

VOLATILIZATION OF GERMANIUM, ZINC, AND LITHIUM IN MARTIAN BASALTS AND ASSOCIATED SURFACE ALTERATION DURING FUMAROLIC DEGASSING Alexander Rogaski¹, Gokce K Ustunisik^{1,2}, Shuying Yang³, and Munir Humayun³, ¹South Dakota School of Mines and Technology, Rapid City, SD, United States; ²American Museum of Natural History, New York, NY, United States; ³Florida State University, Dept. of EOAS & National High Magnetic Field Laboratory, Tallahassee, FL, United States

Introduction: High concentrations of Li, Zn, Ge, Fe, Cl, and S were measured in Martian rocks by the MSL Curiosity rover [1]. Laboratory analysis of shergottites revealed Ge concentrations are lower than expected, relative to nakhlites and chassignites. This suggests that Ge was degassed from shergottite magmas at the Martian surface while concentrations of Ge in nakhlites and chassignites were established by closed-system fractionation [2]. Ge forms volatile chlorides, and possibly sulfides, and may be volatile independent of S or Cl. While its partitioning into the Martian core has been studied [3], little data has been produced to understand the volatility of Ge in silicate melts during degassing of Martian magmas.

To constrain the role of Cl and S on the loss of Ge and Zn from Martian lavas, we first evaluated the elemental losses during degassing of a Martian basaltic magma with trace amounts of Ge and Zn using both low and high Cl, S-bearing volatile system (run times 6 and 12 hours) [4]. These experiments exhibited significant losses of Na, Cl, S, K and Fe. However, they were designed to only investigate the combined effects of Cl and S on degassing of major and trace volatile species. As a next step [5], we focused on constraining the individual effects of Cl and S on the volatility of alkalis, Fe, Ge, Li, and Zn from after 6 hours of degassing. These experiments showed that Li was not lost between initial and final melts. Highest % loss of Zn occurred in the Cl-only run, implying the volatility of Zn chlorides. Volatility of Ge was lower in S-only runs compared to that in Cl-only and Cl-, S-free runs. 6-hour degassing experiments exhibited near-total loss of volatiles and trace metals, therefore degassing pathways were indistinguishable.

We present a new set of degassing experiments aimed at categorizing degassing pathways at shorter time intervals in order to assess the individual and combined effects of Cl and S on the degassing rates of Ge, Zn, and Li.

Experimental Design and Details:

Synthesis of Starting Materials: Irvine, an alkali basalt identified by the Spirit rover, was selected as a starting composition since it has been identified as a ubiquitous lithology on the Martian surface. Four separate starting mixes (Cl-,S-free, Cl-bearing, S-bearing, Cl-, S-bearing) were synthesized from oxides, silicates, and iron sponge. Chlorine and Sulfur were added to the starting material to ensure detectable amounts of vapor

deposits. In addition to the four mixes, a stock solution mix was prepared without Cl and S but with increased concentrations (9000 ppm) of Ge, Zn, and Li. These were added in the form of GeO₂, ZnO, and LiCO₃. To ensure homogeneity, starting mixes and the stock solution were each melted at 1100°C for 10 minutes and quenched to produce a glass that was subsequently ground into a powder. This process was repeated three times. The stock solution was then added in a 1:7 ratio to the four dry mixes.

All starting materials were synthesized as glasses at low pressure. Aliquots of starting powders were packed into Au₇₅Pd₂₅ capsules, crimped in both ends and set in a short (~6 cm) silica tube. The silica tube was evacuated for 20 minutes, sealed, and suspended by a Pt-wire in a vertical furnace at 1300 °C in the hot spot for 2 hours before quenching in water.

Low-Pressure Degassing: A hybrid (controlled open) system was designed to simulate a degassing process which allowed for the concentration and re-equilibration of the degassed vapor with the silicate melt. For the degassing experiments, pieces of synthesized glasses were loaded into Au₇₅Pd₂₅ capsules and placed at the bottom of 30 cm long silica tube. This was then placed into a vertical quench furnace at 1300°C after evacuation as described above. For each starting composition, experiments were run for 10 min, 30 min, and 1 hr.

At the end of each experiment both starting and degassed glasses 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 [2].

Fumarolic Interaction with Target Minerals: Mineral - vapor interaction experiments were conducted in conjunction with the degassing experiments. Temperature gradient within the silica tube allowed the degassed vapor to travel upwards, expand, and interact with the representative minerals for the surface lithologies on Mars. Since basalts are pervasive on the Martian surface; olivine, plagioclase and clinopyroxene were used as the target minerals. To simulate fumarolic interaction, a capillary was created 15 cm above the bottom of the silica tube. Pieces of augite, labradorite, and olivine (Fo₉₇) were wrapped in Pt-wire and set above the capillary. At the end of each run, the minerals were re-

moved and mounted for SEM analysis to identify any alteration phases.

Preliminary Results: Figure 1 shows the ratio of melt abundances of major oxides (refractory and alkalis) and trace and volatile elements (Li, Ge, Zn, Cl, S) showing changes between initial and final degassed melts.

