

A TWO GIGAYEAR HISTORY OF GERMANIUM OUTGASSING FROM SHERGOTTITES. S. Yang¹, M. Humayun¹, A. J. Irving², K. Righter³, A. H. Peslier⁴, B. Zanda^{5,6}, and R. H. Hewins^{5,7} ¹Florida State University, Tallahassee, FL 32310, USA (syang@magnet.fsu.edu); ²Department of Earth & Space Science, University of Washington, Seattle, WA 98195, USA; ³NASA Johnson Space Center, Mailcode XI2, 2101 NASA Parkway, Houston, TX 77058, USA; ⁴Jacobs Technology, NASA Johnson Space Center, Mailcode X13, Houston, TX 77085, USA; ⁵IMPMC, Sorbonne Université, MNHN-UPMC, 75005 Paris, France; ⁶IMCCE, Observatoire de Paris - CNRS UMR 8028, 75014 Paris, France; ⁷Rutgers University, Piscataway, NJ 08854, USA.

Introduction: Germanium (Ge) and Zn enrichment in martian sedimentary rocks has been reported from rocks at Gale Crater, showing concentrations of Ge from tens to hundreds ppm [1]. The Ge concentrations in martian meteorites are significantly lower (0.5-2.5 ppm) [2]. Our recent studies [3-4] have revealed that Ge is lost from shergottites due to volatility. Recent experimental studies confirm that Ge and Zn are both significantly volatile under magmatic conditions [5-7]. Further, Ge is moderately incompatible during magmatic differentiation [8] so Ge contents in olivines or pyroxenes increase during igneous fractionation in nakhlites and chassignites [4]. Shergottites for which Ge abundances had been determined included rocks with ages of 150-600 Ma, while the enrichments reported from Gale Crater rocks likely occurred over 3 Ga ago. The recent discovery of two unpaired ancient (2.4 Ga) depleted shergottites, NWA 7635 [9] and NWA 8159 [10], afforded the prospect of obtaining an extended history of martian volcanic outgassing. Both of the ancient shergottites are depleted in incompatible elements and share a similar GCR exposure age to younger depleted shergottites implying derivation from a single, long-lived (>2 Ga) volcanic center [9].

Analytical Methodology: Where available, olivine, pyroxene, maskelynite, ilmenite and phosphate in nine shergottites (NWA 7635, NWA 8159, QUE 94201, LEW 88516, LAR 12011, LAR 12095, LAR 06319, ALHA 77005 and RBT 04261) and two nakhlites (MIL 090032 and NWA 10153) were analyzed with a New WaveTM UP193FX excimer (193 nm) laser ablation system coupled to a high-resolution ICP-MS at the Plasma Analytical Facility, FSU [2]. All analyses were obtained using the laser spot mode at 50 Hz repetition rate with varying spot sizes (25 μ m, 50 μ m and 100 μ m). The abundances of 70 elements were analyzed at each spot. Germanium was measured at ⁷⁴Ge, with corrections for isobaric interferences [2]. Three USGS glasses (BCR-2g, BHVO-2g and BIR-1g) and a synthetic glass GSD-1g were used as the external standards. Every measurement at a given spot size was calibrated against the external standards analyzed with the same spot size and repetition rate to avoid mass loading effects [11]. Since GSD-1g was substituted for NIST SRM 610 [3-4] as the external standard for Ge, NIST SRM 610 was analyzed daily, to avoid meas-

urement bias. We noticed Ge measurements calibrated against the reference values of Ge in NIST SRM 610 are consistently 17 % higher than that calibrated against reference value for Ge in GSD-1g, so that all Ge data collected in this study were multiplied by 1.17 to eliminate the analytical bias between this study and our previous studies [3-4]. Some minerals previously analyzed were measured for comparison.

Results: Olivines were analyzed in seven, and pyroxenes in all nine measured shergottites. The Ge abundances of Martian meteorites measured in this study and in our previous studies [3-4] are plotted vs. Mg# for olivine (Fig. 1a) and for pyroxene (Fig. 1b). Olivines were not available for analysis in Zagami, NWA 2975, NWA 8657, QUE 94201 and NWA 8159.

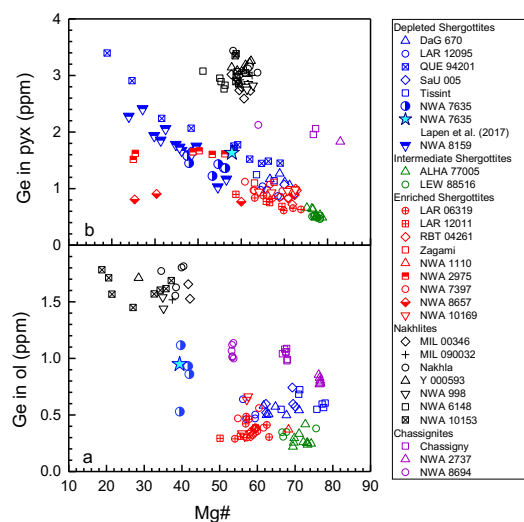


Figure 1: Ge content vs. Mg# of Ol (a) and Pyx (b) of martian meteorites analyzed in this study and in [3, 4, 9].

In Fig. 1, shergottites are color-coded by chemical enrichment to detect compositional relations [12]. Experimental studies [8,13] of Ge partitioning showed Ge is less compatible in olivine ($D_{Ge}^{ol/l} = 0.4$) than in pyroxene ($D_{Ge}^{pyx/l} = 0.9$) and that Ge contents of pyroxenes are independent of their Ca-contents (Fig. 1). The Ge contents of olivines and pyroxenes from shergottites plot below the fractionation trends defined by olivines and pyroxenes from nakhlites and chassignites (NC-

trend) (Fig. 1). Olivines from depleted shergottites exhibit a trend of decreasing Ge vs. Mg#, implying increasing losses of volatiles with increasing fractionation, compatible with the magma having resided near the surface. Olivines from the ancient shergottite, NWA 7635, have variable Ge contents (0.5-1.1 ppm) that plot below the NC-trend but do not plot along an extension of the depleted shergottite trend.

