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Experimental constraints on the volatility of germanium, zinc, and lithium in Martian basalts and the role of degassing in alteration of surface minerals

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Abstract-The surface of Mars is enriched in Cl and S which is linked to volcanic activity and degassing. Similarly, elevated Ge and Zn levels in Gale crater sedimentary bedrock indicate a magmatic source for these elements. To constrain the relative effects of Cl and S on the outgassing of these trace metals and chemical characteristics of primary magmatic vapor deposits incorporated to Martian surface, we conducted a set of degassing and fumarolic alteration experiments. Ge is found to be more volatile than Zn in all experiments. In S-bearing runs, the loss of Ge and Zn was less than any other experiments. In Cl-only runs, degassing of Zn was more than twice that of Ge within the first 10 min and percent loss increased for both elements with increasing time. In Cl + S runs, S-induced reduction of GeO₂ and ZnO to metallic Ge and Zn switches the preference of chloride formation from Zn to Ge. Up to 90% of Ge and Zn loss in the 1-h no volatile-added (NVA) experiments might be due to the small amounts of Cl contamination in NVA mixes via other oxides used for synthesis. Alteration experiments show different phases between 1-h and 24-/72-h runs. In 1-h runs, anhydrite and langbeinite dominate while in 24-/72-h runs halite and sylvite dominate the condensate assemblages. S-bearing phases form as the intermediate products of fumarolic deposition, while chlorides are common when the system is allowed to cool gradually. One-hour exposure was sufficient to form alteration phases and vapor deposits such as NaCl, KCl, CaSO₄, and langbeinites on the Martian analog minerals. These salts were identified in Martian meteorites and in situ measurements. Our results provide evidence that volcanic degassing along with fumarolic alteration could be a potential source for the enrichment and varying abundances of Cl, S, Fe, Zn, Ge in Martian surface, as well as a cause for Ge depletion in shergottites.

INTRODUCTION

Volatile element enrichment in Martian materials has been well established by robotic exploration and Martian meteorite studies. Bulk Mars itself is a volatile-rich planet with abundant sulfur and halogens, based in part on evidence from Martian meteorites (e.g., Bridges et al., 2001; Dreibus & Wanke, 1985; Lodders & Fegley, 1997;



FIGURE 1. Alpha Particle X-ray Spectrometer (APXS) results for SO₃, Cl, Zn, and Ge in rocks and soils at the Gale, Gusev, and Meridiani landing sites. Bulk analyses of a subset of Martian meteorites by Yang et al. (2015) are shown to illustrate the magnitude and ubiquity of volatile enrichment on the Martian surface. Results for SO₃, Cl, and Zn are compiled from the PDS Geosciences node (Gellert et al., 2013; Gellert et al., 2006). All rock targets with detectable Ge (~ \geq 30 ppm) reported for MER (Ming et al., 2008; Mittlefehldt et al., 2021) and MSL up to sol 1340 (Berger et al., 2017) are shown in (c). Ellipses denote the range of SO₃, Cl, and Zn in basaltic soils in (a, b); Ge in soils is below the detection limit in soils. (Color figure can be viewed at wileyonlinelibrary.com)

Taylor et al., 2003; Yoshizaki & McDonough, 2020). Basaltic soils analyzed on the Martian surface at six landing sites show that the average modern Martian soil is enriched in S, Cl, Zn, and P relative to typical planetary basalts (Clark et al., 1982; Foley et al., 2003; Ming et al., 2008; O'Connell-Cooper et al., 2017; Yen et al., 2005). High S and Cl in basaltic airfall dust, and the consistent molar S:Cl of 3.4 ± 0.3 across the planet, is further evidence that the surface of Mars is characterized by elevated volatile elements that have been averaged by eolian mixing of surface materials (Berger et al., 2016; Yen et al., 2005). In situ measurements indicate that volatiles in Martian soils are significantly enriched relative to Martian basalts; the average SO_3 (~8.0 wt%) and Cl (~1.1 wt%) of the surface materials can be estimated from airfall dust (Berger et al., 2016), which exhibit enrichments ~20-30 times greater than basaltic Martian meteorites (Figure 1). Sulfur-bearing units have been identified by orbital spectroscopy and often occur in layered deposits (e.g., Gendrin et al., 2005; Karunatillake et al., 2014; Mangold et al., 2008; Milliken et al., 2010). Gamma-ray spectrometry indicates an average Cl concentration of ~0.5 wt% (Taylor et al., 2010), and hundreds of chloride-bearing deposits have been inferred by mid-infrared orbital spectrometry (Glotch et al., 2016; Osterloo et al., 2010). Volatile-rich sedimentary deposits often have mixed distribution of S and Cl and are found in association with secondary phyllosilicates and/or ferric oxides indicative of aqueous processes (e.g., Ojha et al., 2018; Thollot et al., 2012; Weitz et al., 2013). Volatile enrichment in the soil and dust is also reflected in ancient lithified materials, where elevated S, Cl, and Zn is ubiquitous (Figure 1).

Some of the volatile enrichments include trace elements in addition to the elevated S and Cl relative to Martian meteorites. In situ rover exploration has found remarkable enrichments of Ge (up to ~850 ppm) and Zn (up to $\sim 5 \text{ wt\%}$) in rocks at three landing sites, and localized Cu enrichments (>500 ppm) in Gale crater (Figure 1; Berger et al., 2017; Lasue et al., 2016; Ming et al., 2008; Mittlefehldt et al., 2021; Payré et al., 2019). The processes by which Ge, Zn, and Cu were enriched are not well constrained. The overall interpretation is that these elements were enriched by hydrothermal fluids, but distinctive processes are apparent in the Ge and Zn occurrence at different landing sites (Berger et al., 2017; Mittlefehldt et al., 2021). At Home Plate in Gusev crater, the Spirit rover found high Ge (190 ppm) is associated with moderately enriched Zn (680 ppm) in localized silica-rich materials (Ming et al., 2008). In Endeavor crater, the Opportunity rover discovered very high Ge (~850 ppm) with low Zn (~100 ppm) in a hydrothermally altered deposit (Mittlefehldt et al., 2021). In Gale crater, elevated Ge (~100 ppm) occurs with high Zn (~1000 to 2000 ppm) dispersed throughout >100 vertical meters of Gale crater sedimentary rock (Berger et al., 2017) and may be a characteristic of >350 m of the Mt. Sharp sedimentary group (Gellert et al., 2022; Thompson et al., 2020). An added complexity in the Gale crater record is the hypothesized mobility of Zn and Ge/Zn fractionation in diagenetic fluids (Berger et al., 2017; Rampe et al., 2017). An improved understanding of magmatic and

volcanic enrichment processes would likely constrain the geologic processes recorded by the Ge and Zn enrichments. Since S and Cl were most likely concentrated at the surface via magmatic and volcanic processes (e.g., Nekvasil et al., 2019; Righter et al., 2009), an understanding of the origin of Ge, Zn, and Cu is linked to that of S and Cl.

Evidence of volcanism, a primary source of volatiles, is abundant at the Martian surface (Cattermole, 1990; Mouginis-Mark & Christensen, 2005; Robbins et al., 2011); it is mainly basaltic (McEwen et al., 1999; McSween et al., 2009) and long-lived, with evidence of volcanic activity extending into the Amazonian (Bleacher et al., 2007; Hartmann, 1999; Hauber et al., 2011; Werner et al., 2009) and young 150 Ma crystallization ages from Martian meteorites (McSween, 2002). The abundance of volatile elements at the surface is suggestive of extensive volcanogenic inputs into the surface materials of Mars over much of its history, which were likely reworked by mass wasting, eolian, impact, and fluvial processes, and further affected by diagenesis (e.g., lithification, alteration, vein and nodule formation). While the detailed petrogenesis of these units is debated, a magmatic origin for volatiles is sensible and can account for nearly all of the surface volatile load on Mars (Craddock & Greeley, 2009; Righter et al., 2009). Our understanding of the origin of the volatile enrichment has been limited by several factors: (a) focus on secondary processes rather than primary magmatic processes, (b) an abundance of studies on terrestrial systems rather than Martian compositions, and (c) an overall dearth of data for Ge, all of which are elaborated on below.

First, significant effort has gone into consideration of secondary processes that could have concentrated sulfur and chlorine in Martian soil and bedrock. Hypothesized sulfur enrichment processes include water-rock or icerock interaction with preexisting sulfide-bearing sources, such as aqueous alteration and weathering of sulfur-rich bedrock (Dehouck et al., 2012) (e.g., basalts containing pyrrhotite; Chevrier & Mathé, 2007), interaction of mildly acidic waters with olivine-normative basalts (McLennan et al., 2005) during groundwater surge or ephemeral surface waters (e.g., Arvidson et al., 2005; Bibring et al., 2006; Mangold et al., 2008). Other proposed processes include acidic weathering of ash and clastic sediments (McCollom & Hynek, 2005), and weathering of dust within massive, ancient ice deposits, englacial environments (Baccolo et al., 2021; Massé et al., 2010; Niles & Michalski, 2009). However, these processes likely cannot account for the total sulfur mass in layered sulfates, as indicated by the estimated sulfur at Meridiani Planum, so fundamental questions about sulfur cycling are poorly constrained (Hynek et al., 2019). Similarly, the chloride of the Martian surface is generally considered secondary to an original chloride-bearing source and produced by aqueous dissolution followed by evaporation either in situ (e.g., Tosca & McLennan, 2006; Wang et al., 2021), volatilization during soil-atmosphere multiphase reactions (e.g., Smith et al., 2014; Zhao et al., 2018), or after significant transport to lake beds and deltaic regions (e.g., Hynek et al., 2015). Perchlorates are likewise considered to require reworking of existing chloride material at the surface and/or in the atmosphere (Glavin et al., 2013; Hecht et al., 2009; Wilson et al., 2016). Before we can use the presence of sulfates and chlorides in Martian soil and bedrock to reliably constrain low temperature alteration processes, we need to know what portion of the chloride and sulfate in Martian surface materials could be primary, that is, contributed directly as vapor deposits during magmatic degassing, and thus, whose origin and dispersion require minimal water and bedrock interaction, chemical modification, or major fluvially induced erosional events.