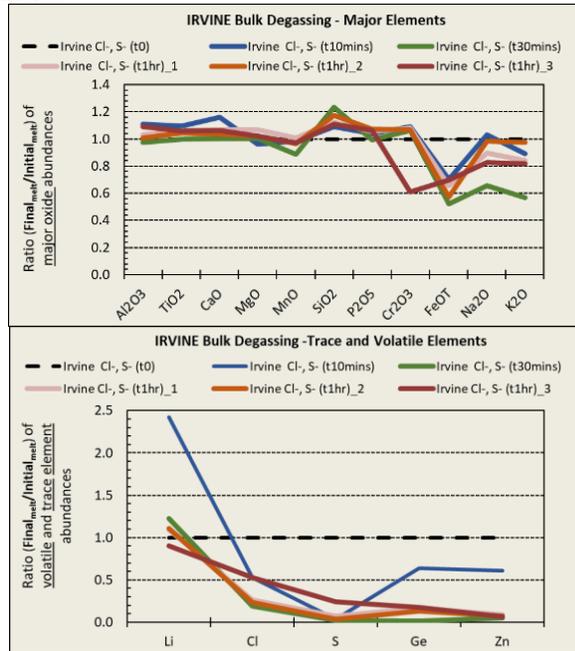


Figure 1: Changes in major oxide abundances as well as the change in abundance for volatile elements. Solid colored lines show degassing trends for each run and dashed lines show the initial composition.

Progressive degassing is observed as a function of time up to 30 minutes. The deviation of the 1 hr runs is likely a result of heterogeneity in the glasses synthesized at low pressure (Table 1).

Cl, S (10min)	Cl (ppm)	S (ppm)	Ge (ppm)	Zn (ppm)	FeO (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)
initial melt	944	5400	544	747	19.18	2.12	0.46
final melt	498	200	347	454	13.47	2.18	0.41
vapor	6454	70046	2973	4363	89.35	1.22	1.05
% lost on weight basis	47	96	36	39	30	-3	11
Cl, S (30min)	Cl (ppm)	S (ppm)	Ge (ppm)	Zn (ppm)	FeO	Na ₂ O (wt%)	K ₂ O (wt%)
initial melt	944	5400	544	747	19.18	2.12	0.46
final melt	181	100	7	41	10.03	1.39	0.26
vapor	6453	43758	4431	5855	84.77	7.29	1.89
% lost on weight basis	81	98	99	94	48	34	43
Cl, S (1hr)	Cl (ppm)	S (ppm)	Ge (ppm)	Zn (ppm)	FeO	Na ₂ O (wt%)	K ₂ O (wt%)
initial melt	944	5400	544	747	19.18	2.12	0.46
final melt	247	401	91	67	12.63	1.90	0.39
vapor	8140	57030	5218	7772	86.69	4.32	1.17
% lost on weight basis	74	93	83	91	34	10	15

Table 1: Concentrations of trace and volatile elements in the initial and final glasses, composition of the vapor, and the partitioning of volatile elements between the melt and vapor phase after mass balance calculations.

Loss of K₂O is greater than Na₂O, consistent with its lower volatility [6]. However, Na₂O comprises a greater portion of the vapor phase. Iron and S (Figure 1) are correlated, suggesting that Fe-sulfides may be a product of this degassing. For the 30-minute run for Irvine with Cl+S, olivine, augite, and labradorite were included to incorporate the fumarolic alteration process. After quenching the run, the mineral specimens were analyzed with SEM/EDS to identify any alteration products.

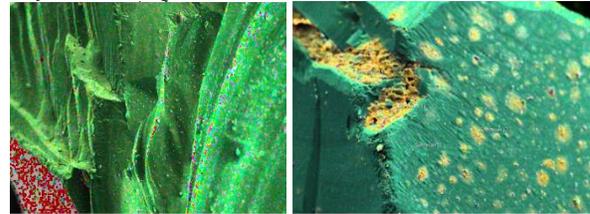


Figure 2: EDS Element Map of original Olivine (left) and a piece exposed to degassed material for 30min (right). Yellow coloration indicates surface concentrations of Cl, S, and Ca.

On all three minerals, patches of Ca, Cl, and S enrichments were observed. In some instances, these concentrations were visible as nodular masses. There were also minor concentrations of KCl and NaCl.

Discussion: The results of our degassing experiments confirm that the selected time series for degassing are appropriate for gauging the volatility of Ge and Zn in the presence of volatile elements. In addition, there is evidence to suggest that Fe preferentially leaves the melt as a sulfide rather than a chloride. Morphologically, the surface deposits appear to be condensates rather than the products of alteration. More and longer experiments will allow for an understanding of the phases present, just as the additional degassing experiments will allow for a full understanding of the behavior of Ge and Zn in the presence of Cl and S.

Acknowledgements: The authors would like to thank the South Dakota Space Grant Consortium for funding this work and the American Museum of Natural History for assisting in sample analysis.

References: [1] McLennan et al. (2014) *Science* Volume 343, Issue 6169 [2] Yang S., et al. (2019) *50th Lunar & Planetary Science Conference*, Abstract# 1908. [3] Yang et al. (2015) *Meteoritics & Planetary Science*, Volume 50, Issue 4 [4] DiFrancesco N. J. et al. (2016) *47th Lunar & Planetary Science Conference*, Abstract#1517. [5] Ustunisik et al. (2018) *49th Lunar & Planetary Science Conference*, Abstract #2083 [6] Gibson, E. K. et al. (1972) *Proceedings of the Lunar Science Conference*, vol. 4, p.1263.