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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 XI2, 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 Nakhla 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.

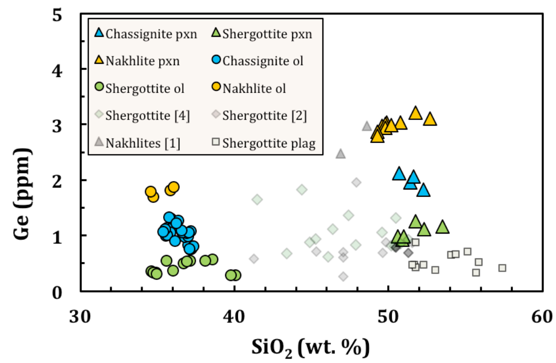

Fig. 1: Ge vs. SiO_2 in olivines and pyroxenes from shergottites, nakhlites and chassignites, and in plagioclase from shergottites. Literature data for Ge are shown for comparison [1,2,4].

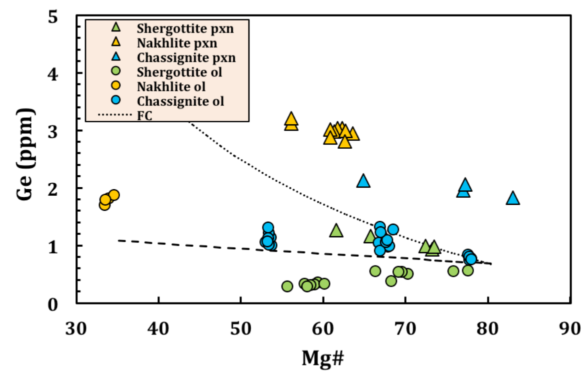

Fig. 2: Ge vs. Mg# for SNC olivines and pyroxenes, with model fractional crystallization curves for olivine.

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

[3], olivine fractionation alone drives up the Ge abundance far more than is observed. Fig. 2 shows that olivines from nakhlites have a higher Ge content because they formed from a more fractionated magma than olivines from the chassignites. Similarly, the Ge in the cpx phase from the nakhlite is an extension of the evolution of Ge in the cpx phases from chassignites. This interpretation of Fig. 2 is consistent with models that derive chassignites and nakhlites from a single magma [e.g., 12]. What is remarkable is that shergottite olivines define a trend of decreasing Ge with decreasing Mg# in Fig. 2, which cannot be interpreted as a fractional crystallization effect, since Ge is incompatible in all the likely fractionating phases. Further, bulk shergottite Ge abundances are not consistent with decreasing Ge in the melts (Fig. 1). In Fig. 2, shergottite pyroxenes form a trend that is consistent with fractional crystallization but from a melt with ~1 ppm Ge, while chassignite cpx must have formed from a melt with ~2 ppm Ge, a clear offset that implies the magma sources were different. Experimental partitioning of Ge between high-Ca pyroxene and low-Ca pyroxene indicates that the pyroxenes partition Ge about equally [3], so that this dichotomy is not the result of different pyroxene Ca contents. Thus, the dichotomy between bulk shergottites and nakhlites is real: there exists a distinct difference in Ge content between the shergottites and the nakhlites and chassignites.

We evaluate several models for the dichotomy: A. the Nakhlite-Chassignite (NC) parent was a thick impact melt sheet formed at ~1.4 Ga; B. the mantle of Mars was not homogenized after core formation, so that the NC magma source had higher redox which increased the Ge contents, relative to that of the shergottites; C. magma outgassing of Ge from shergottites or assimilation of Ge-rich sediments by nakhlite-chassignites. If the NC body is an impact melt sheet derived by melting breccias like NWA 7533 [5], additional siderophile element constraints can be applied. Fig. 3 shows that the Ni contents for olivines, and for pyroxenes, from shergottites, nakhlites and chassignites form a single trend with no clear offset between the groups. Other siderophile elements that are less sensitive to impactor contributions, like Ga/Al ratios and Co abundances, are also consistent between the S and NC meteorites. Thus, there is no corroborative evidence for an impact origin for the Ge dichotomy.

It is well known that NC magmas exhibit higher oxygen fugacities than shergottites, although shergottites span a broad range of fO_2 from FMQ-4 to FMQ-1 [13]. Herd [13] considers models that allow this fO_2 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 fO_2 and depths following [15, 4]. The models showed that Ni and Ge abundances both doubled for a change of a ~1 log unit of fO_2 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.

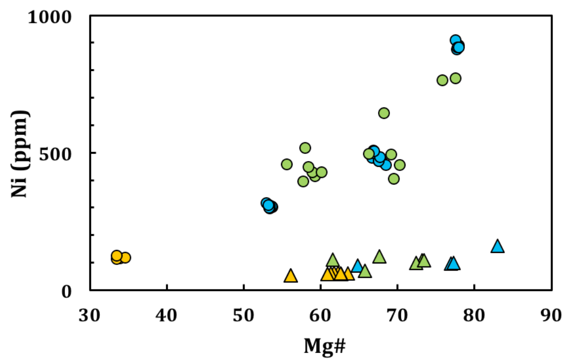

Fig. 3: Ni vs. Mg# for SNC olivines and pyroxenes.

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:

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