

## ROLE OF CL AND S ON THE VOLATILITY OF GE, ZN, AND LI IN MARTIAN BASALTIC MAGMAS: IMPLICATIONS FOR VOLATILE CONTRIBUTION TO MARTIAN SURFACE LITHOLOGIES

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**Introduction:** The successes of the rover and orbital Martian missions have provided a wealth of information on physical and chemical processes that led the formation of the Martian surface through the roles of both igneous and sedimentary processes. An important observation that is still poorly understood is the large concentrations of metals (Li, Zn, Ge), sulfur and halogens (Cl, Br) in Martian breccias measured in situ by rover missions. This pattern of enrichment is not known from the only meteoritic Martian regolith breccia currently available for study.

Recent chemical studies by the MSL Curiosity rover reported high abundances of Li, Cl, S, Fe, Zn and Ge in Martian rocks [1]. Germanium abundances measured in situ in Martian breccias range from a few tens of ppm to hundreds of ppm, 1-2 orders of magnitude higher than in Martian igneous rocks [2]. Local mobility of Ge has been observed to create enrichments of 850 ppm [3]. Such excesses of Ge are much larger than that expected from any chondritic input to the Martian surface. Recently, laboratory analysis of Ge in Martian meteorites revealed that shergottites were increasingly depleted in Ge (~1 ppm) with higher degrees of fractionation, relative to nakhlites and chassignites (2-3 ppm) [4, 5]. This raised the possibility of degassing of Ge from shergottite magmas during eruption at the Martian surface.

Germanium is known to form volatile chlorides, and possibly sulfides, and may even be volatile without the addition of S or Cl. In order to constrain the role of Cl and S on the loss of Ge and Zn from martian lavas, we first experimentally determined the elemental losses during degassing of a martian basaltic composition containing trace amounts of Ge and Zn both in almost volatile-free and mixed Cl-S-bearing systems heated for 6 or 12 hours [6]. Degassing at 6 or 12 hours resulted in significant losses of Na, Cl, S, K and Fe, similar to what was reported previously in volatile-bearing experiments [7].

These experiments failed to distinguish the separate effects of Cl and S on degassing of major and trace volatile species. Here we report on new experiments that focused on constraining the individual effects of Cl and S on the volatility of alkalis, Fe, Ge, Li, and Zn from martian magmas after 6 hours of degassing.

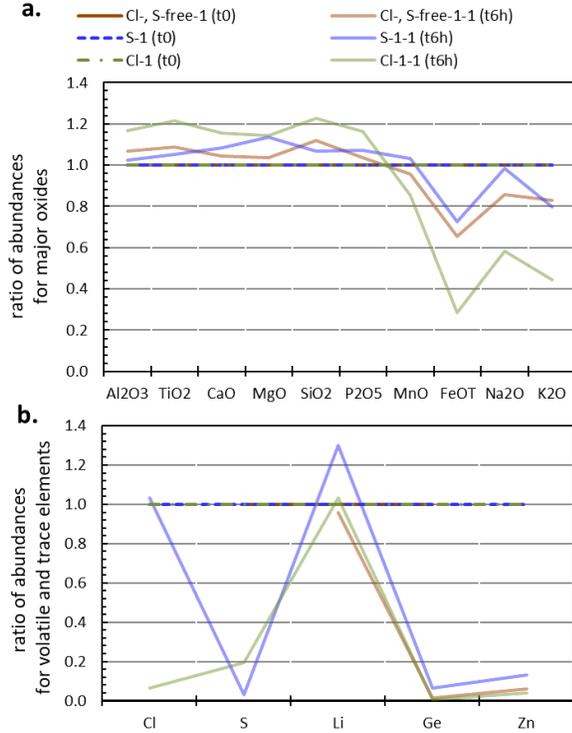
**Experimental Design and Details:** Gusev basalt, Irvine was specifically selected as a target composition

since this aphanitic alkali basalt has been identified across the Martian surface which makes it an appropriate candidate to test the volatility of Martian magmas. Four separate powdered starting compositions (Cl-, S-free, Cl-bearing, S-bearing, Cl-, S-bearing) were synthesized from oxides, silicates, and iron sponge. Sufficient abundance of Cl and S were added to starting material to ensure detectable amounts of vapor deposits, but not so much as to cause explosive rupture of the tubes. Ge, Zn, and Li were added in the form of GeO, ZnO, and LiCO<sub>3</sub> respectively. In order not to affect the phase equilibria of the mixes, the total amount of trace elements was limited to <1000 ppm. Synthesis experiments were done in Au<sub>80</sub>Pd<sub>20</sub> capsules in a large volume piston-cylinder at 0.5 GPa and ~1260°C. For degassing experiments, pieces of synthesized glasses were loaded into new Au<sub>80</sub>Pd<sub>20</sub> capsules and placed at the bottom of 25 cm long silica tube. Each tube was evacuated for 20 minutes, sealed, and suspended by a Pt-wire to the hot spot in a vertical furnace at 1230 °C for 6 hours before quenching into cold water.

Both starting and degassed glasses at the end of each experiment were analyzed by electron microprobe (EMPA) for major oxides at AMNH. Starting and degassed glasses were analyzed for their trace element abundances by laser ablation ICP-MS at the National High Magnetic Field Laboratory at FSU [7].

