

**AN ANCIENT MARTIAN OCEAN INFERRED FROM SULFIDE IMMISCIBILITY IN METEORITES.**

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**Introduction:** Reconstruction of paleoshorelines indicates that Mars may have had a boreal ocean in the Noachian [Citron]. Igneous rocks assimilate material from the surrounding environment during emplacement in sub-volcanic magma chambers. With exception of brecciated meteorites [2], martian meteorites are igneous rocks that bear information on the environments in which these magmas were emplaced. The depleted shergottites form a compositionally coherent group that share the same cosmic ray exposure age, 1.1 Ma, but span about 2 billion years in crystallization ages [3]. Elemental abundances acquired by LA-ICP-MS of a large suite of martian meteorites lead us to conclude that several martian meteorites belonging to the depleted shergottites, and the 2.4 Ga depleted meteorites [3-4], assimilated exogenous sulfides that appear to be volcanogenic massive sulfide ores deposited in an ancient martian ocean [5].

**Evidence for assimilation:** Abundances of Ni and Co for olivines (and pyroxenes) vs. Mg# show distinct fractionation trends for the various shergottite chemical groups. The depleted shergottites exhibit the highest bulk D(Ni) indicating that a phase more potent than olivine at removing Ni from the melt was variably present in the earliest stages of fractionation onwards. This phase is likely to be immiscible sulfide liquid. The two amazonian meteorites, NWA 7635 and NWA 8159, have olivines with the lowest Ni contents of any martian igneous rocks, ~ 5-10 ppm. At the same Mg# (~ 40) nakhilite olivines have about 100 ppm Ni, so fractionation of olivine alone is insufficient to create such extreme Ni depletions. The fractionation of Co by olivine is not significant and olivines from all martian meteorites define a Co vs. Mg# trend around 100 ppm Co, with the exception of NWA 7635 and NWA 8149 that exhibit Co contents in their olivines of ~ 50 ppm. In addition to the low Ni and Co contents, Zn contents of olivines in NWA 7635 and NWA 8149 are three times higher than that of olivines from nakhilites at the same Mg#, whereas olivines from other martian meteorites at higher Mg# have lower Zn contents. The depleted shergottite, QUE 94201, has no olivine but its pyroxene exhibits similarly low Ni contents to pyroxenes in NWA 7635 and NWA 8149, < 20 ppm Ni. Other elements (Co, Zn) in the pyroxenes of QUE 94201 are in line with other shergottite pyroxenes. Finally, plagioclases from NWA 7635 and NWA 8149 have higher Cd and Pb abundances than pyroxenes from other martian meteorites.

Corroborative evidence for assimilation is provided by S [6] and Pb [7] isotopic compositions that indicate that exogenous S and Pb dominate the amazonian meteorites, NWA 7635 and NWA 8159.

**Implications:** Assimilation of sulfides rich in Fe-Zn-Pb are indicated by the data for the amazonian meteorites. The presence of an ancient boreal ocean implies that the earliest lava flows erupted from large Mons-type volcanoes would have been submarine eruptions. Such eruptions would create extensive hydrothermal circulation systems that fractured and cooled the lava pile depositing volcanogenic massive sulfide ores above the lava pile. None of this material has been directly sampled, because it is now deeply buried beneath younger episodes of volcanism. The Amazonian (2.4 Ga) intrusive or eruptive bodies from which NWA 7635 and NWA 8159 are derived would have been emplaced through the older (> 3.9 Ga), hydrothermally altered flows and their massive sulfide ores. Assimilation of ~ 1 % Fe-Zn-Pb sulfide would have induced sulfide saturation in the assimilating magmas exsolving an immiscible Ni-sulfide liquid that stripped the magmas of Ni and, to a lesser extent, Co, while adding Zn and Pb to the magma. One implication of this process is that martian volcanoes that exhibit Ni-Co depletions must have formed orthomagmatic Ni-Cu-PGE ores that are stratigraphically higher than the Fe-Zn sulfides. A second implication is that the depleted shergottites must have formed from one of the topographically lowest bases on Mars.

**References:** [1] Citron R. I. et al. (2018) *Nature* 555, 643-646. [2] Humayun M. et al. (2013) *Nature* 503, 513-516. [3] T. Lapen et al. (2017) *Sci. Adv.* 3, e1600922. [4] C. Herd et al. (2017) *GCA* 218, 1-26. [5] Humayun M. et al. (2021) *LPSC LII*, Abstract #1390. [6] Franz H. B. et al. (2019) In Filiberto J. and Schwenzer S. P. (eds.) *Volatiles in the Martian Crust*, pp. 119-184. [7] Bellucci J. J. et al. (2020) *Chem. Geol.* 545, 119638.