

ASSIMILATION OF FOSSIL HYDROTHERMAL SULFIDE BY EARLY AMAZONIAN MARTIAN MAGMAS: IMPLICATIONS FOR ORE MINERALIZATION ON MARS. M. Humayun¹, S. Yang¹, A. J. Irving² and K. Righter³, ¹National High Magnetic Field Laboratory and Dept. of Earth, Ocean & Atmospheric Science, Florida State University, Tallahassee, FL 32310-3706, USA (humayun@magnet.fsu.edu); ²Dept. of Earth and Space Sciences, University of Washington, Seattle, WA 98195, USA; ³NASA Johnson Space Center, Houston, TX 77058, USA.

Introduction: Martian magmas would interact with any hydrosphere present, whether a global ocean [e.g., 1] or an icy (subterranean) hydrosphere [2] creating hydrothermal systems. Volcanogenic massive sulfide (VMS) ores, with Fe-Zn-Pb sulfides, created by hydrothermal deposition associated with a wide range of volcanism would be expected on Mars [3]. Similar to terrestrial komatiites, martian igneous rocks could generate orthomagmatic Ni-sulfide ore deposits by immiscible sulfide liquid segregation [4]. For this to occur, a martian magma would need to flow over (or intrude into) a pre-existing sulfur-rich formation. Here, we elaborate on the first evidence [5-6] of potential orthomagmatic mineralization in two Early Amazonian (2.4 Ga) igneous meteorites [7-8] involving a three-step process: i) formation of Fe-Zn-Pb sulfides, (ii) assimilated by the 2.4 Ga magmas leading to (iii) formation of orthomagmatic Ni-sulfide deposits. These deposits may remain on Mars, but the telltale signs of Zn-Pb enrichment and Ni-Co depletion in the two meteorites provide important insights into martian geology.

Samples and Analytical Methodology: The 2.4 Ga meteorites NWA 7635 [7] and NWA 8159 [8] were analyzed for elemental abundances in their plagioclase, pyroxene and olivine mineral grains by laser ablation ICP-MS [9]. Plagioclase and pyroxene from other martian meteorites, particularly QUE 94201, were analyzed to establish martian magmatic trends.

Modeling methods: The fractional crystallization of the composition of the Tissint groundmass [10], representative of a depleted shergottite parental melt, was modeled using Rhyolite-MELTS [11, 12]. The sulfur content at sulfide saturation (SCSS) was calculated [13-15] for variable amounts of assimilated Fe-sulfide assuming batch equilibrium since the two immiscible liquids remained in contact. The initial sulfur content was set at zero (outgassed magma). The elemental partitioning between immiscible sulfide liquid and silicate melt was taken from [16]. The Mg# for olivine and melt was calculated offline using [17] that yielded better agreement with FeO vs. MgO trends than Rhyolite-MELTS. Partition coefficients for silicates were obtained from [18-19, 23].

Results: Ni and Co abundances in olivines (Fig. 1), and in bulk rocks from NWA 7635 and NWA 8159 are

exceptionally low, whereas Zn is higher than a magmatic trend would predict (Fig. 1). The bulk rock Pb/Ce ratios of NWA 7635 (1.2) and NWA 8159 (2.4) are higher than in other martian meteorites (0.1-0.6). Olivine (and pyroxene) in NWA 7635 and NWA 8159 have Co a factor of two lower than for other martian meteorites (Fig. 1).

