gudmundsson, G., 1992. High pressure fluid-absent melting experiments in the presence of graphite–oxygen fugacity, ferric/ferrous ratio and dissolved CO₂. *European Journal of Mineralogy* 4 (1), 105–114.
- Icenhower, J.P., London, D., 1997. Partitioning of fluorine and chlorine between biotite and granitic melt: experimental calibration at 200 MPa H₂O. *Contributions to Mineralogy and Petrology* 127, 17–29.
- Jambon, A., Deruelle, B., Dreibus, G., Pineau, F., 1995. Chlorine and bromine abundance in MORB: the contrasting behaviour of the Mid-Atlantic Ridge and East Pacific Rise and implications for chlorine geodynamic cycle. *Chemical Geology* 126 (2), 101–117.
- Johnson, M.C., Rutherford, M.J., Hess, P.C., 1991. Chassigny petrogenesis—melt compositions, intensive parameters, and water contents of martian (questionable) magmas. *Geochimica et Cosmochimica Acta* 55 (1), 349–366.
- Johnston, D.A., 1980. Volcanic contribution of chlorine to the stratosphere: more significant to ozone than previously estimated? *Science* 209 (4455), 491–493.
- Jones, J.H., 1984. Temperature-independent and pressure-independent correlations of olivine liquid partition coefficients and their application to trace-element partitioning. *Contributions to Mineralogy and Petrology* 88 (1–2), 126–132.
- Jones, J.H., 1995. Experimental trace element partitioning. In: Ahrens, T.J. (Ed.), *Rock physics and phase relations: a handbook of physical constants*. American Geophysical Union, Washington D.C., pp. 73–104.
- Jones, J.H., 2004. The edge of wetness: the case for dry magmatism on Mars. *Lunar and Planetary Science*, 35th: Abstract # 1798.
- Jones, J.H., 2007. The edge of wetness: the case for dry magmatism on Mars, II. Workshop on Water in Planetary Basalts: Abstract # 2006.
- Karlsön, H.R., Clayton, R.N., Gibson Jr., E.K., Mayeda, T.K., 1992. Water in SNC meteorites: evidence for a martian hydrosphere. *Science* 255 (5050), 1409–1411.
- Keller, J.M., et al., 2007. Equatorial and midlatitude distribution of chlorine measured by Mars Odyssey GRS. *Journal of Geophysical Research* 111 (E03S08).
- Lentz, R.C.F., McSween, H.Y., Ryan, J., Riciputi, L.R., 2001. Water in martian magmas: clues from light lithophile elements in shergottite and nakhlite pyroxenes. *Geochimica et Cosmochimica Acta* 65 (24), 4551–4565.
- Leshin, L.A., 2000. Insights into martian water reservoirs from analyses of martian meteorite QUE94201. *Geophysical Research Letters* 27 (13), 2017.
- Leshin, L.A., Epstein, S., Stolper, E.M., 1996. Hydrogen isotope geochemistry of SNC meteorites. *Geochimica et Cosmochimica Acta* 60 (14), 2635–2650.
- Malinin, S.D., Kravchuk, I.F., Delbove, F., 1989. Chloride distribution between phases in hydrated and dry chloride–aluminosilicate melt systems as a function of phase composition. *Geochemistry International* 26, 32–38.
- Mandeville, C.W., et al., 2002. Determination of molar absorptivities in infrared absorption bands of H₂O in andesitic glasses. *American Mineralogist* 87, 813–821.
- Mathez, E.A., Webster, J.D., 2005. Partitioning behavior of chlorine and fluorine in the system apatite–silicate melt–fluid. *Geochimica et Cosmochimica Acta* 69 (5), 1275–1286.
- McCubbin, F.M., Nekvasil, H., 2008. Maskelynite-hosted apatite in the Chassigny meteorite: insights into late-stage magmatic volatile evolution in martian magmas. *American Mineralogist* 93, 676–684.
- McLennan, S., et al., 2005. Provenance and diagenesis of the evaporite-bearing Burns formation, Meridiani Planum, Mars. *Earth and Planetary Science Letters* 240, 95–121.
- McSween, H.Y., et al., 2001. Geochemical evidence for magmatic water within Mars from pyroxenes in the Shergottite meteorite. *Nature* 409 (6819), 487–490.
- McSween, H.Y., et al., 2006. Characterization and petrologic interpretation of olivine-rich basalts at Gusev Crater, Mars. *Journal of Geophysical Research-Planets* 111 (E2), E02510. doi:10.1029/2005E02477.
- Médard, E., Grove, T., 2007. The effect of H₂O on the olivine liquidus of basaltic melts: experiments and thermodynamic models. *Contributions to Mineralogy and Petrology*.
- Monders, A.G., Médard, E., Grove, T.L., 2007. Phase equilibrium investigations of the Adirondack-class basalts from the Gusev plains, Gusev crater, Mars. *Meteoritics & Planetary Science* 42 (1), 131–148.
- Morris, R.V., et al., 2004. Mineralogy at Gusev crater from the Mössbauer spectrometer on the Spirit Rover. *Science* 305 (5685), 833–836.
- Morris, R.V., et al., 2006. Mössbauer mineralogy of rock, soil, and dust at Gusev crater, Mars: Spirit's journey through weakly altered olivine basalt on the plains and pervasively altered basalt in the Columbia Hills. *Journal of Geophysical Research* 111 (E02S13). doi:10.1029/2005JE002584.
- Nekvasil, H., et al., 2004. The origin and evolution of silica-saturated alkalic suites: an experimental study. *Journal of Petrology* 45 (4), 693–721.