Second, although the origin of the high Ge, Zn, and Cu is likely primarily due to magmatic and volcanic processes, most available data for these elements are relevant to terrestrial magmatic systems, compositions, and volatile loads. While many gas analyses, experimental simulations, and modeling efforts have elucidated the nature of precipitates from water-rich magmatic degassing (e.g., Peregoedova et al., 2006), terrestrial volcanic outgassing does not provide a good analog for exhalatives formed from "dry," Cl-and S-rich magmas that exist on Mars. Identifying the nature of the precipitates from OH-poor degassing is a vital prerequisite to understanding the primary magmatic and volcanic contributions of Cl- and S- to the Martian surface and the secondary processes (e.g., physical sedimentary/impact reworking, low temperature alteration, and hydrothermal remobilization) that may have modified the stability of these primary phases. Furthermore, fumarolic activity associated with hydrothermal systems is well documented on Earth and was a geologically significant process on Mars. Fluids exsolve from hydrous magmas by magmatic boiling at depth. These liquids themselves will rise and produce a gas rich in HCl as well as SO₂ and H₂S (e.g., Halmer et al., 2002) and a more oxidized aqueous liquid phase (brine) in which sulfate and chlorides are dissolved (e.g., Allard et al., 2000). The gas phase can escape in fumaroles and contribute to the formation of acid lakes comprised primarily of meteoric water. The liquid phase can escape from the subsurface, giving rise to hot springs depositing near neutral water-dominated sinter and amorphous phases. Both types can be part of the same hydrothermal system (e.g., at Lassen Volcanic park, McHenry et al., 2014) that contains fumaroles and hot springs. This type of mixed behavior on Mars may be exemplified by Home Plate (Morris et al., 2008; Ruff et al., 2011) in the Columbia Hills of Gusev crater. Much degassing would likely have taken place from magma ponds and lakes and minor fumarolic vents via open vent degassing which can be primarily active during the period of secondary crust formation. In the absence of crustal recycling, this inactive exhalation of volatiles could have contributed greatly to the Martian atmosphere and surface.

Third, there is a dearth of data for Ge in Martian meteorites, yet Ge exhibits some of the most interesting behavior known for Martian volatile elements. Laboratory analysis of Ge in Martian meteorites reveals that shergottites are depleted in Ge (~1 ppm) relative to nakhlites and chassignites (2-3 ppm) at the same degree of magmatic fractionation (e.g., Yang et al., 2019). This raises the idea of degassing of Ge from shergottite magmas during eruption at the Martian surface while concentration of Ge in nakhlites and chassignites was established by closed-system fractionation. Ge is known to form volatile chlorides, and possibly sulfides, and may even be volatile without the addition of S or Cl (e.g., Renggli & Klemme, 2020). While Ge partitioning into the Martian core has been studied by Righter et al. (2011) and Yang et al. (2015), little data have been produced to understand the volatility of Ge in silicate melts during degassing of Martian magmas. The chemical controls on the outgassing of Ge. Zn. and other volatile elements from magmas are not understood due to lack of experiments on Martian composition magmas that are rich in FeO, S, and Cl and poor in Al₂O₃ compared to the synthetic melts or hydrous terrestrial magmas that have been studied (e.g., Candela & Holland, 1984; Iveson et al., 2019; Johnson & Canil, 2011; Scholtysik & Canil, 2021; Zajacz et al., 2013). Furthermore, Ge is rarely included in the elements studied under any conditions, and Ge is highly relevant to Mars exploration given the enrichments measured at the surface.

Given all the background of these three areas, what is clearly missing are experimental studies of the partitioning of Ge and Zn between Martian composition basaltic melt and exsolved S- and Cl-rich gas and the subsequent interaction among this gas, its condensates, and mineral substrates. Here, we report the findings of an experimental study on the contribution of magmatic volatiles to the Martian surface focused on the volatility of trace metals (Li, Zn, and Ge) in the presence of Cl and S. The results provide constraints on the compositional and time (t) dependence of the volatility of trace metals, particularly those recently identified at the Martian surface. Specifically, we constrained the individual and relative effects of Cl and S, with the possible formation of metal chlorides and sulfides, which, in turn, influence the partitioning of these trace metals between the melt and vapor phase. In addition, we documented the mineral alteration and condensate assemblages that arise from interaction between common surface minerals on Mars and the vapors produced from Martian basaltic degassing.

EXPERIMENTAL DESIGN AND DETAILS

Our experiments were designed to (1) determine the extent of volatile element loss as magma ascends to the Martian surface and degasses, (2) calculate the composition of exsolved vapors in terms of their volatile and trace element components (not species), and (3) characterize the alteration assemblages or coatings produced by the interaction of this vapor with common surface minerals (olivine, clinopyroxene, and plagioclase). These processes were simulated by heating synthesized glasses that represent common Martian basalt (Irvine) (McSween et al., 2006) above their liquidus temperature $(\sim 1300^{\circ}C)$ at <1 bar. Volatile-bearing (Cl, S, and Cl + S) and non-volatile-bearing glasses were prepared with varying Cl:S ratios along with added trace metals (Ge, Li, and Zn) to determine the individual and relative effects of volatile load (Cl and/or S) on degassing rates. Compositionally, these glasses were intended to produce vapor with a high Cl/S content; a characteristic of late Martian magmas (Filiberto & Treiman, 2009). In addition to testing the degassing behavior of volatile trace metals (Ge. Li, and Zn) in the presence of Cl and S, we investigated the change in vapor composition and formation of sublimate assemblages (mineral coatings) that may arise from magmatic degassing on Mars. Fumarolic alteration experiments were designed as part of the low-pressure degassing to determine how these degassed magmatic vapors interact with mafic minerals at the Martian surface. Low-pressure synthesis (for volatilefree no volatile-added [NVA] runs), degassing, and fumarolic alteration experiments; petrographic examination of the run products; and sample preparation were conducted at the experimental petrology laboratory in the Department of Geology and Geological Engineering at SDSM&T. High-pressure synthesis (for volatile-bearing runs), experiments were completed at Lamont Doherty Earth Observatory (LDEO) of Columbia University.

The degassing experiments of the synthetized volatile-bearing glasses were conducted in long (28 cm) evacuated silica glass tubes (Figure 2) to build up a small partial pressure of exsolved gases locally and to slow the effects of Rayleigh distillation that would come from boiling in an unconfined system. The length of the evacuated silica glass tube was computed to provide up to one-third of a bar pressure during the experiment, based on the amount of glass loaded, the volatile content of that glass, the assumption of complete loss of all volatiles from the glass, the average temperature in the tube, and the assumption of ideal mixing of components in the vapor phase at high temperature. Since temperature varied along the length of the silica glass tube, the pressure was approximated using the average temperature (650°C). This experimental setup (Ustunisik et al., 2011, 2015) was



FIGURE 2. Design of the glass silica tube for the evaporation and volatile condensation experiments. The diameter of the tube has been exaggerated to better show the interior components. (a) Schematic showing the low-pressure (P) experimental design and components within the silica tube along with the quench furnace. (b) Experimental assembly. (c) Close up view of low-P degassing and fumarolic alteration setup and silica tube holding the sample; arrows show the target minerals just above the capillary. (d) Target minerals, forsterite, labradorite, and augite reacting with degassed vapors. (Color figure can be viewed at wileyonlinelibrary.com)

designed to simulate degassing under Martian conditions where a degassed vapor cloud expands, cools, and deposits vapor components in the cooler regions (away from the hot spot), which drive further devolatilization from the magma in contact with the vapor. Consequently, the degassing is occurring in an analogous manner to what would be expected during Rayleigh fractionation, but the fractionation is much slower than it would be in an unconfined open system like that provided by a gas-mixing furnace with a continuous gas flow. More importantly, it allows for the degassing path to be observed at longer time scales than would be provided in an unconfined system (Ustunisik et al., 2015). The volcanic environment that we envisioned was the natural cooling of magmatic gas proximal to a lava flow or cooling in a small fire fountain, starting with a gas phase whose composition is initially dictated by the equilibrium magma and then modified due to thermal diffusion and precipitation of vapor-deposited minerals (Nekvasil et al., 2019). It also allowed us to simulate the mixing of high- and low-temperature vapor-deposited phases and the reactions among them as the local gas column cools.

Each of these experiments involved a "source" magma generated from the previously described synthetic glasses and a "target" mineral assemblage, designed to simulate likely mineral assemblages on Mars. The source capsule seated at the bottom of a silica tube at the hot spot of a vertical quench furnace (Figure 2a,b). During each experiment, the source magma is allowed to boil above its liquidus temperature while the target minerals (Figure 2c,d) are suspended above it at a lower temperature (just above the capillary), simulating crustal material in contact with heat and vapor from a lava flow. The experimental charge with source material at the hot spot was heated for the designated duration for that run and allowed to degas, then rapidly quenched in water, and allowed to cool. Following the quench, each silica glass tube was optically inspected to check for any cracks that might indicate a failure to maintain a closed system. Tubes that remained sealed were opened, and the material inside recovered for analysis. Target minerals were analyzed by scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) to determine morphological and compositional changes.

In a multicomponent melt, volatiles including Cl and S will compete to bind with suitable cations to escape the melt. Given that the composition of magmatic vapors is dependent on the composition of their melt of origin (Giggenbach, 1996), we decided to use basalt as a source material, due to its predominance in Martian volcanism. The Mars Exploration Rover (MER) Spirit identified a minimally altered basalts in Gusev crater (McSween et al., 2006). Of these, the rock named Irvine appeared to show little to no visible evidence of chemical weathering. In addition, Irvine displayed an aphanitic texture, indicative of a surficial lava. The "Soil-Corrected" Irvine composition (McSween et al., 2006), which represents the calculated composition after the removal of dust effects (in particular, major and minor oxides are renormalized to 100 wt% without the 1.4 wt% S + Cl measured by the APXS), was used for source magma synthesis.