**Results:** Figure 1 shows ratio of abundances of major oxides (refractory and alkalis) (Fig. 1a) and trace and volatile elements (Li, Ge, Zn, Cl, S) (Fig. 1b) showing changes with respect 1 between initial ( $t_0$ ) and final degassed ( $t_{6hr}$ ) melts. The percentage loss for each run is shown in Table 1. Dark colored solid and dashed lines show the abundances in initial glasses while light colored solid lines shows that of final degassed glasses. Relative to the starting compositions, the Cl-bearing runs lost larger fractions of Na, K, and Fe, than the Cl-, S-free and S-free runs. The order of loss for the alkalis was K<sub>2</sub>O > Na<sub>2</sub>O which is consistent with the lower vaporization temperature of K<sub>2</sub>O (877°C) compared to Na<sub>2</sub>O (1057°C) at 10<sup>-3</sup> atm [8]. Refractory element abundances (Si, Ti, Al, Mg, Ca, etc.) increased up to 20% in proportion to the loss of Fe (Fig. 1a). Zn and Ge were lost almost completely after 6 hours from both volatile-free and volatile-bearing runs, while the highest percentage loss of Zn occurred in the Cl-bearing system implying the volatility of Zn in the form

of Zn chlorides (Fig. 1b). For all three experiments, Li was not lost measurably between initial and final melts. Volatility of Ge was lower in S-bearing runs (94%) compared to loss of Ge in Cl-bearing (100%) and Cl-, S-free systems (99%) (Table 1).



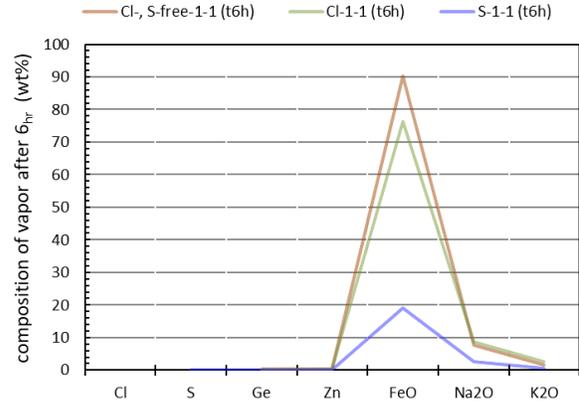
**Figure 1.** Ratio of melt abundances for **a.** major and **b.** volatile and trace elements and volatile elements.  $t_0$ =initial melt and  $t_{6hr}$ =degassed melt.

**Table 1.** Percent volatile loss for major, trace, and volatile elements after 6 hours degassing.

% Loss	Cl	S	Ge	Zn	FeO	Na <sub>2</sub> O	K <sub>2</sub> O
Cl-, S-free (6 <sub>hr</sub> )			99	94	40	22	24
only Cl (6 <sub>hr</sub> )	95		100	97	76	51	63
only S (6 <sub>hr</sub> )		97	94	88	32	8	25

**Discussion:** Compositional changes in the vapors after degassing clearly show the possibility of surficial enrichments of Cl, S, Fe, Zn and Ge, and alkalis, from the outgassing of metal halides from martian volcanics. Magmatic outgassing, particularly of Cl-rich magmas, results in the rapid loss of Na, K, Fe, and Zn, but not of Li. Therefore the high Li concentrations observed are not likely to be connected to volcanic outgassing. While presence of Cl enhanced the volatility of Ge compared to the S-bearing system; the percentage loss of Ge in Cl-bearing runs and Cl-S-free runs being equal implies the possibility of Ge loss in the GeO form. Mass balance calculations using composition of initial and final melts made it possible to assess the changes in composition of the vapor phase produced over time for both volatile-free and volatile-bearing systems (Fig.

2). Even though, the loss of Zn was the highest in the Cl-bearing experiments and the loss of Ge was same for Cl-, S-free and Cl-bearing runs; the Ge content of vapor phase in volatile-free and even S-bearing experiments were larger compared to the Ge content of vapor in Cl-bearing system.



**Figure 2.** Calculated compositions of vapors for each experiment in terms of its trace element (Ge, Zn), volatiles (Cl, S), alkalis (Na<sub>2</sub>O, K<sub>2</sub>O) and FeO abundances (wt%) after 6 hours degassing.

This is due to the lower weight fraction of vapor (fv) in Cl-, S-free and S-bearing experiments compared to that of Cl-bearing runs. Even though the percent loss of Ge from all three melts seems to be the same, the amount of Ge in a smaller weight fraction caused significant enrichments in the Ge content of S-bearing ( $Ge_{vapor}$ : 1.24 wt%) and Cl-, S-free ( $Ge_{vapor}$ : 0.34 wt%) vapors compared to the Cl-bearing ( $Ge_{vapor}$ : 0.05 wt%) vapors. Therefore constraining the composition of vapor phase in terms of its volatile components becomes critical to understand the variations in Ge and Zn enrichments in martian surface lithologies in addition to checking the bulk volatile loss. The extent of Ge loss in shergottites is estimated to be about 50%, while Zn was not noted to be lost [4] both elements were lost to much greater extents (90-100%) in these experiments. This shows the importance of shorter duration experiments to better assess the relative rates of loss for Ge and Zn from martian basalts.

**References:** [1] McLennan S. M. et al. (2013) *Science* 343: p. 1244734. [2] Berger J. A. et al. (2017) *JGR Planets* 122, 1747-1772.. [3] Mittlefehldt D. W. et al. (2016). 47th Lunar & Planetary Science Conference, Abstract #2086. [4] Humayun M. et al. 2016. 47th Lunar & Planetary Science Conference, Abstract #2459. [5] Yang S. et al. (2018) LPSC XLIX, this volume. [6] Humayun M. et al. 2016. 79th MetSoc Conference, Abstract #6491. [7] DiFrancesco N. J. et al. 2016. 47th Lunar & Planetary Science Conference, Abstract #1517. [8] Gibson E.K. and Hubbard N.J. (1972) Proc. 3rd LPSC.