Zoned pyroxenes from the evolved depleted shergottite, QUE 94201, define a fractionation trend that is parallel but lower than the NC-trend. Zoned pyroxenes from the ancient NWA 8159 shergottite form a trend below that of the pyroxenes from QUE 94201, overlapping pyroxenes from NWA 7635. Zoned pyroxenes from two highly evolved enriched shergottites (NWA 8657 and NWA 2975) exhibit a large range in Mg# without a corresponding change in Ge.

The equilibrium partitioning of Zn is $D_{ol} > D_{opx} > D_{cpx}$ [8, 13]. Accordingly, olivines (Fig. 2a) are shown separately from pyroxenes (Fig. 2b), and pyroxenes form two distinct trends based on their CaO contents. Unlike Ge, Zn contents of olivines and pyroxenes have no clear offset between shergottites and nakhlites/chassignites (Fig. 2). Zinc contents of Martian olivines and pyroxenes increase with decreasing Mg# (Fig. 2). In shergottites RBT 04261, NWA 7397, Zagami and NWA 10169, high-CaO pyroxenes are lower in Zn than that of low-CaO pyroxenes consistent with igneous fractionation (Fig. 2b). Notably, olivines from ancient shergottite NWA 7635 have Zn contents (500-700 ppm) that are higher than the fractionation trend (Fig. 2a), which appears to be due to Zn contamination of the magma.

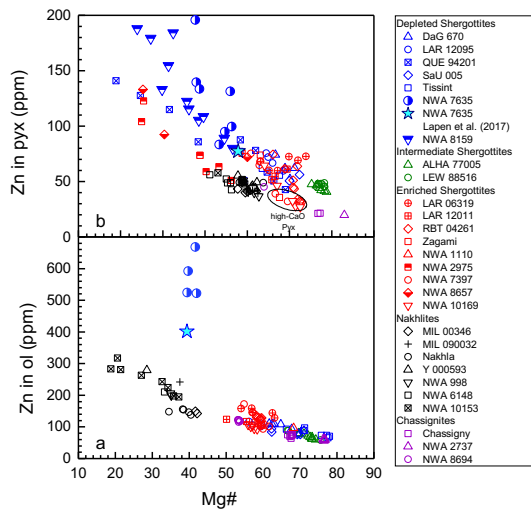


Figure 2: Zn content vs. Mg# of Ol (a) and Pyx (b) of Martian meteorites analyzed in this study and in [3, 4].

Note that low-Ca pyroxenes have higher Zn contents than high-Ca pyroxenes.

Discussion: Volatility and crystal fractionation appear to be the two factors that control the Ge abundances of shergottites. Germanium abundances reflect variable levels (50%-80%) of magmatic degassing from shergottites (Fig. 1). Zinc abundances do not reveal any measurable losses of Zn during degassing for any of the meteorites studied here. This is interesting since ancient rocks around Gale Crater are enriched in Zn [1]. Our results show that Zn is not outgassed from volcanoes in sufficient quantities to increase Zn abundances in sediments. The higher Zn may then be due entirely to hydrothermal fluids percolating through brecciated sediments [1].

Since most shergottites analyzed previously [3-4] are moderately fractionated (Mg# 60-70), the magmatic differentiation trends of Ge were incompletely defined. Our new data of highly evolved depleted shergottites (QUE 94201, NWA 7635 and NWA 8159) produced a more comprehensive fractionation trend of Ge contents in pyroxene from shergottites (Fig. 1b). A simple expectation is that shergottites magmas should continuously outgas during differentiation so that pyroxenes with lower Mg# have lower Ge. Zoned pyroxenes from the enriched shergottites, NWA 8657 and NWA 2975, do not follow the fractionation trend with other shergottites in Fig. 1(b) but exhibit constant Ge contents within a large range of Mg#, perhaps due to outgassing during fractionation. Pyroxenes from NWA 7635 and NWA 8159 form parallel trends to that of QUE 94201 (Fig. 1b), indicating closed system fractionation from parental magmas that previously underwent outgassing. This would require that all three highly evolved depleted shergottites, NWA 7635, NWA 8159 and QUE 94201, were shallow intrusives from magmas that had outgassed near a summit caldera.

References: [1] Berger J. A. et al. (2017) *JGR: Planets* 122, 1747-1772. [2] Yang S. et al. (2015) *MAPS* 50, 691-714. [3] Humayun M. et al. (2016a) LPSC XLVII, Abstract #2459. [4] Yang S. et al. (2018) LPS XLIX, Abstract #1681. [5] Humayun M. et al. (2016b) 79th Ann. Meeting Met. Soc., Berlin, Abstract #6491. [6] Norris C. A. and Wood B. J. (2017) *Nature* 549, 507-510. [7] Ustunisik et al. (2018) LPSC XLIX, Abstract #2659. [8] Davis F. A. et al. *GCA* 104, 232-260. [9] Lapen et al. (2017) *Sci. Adv.* 3, e1600922. [10] Herd et al. (2017) *GCA* 218, 1-26. [11] Yang S. et al. (2018) *Geochem. Geophys. Geosyst.* [12] Symes S. J. K. et al. (2008) *GCA* 72, 1696-1710 [13] Le Roux V. et al. (2015) *Am. Min.* 100, 2533-2544.