Preparation of Starting Glasses

Four separate aliquots of source mix based on the Irvine composition (Table 1) but containing different proportions of Cl and/or S (no volatile added [NVA], Cl bearing, S bearing, and Cl + S bearing) were prepared as the source magmas by combining oxides, silicates, chlorides, and sulfates together in ethanol, and homogenizing this in agate mortars for approximately 2 h. To maintain homogeneous starting compositions, in addition to the four separate dry mixes above, a stock solution mix was prepared without Cl and S but with

bearing exj	periments.				
Oxide	Target ^a	NVA initial (t_0)	Cl initial (t_0)	S initial (t_0)	Cl,S initial (t_0)
SiO ₂ ^b	47.77	49.43 (0.25) ^c	48.85 (0.21)	49.99 (0.26)	49.68 (0.25)
TiO ₂	1.08	1.08 (0.02)	1.09 (0.02)	1.11 (0.02)	1.13 (0.02)
Al_2O_3	10.76	11.57 (0.08)	11.59 (0.11)	11.92 (0.06)	12.08 (0.35)
FeO _T	19.15	17.60 (0.25)	17.84 (0.19)	15.90 (0.17)	16.80 (0.29)
MgO	10.33	9.86 (0.11)	10.18 (0.04)	10.18 (0.05)	10.03 (0.09)
CaO	6.13	6.27 (0.06)	6.10 (0.04)	6.32 (0.05)	5.94 (0.07)
Na ₂ O	2.73	2.69 (0.14)	2.81 (0.15)	2.95 (0.11)	2.76 (0.09)
K ₂ O	0.70	0.67 (0.08)	0.75 (0.09)	0.72 (0.13)	0.76 (0.08)
MnO	0.37	0.35 (0.05)	0.36 (0.06)	0.42 (0.05)	0.36 (0.06)
P_2O_5	0.99	0.48 (0.03)	0.45 (0.04)	0.49 (0.05)	0.48 (0.03)
Total	100	100	100	100	100
Cl	2.5		14,522 (340)		10,493 (277)
S	1.5			4367 (115)	5267 (321)
Li	300	258 (3)	252 (5)	269 (8)	262 (3)
Ge	900	919 (3)	927 (2)	1038 (14)	1075 (12)
Zn	900	860 (15)	1125 (23)	1127 (22)	1169 (18)

TABLE 1. Target composition (Irvine) and mean compositions of initial melts for NVA, Cl-, S-, and Cl + S-bearing experiments.

Abbreviation: NVA, no volatile added.

^aIrvine composition (McSween et al., 2006).

^bOxides in wt%; Cl, S, Ge, Li, Zn in ppm.

 $^{c}(1\sigma).$

high concentrations (9000 ppm) of Ge, Zn, and Li in the form of GeO, ZnO, and LiCO₃, respectively. Fe^o sponge (to combine with hematite to provide the desired ferrous/ ferric ratio) was added in the last hour to both stock solution mix and dry mix to mitigate any oxidation of the components. Before the addition of volatile-bearing agents (MgCl₂ and CaSO₄), starting mixes and the stock solution were each melted in a graphite crucible in a box furnace at 1300°C for 5-10 min and quenched to produce a glass. The resulting glasses were ground to a powder (1– 3 µm) in an agate mortar with minimal ethanol before being allowed to dry. This melting and grinding was repeated three times for both stock solution mix and dry mixes to ensure a homogeneous final starting composition especially in trace elements. As a last step, the stock solution mix was added to four dry mixes in 1:7 ratio, before being melted and re-ground as a "final mix." For Cl- and S-bearing mixes, MgCl₂ and CaSO₄ were added to these four final mixes at the last stage, adding minimal ethanol to mitigate the dissolution of the Cl component. 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. Martian shergottite magmas are thought to have equilibrated at conditions as oxidized as FMQ (Herd et al., 2017; Righter et al., 2008) while nakhlites and chassignites crystallized under more oxidized conditions at or above the FMQ buffer (Righter et al., 2014). The correlation between oxygen fugacity and

 $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ for Martian basaltic compositions was established by Righter et al. (2013). The $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ expected for a near liquidus Martian basaltic magma buffered at FMQ and 1 bar pressure would be 0.8. Therefore, both stock solution mix and dry mixes were prepared to have the $Fe^{2+}/(Fe^{2+}+Fe^{3+})$ of 0.8 in the source material by appropriately apportioning hematite (Fe₂O₃), and metallic Fe "sponge" in the mixes. Because the sealed silica tube experiments are not buffered, the oxygen fugacity within the tube will change with changes in temperature or re-equilibration. Nekvasil et al. (2019) carried out similar experiments in sealed silica tubes and presented evidence that fO_2 within the tubes decreased at the lower temperatures along the length of the tube and during cooling, but the decrease was less than expected, so overall the fO_2 conditions in the tube exhibited oxidation relative to a buffer. As a result, the fO_2 conditions increased from FMQ + 1 to values near FMO + 2. Given the identical silica tube design, materials, and temperatures and cooling profiles, we expect these conditions in our experiments as well, and note their relevance to fO_2 range documented in degassed Martian magmas (FMQ to FMQ + 4; e.g., Peslier et al., 2010; Righter et al., 2014).

Synthesis of Source Magmas

For mixes containing Cl and/or S, the synthesis of glasses was conducted at high pressure to ensure

retention of the volatile elements, which readily soluble in silicate melts at 10 kbar. For these experiments, final homogenized source mix was placed into graphite capsules and heated to 1400°C at 10 kbar for 2 h to ensure complete melting and incorporation of the components, before being quenched to produce glasses of the desired composition. No contamination was observed in the melts with the crucible material. Synthesis experiments were performed in $\frac{1}{2}''$ inner diameter Boyd-England compound pressure vessel, piston cylinder apparatus, with cylindrical Pb-wrapped BaCO₃/MgO pressure medium, graphite furnace, high-density Al₂O₃ sleeve, one-hole and solid MgO spacers, MgO wafer, and graphite sample capsule (0.25'' with 0.188 internal cavity), with continuous external H2-N2 flow to protect the thermocouple from oxidation. Experiments were pressurized cold then heated incrementally to 850°C for over an hour after which the assembly was left at 850°C overnight to stabilize and close porosity in the pressure media and graphite capsules. After repressurization, temperature was raised in 50°C steps of approximately 20 min to the run temperature, held for 2 h at 1400°C and then power quenched.

Our preliminary work (Rogaski et al., 2018) showed that the synthesis of Cl- and S-free glasses can be conducted in a short, sealed silica tube and still retain the volatile trace (Li, Ge, and Zn) and volatile major elements (Na₂O and K₂O). Therefore, NVA starting glass was synthesized at low pressure (<1 bar) in Au₇₅Pd₂₅ capsules (melting temperature ~1400°C with minimal Feloss compared to Pt and/or Au₈₀Pd₂₀ capsules). For lowpressure synthesis, capsules with starting material were placed at the bottom of 6-cm-long silica tube. The tube was evacuated and sealed to create a vacuum within, which prevented the explosive expansion of the exsolved vapors during heating. The tube was then suspended in a vertical quench furnace, with the capsule-bearing portion of the tube in the hot spot and heated at 1300°C for 2 h. Quench was conducted by immediately inserting the silica tube into cold water. The resulting glasses were used as the starting material for low-pressure degassing and alteration experiments.

Low-Pressure Degassing Experiments

Evaporation experiments were carried out above the liquidus temperature of the starting glasses in a vertical quench furnace in which the thermal gradient is well characterized. Carefully weighed and sorted (500–650 μ m) (to normalize any effects of sample size and surface area on the evaporation rate) aliquots of the synthetic Irvine glasses were placed in Au₇₅Pd₂₅ capsules. Capsules were lightly crimped, leaving enough space for vapor to escape during degassing. Each capsule was placed at the bottom

of the 28-cm long (2.5 mm, ID) silica glass tube sealed at the bottom (Figure 2). Long tubes, with relatively large interior volumes were used to maximize the amount of degassing of volatiles from the liquid, without building up substantial pressure within the tube, which can slow down the volatile offgassing from the melt. The length of the tube was determined by previous experimental work (Ustunisik et al., 2011) to provide the ideal pressure conditions in the setup and accommodate expansion of vapor during heating.

A small mesh trap of platinum wire containing the minerals for the alteration experiments was inserted into the glass tube 15 cm above the source. The silica tube was then evacuated for 20 min and sealed to maintain a vacuum of less than 1 atm. The sealed silica glass tube was suspended such that the source capsule sat at the hot spot of the furnace. The sample was kept entirely in the "isothermal" zone throughout the duration of each experiment. This isothermal zone was determined for the furnace prior to the experimental work. Maintaining a low pressure in spite of devolatilization was facilitated by the use of a long silica glass tube; however, this resulted in the tube not being fully contained in the isothermal zone. This thermal gradient in the overlying silica glass tube (1320°C at the hot spot and 200°C at the uppermost end) made it impossible to collect, analyze, or computationally predict the composition of the vapor phase directly. But the isothermal condition of the melt allowed for careful evaluation of the loss of volatiles from the melt. The sample was held at 1320°C while the target material was exposed to a temperature range of 620-650°C. Samples from each set of volatile and nonvolatile-bearing glasses were heated for durations of 10 min or 1 h, each. Upon the completion of each degassing run, the sample was quenched in cold water. Pieces of degassed glass were mounted in epoxy after optical examination and polished and carbon-coated for electron microprobe (EMP) and laser inductively coupled plasma mass spectroscopy (ICP-MS) analysis.

