EXPERIMENTAL CONFIRMATION OF THE VOLATILITY OF GERMANIUM IN MARTIAN BASALTS.

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Introduction: Chemical studies by the MSL *Curiosity* rover have reported high abundances of Li, Cl, S, Fe, Zn and Ge in martian rocks [1]. Germanium abundances in martian breccias range from a few tens of ppm to hundreds of ppm, 1-2 orders of magnitude higher than in martian igneous rocks [2]. Local mobility of Ge has been observed to create enrichments of 850 ppm [3]. Such excesses of Ge are much larger than that expected from any chondritic input to the martian surface, which has been observed in the martian meteoritic breccia, NWA 7533, producing modest enrichments of 2-5 ppm in various clasts [4]. It has been quite unclear how the Ge excesses in martian sedimentary rocks have originated. 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 (clinopyroxenite cumulates) and chassignites (olivine cumulates) [4]. Since nakhlite and chassignite meteorites exhibited a closed system internal fractionation of Ge, i.e., Ge contents increasing with increasing fractionation, Humayun et al. [4] proposed that shergottites may have outgassed Ge during eruption at the martian surface. Like Zn chloride, Ge chloride ($GeCl_4$) is known to be highly volatile but direct evidence of Ge volatility has not been reported from terrestrial magmas. The paucity of information about Ge in volcanic exhalatives on Earth is largely due to the lack of analytical data collected on Ge in volcanic aerosols, etc. DiFranceso et al. [5] experimentally investigated the volatile outgassing of alkalis, Fe, Cl and S from a synthetic martian basalt. To better understand the factors controlling Ge and Zn loss from martian lavas, this study reports new experimental results on elemental losses during degassing of a martian basaltic composition containing trace amounts of Li, Zn and Ge.

Experimental and Analytical Methodology: Experimental methodology at Stony Brook followed previous methods [5, 6]. Two batches of glass corresponding to the composition of the martian rock "Irvine" were prepared from synthetic oxides, etc., and melted at 5 kb in a piston cylinder apparatus at FMQ+0.5. One batch (MTE-1) was prepared volatile-free and the other containing Cl (~4%) and S (0.4%) as added volatiles (MTE-2). The trace elements Li, Zn and Ge were added at 200-400 ppm concentrations in both starting compositions. Aliquots prepared from these two sets of glasses were loaded into Au-Pd capsules, sealed inside a 25 cm long silica glass tube, suspended in a furnace at 1230°C for either 6 or 12 hours, and then quenched in air. The resulting glasses were analyzed for major and trace elements by LA-ICP-MS at FSU using procedures described elsewhere [4].

Results: Both sets of starting compositions were found to contain additional trace elements, including Sc, Co, Cu, Ga, Rb and Cs, and the volatile-free composition (MTE-1) also contained small amounts of Cl and S. Relative to the starting compositions, degassing at 6 or 12 hours resulted in significant losses of Na, Cl, S, K and Fe, similar to what was reported previously [5]. The volatile-bearing runs lost larger fractions of Na, Cl, S, K, and Fe, than the volatile-free runs. Zinc (93% volatilized) and Ge (97% volatilized) were both lost nearly totally after only 6 hours from both volatile-free and volatile-bearing glasses. Copper (not added) was also noted to be lost (>97%) after 6 hours of heating. The order of loss for the alkalis was Cs>Rb~K>Na, while Li was not lost during the outgassing experiments. A number of trace elements, including B and Ni, were gained during the runs from unknown sources. Refractory element abundances (Al, Ca, Ti, Sc, Co, Ga, etc.) increased in proportion to the loss of Fe by 10-20%.

Discussion: Magmatic outgassing, particularly of Cl-rich magmas, results in the rapid loss of Ge, together with Cu, Zn, Fe and alkalis, excluding Li. The extent of Ge loss in shergottites is estimated to be about 50%, while Zn was not noted to be lost [4]. Shorter duration experiments are needed to assess the rates of loss for Ge and Zn from shergottites. The high Li concentrations observed in some K-rich conglomerates are not likely to be connected to volcanic outgassing [7]. These experiments clearly show the potential of forming surficial enrichments of Cl, S, Fe, Zn and Ge, possibly of some alkalis, from the outgassing of metal halides from martian volcanics. Subsequently, the surficial reservoir of Zn and Ge may be remobilized and further concentrated to form the extreme enrichments observed in some martian rocks [e.g., 3]. Our experiments indicate that the enrichments of Cu reported in some Kimberley rocks, Gale Crater, may also be exhalative in origin.

References: [1] McLennan S. M. et al. (2013) *Science* 343: p. 1244734. [2] Berger J. A. et al. 2015. 46th Lunar & Planetary Science Conference, Abstract #1564. [3] Mittlefehldt D. W. et al. (2016). 47th Lunar & Planetary Science Conference, Abstract #2086. [4] Humayun M. et al. 2016. 47th Lunar & Planetary Science Conference, Abstract #2459. [5] DiFrancesco N. J. et al. 2016. 47th Lunar & Planetary Science Conference, Abstract #1517. [6] Ustunisik G. et al. (2015) Am. Mineral. 100, 1717-1727. [7] Ollila A. M. et al. 2014. *JGR Planets* 119: 255-285. [8] Goetz W. et al. 2016. 47th Lunar & Planetary Science Conference, Abstract #2942.