- Nekvasil, H., Filiberto, J., McCubbin, F.M., Lindsley, D.H., 2007. Alkalic parental magmas for the chassignites? *Meteoritics & Planetary Science* 42 (6), 979–992.
- Nelson, M.J., Newsom, H.E., Draper, D.S., 2005. Incipient hydrothermal alteration of basalts and the origin of martian soil. *Geochimica et Cosmochimica Acta* 69 (10), 2701–2711.
- Onuma, K., Tohara, T., 1983. Effect of chromium on phase relations in the join forsterite–anorthite–diopside in air at 1 atm. *Contributions to Mineralogy and Petrology* 84 (2), 174–181.
- Patino Douce, A.E., Roden, M., 2006. Apatite as a probe of halogen and water fugacities in the terrestrial planets. *Geochimica et Cosmochimica Acta* 70 (12), 3173–3196.
- Rao, M.N., Nyquist, L.E., Wentworth, S.J., Sutton, S.R., Garrison, D.H., 2008. The nature of martian fluids based on mobile element studies in salt-assemblages from Martian meteorites. *Journal of Geophysical Research-Planets* 113 (E06002). doi:10.1029/2007JE002958.
- Rieder, R., et al., 2004. Chemistry of rocks and soils at Meridiani Planum from the alpha particle X-ray spectrometer. *Science* 306, 1746–1749.
- Roeder, P.L., Emslie, R.F., 1970. Olivine–liquid equilibrium. *Contributions to Mineralogy and Petrology* 29 (4), 275–289.
- Sautter, V., Jambon, A., Boudouma, O., 2006. Cl–amphibole in the nakhlite MIL 03346: evidence for sediment contamination in a Martian meteorite. *Earth and Planetary Science Letters* 252 (1–2), 45–55.
- Squyres, S.W., et al., 2004. The Spirit Rovers Athena science investigation at Gusev crater, Mars. *Science* 305 (5685), 794–799.
- Squyres, S.W., et al., 2007. Pyroclastic activity at Home Plate in Gusev crater, Mars. *Science* 316, 738–742.
- Stebbins, J.F., Du, L.S., 2002. Chloride ion sites in silicate and aluminosilicate glasses: a preliminary study by 35Cl solid-state NMR. *American Mineralogist* 87 (2–3), 359–363.
- Stolper, E.M., McSween, H.Y., 1979. Petrology and origin of the shergottite meteorites. *Geochimica et Cosmochimica Acta* 43, 1475–1498.
- Stormer, J.C., Carmichael, I.S.E., 1971. Fluorine–hydroxyl exchange in apatite and biotite: a potential igneous geothermometer. *Contributions to Mineralogy and Petrology* 31 (2), 121–131.
- Tosca, N.J., McLennan, S.M., Lindsley, D.H., Schoonen, M.A.A., 2004. Acid–sulfate weathering of synthetic Martian basalt: the acid fog model revisited. *Journal of Geophysical Research-Planets* 109 (E5).
- Treiman, A.H., 2005. The nakhlite meteorites: augite-rich igneous rocks from Mars. *Chemie der Erde-Geochemistry* 65 (3), 203–270.
- Treiman, A., Barrett, R., Gooding, J., 1993. Preterrestrial aqueous alteration of the Lafayette(SNC) meteorite. *Meteoritics* 28 (1), 86–97.
- Treiman, A.H., Amundsen, H.E.F., Blake, D.F., Bunch, T., 2002. Hydrothermal origin for carbonate globules in Martian meteorite ALH84001: a terrestrial analogue from Spitsbergen (Norway). *Earth and Planetary Science Letters* 204 (3–4), 323–332.
- Watson, L.L., Hutcheon, I.D., Epstein, S., Stolper, E.M., 1994. Water on Mars: clues from deuterium/hydrogen and water contents of hydrous phases in SNC meteorites. *Science* 265 (5168), 86–90.
- Webster, J.D., De Vivo, B., 2002. Experimental and modeled solubilities of chlorine in aluminosilicate melts, consequences of magma evolution, and implications for exsolution of hydrous chloride melt at Mt. Somma–Vesuvius. *American Mineralogist* 87, 1046–1061.
- Webster, J.D., Rebbert, C.R., 1998. Experimental investigation of H₂O and Cl₂ solubilities in F-enriched silicate liquids; implications for volatile saturation of topaz rhyolite magmas. *Contributions to Mineralogy and Petrology* 132 (2), 198–207.
- Webster, J.D., Rebbert, C.R., 2001. The geochemical signature of fluid-saturated magma determined from silicate melt-inclusions in ascension island granite xenoliths. *Geochimica et Cosmochimica Acta* 65 (1), 123–136.
- Webster, J.D., Kinzler, R.J., Mathez, E.A., 1999. Chloride and water solubility in basalt and andesite melts and implications for magmatic degassing. *Geochimica et Cosmochimica Acta* 63 (5), 729–738.
- Whitaker, M., Nekvasil, H., Lindsley, D., McCurry, M., 2008. Can crystallization of olivine tholeiite give rise to potassic rhyolites?—an experimental investigation. *Bulletin of Volcanology* 70 (3), 417–434.
- Zeng, Q., Nekvasil, H., Grey, C.P., 1999. Proton environments in hydrous aluminosilicate glasses: A H-1 MAS, H-1/Al-27, and H-1/Na-23 TRAPDOR NMR study. *Journal of Physical Chemistry B* 103 (35), 7406–7415.
- Zimova, M., Webb, S., 2006. The effect of chlorine on the viscosity of Na₂O–Fe₂O₃–Al₂O₃–SiO₂ melts. *American Mineralogist* 91 (2–3), 344–352.