

**THE EFFECT OF S AND Cl ON MINERAL STABILITY IN MARTIAN MAGMAS** G. Ustunisi<sup>1</sup>, H. Nekvasil<sup>1</sup>, F. M. McCubbin<sup>2</sup> and D. H. Lindsley<sup>1</sup>, <sup>1</sup>Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, Hanna.Nekvasil@stonybrook.edu, Gokce.Ustunisi@sunysb.edu, <sup>2</sup>Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd., NW, Washington, DC 20015, fmccubbin@ciw.edu

**Introduction:** Orbiter and rover data have shown that sulfur is abundant on the Martian surface (e.g., [1]-[3]). The abundance of sulfides and the presence of sulfates in martian meteorites (e.g., [4]-[6]) confirm the presence of significant amount of S in martian igneous rocks. Chlorine is also found in abundance on Mars, both on the surface, as evidenced by chlorides (e.g., [7]-[9]), and within martian lithologies in minerals such as apatite, biotite, and some amphibole (e.g., [10], [11]).

The source of surficial S and Cl is generally ascribed to volcanic emissions upon decompression and degassing of magma (e.g., [12]). This characteristic may have been inherited from the mantle source or produced by secondary processes such as extraneous fluid/melt interaction. Specific evidence for Cl- and S-rich magmas is seen in crystallized melt inclusions of MIL 03346 [6] and the intercumulate melt of the Chassigny dunite [11]. But what effect did these volatiles have on mineral stability? How do we identify rocks on the surface that have originated from Cl- and S-rich magmas? Certainly the presence of Cl- and S-bearing phases makes such identification straightforward; however, the abundance of such phases may be too small for reliable identification from orbiter spectra. Furthermore, Cl- and S- can be readily lost from magmas during fluid exsolution. In fact, the presence of a significant amount of HCl in the melt can cause early second boiling to produce a supercritical fluid even at elevated pressure [13]. Loss of such a fluid can destabilize Cl- and S-rich phases. In this case, the absence of Cl- and S-rich phases would not necessarily indicate low Cl and S contents in the parental magmas and evaluation of the Cl- and S- bearing nature of the parental magmas must be based on the effect of these volatiles on the stability of S- and Cl- poor minerals.

There is some evidence that Cl can have high solubility in basaltic melts and can affect mineral stability by complexing with divalent network-modifying cations [14]. This was observed for the Humphrey composition by enhanced pigeonite stability relative to olivine [15]. These results suggest that the minerals of igneous protoliths prior to alteration rocks and available for alteration may differ depending upon the Cl/water ratio of the magma from which they crystallized. Less is known about the effect of S and the complexities induced by its potential for two valence states in silicate melts.

Experiments were conducted here to investigate the effect of Cl and S on the stability of both Cl- and S-bearing and Cl- and S-poor silicates. The results provide insights into the nature of the mineralogy of surface lithologies that could act as precursors to alteration assemblages.

**Experimental design:** The experiments were designed to provide data on mineral/melt equilibria for a S- and Cl- rich composition that can be compared with existing data for the equivalent Cl- and S-free composition. An additional major goal of the design was to simulate a process that has relevance to a known martian lithology, chosen here to be the Chassigny dunite. In their study of the apatite of the Chassigny dunite, [11] concluded that Cl-rich high temperature fluids percolating upward from deeper hotter parts of the magma plumbing system interacted with the interstitial melt of the cumulus pile and exchanged water and Cl. They noted that the melt inclusion and interstitial mineral phases departed in composition just before feldspar and kaersutite crystallized and placed the timing of this fluid/melt interaction at this stage. The melt composition at this point is inferred from the experiments and conclusions of [16]. These workers experimentally determined the phase equilibria of a magma with the composition of the Columbia Hills rock Backstay [17]. They concluded that it is a reasonable analog to the type of melt that gave rise to the Chassigny dunite and was trapped in melt inclusions. Their experiments indicate that the liquid residual to crystallization of Backstay with 2.6 wt% water at the base of ~65 km crust at 1050°C crystallizes olivine, and two pyroxenes, but is not yet saturated with feldspar or kaersutite. The experiments conducted here were based on this composition but with a volatile content modified to reflect fluid/melt interaction in the intercumulus zone: 1.5 wt% Cl, 0.3 wt% S, 0.4 wt% water (Table 1).

**Experimental details:** The composition shown in Table 1 was prepared in two stages. First, a mixture of oxides and silicates was made to replicate the liquid composition residual to Backstay crystallization at 1050°C (based on the data of [16]). This mixture was added to a graphite-lined Pt capsule into which water was syringed on sufficient quantity to yield 2 wt% water. A hydrous glass was made of this at 9.3 kbar and 1250°C. This synthesis of a Cl-, S-, F-free glass avoided the possible complication of early exsolution of a Cl-rich fluid phase [14] and concomitant loss of at least some Cl and S. Second, a dry mixture of oxides,