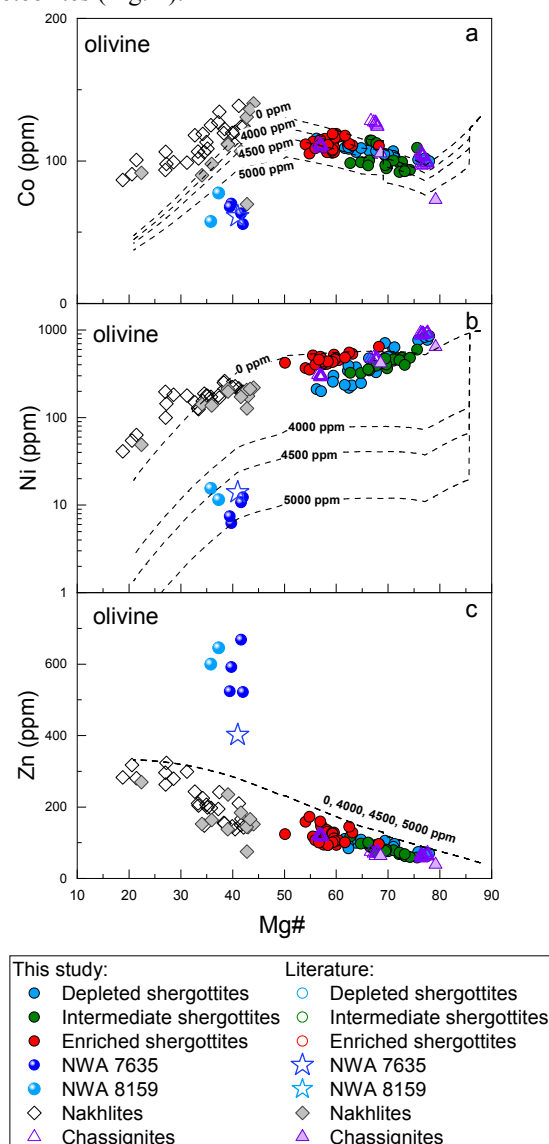


Figure 1: Abundances of (a) Co, (b) Ni and (c) Zn as a function of Mg# in martian olivines with fractionation trends for sulfur addition of 0-5,000 ppm.

There are striking enrichments of Zn in olivine (400-700 ppm Zn vs. 200 ppm Zn in depleted shergottites), and in pyroxene, from NWA 7635 relative to the trends defined by other martian meteorites [5-6]. The Mg# obtained by LA-ICP-MS was found to be identical to that reported by EMP for both meteorites [7-8], indicating no beam overlap on magnetite. Higher Zn, Cd and Pb are also evident in plagioclase grains from NWA 7635 and NWA 8159, but not in plagioclases from depleted shergottites.

Discussion: Modeling showed that fractional crystallization of silicates alone was insufficient to lower the Ni or Co contents of olivines to the observed values, while the enhanced abundances of Zn or Pb require assimilation of Pb-Zn-enriched material. Segregation of immiscible sulfide liquid effectively lowers Ni (Cu, PGE) abundances in magmas. When there is no initial sulfur, assimilation of > 0.5 % extraneous sulfide saturates the magma with sulfur.

The SCSS for martian magmas [13-15] is around 3,500-5,600 ppm at 1,460 °C near the liquidus of the Tissint groundmass but diminishes near the solidus below 1,000 ppm S. The model was insensitive to where in the fractionation sequence sulfide addition occurred since the magma exsolved most of the added sulfur on cooling. The partitioning between immiscible sulfide liquid and silicate liquid yielded a D(sulfide/silicate) ~ 30 for Co, ~ 300 for Ni and ~ 1 for Zn with little variation during crystallization as the partition coefficients depend only on FeO in the liquid [16] and FeO remains constant in martian magmas [5]. Fig. 1 shows calculated fractionation trends for Co, Ni and Zn vs. Mg# in martian magmas. Even small amounts of sulfide (~ 1 wt. %) added to a fully degassed magma effectively removed the Ni from the silicate melt, but did not sufficiently reduce the Co content, nor impact the Zn abundances.

