

THE CONTRAST IN OUTGASSING OF GERMANIUM BETWEEN SHERGOTTITES AND NAKHLITES

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Introduction: Germanium is generally thought to follow Si in its geochemical behavior, but little data has existed to rigorously understand the behavior of Ge in the Martian mantle. Germanium is known to be more siderophile than Si [1], and its partitioning into the martian core has been studied by [2]. Typical abundances in igneous martian meteorites range from 0.5-3 ppm, a larger range than what is observed in terrestrial basalts (1.5 ± 0.1 ppm) [2]. In situ measurements by the MER and MSL rovers have revealed a surprisingly large range in Ge abundances in surface rocks (30-650 ppm), but many igneous rocks and soils are shown to have <30 ppm Ge (the detection limit of the APXS) [3]. Recently, [4] reported that shergottite minerals showed a depletion of Ge with increasing fractionation, while nakhlites and chassignites exhibited Ge behavior compatible with closed system igneous differentiation. They interpreted their observations as tentatively indicating volcanic outgassing of Ge from shergottites (but not from nakhlite-chassignites) with recondensation of the Ge vapor into soils and breccias. Recent experimental studies show that Ge is significantly volatile from magmas [5-7]. In this study, we followed up on those results by analyzing minerals in five nakhlites and five shergottites by laser ablation ICP-MS (LA-ICP-MS).

Analytical Method: The shergottites NWA 7397, NWA 2975, NWA 8657, DaG 670 and Sau 005, and mineral separates of olivine and pyroxene from the nakhlites Nakhla, MIL 00346, NWA 998, NWA 6148, and Y 000593 were analyzed by a New Wave UP193FX excimer (193nm) laser ablation system coupled to a high-resolution ICP-MS at the Plasma Analytical Facility, FSU [2]. The concentrations of 70 elements in olivine (Ol), pyroxene (Pyx), plagioclase and multiple minor phases, such as phosphate and Fe-Ti oxides, were analyzed using a spot mode at 50 Hz repetition rate. Varying laser spot sizes (25 μ m, 50 μ m and 100 μ m) were used depending on the sizes of mineral phases. Ge was measured at m/e 74. Isobaric interferences from $^{148}\text{Nd}^{++}$ and $^{148}\text{Sm}^{++}$ on ^{74}Ge were corrected by monitoring the doubly charged odd isotopes $^{145}\text{Nd}^{++}$ and $^{149}\text{Sm}^{++}$. Every measurement of Ge at a given spot size was calibrated against NIST SRM 610 analyzed with the same spot size and repetition rate to avoid mass loading effects. After accounting for spot size differences, the variation of Ge abundances of a single phase measured with varying spot sizes is 2-3%.

Results: The Ge abundances are plotted against the Mg# of olivine (Fig. 1a) and pyroxene (Fig. 1b) from SNC meteorites measured in this study and by [4]. Abundances of Zn in these same minerals are plotted against Mg# in Fig. 2. Several contrasts between minerals in the nakhlite-chassignite (NC) meteorites and minerals from the shergottites (S) are observed: (1) Ge contents of NC-minerals are higher than that of S-minerals, consistent with the observation of [4]; (2) fractionation trends defined by NC-minerals are separated from that defined by S-minerals; and (3) as Mg# decreases, the Ge contents of NC-minerals increase while that of S-olivines decrease, and the variation of Ge against Mg# of S-pyroxenes is quite variable.

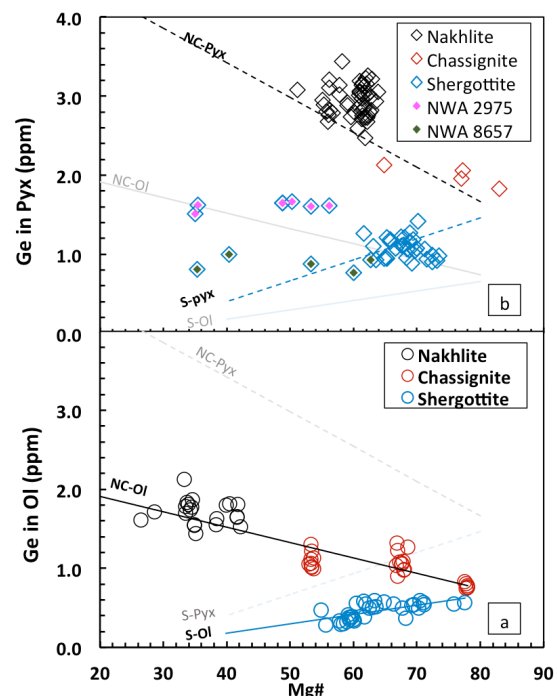


Figure 1: Ge content vs. Mg# of Ol (a) and Pyx (b) of SNC meteorites. The olivine (Ol) trends are linear fits to the data, while the pyroxene (Pyx) trends were calculated using the equilibrium partition coefficient ($K_D \sim 0.45$) between Ol and Pyx determined by recent experimental studies at magmatic conditions [8-9].