Alteration Experiments

Mineral-vapor interaction experiments were conducted as part of the low-pressure degassing design. The target minerals placed in this closed system were selected to be representative of those extant on the Martian surface. Olivine, plagioclase, and clinopyroxene dominate the weakly altered basaltic rocks in Gusev Crater (McSween et al., 2008) and are major components of basaltic sand and soil in Gale crater (Bish et al., 2013; Rampe et al., 2017); therefore, these minerals were selected as targets for the alteration experiments. Further constraint on the mineralogy at the Martian surface was obtained from data gathered by the MSL ChemMin instrument (Bish et al., 2013). According to their observations, olivine at Rocknest was found to be forsteritic, along with labradorite plagioclase, and high-Ca augitic pyroxene. Therefore, for target minerals, terrestrial samples matching these minerals, olivine (Mogok forsterite), plagioclase (Ward's Scientific labradorite), and high-Ca pyroxene (Milesovka Mountain, Czech Republic augite) were used. We acknowledge that ~20%–50% of Martian surface materials are X-ray amorphous (e.g., Rampe et al., 2017). However, the fact that both the mineral chemistry and the processes that formed the amorphous material are not well understood, these three minerals are still a reasonable proxy for the primary materials on the Martian surface and showing the alteration on the crystalline fraction.

pieces Target minerals were broken into approximately 0.5 cm wide, avoiding any discolored/ weathered areas or coatings, and then rinsed and dried in ethanol. Cleaned target samples were loosely wrapped in a cleaned Pt₉₀-Rh₁₀ (thermocouple) wire before being inserted into the tube, to reduce interaction with the walls. Based on the measurement of the temperature 15 cm above the hot spot, target samples were held at approximately 620-650°C. The minerals were included in the 1-h degassing runs and extracted right after quenching. To assess prolonged exposure and cooling effects, separate 24- and 72-h experiments were run. 24and 72-h experiments were not quenched immediately like the 10-min and 1-h ones instead they were cooled gradually in air prior to opening the evacuated silica tube and extracting the minerals. This allowed for analysis of the intermediate phases that form during active degassing in the 1-h experiments and the final phases that coalesce further away from the source magma. Since the 24- and 72-h experiments were not quenched as the shorter experiments, the final glasses did not provide relevant degassing data and were not analyzed.

ANALYTICAL PROCEDURES

All experimental products were first observed optically, with detailed analysis followed by SEM-EDS for the target minerals and EMP and laser ablation (LA)-ICP-MS for the glasses. After each high-pressure synthesis, pieces of recovered glasses were mounted in epoxy and prepared as polished probe mounts. The samples were analyzed by EMP for major element and LA-ICP-MS for trace element abundances prior to the low-pressure degassing. Composition of the source material was verified by EMP analysis of the synthesized glass. Only the tubes that remained sealed after quench had their products analyzed. Degassed glasses were prepared the same way described above as polished probe mounts and were analyzed with EMP and LA-ICP-MS, respectively. Vapor condensates on the target minerals were only analyzed with SEM-EDS as salt sublimates, coatings, and trace metals are highly soluble in water. All experimental run products were kept in a desiccator connected to a vacuum pump between high-pressure synthesis and low-pressure degassing and fumarolic alteration experiments as well as prior to sample preparation and analysis to preserve the record of gassolid reactions. This was critical to avoid transformation of especially the vapor condensates (salt coatings) on the target minerals following the gas-solid interactions to hydrated minerals which can cause the micron-scale changes in the chemistry and textural changes with the development of possible relict textures (olivine), pores (Ca- and Mg-sulfates), and formation of clay mineral (plagioclase) (Dalby et al., 2018).

EMP analysis was completed at Oregon State University, using a Cameca SX-100 EMP. Analytical conditions include an accelerating voltage of 15 kV, a beam current of 20 nA (10 nA for Cl, Na, and K), and a beam size of 5 μ m for glass and larger phases and 1 μ m for finer crystals. The following minerals were used for standardization: McKee jadeite, Na; potassium feldspar, K; San Carlos olivine, Mg; Wakefield plagioclase, Si and Ca; Apatite, P; Barite, S; Scapolite, Cl; Ilmenite, Ti; MgCr₂O₄, Cr; Rhodonite, Mn; Rockport fayalite, Fe.

After EMP analysis, the starting glasses and experimental charges were analyzed for elemental abundances (Ge, Li, and Zn) using the high-resolution Thermo Finnigan Element XR[™] ICP-MS equipped with an Electro Scientific Lasers (ESL) New Wave[™] UP193FX ArF (193 nm) excimer laser ablation system at the National High Magnetic Field Laboratory (Humayun, 2012; Humayun et al., 2010; Yang et al., 2015, 2018). The starting and experimental glasses were ablated with 50 µm laser spots at a repetition rate of 50 Hz for 10 s. Each glass was analyzed at multiple spots (4-6) repeatedly and the averaged values were used as the measured compositions of the glasses. The standard deviations of the repeated measurements were used to access the uncertainties of analyzed elemental concentrations. Mass peaks of Li, Zn, and Ge were acquired at ⁷Li, ⁶⁶Zn, and ⁷⁴Ge. The isobaric interferences of doubly charged ions 148 Nd⁺⁺ and 148 Sm⁺⁺ on 74 Ge were corrected by monitoring ¹⁴⁵Nd⁺⁺ and ¹⁴⁹Sm⁺⁺ within a multielement routine (Yang et al., 2015, 2018). A synthetic glass GSD-1 g and three USGS glasses (BHVO-2 g, BCR-2 g and BIR-1 g) were analyzed as external standards using the same laser properties as for samples. For elements that are poorly constrained in USGS glasses (e.g., Li, Ge) (Jochum et al., 2005), GSD-1 g was used as the external standard; for elements that have been precisely determined in USGS glasses (e.g., major elements, Zn), USGS glasses were used as the calibration materials. The chemical compositions of GSD-1 g and of USGS glasses are provided in Jochum et al. (2005). The relative sensitivity factors (RSFs) obtained from the external standards were used to calculate elemental abundances of the glasses (Humayun et al., 2010). The intensity ratios between analyzed elements against Si were multiplied by RSFs to obtain elemental ratios with respect to SiO₂. These elemental ratios were converted to elemental concentrations by multiplying by SiO₂ contents determined by normalization of major element oxides to 100% (Humayun et al., 2010).

Target minerals which interacted with the degassed vapors were characterized with SEM-EDS for their mineralogy and semi-quantitative chemistry for the identification of surficial alteration phases. For this procedure, grains were secured to aluminum stubs on conductive carbon tape and coated with carbon for the analysis. SEM-EDS analysis was conducted at the Engineering and Mining Experiment Station at South Dakota School of Mines and Technology. These analyses were performed using a Zeiss Supra 40 variable-pressure field-emission SEM, with an Oxford AZtec energy dispersive X-ray spectrometer.

RESULTS

Geochemical Observations

Compositions of the initial and final degassed glasses are produced by taking the average of ~10 EMP analyses for each run product (Table 2). The 1σ values presented parenthetically represent the standard deviation of the mean for each oxide value, which was larger than the analytical uncertainty determined by counting statistics. After degassing and quench, the silica glass tube used in the 1-h runs showed some devitrification in the bottom 2-3 cm. The fact that the capsule remained shiny in each experiment, suggested that the silica glass tube retained its integrity for the duration of the experiment. No macroscopic condensates were formed on the tube walls in the 10-min and 1-h runs. The degassed samples consisted of glass, irregular blobs of metallic iron, and vesicles (rare). Immiscible Fe-droplets were found during backscattered electron (BSE) imaging (Figure 3) of the final glasses for the Cl + S 10-min and 1-h runs, the Clonly 10-min and 1-h runs, and the S-only 1-h run. The fact that there were no immiscible Fe-droplets in NVA starting glasses which were both synthesized and degassed at low pressure (<1 bar) in Au₇₅Pd₂₅ capsules, we attributed the formation of these Fe-droplets in volatile bearing runs due to the shift in fO_2 between highpressure synthesis in the graphite capsules (low fO_2) and degassing at FMQ + 1 (high fO_2). To account for this loss, mass balance calculations were done to quantify the amount of metallic Fe in the final glasses and add it back to the bulk composition of the glass (Table 2). We did not measure Ge or Zn in the metallic Fe-droplets; therefore, mass balance calculations did not include the partitioning of Ge or Zn into metallic Fe phase. After Fe correction, we still observed some amount of loss in FeO, especially in 1-h degassing experiments and attributed remaining amount of loss of FeO to the degassing.

Mass Balance Calculations

To compute the composition of the vapor, proportion of vapor and melt phases, and convert the system back onto a metallic Fe-free basis, mass balance calculations were conducted through correction of the major oxide constituents of the final degassed melt for FeO_T loss due to iron reduction as discussed previously (Ustunisik et al., 2011). The weight fraction of silicate melt after degassing (fm) was computed for each likely refractory oxide (e.g., MgO, Al₂O₃, CaO) as the weight ratio in the initial and final (degassed) silicate glasses. The actual fm used (Table 3) lies between the values obtained from MgO and was chosen because it vielded the best overall mass balance for each experiment. The weight fraction of FeO lost as Fe^0 and oxygen (*f*FeO^r) was computed as $fFeO^r = (FeO^{initial} - fm^*FeO^{final melt})/100$, and the degassed glass composition was corrected for this. With the fm and $f \text{FeO}^{r}$ calculated, the weight fraction of vapor (fv) is obtained through the relation $fv = 1 - (fm + fFeO^{r})$. With the consideration of the chemical components, i = Cl, S, Ge, Zn, and FeO, the composition of thevapor phase and the percentage volatile loss are calculated as $i^{vapor} = (i^{initial melt} - fm^*i^{inal melt})/fv$.

Changes in Melt Composition

The relative changes in major oxide abundance are shown with the dashed line representing the initial melt composition and the colored lines representing the relative changes in abundance for each oxide in the 10min (light color) and 1-h (dark color) runs (Figure 4). In the NVA experiment, there was very little change observed in the major oxides. However, in the volatilebearing runs (Cl-only, S-only, and Cl + S), there is a noticeable loss of Na₂O and K₂O. This change in relative abundances is accentuated between the 10-min experiments and the 1-h experiments. This loss is a result of the volatile nature of the alkali oxides, compared with the more refractory oxides such as MgO, Al₂O₃, and CaO.

In the volatile-bearing runs, most of the Cl and S is lost in the first 10 min of degassing (Figure 5; Table 3). For Cl-only, 92% of the Cl was lost in the first 10 min, increasing to 95% after an hour. For the S-only run, 96% of the S was lost in the first 10 min and this loss stayed

TABL	E 2. Mean co	mpositions o	f initial, final, a	and final Fe ⁰	corrected d	legassed melts	s for NVA, 0	Cl-, S-, ar	nd Cl + S-bearing	g experiments	
	NVA initial	NVA final		Cl final	Cl final	S initial	S final	S final		Cl,S final	Cl,S final
Oxide	(t_0)	$(t_{1 h})^{c}$	Cl initial (t_0)	$(t_{10 min})^{d}$	$(t_{1 h})^{\mathbf{d}}$	(t_0)	$(t_{10 min})^{d}$	$(t_{1 h})^{\mathbf{d}}$	Cl,S initial (t_0)	$(t_{10 min})^{d}$	$(t_{1 h})^{\mathbf{d}}$
SiO_2^{a}	49.43 (0.25) ^b	49.73 (0.21)	48.85 (0.21)	49.14	49.14	49.99 (0.26)	50.30 (0.48)	50.30	49.68 (0.25)	49.98	49.98
TiO_2	1.08 (0.02)	1.07 (0.02)	1.09(0.02)	1.10	1.18	1.11 (0.02)	1.16 (0.02)	1.19	1.13(0.02)	1.17	1.25
Al_2O_3	11.57 (0.08)	11.56 (0.06)	11.59(0.11)	11.63	12.27	11.92 (0.06)	12.00 (0.17)	12.16	12.08 (0.35)	12.44	11.99
FeO_T	17.60 (0.25)	17.54 (0.28)	17.84 (0.19)	16.92	16.18	15.90 (0.17)	15.26 (0.55)	15.33	16.80(0.29)	16.13	16.01
MgO	9.86(0.11)	9.79 (0.12)	10.18 (0.04)	10.79	11.04	10.18 (0.05)	10.38 (0.12)	10.61	10.03(0.09)	10.42	10.73
CaO	6.27 (0.06)	6.22 (0.07)	6.10(0.04)	6.68	6.64	6.32 (0.05)	6.71 (0.16)	6.73	5.94 (0.07)	6.41	6.73
Na_2O	2.69(0.14)	2.63(0.14)	2.81 (0.15)	2.35	2.10	2.95 (0.11)	2.73 (0.15)	2.23	2.76 (0.09)	2.08	1.83
$\rm K_2O$	0.67(0.08)	0.62(0.08)	0.75(0.09)	0.55	0.57	0.72(0.13)	0.55 (0.07)	0.51	0.76(0.08)	0.53	0.55
MnO	0.35(0.05)	0.34 (0.04)	0.36(0.06)	0.35	0.40	0.42(0.05)	0.43 (0.05)	0.43	0.36(0.06)	0.36	0.44
P_2O_5	0.48(0.03)	0.49 (0.04)	0.45(0.04)	0.49	0.47	0.49(0.05)	0.49(0.03)	0.51	0.48(0.03)	0.49	0.50
Total	100			100	100			100		100	100
ū			14,522 (340)	1172	807				10,493 (277)	820	550
S						4367 (115)	175 (50)	195	5267 (321)	100	149
Ŀi	258 (3)	277 (4)	252 (5)	444	333	269 (8)	384 (5)	238	262 (3)	405	359
Ge	919 (3)	48 (3)	927 (2)	718	23	1038 (14)	761 (77)	371	1075 (12)	317	25
Zn	860 (15)	127 (2)	1125 (23)	535	104	1127 (22)	862 (34)	598	1169 (18)	708	112
Abbre ^a Oxide	viation: NVA, no s in wt%; Cl, S, 6	volatile added. Ge, Li, Zn in ppı	ш.								

 ${}^{b}(1\sigma)$. ${}^{c}NVA$ final $(t_{1 h})$ and S final $(t_{10 min})$ degassing experimental products do not contain metallic Fe (FeO'). d Final glasses after Fe⁰ correction.



FIGURE 3. Backscattered electron (BSE) images of initial (a. NVA_I, c. Cl₀, f. S₀, i. Cl + S₀) and degassed glasses after 10 min (d. $Cl_{10 \text{ min}}$, g. S_{10 min}, j. Cl + S_{10 min}) and 1 h (b. NVA₁ h, e. Cl₁ h, h. S₁ h, k. Cl + S₁ h) of degassing. Numbers and lines show locations of point and line analyses. The white speckling in the degassed glasses indicate metallic Fe droplets. (Color figure can be viewed at wileyonlinelibrary.com)

the same in the 1-h run. In the Cl + S system, 98% of the S was lost in both the 10-min and stayed the same during 1-h experiments, while Cl loss was near 100% for both set of starting compositions and time series (Cl-only, Cl + S for 10 min and 1 h; Table 3).

The relative abundance of Li in the melt increases in all experiments especially in S-bearing runs. This is contrary to the fast-diffusing behavior of Li and may indicate contamination. One possible contamination source for Li can be through the silica glass tube which

				f^{a}	Cl	S	Ge	Zn	FeO
Irvine no volatile	<i>t</i> _{1 h}	Vapor Final melt	Composition (ppm) Volatile abundance (ppm) Volatile loss (%)				3,60,000 50 95	3,04,000 131 85	3,37,000 1,76,000
(NVA)		Contribution to the system	Vapor Melt	0.003 0.998			899 49	759 130	843 1,75,000
Irvine Cl	$t_{10 \min}$	(ppm) Vapor Final melt	Composition (ppm) Volatile abundance (ppm) Volatile loss (%)		5,49,000 1170 92		9400 718 25	25,000 535 54	4,17,000 1,69,000 6
		Contribution to the system (ppm)	Vapor Melt	0.025 0.968	13,500 1140		230 701	608 521	10,200 1,65,000
	<i>t</i> _{1 h}	Vapor Final melt	Composition (ppm) Volatile abundance (ppm) Volatile loss (%)		4,39,000 807 95		29,000 23 98	33,000 104 91	5,00,000 1,62,000 11
		Contribution to the system (ppm)	Vapor Melt	0.032 0.968	13,900 782		914 22	1000 101	16,000 1,56,000
Irvine S	<i>t</i> _{10 min}	Vapor Final melt	Composition (ppm) Volatile abundance (ppm) Volatile loss (%)			3,59,000 177 96	25,000 771 27	24,000 873 24	5,93,000 1,52,000 5
		Contribution to the system (ppm)	Vapor Melt	0.012 0.988		4300 175	297 762	287 863	7100 1,51,000
	<i>t</i> _{1 h}	Vapor Final melt	Composition (ppm) Volatile abundance (ppm) Volatile loss (%)			5,18,000 195 96	83,000 371 65	65,000 598 48	3,34,000 1,53,000 5
		Contribution to the system (ppm)	Vapor Melt	0.008 0.992		4300 193	678 368	536 593	2700 1,52,000
Irvine Cl + S	$t_{10 \min}$	Vapor Final melt	Composition (ppm) Volatile abundance (ppm) Volatile loss (%)		4,25,000 820 100	2,27,000 100 98	34,000 317 71	21,000 708 41	2,94,000 1,61,000 5
		Contribution to the system (ppm)	Vapor Melt	0.023 0.992	9800 801	5200 98	772 309	482 692	6800 1,57,000
	<i>t</i> _{1 h}	Vapor Final melt	Composition (ppm) Volatile abundance (ppm) Volatile loss (%)		4,42,500 550 100	2,28,000 149 98	46,700 25 98	47,000 112 91	2,36,000 1,60,000 5
		Contribution to the system (ppm)	Vapor Melt	0.023 0.977	10,100 537	5200 145	1100 24	1100 110	5400 1,56,000

TABLE 3. Mass balance results for each of the experiments.

Note: Changes in melt and vapor composition are presented in terms of Cl, S, Ge, Zn, and FeO. Calculations were used to determine the weight fractions (*f*) of the melt and vapor as well as their composition in relation to these five components.

^aWeight fraction (*f*) of phase in system (only vapor and melt are given, not FeOr); digits beyond two decimal places are given only for mass balance purposes and rounded to the nearest decimal point.

may include trace amounts of Li. However, we did not analyze the silica tube for this possible Li contamination prior to the experiments.

Loss of Ge depends on the degassing time and volatile speciation of the melt (Figures 5 and 6a). In all 1-h runs, the total loss of Ge is greater than the loss of Zn

(Figure 5b–d). Within 1 h of degassing surprisingly the amount of Ge loss in S-only experiment is lower (65%) compared to much higher percentages of Ge loss in NVA (95%) and both Cl-only and Cl + S (98%) runs. Greater variation in the loss of Ge is observed in the 10-min runs (Cl-only, S-only, and Cl + S), where 25% of Ge is lost in



FIGURE 4. Volatile losses for major oxides in degassed glasses in each of the four experiments for the Irvine composition. Results are compared to the initial melt composition (dashed line): (a) Irvine NVA (no volatiles added); (b) Irvine Cl (doped with 15,000 ppm Cl); (c) Irvine S (doped with 5000 ppm S); (d) Irvine Cl + S (doped with both 10,000 ppm Cl and 5000 ppm S). (Color figure can be viewed at wileyonlinelibrary.com)

the Cl-only and 27% in the S-only runs, while Ge loss is 71% in the Cl + S run (Figure 6a; Table 3). Note that 10-min NVA run was not performed.