SiO <sub>2</sub>	51.74
TiO <sub>2</sub>	1.10
Al <sub>2</sub> O <sub>3</sub>	16.84
FeO <sub>T</sub>	9.99
MnO	0.12
MgO	3.12
CaO	6.08
Na <sub>2</sub> O	5.28
K <sub>2</sub> O	1.28
P <sub>2</sub> O <sub>5</sub>	1.79
Cl	1.51
F	0.30
Cr <sub>2</sub> O <sub>3</sub>	0.15
S	0.30
H <sub>2</sub> O	0.40
	100.00

**Table 1.** Bulk composition used for experiments.

silicates, MgCl<sub>2</sub>, MgF<sub>2</sub>, and CaSO<sub>4</sub> was prepared. This was ground together with the hydrous glass in a 4:1 ratio with a small amount of alcohol to achieve the composition of Table 1. The starting mixture was loaded into graphite-lined cobalt capsules in order to ensure similar fO<sub>2</sub> conditions as the experiments on Backstay of [16] (and thereby, facilitate comparison of phase assemblages of the Cl- and S-free

**Table 2.** Phase assemblages for Cl-S-rich composition of Table 1. at 9.3 kbar compared with the Cl- and S-free assemblages of [16].

T (°C)	Cl-, S- free Backstay (1050)	Cl-, S- rich Backstay (1050)
1125		FeS immisc. liquid
1050	Cr-spinel olivine augite orthopyroxene glass	Cr-spinel x x x glass FeS immisc. liquid
1000	olivine orthopyroxene (En58Wo5Fs37) plagioclase (An37Ab62Or2) Ti-amph apatite	Cr-spinel x orthopyroxene (En58Wo3Fs39) x x apatite FeS immisc. liquid
980	olivine orthopyroxene (En56Wo4Fs40) plagioclase (An35Ab63Or2) Ti-amph apatite	
960		FeS immisc. liquid orthopyroxene (En47Wo4 Fs49) sodic plagioclase (An23Ab74Or3) amphibole apatite

and Cl- and S-bearing compositions). The cobalt was used as an exterior jacket to prevent Fe-alloying with the cobalt and to prevent the runaway fluid loss and thermocouple problems that occurred in unjacketed graphite capsules.

Crystallization experiments were run under the same pressure conditions as [16] (i.e., 9.3 kbar) in piston-cylinder apparatus, by first melting at 1250°C, then dropping to the final equilibration temperature and crystallizing for several days. All run products were analyzed optically and by electron microprobe.

**Results:** The experiments yielded crystals plus glass with no zoning of crystals. Experiments at 1000 and 960°C showed evidence of fluid exsolution and fracturing of interior graphite capsule with vein formation in the open spaces created. There was no evidence of rupture of the cobalt exterior capsule.

Table 2 shows the phase equilibria obtained thus far on the Cl- and S-bearing composition compared to the Cl-S-free composition of [16]. The suppression of the saturation temperatures of olivine, plagioclase, and amphibole shown in Table 2 confirm Cl complexing with Mg, Ca, and Fe in the melt as determined experimentally by [14]. The lack of olivine in the lithology would have a major impact on alteration assemblages as this mineral is highly susceptible to weathering. Of additional note is the delay in plagioclase crystallization.

Glass compositions show silica enrichment with decreasing temperature and the formation of increasingly peraluminous compositions. In spite of the obvious differences in mineral assemblages, the residual liquids are similar for both the Cl- and S- free and the Cl- and S-rich compositions.

**References:** [1] Yen R. G. et al. (2005) *Nature*, 436, 49–54. [2] Gendrin A. et al. (2005) *Science*, 307, 1587–1591. [3] Bishop, J. L. et al. (2009) *Jour. Geophys. Res. Planets*, 114, E00D09, doi:10.1029/2009JE003352. [4] Greenwood J. P. et al. (2000) *Geochim. Cosmochim. Acta*, 64, 1121–1131. [5] Wentworth S. J. and Gooding J. L. (1988) *Meteoritics*, 23, 310. [6] McCubbin F. M. et al. (2009) *Geochim. et Cosmochim. Acta*, 73, 4907–4917. [7] Keller J. M. et al. (2006) *Jour. Geophys. Res. Planets*, 111, E03S08, doi:10.1029/2006JE002679. [8] Gellert R (2006) *J. Geophys. Res.*, 111, doi: 10.1029/2005JE002555. [9] Schmidt M. E. et al. (2008) *J. Geophys. Res.*, 113, E06S12, doi:10.1029/2007JE003027. [10] Rao M. N. et al. (2005) *J. Geophys. Res.*, 110, E12S06, doi:10.1029/2005JE002470. [11] McCubbin F M and Nekvasil H (2008) *Am. Min.* 93, 676–684. [12] Gailard F. and Scaillet B. (2009) *EPSL*, 279, 34–43. [13] Webster J. D. and Rebert R. (1998) *Contrib. Mineral. Petrol.* 132, 198–207. [14] Webster J. D. and DeVivo B. (2002) *Am. Min.* 87, 1046–1061. [15] Filiberto J. and Treiman A.H. (2009) *Chem. Geol.* 263, 60–68. [16] Nekvasil H. et al. (2009) *Meteoritics & Planet. Sci.*, 44, 853–869. [17] McSween H. Y. et al. (2006) *J. Geophys. Res.*, 111, E09S91.