

**MARTIAN MAGMAS: WATER-POOR BUT CHLORINE-RICH.** J. Filiberto<sup>1</sup> and A.H. Treiman<sup>1</sup>, <sup>1</sup>Lunar and Planetary Institute, Houston, TX 77058. [Filiberto@lpi.usra.edu](mailto:Filiberto@lpi.usra.edu).

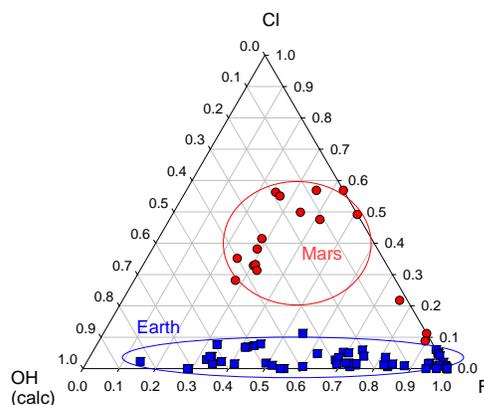
**Introduction:** Understanding the abundance of volatiles (H<sub>2</sub>O, Cl, and F) in martian basalts is crucial to understanding the martian volatile cycle, and thus Mars' habitability [1]. Martian meteorites contain only ~100 ppm H<sub>2</sub>O [2-5] but some studies have suggested that the parental magmas contained up to 2 wt % water [6-9]. Here, we integrate evidence from mineral chemistry, cosmochemistry, and experimental results to show that chlorine, not water, was the dominant volatile species in martian basalts. As a consequence, eruption and degassing of the basalts would have increased the acidic nature and contributed only minimal amounts of H<sub>2</sub>O to Mars' surface environment. Such acidic conditions are consistent with the 'acid fog' model that produced the halogen-rich, sulfur-rich regolith [10-12].

**Evidence from Mineral Chemistry:** Hydrous minerals, such as apatite and amphibole, act as a monitor of a magmas' volatile content because of their dependency on the availability of volatiles (OH, F, Cl) in the melt. Therefore, the minerals' chemistry can be used to evaluate the pre-eruptive volatile content of basaltic magmas [13-16]. Further, comparisons of the volatile contents of apatites and amphiboles from different planets can be used to evaluate the relative volatile enrichment of each planetary body

**Apatite:** The volatile content of the apatite, a late stage magmatic mineral, reflects the Cl:F:OH content of the parent magma. Apatite preferentially accepts volatiles from magmas in the order F > OH > Cl [13, 15, 17] and can be used to compare the halogen contents of the parental basalts from different planets [14]. Martian meteorite apatites contain little OH with an average Cl:F:OH ratio of ~5:3:2 (figure 1). In contrast, apatites from terrestrial basaltic rocks contain little Cl and variable OH:F ratios. This suggests that Martian magmas are Cl-rich and water-poor, while terrestrial magmas are Cl-poor.

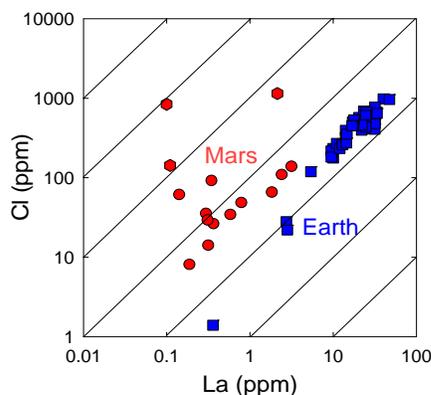
**Amphibole:** Similar to the volatiles in apatite, the volatile composition of amphiboles can also be used to compare the volatile contents of basalts from different planets. Amphibole preferentially accepts volatiles in the order OH > F > Cl [16-18]. The amphiboles in the martian meteorites are chlor-, chlor-fluor- or oxy-amphiboles [2, 19]; for example, Ti-rich amphibole (kaersutite) in the Chassigny meteorite contains 0.1 wt % Cl [7] and similar concentrations of water (0.1–0.2 wt % H<sub>2</sub>O) [2], the kaersutite in the NWA 2737 dunitite meteorite has up to 0.31 wt % Cl [20], and the amphibole (chloro-potassic-hastingsite) in the nakhlite MIL 03346 contains up to 7.0 wt % Cl [19]. Water analyses on amphiboles from NWA 2737 and MIL 03346 meteorites are not available. Since, amphiboles reflect the

orites are not available. Since, amphiboles reflect the volatile contents of their parental magmas, these chlorine-rich, water-poor martian amphiboles suggest that their parental magmas were chlorine-rich and water-poor. In contrast, terrestrial amphiboles tend to be hydroxy-amphiboles which formed under hydrous conditions [e.g. 21].



**Figure 1.** Proportions of Cl, F, and OH in apatite grains in martian meteorites (red circles; [14, 20, 22-26]) and in terrestrial basaltic rocks (blue squares; [27-33]); OH is rarely analyzed directly, but is calculated by difference/stoichiometry. Terrestrial sample suites that have been altered or metasomatized are excluded.