Zinc shows similar trends to Ge (Figures 5b and 6b) in the 1-h experiments, where the greatest loss of Zn occurs in the Cl + S and Cl-only runs (91%), with a lesser degree of loss in the NVA system (85%), and a significantly lesser amount of loss in the S-only run (48%). For the 10-min runs, Zn loss is variable among the Cl-only (54%), S-only (24%), and Cl + S (41%) runs (Table 3).

Changes in Vapor Composition

Mass balance calculations using the composition of initial and final melts make it possible to calculate the changes in composition of the vapor phase in terms of its volatile and trace metal components over time (10 min and 1 h) for the various starting compositions (Table 3; Figure 7). Using the weight fraction of melt (f_M) and vapor phases (f_v) produced, the contribution of vapor components (dashed boxes in Figure 7) is calculated

through their loss from the melt. Vapor content is presented (Table 3) as both vapor composition and vapor contribution. Prior to further discussion on changes in vapor composition, we define the vapor contribution and vapor composition terms. The vapor contribution represents how much of a given volatile component entered to the vapor phase from the bulk composition of the initial melt. In other words, the vapor contribution for any component is calculated by multiplying the concentration of this volatile component in the vapor (vapor composition) with the weight fraction of vapor. Therefore, vapor contribution (Figures 7 and 8) provides an accurate representation of the volatile element input from the melt to the vapor phase which will be available to condensate as deposits and coatings or involved in target mineral alteration when compared to percentage loss of composition of vapor.

The calculated f_v vapor varies between experiments as a result of changing volatile load and degassing time. In the 10-min runs, the f_v for the Cl-only and Cl + S runs are similar (0.025, 0.023) (Figure 7a,d; Table 3); however,



FIGURE 5. Effects of outgassing on volatile and trace element abundances in each of the four experiments for the Irvine composition. Results are compared to the initial melt composition (dashed line): (a) Irvine NVA (no volatiles added); (b) Irvine Cl (doped with 15,000 ppm Cl); (c) Irvine S (doped with 5000 ppm S); (d) Irvine Cl + S (doped with both 10,000 ppm Cl and 5000 ppm S). (Color figure can be viewed at wileyonlinelibrary.com)



FIGURE 6. Changes in the concentrations of Ge (a) and Zn (b) in the melt as a function of time for each of the four experiments. (Color figure can be viewed at wileyonlinelibrary.com)

the S-only experiment has about half the total f_v (0.012) (Figure 7b; Table 3). For the 1-h experiments, the trend of S-only run (Figure 7b) having a smaller f_v than the Cl-only (Figure 7a) and Cl + S (Figure 7d) experiments is

repeated (Table 3). The NVA run had a lower f_v (0.0025) (Figure 7c; Table 3) than the volatile-bearing runs.

The vapor composition of the trace elements (Ge and Zn) is influenced by the f_v and the presence of other



FIGURE 7. Schematic showing the results of mass balance calculations for the starting and degassed Irvine glasses for no volatile added (NVA) (a), and with Cl + S (b), Cl (c), and S (d). Pathways show the change in composition between the initial melt and the final degassed melts. In addition, the composition weight fraction of the vapor phase is shown. (Color figure can be viewed at wileyonlinelibrary.com)

1197



FIGURE 8. Loss of volatile and trace elements (a) during degassing along with the contribution of these elements to the vapor (b) for Cl-only, S-only, no volatile added (NVA), and Cl + S runs. Lighter colors show the 10-min experiments while darker colors show the 1-h experiments. (Color figure can be viewed at wileyonlinelibrary.com)

volatile components in the vapor. In the 10-min runs, the vapor contribution of Ge is nearly the same between the Cl-only (230 ppm; Figure 7a; Table 3) and S-only (297 ppm) (Figure 7b; Table 3). However, the vapor composition of Ge in the S-only (25,000 ppm) is

more than double the Cl-only (9400 ppm) run (Table 3). This discrepancy is a result of more than twice of f_v in the Cl-only ($f_v = 0.025$) run compared to the S-only ($f_v = 0.012$) run which decreases (dilutes) the contribution of Ge carried in S-only vapor (Figure 7a,b; Table 3).

The calculated vapor compositions for each of the experiments represent the material lost from the melt as well as the components available to alter and condense on common surface minerals. The alteration experiments included plagioclase (labradorite), clinopyroxene (augite), and olivine (forsterite). These minerals were included in the 1-h degassing experiments for Cl-only, S-only, and Cl + S-bearing runs.

Before discussing the details of alteration experiments, we first outline the specific terminology used for these experiments. For the purposes of this discussion, we define "alteration phases" as any phase not native to the target mineral, with a chemical composition that includes an elemental component that is most likely derived from the target mineral yet not from the vapor. However, "vapor deposits/coating" are here defined as new phases with a chemical signature independent of the target material or considered to be exclusively sourced from the condensation of vapor.

The Cl + S experiments showed the largest degree of alteration and vapor deposition in 1-h runs. To better constrain the long-term alteration effects, a 24- and 72-h alteration experiments were run with the Cl + S starting glasses in addition to the 1-h experiments. At the end of alteration experiments, the target materials were slightly discolored and appeared to have surficial coatings of other minerals. Therefore, we identified evidence for both mineral alteration and vapor deposits on the surface of the minerals after the experiments.

Target Mineral Alteration

Composite element maps were generated from SEM-EDS of minerals prior to (forsterite—Figure 9a, augite— Figure 10a, and labradorite—Figure 11a) and after (Figures 9b–e, 10b–e, 11b–d) the fumarolic alteration experiments. Compared to Cl-only and S-only runs for all three minerals, the greatest degree of mineral alteration and vapor precipitation were observed for Cl + S runs (Figures 8b,c, 9b,c, 10b).

In all the experiments, the target olivine showed the largest degree of alteration compared to the augite and plagioclase, with the phases varying depending on the vapor composition. In the Cl-only run, the target olivine showed minor development of Ca-chloride associated with rough surfaces and cracks on the mineral (Figure 9d). Ca-chloride precipitations lacked discernable crystal structure and developed as amorphous masses. In the S-only experiment, we observed amorphous development of Mg-sulfate and Ca-sulfate (anhydrite) on olivine, with the anhydrite comprising more than 90% of the observable alteration (Figure 9e). In the Cl + S experiment, the development of ordered mineral phases

was detected on the target olivine. Two distinct phases, anhydrite and langbeinite $(K_2Mg_2[SO_4]_3)$ group minerals, were detected on the mineral surface (Figure 9b,c). The anhydrite was amorphous on some surfaces, yet more crystalline on others. The langbeinite group minerals ranged in composition between langbeinite and calciolangbeinite and formed vermicular patterns on the surface of the target olivine (Figure 9c).

The target augite generally displayed a lesser degree of alteration than the olivine but displayed clear evidence of vapor deposit formation (Figure 10b-e). In the Cl-only experiment, halite and Ca-chloride were detected. These phases were not abundant and lacked any discernable crystal structure (Figure 10d). The S-only experiment showed minor patches of amorphous anhydrite along intersecting cleavage planes on the augite. A single piece of pyrite (Fe sulfide) with a width of about 20 µm was also detected (Figure 10e). In the Cl + S experiment, alteration to anhydrite was more extensive than in the Sonly experiment, forming large (100 µm) flower structures (Figure 10b). The target augite also showed generation of the langbeinite phases observed on the olivine in the same Cl + S experiment, though not to the same spatial extent (Figure 10c).

In the Cl + S experiment, development of anhydrite was observed (Figure 11b), on the target plagioclase seemingly beginning to form the base of the flower structures previously noted on the augite. In both the Clonly (Figure 11c) and S-only (Figure 11d) experiments, there was no detectable alteration or vapor deposition.

To observe a wider range of phases that could arise from outgassing of volatile-rich Martian basalts, additional alteration experiments were run for 24- and 72-h with the Cl + S composition (Figures 12 and 13). For these runs, only Cl + S composition was used since it showed the most alteration in the 1-h experiments and contained both of the volatiles of interest (Cl, S). In addition, unlike the 1-h experiments in which the minerals were extracted immediately after quenching of the tube in water, the sealed silica tube was allowed to cool gradually for several hours before being opened. 24-h experiments did not show noticeable mineral alteration of target minerals. Instead, pyrite (FeS₂) was observed in greater abundance than the 1-h runs, again on the augite (Figure 12a). Growth of various salts was more extensive after 24-h than in the shorter (1-h) experiments. These were primarily mixed salts (halite and sylvite) with a varying Na/ K content. Individual salt crystals on the target olivine were near 100 µm across and covered much of one side of the sample (Figure 12b) while these deposits were sparse on the target augite along with minor CaCl₂ (Figure 12c). The loss of alkalis during degassing was thought to be the source for the formation of NaCl and KCl crystal deposits on olivine and NaCl crystal deposits in augite. The formation of

Forsterite after 1-hour alteration



FIGURE 9. Composite element maps of original (a) and altered forsterite after being exposed to Irvine Cl + S- (b, c), Cl- (d), and S- (e) following 1-h fumarolic alteration experiments. Forsterite shows Ca- and Mg-sulfate, and Ca-chloride coatings in addition to langbeinite group mineral formations as red patches seen in composite element maps. (Color figure can be viewed at wileyonlinelibrary.com)

minor CaCl₂ on augite was thought to be mineral alteration via Ca content of augite.