Silicate fractionation trends for martian magmas both sulfide-free and with added sulfide are shown on Fig. 1. Sulfide-free fractionation captures olivine compositions of chassignites, nakhlites and enriched shergottites spanning Mg# 80-20. Olivines from intermediate and depleted shergottites have experienced greater loss of Ni at a given Mg# than olivines from enriched shergottites, possibly due to traces (<0.1 %) of immiscible sulfide separation [22]. The olivine compositions of NWA 7635 and NWA 8159 are consistent with Ni depletion in their parent melts caused by batch removal of a small fraction (<1.5 %) of immiscible sulfide liquid. Olivine and melt compositions from NWA 7635 require larger immiscible sulfide removal than those from NWA 8159 (1.3 vs. 1.2 %).

The presence of excess Zn in olivines and bulk rock compositions, excess Pb in plagioclases and bulk rock compositions, and higher Cd in plagioclases from NWA 7635 and NWA 8159 attest to the contamination of the parent melts with a sulfide-rich (Fe-Zn-Pb) lithology. The depleted incompatible lithophile element compositions of these ancient meteorites limit the possible assimilation of silicates to lithologies that were similarly depleted. If the contaminants had included regolith, aeolian dust or other incompatible element-enriched lithologies the effect on highly incompatible elements (e.g., Th) would be evident. We conclude from this that the sulfide-rich assimilants were hosted by older volcanic units from a depleted source. The ubiquitous presence of assimilated sulfide in two distinct 2.4 Ga magmas that share the same ejection age [7], but not in later (0.4-0.6 Ga) depleted shergottites from the same ejection event, may result from shielding of a fossil hydrothermal system by the 2.4 Ga formations. The presence of a fossil hydrothermal system formed during submarine eruption of the earliest (>3.8 Ga) stages of volcanic edifice construction implies the existence of an ancient ocean on early Mars that had sufficient dissolved sulfate to create the hydrothermal sulfides.

References: [1] Citron R. I. et al. (2018) *Nature* 555, 643-646. [2] Ehlmann B. L. et al. (2011) *Nature* 479, 53-60. [3] Ehlmann B. L. et al. (2013) *Space Sci. Rev.* 174, 329-364. [4] Baumgartner R. J. et al. (2015) *Ore Geology Reviews* 65: 400-412. [5] S. Yang et al. (2019) *LPSC 50*, abstract # 1908. [6] M. Humayun et al. (2019) *82nd Meteoritical Society Meeting, Sapporo, Japan*, Abstract# 6380. [7] T. Lapen et al. (2017) *Sci. Adv.* 3, e1600922. [8] C. Herd et al. (2017) *GCA* 218, 1-26. [9] Yang S. et al. (2018) *Geochem. Geophys. Geosyst.* 19, (<https://doi.org/10.1029/2018GC007593>). [10] Aoudjehane H. C. et al. (2012) *Science* 338, 785-788. [11] Gualda G. A. R. et al. (2012) *J. Petrol.* 53, 875-890. [12] Balta J. B. and McSween H. Y., Jr. (2013) *JGR Planets* 118, 2502-2519. [13] Righter K. et al. (2009) *EPSL* 288, 235-243. [14] Ding S. et al. (2014) *GCA* 131, 227-246. [15] Liu K. et al. (2021) *Chem. Geol.* 559, 119913. [16] Kiseeva E. and Wood B. J. (2015) *Earth Planet. Sci. Lett.* 424, 280-294. [17] Filiberto J. and Dasgupta R. (2011) *Earth Planet. Sci. Lett.* 304, 527-537. [18] Matzen A. K. et al. (2017) *Contrib. Mineral. Petrol.* 172:3. [19] Le Roux V. et al. 5) *Am. Mineral.* 100, 2533-2544. [20] Franz H. B. et al. (2019) In Filiberto J. and Schwenzer S. P. (eds.) *Volatiles in the Martian Crust*, pp. 119-184. [21] Wang Z. and Becker H. (2017) *EPSL* 463, 56-68. [22] Paquet M. et al. (2021) *GCA* 293, 379-398. [23] Herd C. D. K. et al. (2009) *Am. Mineral.* 94, 244-255.