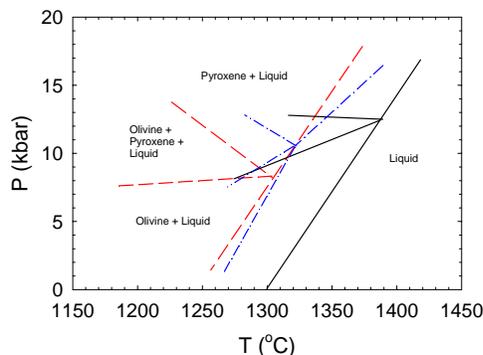
**Cosmochemical Evidence:** Higher Cl contents of martian minerals compared with terrestrial minerals are consistent with the Cl-enriched inferred composition of the martian mantle [34]. Nearly all martian meteorites have the same Cl/La ratio  $\approx 45$  (Figure 2). The few meteorites with higher ratios reflect terrestrial or martian alteration. This Cl/La ratio is taken as that of the martian mantle, because both Cl and La are highly incompatible during partial melting and basalt crystallization.



**Figure 2.** Average bulk chlorine and lanthanum abundances in martian meteorites (red circles; [34-38]), martian meteorites affected by weathering (red hexagons; [34, 39, 40]), and in terrestrial basaltic rocks (blue squares; [34, 41, 42]). The unaltered martian meteorites average Cl/La  $\approx 45$ . Terrestrial lavas average Cl/La  $\approx 20$ .

The martian Cl/La ratio is ~2–3 times the average Cl/La of terrestrial basaltic rocks (Figure 2), consistent with Mars' overall enrichment in volatile elements compared to the Earth [34]. Therefore, Cl should be more important in basalt petrogenesis on Mars than on Earth.

**Experimental Evidence:** The results of some previous crystallization experiments on martian meteorites suggest that parent magmas contained up to 2 wt % water, in order to produce the mineral compositions and crystallization temperatures of the martian meteorites [6-9]. If instead, some other volatile, such as chlorine, could produce the mineral compositions and crystallization temperatures of the martian meteorites, then large quantities of magmatic water would not be required.



**Figure 3.** Experimentally determined phase relations for the Humphrey bulk rock composition with 0.7 wt % Cl (red dashed lines) [43], compared with anhydrous (0.1 wt % H<sub>2</sub>O; 0 wt% Cl) experimental work (black solid lines; [44]), and hydrous (0.8 wt % H<sub>2</sub>O; 0 wt % Cl) experimental work (blue dashed lines; [45]).

Our recent experiments have shown that chlorine and water do have similar effects on crystallization temperatures and mineral compositions [43]. Figure 3 shows the experimental near-liquidus phase equilibria for a martian basalt (Humphrey): anhydrous and chlorine-free [44], anhydrous with 0.7 wt % Cl [43], and with 0.8 wt % H<sub>2</sub>O and chlorine-free [45]. In all sets of experiments, olivine is the liquidus phase at low pressure and low-Ca pyroxene is on the liquidus at high pressure. Addition of 0.7 wt % Cl moves the olivine-low-Ca-pyroxene (pigeonite) liquidus point from 1385°C and 12.5 kbar (anhydrous) to 1305°C and 8.5 kbar, which greatly enlarges the stability field of low-Ca pyroxene. The effect of adding 0.8 wt % H<sub>2</sub>O is similar: it depresses the olivine-low-Ca-pyroxene (orthopyroxene) liquidus point from 1385°C and 12.5 kbar to 1325°C and 10.6 kbar. Thus, comparable amounts by weight of Cl and H<sub>2</sub>O result in equivalent depressions of the liquidus. Though, on a molar basis Cl causes twice the liquidus depression that H<sub>2</sub>O causes. This suggests that chlorine-bearing experiments do produce the same mineral compositions and crystallization temperatures as water-bearing experi-

ments. Therefore, large amounts of water are not needed to explain the mineralogy of the meteorites.

**Conclusions:** The analyses of mineral chemistry and cosmochemical constraints suggest that martian magmas were rich in chlorine and contained little water. Melting and crystallization experiments on martian basalts, previously interpreted in terms of water-rich magmas [6-9], are equally-well explained in terms of chlorine-rich magmas [43]. Together, mineralogical, cosmochemical, and experimental results suggest that parental magmas of martian meteorites were chlorine-rich and water-poor. The concept of Cl-rich martian basalts is consistent with spacecraft data from Mars [46-48]. Results from the gamma ray spectrometer (GRS) on the Mars Odyssey orbiter show that Mars's surface is Cl-rich, with abundances from 0.2 to 1 wt %. The Mars Exploration Rover (MER) Spirit' analyses demonstrate that the average basaltic rock in Gusev crater [Adirondack class] contains ~0.2 wt % Cl. These results imply that chlorine is important during basalt genesis, crystallization, and eruption on Mars. Eruption of chlorine-rich, water-poor martian basalts would have increased the acidic nature of the surface and not contributed significant amounts of water; this supports the 'acid fog' model and limits the availability of water for habitability.

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