Vapor Deposit Mineralogy within Silica Tube

Because the results of the 24-h alteration experiment differed significantly from the 1-h experiments, we conducted a 72-h alteration experiment for the Cl + S composition. Similar to the 24-h run, after the experiment, the sealed silica tube was allowed to cool gradually over the course of several hours before being opened to extract the minerals. The 72-h experiment was the only one to have macroscopic growth of condensate material within the interior walls of the silica tube (Figure 12a) and therefore for this one, we only reported the chemical characterization of condensates within the silica tube for 72-h run. Two distinct clusters of condensates were observed, with one cluster located within the interior walls ~ 2 cm above the target minerals (cooler portion of silica tube) and the other located the same distance below the target minerals (hotter portion of the silica tube—relatively closer to hot spot) (Figure 13a). Both groups of condensates were comprised of mixed salts (Na/K chlorides). Rather than a random turbulent flow within the silica tube, the flow direction was assumed to be from the hot spot to the cooler regions driven by thermal gradient. In the cluster above the minerals, relatively cooler regions, the condensates were single, euhedral, cubic salts with variable Na/K ratio (Figure 13b). Below the target minerals within the hotter portions of the silica tube, condensate salts formed as branching structures as well the large single euhedral crystals (Figure 12). When branching salt crystals were examined closely (Figure 13c), they were found to be individual cubic salt crystals in a chain structure (Figure 13d) in the direction of vapor exsolving from the melt and expanding to the cooler portions of the silica tube.

DISCUSSION

Low-Pressure Degassing Experiments

The near-complete loss of volatiles in the 10-min experiments shows that nearly all volatile-assisted transport of trace metals (chloride and sulfide formation) occurs in the first few minutes, with loss as oxides becoming the dominant vapor contributor afterwards in the 1-h experiments. Since nearly all volatile loss occurs in the first 10 min, these shorter runs are key to understanding the volatile-assisted transport of the trace



FIGURE 10. Composite element maps of original (a) and altered augite after being exposed to Irvine Cl + S- (b, c), Cl- (d), and S- (e) after 1-h fumarolic alteration experiments. In addition to Ca- and Mg-sulfate, Ca-chloride coatings, and langbeinite group mineral formations, augite also Pyrite (FeS₂) and halite (NaCl) are observed as coatings. (Color figure can be viewed at wileyonlinelibrary.com)

metals (Ge and Zn) from the melt to the vapor phase. In the Cl-only experiments, Zn loss (54%) is more than twice that of Ge (25%). The loss of Zn demonstrates a preference for the formation of Zn-chloride rather than Ge-chloride. This phenomenon is likely a result of the shorter, and therefore stronger, bonds between Ge and O (1.74 Å; Smith & Isaacs, 1964) compared to Zn and O (2.00 Å; Supatutkul et al., 2017). Chlorine preferentially breaks these weaker bonds to form chloride complexes with Zn.

In the S-only experiments, the maximum loss of Ge (65%) and Zn (48%) is consistently less than in any other experiments, including the NVA run. One possible explanation for this is that the S-only experiments might have melts with the most dissolved S compared to the Cl + S-bearing runs. The possible complexing of dissolved S in the melt with Ge and Zn might decrease the degassing of Ge and Zn in S-only experiments compared to rates that the Cl and Cl-S experiments exhibit.

The differences in the volatility of Ge and Zn between Cl-bearing and Cl-free (S-only or NVA) runs could be attributed to the shift in the oxygen fugacity during degassing of volatile and trace elements from Cl-bearing and Cl-free melts. In Cl-bearing experiments, some of the FeO loss is due to the Fe complexing with Cl in the melt. This reaction of FeO + 2Cl \rightarrow FeCl₂ + 0.5O₂ (Bell et al., 2011) could lead to a slightly more oxidized melt in Cl-bearing runs. So, it is possible to have some differences in the redox state between the Cl-bearing and Cl-free (S-only or NVA) experiments that, in turn, will decrease the loss of Ge and Zn in Cl-bearing runs with respect to Cl + Sbearing ones.

The Cl + S experiments show the largest amount of loss of trace and volatile elements in the 1-h experiments. In the 10-min experiment, Ge loss (71%) was greater than the Zn loss (41%), as opposed to the results of the Clonly run at 10-min, where Ge loss (25%) was less than that of Zn (54%). This shift may be the result of the combined effects of Cl and S on melt chemistry. In S-only runs, the complexing Ge and Zn with dissolved S in melt and in Cl-only runs, Cl being lost in the form Fe chlorides before complexing with Ge or Zn could both lead to the lower loss of Ge and Zn. Sulfur complexing in the melt for the S-bearing versus Cl-bearing runs might hold back on the loss of Zn and Ge compared to other Cl-bearing melts. As the system becomes more oxidized with FeCl₂

Labrodorite after 1-hour alteration



FIGURE 11. Composite element maps of original (a) and altered labradorite after being exposed to Irvine Cl + S- (b), Cl- (c), and S- (d) after 1-h fumarolic alteration experiments. Labradorite shows no discernable alteration or crystalline deposits. In the Cl + S experiments, minimal amount of Ca-sulfate is detected principally as coatings and clusters that lack distinct crystal development. (Color figure can be viewed at wileyonlinelibrary.com)



50 μm

FIGURE 12. Composite element maps of augite (a, c) and forsterite (b) after being exposed to Irvine with Cl + S for 24 h fumarolic alteration experiments. 24-h alteration runs show that NaCl and CaCl₂ crystals grow on the surface of forsterite and augite, respectively, rather than simple coatings formed on the surface of both minerals during 1-h experiments. (Color figure can be viewed at wileyonlinelibrary.com)

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FIGURE 13. Composite element map of mixed salt condensates forming on the inner walls of silica tube from Irvine with Cl + S after 72-h fumarolic alteration experiments. In the 72-h experiment, two distinct clusters of halite/sylvite condensate were observed. The dichotomy in crystal morphology is a result of varying temperature conditions. The cluster of condensates lower in the tube formed at higher temperatures, consistent with more rapid formation of smaller salt crystals that clustered into the branching patterns (a, c, d) observed. In the upper cluster, the cooler temperature allowed for gradual growth of larger single crystals (a, b). (Color figure can be viewed at wileyonlinelibrary.com)

loss, S in melt will be stable as sulfate and complexing may disappear.

The NVA experiments show similar amounts of Ge (95%) and Zn (85%) loss to the 1 h Cl-only and Cl + Sbearing runs and the loss of both elements in NVA runs are still larger than Ge (65%) and Zn (48%) loss in 1 h Sonly experiments. This unexpected high volatility of Ge and Zn in NVA experiments raises the possibility of small amount of Cl contamination in the NVA starting material from the oxides used for synthesis but we did not measure any Cl in the initial and degassed glasses for NVA runs. Another explanation is the loss of Ge as GeO₂. Solid–gas reaction experiments by N. Zimmermann (personal communication) have shown the possibility of condensation of Ge-bearing phases such as GeO2-Ge microcubes and hexagonal GeO₂ crystals over the temperature range of 300-750°C during the degassing of Br-, Ca-, Ti-, and P-enriched basaltic magma after 96 h.

The calculated WF_v vapor for each experiment is predominantly controlled by the initial melt chemistry. For example, in the 10-min runs, the WF_v for the Cl-only and Cl + S runs are similar (0.025, 0.023); however, the S-only experiment has about half the total WF_v (0.012). We interpret this to be a result of early complexing of sulfur in the melt where the formation and loss of SO_2 may decrease the percent loss of Ge and Zn. In the Cl + S experiment, the combined loss of two volatiles results in a near doubling of the WF_v, while in the Cl-only, the extensive loss of Fe as Fe-chlorides allows for the generation of a greater amount of vapor than in the S-only run. For all the volatile-bearing runs, the principal component of the vapor phase is the Cl and/or S, which is absent in the NVA melt, resulting in a smaller amount of vapor produced.

Partitioning of chlorides to the vapor phase would explain its widespread distribution on the Martian surface independent of hydrothermal processes. In addition, the confirmation that Ge and Zn leave the melt as chlorides provides a mechanism for the distribution of these trace metals on the surface, which may then be further concentrated by hydrothermal or aqueous processes. As such, the positive correlation of Cl and Zn in Martian soils (Berger et al., 2020; O'Connell-Cooper et al., 2017; Yen et al., 2005) and the enrichment of volatiles in the global dust (Berger et al., 2016) are consistent with an overall enrichment across the entire surface. An overall enrichment of 2–10 times the concentrations found in the basaltic crust could have been an enhancement that facilitated the observed localized enrichments of 100–1000 times the average crust. However, this work exclusively investigates the partitioning of these trace metals to the vapor phase from the melt in a system independent of crystallization. Future work is necessary to determine the capacity for mineral crystallization to remove Ge and Zn from the melt prior to fumarolic degassing.

A potential source for the primary Ge and Zn enrichment at the Martian surface is outgassing of Noachian and Hesperian lavas. The high concentrations of Ge and Zn discovered by the APXS instruments support this hypothesis in general, but the enrichment pathways are not entirely clear owing to the relative diversity of the enriched deposits and remobilization via hydrothermal and diagenetic processes (Berger et al., 2017; Mittlefehldt et al., 2021). Shergottites provide a point of comparison to the in situ rover samples, having 1-3 ppm and 40-90 ppm of Ge and Zn, respectively (Yang et al., 2015). This is comparable to analog terrestrial basalts, which contain 1.4 ± 0.3 ppm Ge and 90-130 ppm Zn (e.g., Bernstein, 1985; Heinrichs et al., 1980). Shergottites indicate that as much as half of the Ge in shergottite magmas might have been outgassed prior to solidification (Yang et al., 2019). Such volcanic exhalations are a potent source for the huge excesses of Ge observed in the Martian sedimentary rocks (Berger et al., 2017; Humayun et al., 2016a, 2016b; Yang et al., 2019), although experimental confirmation that Ge is sufficiently volatile has been lacking. Martian regolith breccia meteorites provide constraints because they incorporated regolith with the evidence of hydrothermal alteration, but without the volatile element enrichments observed by rovers (Humayun et al., 2013; McCubbin et al., 2016; Yang et al., 2015). Two models proposed for the lithification age (e.g., Hewins et al., 2017; McCubbin et al., 2016) have very different implications: (i) Annealing the rock at ~ 4.3 Ga is consistent with the absence of high Cl, S, Zn, and Ge in the breccia (Humayun et al., 2013) and likely occurred before significant outgassing and incorporation of volatiles into sediments of late Noachian/early Hesperian age. (ii) Annealing the rock at ~1.4 Ga indicates that Cl, S, Zn, and Ge enrichments were not uniformly distributed in surface materials such that they were incorporated in the breccia.

