THE GERMANIUM DICHOTOMY IN MARTIAN METEORITES. M. Humayun\(^1\), S. Yang\(^1\), K. Righter\(^2\), B. Zanda\(^3\), and R. H. Hewins\(^3,4\), \(^1\)Florida State University, Tallahassee, FL 32310, USA (humayun@magnet.fsu.edu); \(^2\)NASA Johnson Space Center, Mailcode X12, 2101 NASA Parkway, Houston, TX 77058, USA; \(^3\)Muséum National d’Histoire Naturelle-UPMC, 75005 Paris, France; \(^4\)Rutgers University, Piscataway, NJ 08854, USA.

**Introduction:** Germanium is a moderately volatile and siderophile element \([1,2]\) that follows Si in its compatibility during partial melting of planetary mantles \([3]\). Despite its obvious usefulness in planetary geochemistry Ge is not analyzed routinely, with there being only three prior studies reporting Ge abundances in Martian meteorites \([1,2,4]\). The broad range (1-3 ppm \([4]\)) observed in Martian igneous rocks is in stark contrast to the narrow range of Ge observed in terrestrial basalts (1.5±0.1 ppm \([4]\)). The Ge data from these studies indicates that nakhlites contain 2-3 ppm Ge \([1,4]\), while shergottites contain ~1 ppm Ge \([1,2,4]\), a dichotomy with important implications for core formation models \([4]\). There have been no reliable Ge abundances on chassignites. The ancient meteoritic breccia, NWA 7533 (and paired meteorites) contains numerous clasts, some pristine and some impact melt rocks \([5-8]\), that are being studied individually. Because Ge is depleted in the Martian crust relative to chondritic impactors, it has proven useful as an indicator of meteoritic contamination of impact melt clasts in NWA 7533 \([9]\). The Ge/Si ratio can be applied to minerals that might not partition Ni and Ir, like feldspars \([9]\). We report Ge in minerals from the 3 known chassignites \([10]\), 2 nakhlites and 5 shergottites by LA-ICP-MS using a method optimized for precise Ge analysis.

**Analytical Methodology:** The chassignites Chassigny 2525 (SP-1 and SP-2), NWA 2737 and NWA 8694 \([10]\), the nakhlites NWA 6148 and MIL 090032, and the shergottites Tissint, NWA 10169 \([11]\), NWA 1110, SaU 005 and Zagami, were analyzed by LA-ICP-MS at FSU. An ESI™ UP193FX excimer laser system coupled to a Thermo Finnigan Element XR™ operated in low resolution mode was used to obtain data for over 70 major and trace elements on the same spot. The principle limitation to precise Ge abundances is an isobaric interference from \(^{36}\)Ar\(^{38}\)Ar\(^{-}\) at m/e=74 with ~4,000 cps. To overwhelm this background signal, a spot size of 100 μm and 50 Hz repetition rate were used. The background correction for Ge is <5% in pyroxenes and <10% in olivines. Standardization for Ge is to the NIST SRM 610 glass \([4]\).

**Results:** New LA-ICP-MS analyses of the abundance of Ge plotted vs. SiO\(_2\) are shown in Fig. 1. The nakhlites have Ge abundances that are higher than those of chassignites, which in turn are higher than those of shergottites. Radiochemical neutron activation analyses (RNAA) of Nakhl and Lafayette \([1]\) have Ge contents (2.5-3.0 ppm) that overlap those of the LA-ICP-MS clinopyroxene spot analyses. Also shown are RNAA Ge data \([1,2]\), and LA-ICP-MS Ge data \([4]\), for bulk shergottites that plot between the new shergottite pyroxene, plagioclase and olivine analyses. Thus, the new data are accurate and reveal a surprising range in Ge contents of SNC meteorites.

![Fig. 1: Ge vs. SiO\(_2\) in olivines and pyroxenes from shergottites, nakhlites and chassignites, and in plagioclase from shergottites. Literature data for Ge are shown for comparison \([1,2,4]\).](https://ntrs.nasa.gov/search.jsp?R=20160003883)

Plagioclase is the phase with the lowest Ge contents, while cpx is the phase with the highest Ge content.

**Discussion:** Fig. 2 shows that the variable abundances of Ge in nakhlite and chassignite olivine or pyroxene are controlled by crystal fractionation trends. Because the ol/cpx ratio during crystallization is not well constrained, we have chosen to model olivine composition with a model that assumes only olivine crystallizing (upper dotted curve) and one with mainly cpx crystallizing (lower dashed curve) from the melt. Since Ge is more incompatible in olivine than in cpx
modeled the abundances of Co, Ni, Ga and Ge in a magma ocean. This fO2 range to be consistent with popular models of the magma ocean crystallization for Mars [14]. We modeled the abundances of Co, Ni, Ga and Ge in a Martian magma ocean at variable fO2 and depths following [15, 4]. The models showed that Ni and Ge abundances both doubled for a change of a ~1 log unit of fO2 at 10-20 GPa in a Martian magma ocean [15, 4], with smaller effects on the abundances of Co and none on Ga. Thus, variable core formation conditions (B) also failed to produce the Ge dichotomy while keeping Ni constant.

Fig. 3: Ni vs. Mg# for SNC olivines and pyroxenes.

Models A and B are easier to test rigorously than model C since little is known about Ge volatility during volcanic outgassing. The process is not significant on Earth, but the volatile controls of Martian magmas are distinct from those of terrestrial magmas [12]. Volcanic outgassing on Mars has enriched Martian soils in Cl, S, Zn, Ge and Br [16]. Either, shergottites outgassed volatiles or nakhlites-chassignites assimilated Ge-rich soil, like that at Gusev crater [16]. Fig. 2 shows that the most magnesian shergottite olivines are nearly identical in their Ge with chassignite olivines, but olivines from more evolved shergottites have lower Ge implying that shergottite melts have outgassed Ge.

References: