

THE WATER, VOLATILE ELEMENTS AND OXYGEN FUGACITY (fO_2) IN SNC METEORITES.

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Introduction. One of the important arguments for a Martian origin of SNC is the discovery of a trapped N-Ar component in two meteorites (EETA 79001 [1], and Zagami [2]) having similarities with the Martian atmosphere as measured during the Viking experiment. Impact-melt glasses, rich in Martian atmospheric gases, contain Martian soil fines (MSF) mixed with other coarse-grained regolith fractions which are produced during impact bombardment on Mars surface. An important characteristic of the MSF fraction is the simultaneous enrichment of felsic component accompanied by the depletion of mafic component relative to the host phase in these glasses [3, 4]. These glasses yield large sulfur abundances due to the occurrence of secondary mineral phases such as sulfates produced during acid-sulfate weathering of the regolith material near the Martian surface [5-7]. The high concentration of sulfur in Mars soils measured by Mars Pathfinder (4.0 to 6.5 wt% SO_3) [8] confirms the high concentrations measured at the two Viking landed sites (5.9 to 9 wt. % SO_3) [9]. Volcanic degassing of SO_2 is a mechanism which can explain the high concentrations of sulfur found on the Martian surface by the Pathfinder and Viking missions. Sulfurous gases released into atmosphere by volcanoes on Mars are oxidized to H_2SO_4 which deposit back on the surface of Mars as aerosol particles [10]. Data obtained from Mars orbital missions over the last years suggest that multiple locations on the planet's surface bear evidence for ancient sulfate mineralization [11]. The first reports of jarosite $K_2Fe^{3+}_6(SO_4)_4(OH)_{12}$ were based upon Raman spectroscopic and EPMA identification of micrometer-sized veinlets in the mesostasis of MIL 03346 [12,13]. Cu-Fe-Ni sulfides are minor although important minerals of igneous rocks. Magmatic sulfides control the whole-rock budget of a large panel of chalcophile and siderophile elements [14], while carrying clues to understand sulfur cycling, thanks to sulfur isotope systematic [15]

Water and other volatiles. Volatile elements are of great geochemical importance because they influence a wide range of geological processes. Water and other volatiles play an important role in

partial melting of mantle sources of primary magmas, and their eruption and crystallization history. Melt inclusions trapped in early crystallized minerals, e.g., olivine, preserve a range of compositional and isotopic variability, providing valuable information on their parent melt composition, pre-eruptive volatile abundances of magmas, and their degassing history [16, 17]. Boctor et al. [18, 19] investigated the volatile abundances and hydrogen isotope signatures of the nominally anhydrous minerals, melt inclusions, and glass in the nakhlites and chassignites (Chassigny and NWA 2737). They concluded that nominally anhydrous minerals in Martian meteorites contain trace amounts of OH and may constitute the main H reservoir in the Martian interior. The mineralogy of the SNC meteorites is consistent with these low water contents. Phosphates in SNC's are either merrillite $[Ca_3(PO_4)_2]$ or chlorapatite $[Ca_5(PO_4)_3Cl]$, not hydroxy-apatite. Zagami chlorapatite, for example, only contains about 1000 ppm water [18]. Chlorapatite is the least stable form of apatite. For chlorapatite to form in preference to hydroxy-apatite, the activity of water must be very low. The water content of SNC amphiboles is also low [20]. The argument has been made that significant water may have been liberated from these amphiboles by the shock events that ejected the SNC's from Mars [21]. However, this seems unlikely. The Martian amphiboles discovered thus far are kaersutites with high TiO_2 contents. They are probably best thought of as oxy-amphiboles and necessarily so for Ti charge balance [22]. The SNC amphiboles probably have always had low hydroxyl contents, regardless of how much or how little water was lost due to shock [23]. The amount of water in Martian magmas has significant ramifications for the Martian atmosphere-hydrosphere cycle. Large D-enrichments have been observed in kaersutitic amphiboles in Zagami, Chassigny and Shergotty meteorites (delta-D values up to 4400 per mil) suggesting that substantial amounts of H escaped Mars in its past [24].

The oxygen fugacity (fO_2) of magma. Magmatic oxidation state reflects the degree of oxidation of the source region and, possibly, the additional effects of magma interaction with near

surface rocks and/or fluids. The physical parameter which controls oxidation state is oxygen fugacity (fO_2). fO_2 influences the crystallization sequences of magmas, as well as the composition of the resulting minerals [e.g. 25,26]. Recent studies have shown that Martian magmas had wide range of oxygen fugacities (fO_2) and that this variation is correlated with the variation of La/Yb ratio and isotopic characteristics of the Martian basalts, shergottite meteorites [27, 28].

Amongst Martian meteorites correlations between La/Yb values and initial Sr and Nd isotopic compositions indicate the presence of long-term incompatible element-enriched and -depleted reservoirs, and suggest that Martian magmatism is characterized by mixing between these reservoirs [29-32]. Oxygen fugacity estimates have been based on coexisting Fe-Ti oxides (ulvöspinel-ilmenite) for 5 basaltic shergottites and the groundmasses of olivine-phyric [33] shergottites EETA79001 lithology A (EET-A) and Dhofar 019 [34,35]. Oxygen fugacity was also estimated for olivine-phyric shergottite DaG 476 using coexisting olivine - pyroxene-chromite assemblages [36], which may reflect magmatic conditions more accurately than late-crystallizing Fe-Ti oxides. Herd et al. [37], Herd [38], Wadhwa [39] and Goodrich et al. [40] demonstrated that the fO_2 in Martian basalt represented by the shergottites varies by 2 to 3 log units and is correlated with geochemical parameters such as LREE/HREE, initial $^{87}\text{Sr}/^{86}\text{Sr}$. These correlations have been interpreted as indicating the presence of reduced, incompatible element-depleted and oxidized, incompatible element enriched reservoirs that were produced during early stages of Martian differentiation (~4.5 Ga) [37-43]. Martian basaltic magmatism is thought to represent mixing between these two reservoirs. Whether this mixing process is a product of assimilation (mantle-derived, reduced basalts that assimilated an upper-mantle or lower-crustal oxidized reservoir) or mixing of two mantle reservoirs during melting is still a point of debate. The relationships between fO_2 and incompatible element characteristics have been determined by two largely independent approaches; fO_2 from mineral equilibria or multivalent element behavior (Eu) and bulk elemental-isotopic measurements.

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