Testing the outgassing hypothesis with rover observations has limitations. First, under typical measurement conditions, the MER- and MSL-APXS detection limit is 30 ppm for both elements (Gellert et al., 2006; VanBommel et al., 2019); thus, Ge enrichments (and depletions) that are <20 times higher than common basaltic concentrations are currently not detectable. However, methods are being developed to improve trace element quantification with MER-APXS, and preliminary results indicate that Ge enrichments are more widespread in Gusev Crater and in sedimentary deposits at Meridiani Planum than previously thought (Knight et al., 2023). Second, rover missions are driven by research questions and operational concerns that necessarily lead to sample bias. For example, landing sites are selected to study sites with aqueous activity and potentially habitable environments (e.g., Grotzinger et al., 2012; Squyres et al., 2004), and rover paths and APXS targets are selected to answer specific science questions in a manner that is safe for the rover and payload (e.g., Berger et al., 2020). For these reasons, making a quantitative comparison of the experimentally observed outgassing to the volatile element concentrations observed in Martian meteorites and in situ samples involves considerable uncertainty with many complex parameters. Such a comparison merits further investigation but is beyond the scope of this work. Nevertheless, the widespread S, Cl, Zn, and Ge enrichments on the Martian surface are compelling evidence of significant delivery of volatiles to the surface.

The experiments performed here revealed that both Ge and Zn are volatile from melts of likely Martian igneous compositions in the presence of S or Cl. The Clbearing experiments resulted in near total loss of Ge and Zn from the initial melts in about an hour, with a significant portion of the loss occurring in the first 10 min. Experiments with sulfur as the added volatile lost less of their initial Ge or Zn abundances. The significant losses of both Ge and Zn from the NVA experiment are surprising, and the loss mechanisms for this experiment are not understood sufficiently at present. Since Martian magmas contain both S and Cl (Filiberto et al., 2016), these experiments establish that volatile losses of Ge and Zn are likely under Martian conditions. Elemental abundances for shergottites, admittedly a different melt composition than Irvine, exhibit evidence for progressive loss of up to half the initial Ge inventory of the melt but show no discernable losses of Zn (Yang et al., 2019). In this sense, the present experiments were too aggressive compared to what is known from shergottites. The experiments, therefore, provide supportive evidence that early volcanism could have enriched Martian surface materials in volatile Ge and Zn compounds that were subsequently redistributed during hydrothermal or aqueous processes to yield the high Ge and Zn abundances now ubiquitously observed in Martian sedimentary rocks (Berger et al., 2017).

Fumarolic Alteration Experiments

The alteration experiments provided a variety of information related to the interactions between the vapor and the surface of minerals expected to be present, at variable temperature and time constraints. Anhydrite and langbeinite group minerals were dominant phases in the S-only and Cl + S 1-h runs. Due to the refractory nature of Ca in the melt, it is unlikely that the Ca forming these new phases is sourced from the vapor. Instead, we infer that the Ca was pulled from the target minerals. Henley et al. (2015) suggest that the anhydrite clusters can be formed due to the reaction between SO₂ gas and anorthitic feldspar at 600-800°C during 41- and 96-h experiments. They also observed a corona texture over anhydrite in their 72 hr (3 days) and 700°C runs with the reaction of low anorthitic (An₂₆) glass. Previous experiments and thermodynamic modeling on anhydrous systems by King et al. (2018) have shown that Ca-bearing mineral reacts with SO₂ effectively to produce CaSO₄ in addition SiO₂ and Al₂SiO₅ if the reactant is anorthitic plagioclase. Similarly, when reacted with SO₂ at 600–800 °C, diopside forms large plate-like CaSO₄ crystals while augite forms Na₂SO₄, hematite (Fe₂O₃), and submicron Al-phase. Renggli and King (2018) have also confirmed that CaSO₄ is the dominant phase in most Fe-bearing and Fe-free systems with different grain size and morphologies. Their Fe-bearing experiments form large CaSO₄ grains with diameters of up to tens of microns while Fe-free experiments precipitate continuous coatings of CaSO₄ with small grain sizes of up to several microns. These studies suggest that the formation of sulfate phases on the target olivine in our experiments must be the products of alteration of labradorite and augite crystals which were likely in contact with the target olivine.

The Mg in the Mg-sulfate was inferred to come from the olivine since Mg is assumed to be refractory in the melt. In addition, the lack of Mg-bearing phases on the plagioclase provides further evidence for alteration of the target olivine as opposed to deposition from the vapor. In their olivine alteration experiments with SO₂ gas at 600 and 800°C, King et al. (2018) formed subgrains MgSO₄ while developing porosity associated with elongated Fe₂O₃ crystals.

In the Cl-only experiment, halite and Ca-chloride were observed. The halite was likely condensed directly from the vapor as the target augite on which it appeared lacked a significant Na component. In addition, the mass balance equations confirm that a large portion of the Cl and Na from the melt were lost to the vapor phase, providing the necessary components to form halite condensates. Previous work by Henley and Seward (2018) confirm the halides as dominant ligands for metal transport in high temperature hydrothermal systems while their effect being dependent on their concentration in the single phase gas field. They have shown that HCl and HF dominate the halide species in the volcanic gases. They are followed by alkali halide gas species that could form as surface condensates due to the intersection of the vapor–liquid or vapor-halite fields at <800°C during expansion limits the maximum chloride content of the gas phase.

In the 72-h experiment, two distinct clusters of halite and sylvite condensates were observed. The dichotomy in crystal morphology is a result of varying temperature conditions. The cluster of condensates lower in the tube formed at higher temperatures, consistent with more rapid formation of smaller salt crystals that clustered into the branching patterns observed. In the upper cluster, the cooler temperature allowed for gradual growth of larger single crystals.

In both the 24- and 72-h alteration experiments, no discernable S-bearing phases were detected, despite being the dominant phases in the 1-h experiments. Instead, chlorides, particularly halite and sylvite comprised the majority of vapor deposits on the target minerals and silica tube. We attribute this to the prolonged cooling of the 24and 72-h experiments. While the 1-h runs were quenched and opened after an hour of heating, the longer runs were allowed to cool gradually for several hours before being opened. We infer that the chlorides (halite, sylvite) condense at temperatures lower than those at which the target minerals sit during the experiments (620–650°C) and thus only accumulate when the silica tube is allowed to cool gradually while remaining sealed. The absence of sulfates and langbeinite group minerals in these longer runs suggests that these phases are primarily stable at higher temperatures but degrade as the closed system cools and the chloride component of the vapor condenses.

Similar gas-solid reaction experiments conducted by DiFrancesco (2018) and Nekvasil et al. (2019) reported gas-deposited materials including iron oxides (hematite and maghemite), halides (halite, sylvite, and molysite), iron sulfides (pyrrhotite and pyrite), and native S. One possible explanation for very few sulfide-bearing condensates in our experiments might be due to the small amounts of sulfur in the starting compositions, ~0.4 and ~ 0.5 wt% in S- and Cl + S-bearing runs, respectively. Nekvasil et al. (2019) have shown that starting compositions need 2.54 wt% S to stabilize pyrite or pyrrhotite (or troilite) type of condensates. The fact that we did not stabilize any iron oxides in the form of hematite and maghemite supports the reducing environment in our degassing experiments compared to relatively oxidized (Ni-NiO) conditions by DiFrancesco (2018) and Nekvasil et al. (2019). To understand the range of conditions under which alteration and vapor deposited phases in fumarolic systems form, additional experimental work will need to be done.

CONCLUSIONS

The exploration of Mars has revealed high concentrations of Cl, S, Zn, and Ge in diverse Martian

rocks and soils, consistent with a global enrichment of volatile elements at the Martian surface. Localized enrichments of Ge and Zn further indicate localized mobilization of the trace elements. Such excesses of Ge are much larger than that expected from any chondritic input to the Martian surface, which has been observed in the Martian meteoritic breccia, NWA 7533, producing modest enrichments of 2-5 ppm in various clasts (Humayun et al., 2016a, 2016b). Recently, in situ analysis of Ge abundances in Martian meteorites revealed that shergottites (basaltic meteorites) were increasingly depleted in Ge with higher degrees of fractionation, relative to nakhlites and chassignites (2–3 ppm) (Humayun et al., 2016a, 2016b; Yang et al., 2019). This raised the possibility of degassing of Ge from shergottite magmas during eruption at the Martian surface.

The experiments in the present study replicated this degassing mechanism by conducting several low-pressure degassing experiments on melts mimicking the Irvine basalt composition identified by the Spirit rover. We found that fumarolic degassing of Martian basaltic magmas is a capable agent for the depletion of Ge and Zn that is observed in the SNC meteorites, particularly the shergottites. Chloride formation further increased the quantity of these trace metals that were transferred to the vapor phase, signifying that the increased Cl/OH ratios in Martian magmas can be linked to the extensive surface enrichments of Cl on the Martian surface. Sulfur did not appear to form sulfide complexes with the trace metals and instead acted to reduce the fO_2 of the melt, which, in turn, led to the favorability of Ge-chloride formation instead of Zn-chlorides, whose formation was preferred in the oxidized melt. Further work will need to be conducted to determine the effect that crystallization of mineral phases during magmatic ascent has on the partitioning of Ge and Zn from the melt. The alteration experiments revealed the vapors produced during this degassing were capable of producing a variety of sulfate. sulfide, and chloride deposits on surface minerals. These deposits were produced both through direct vapor deposition and through alteration of the original target minerals. Variable cooling rates of the experiments revealed preferential stability of S-bearing phases at high temperatures, with chlorides dominating at lower temperatures.

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Data Availability Statement—The data set from this work will be available through the traceDs database site (https://www.earthchem.org/communities/experimentalpetrology). This database is part of the Interdisciplinary Earth Data Alliance (IEDA) initiative, focused on the creation of accessible databases of critical community data resources.

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