Pyroxenes from two shergottites (NWA 2975, NWA 8657) that exhibit a wide range of Mg# show essentially constant levels of Ge. Pyroxenes from shergottite NWA 2975 are systematically higher in Ge (~1.5 ppm) relative to Ge (0.5-1.0 ppm) in pyroxenes

from other shergottites measured in this study. Neither of these shergottites has coexisting olivine. It should be noted that coexisting olivine-pyroxene pairs in shergottites are limited to six meteorites in Figs. 1-2.

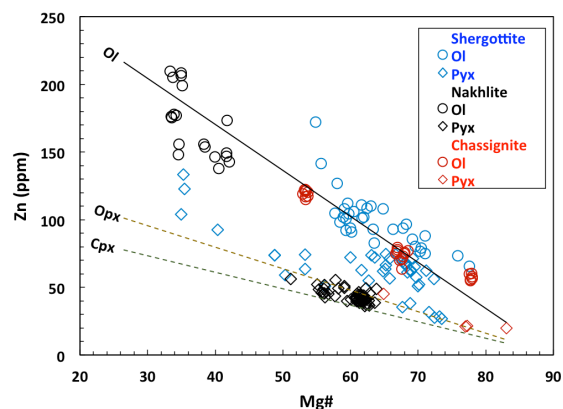


Figure 2. A plot of Zn against Mg# of Ol, opx and cpx of SNC meteorites (this study). Trends calculated as in Fig. 1.

Fig. 2 shows that Zn in SNC olivines defines a single trend. The Zn content of SNC pyroxenes is higher in low-Ca pyroxene than in high-Ca pyroxene as expected from equilibrium partitioning [8-9], but the magnitude calculated from D values of [8-9] yielded lower Zn than if D values from [10] had been used. Thus, Zn contents in SNC minerals are consistent with solid-liquid partitioning during fractional crystallization, and show no evidence of volatile loss.

Discussion: Recent experimental studies [8-9] show that Ge is incompatible in olivine ($D_{Ge} \sim 0.4$), and barely compatible in pyroxenes ($D_{Ge} \sim 0.9$). This is reversed with Zn being barely compatible in olivine ($D_{Zn} \sim 0.96$) and incompatible in the pyroxenes ($D_{Zn} \sim 0.43$ for opx, 0.36 for cpx [8-9]). Thus, Zn and Ge abundances in a magma undergoing either olivine or olivine+pyroxene fractionation would increase with decreasing Mg#. The Zn and Ge abundances of NC-olivines and pyroxenes (Figs. 1-2) are consistent with closed system fractional crystallization, while the Ge abundances of shergottite olivines and pyroxenes are not. This observation that the Zn and Ge composition of olivines and pyroxenes from both nakhilites and chassignites evolved along the igneous fractionation trend of a single magma is consistent with the proposal that these meteorites are cumulates derived from the same magma [e. g., 11].

Notably, the distribution of Ge in olivines and pyroxenes from shergottites contrast with that from nakhilites and chassignites in two aspects. First, as Mg# decreases, the Ge abundances of shergottite olivines decrease (Fig. 1a) and many of the pyroxenes (Fig. 1b)

have Ge contents in equilibrium with olivines that exhibit such a decrease in Ge with decreasing Mg#. Thus, we infer that shergottites in general must outgas about half of the original Ge content of shergottite primary magmas. However, the extent of magmatic outgassing is a function of emplacement depth and gas composition, i.e. presence of other volatiles including S and Cl. Thus, a single degassing trend is not expected. The second observation from Fig. 1b is that two shergottites exhibit a large range in Mg# in their pyroxenes without a corresponding change in Ge. Pyroxenes from NWA 2975 [12] have the highest Ge abundances (1.5 ppm) observed from shergottite pyroxenes, while pyroxenes from NWA 8657 exhibit some of the lowest Ge contents of shergottite pyroxenes (~ 0.5 ppm). One possible explanation is that these pyroxene trends imply that both shergottites were derived from magmas that had undergone outgassing prior to fractionation, but had not continued to outgas during fractionation. An alternative possibility is that pyroxenes in NWA 2975 may have exchanged Mg-Fe-Ca, but not Ge, during shock melting [12]. While Ge diffusivity in pyroxenes is not known, as an element that substitutes for Si on the tetrahedral site, Ge would be expected to be a slow diffuser, slower than even REE in cpx [13].

In contrast to Ge, Zn in shergottites is entirely consistent with equilibrium partitioning between melt and solids, and there is no resolvable volatile loss of Zn. Corroborative evidence for volatile degassing of Ge from magmas is available from experimental studies with or without added Cl or S [5-7]. The experimental durations were long enough to outgas >95% of the Zn and Ge inventories. Experiments of shorter run duration are needed to better constrain the relative losses of Cl, S, Ge and Zn from martian magmas, since evidence for Cl and S degassing from nakhilites has been made [14], but Ge was not affected by this.

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