

**HOW OXIDIZED IS THE MARTIAN MANTLE AND HOW DID IT GET THAT WAY?** M.M. Hirschmann<sup>1</sup><sup>1</sup>Dept. Earth and Env. Sci., U. Minnesota, Minneapolis, MN 55455 USA *mmh@umn.edu*.

**Introduction:** Martian rocks record a spectrum of magmatic oxygen fugacities ranging from  $\sim$ IW for depleted shergottites to above QFM for nakhlites and trachyandesites [1-3]. Because the more reduced values derive from the basalts seemingly least-modified from their mantle sources, they have been taken to represent the typical martian mantle value [2]. The more oxidized basalts are considered as representing either discreet enriched mantle sources or mixing with crust [1,4,5]. Observations from Gusev crater and of newly discovered meteorites have given a wider picture of oxygen fugacities in martian basalts and suggest that relatively oxidized conditions are not uncommon [3,6]. At the same time, geochemical data from new meteorites and rovers suggests that the shergottites are anomalously depleted compared to typical martian basalts [7,8]. More enriched varieties, including alkalic rocks that are more oxidized (e.g., the trachyandesite clasts of NWA7034 [3]) are possibly common components of martian crust [8,9]. Further, correlations between  $f_{O_2}$  and isotopes intersect compositions similar to bulk silicate Mars ( $\epsilon_{Nd}=0$ ,  $^{87}Sr/^{86}Sr=0.709-0.72$ ; [10,11]) at oxidizing conditions (IW+2-3) [2]. Together, these observations suggest (but do not prove) that the “average”  $f_{O_2}$  of martian mantle could be comparatively oxidized. The consequences of a more oxidized average mantle (or alternatively, more oxidized basalt sources) are significant, particularly for the associated masses and compositions of volcanic exhalations.

Although some of the more oxidized signal derived from martian basalts clearly comes from crustal contamination, preservation of early  $f_{O_2}$  indicated by trace element oxybarometers [12, 13] and isotopic arguments [4,5] show that significant  $f_{O_2}$  variations derive from the mantle. Thus, the question arises, what processes may be responsible for setting the  $f_{O_2}$  of martian mantle and for observed variations between different mantle domains?

**“Native” martian mantle  $f_{O_2}$ :** The native oxygen fugacity of the martian mantle is that which was set by core separation during the magma ocean stage. For the molten peridotite with  $\sim$ 18 wt.% FeO\* at low pressure, this is between IW-2 and IW-1 [14]. Unlike for Earth, equilibration at high pressure cannot raise this  $f_{O_2}$  appreciably. The maximum mean pressure of metal-silicate equilibration in the martian magma ocean is 13-14 GPa [15,16, but see also 5], conditions that should produce  $f_{O_2}$  similar to that at ambient pressure [17]. Intermediate equilibration pressures of  $\sim$ 8 GPa would set the  $f_{O_2}$  yet lower [18]. Thus, all of the martian igneous rocks in present collections, including those

that are the most reduced (IW) record  $f_{O_2}$  more oxidized than the native reference condition. All of the sources of these basalts have had their  $f_{O_2}$  raised to lesser or greater degree by some process or combination of processes.

**Processes affecting martian mantle  $f_{O_2}$ :** Magma ocean differentiation, thought possibly to be responsible for development of the diverse geochemical domains represented by the depleted and enriched shergottites, could also potentially elevate martian mantle  $f_{O_2}$ . During magma ocean crystallization, incompatible behavior of  $Fe^{3+}$  produces residual magmas that are more oxidized. However, in contrast to the situation for Earth [19], the conditions of metal-silicate equilibration on Mars (IW-2-IW-1,  $P<14$  GPa), set  $Fe^{3+}/Fe^T$  to a low value (0.002, [17]). For such a low initial ratio, solidified magma ocean cumulates produced by Rayleigh fractionation do not become significantly oxidized; e.g., for an effective partition coefficient of  $Fe^{3+}$  of 0.05-0.3 (the latter corresponding to high trapped liquid, suggested by recent magma ocean compaction modeling [20])  $Fe^{3+}/Fe^T$  in solidified mantle remains low ( $<0.01$ , corresponding to  $\sim$ IW or below) up to at least up to 98% solidification. However, the situation is very different for even a modestly hydrous magma ocean. For a reduced hydrous magma ocean, hydrogen is dissolved chiefly as  $H_2O$  (or  $OH^-$ ), but degases partly as  $H_2$  [21]. Even small amounts of  $H_2$  degassing can lead to appreciable magma oxidation. For example, for a magma ocean with 18% FeO\*, conversion of 0.1 wt.% dissolved  $H_2O$  to  $H_2$  gas will produce magma with  $Fe^{3+}/Fe^T$  of 0.045, sufficient to oxidize to near QFM [17]. The degassing is a natural consequence of magma ocean crystallization, which concentrates volatiles in the residual magma, thereby raising the partial pressure of all volatile species, leading to degassing to the overlying atmosphere [23]. Note that this is not an estimate of the total  $H_2O$  degassed, but rather the total that is degassed as  $H_2$ . This process is self-limiting near QFM, as  $H_2$  degassing becomes negligible as magma  $f_{O_2}$  rises, and further hydrous degassing (if any) takes place chiefly as  $H_2O$ . Thus, the relatively oxidized nature of all martian igneous rocks (compared to the “native” mantle state of IW-1 to IW-2) is most plausibly a signature of  $H_2$  degassing during the magma ocean stage. If more depleted shergottites are derived in part from early-formed magma ocean cumulates, then these may have formed at a time when the magma ocean had not experienced as much  $H_2$  degassing. Also, the sources of more enriched magmas may have been affected by metasomatism, [8,9,22] which also likely enhanced

oxidation of some sources and contributed to redox heterogeneity of martian magmas.

**Discussion:** Uncertainty about the typical oxidation state of the martian mantle raises important questions about martian volcanogenic volatile fluxes. Although I have argued previously that most martian magmas likely came from sources saturated in graphite [23], new data and perspectives suggest that this is not so certain. Because the  $f_{O_2}$  of graphite saturation relative to metal-oxide (e.g., IW) buffers varies with mantle temperature and pressure [23], observations on the  $f_{O_2}$  of erupted basalts are insufficient – we need further constraints to translate these to the redox conditions in their mantle sources. Righter et al. [24] found that decompression of shergottite magmas causes oxidation compared to their sources, but it is not clear whether this applies generally to other martian magmas, as the opposite effect occurs for other natural and synthetic compositions, including those that are very FeO\* rich [25]. If the most reduced mantle sources are near IW, they are not saturated with alloy or with metal-sulfide-carbide liquids in the shallowest mantle, but should become so at modest depths, as the  $f_{O_2}$ /pressure gradient ( $\sim 0.5$ -1 log unit/GPa [26]) for subsolidus mantle is likely be similar for Earth and Mars. Thus, some form of alloy or alloy-liquid saturation is likely at pressures  $>2$ -4 GPa for the more reduced martian mantle domains.

The relatively oxidized condition for Earth is generally considered to be a product of iron disproportionation that is particular to planets in which high pressure metal-silicate equilibration occurs [14,17]. However, this does not discount possible contributions from H<sub>2</sub> magma ocean degassing [27]. The more reduced state of the lunar mantle argues that aggregate H<sub>2</sub> degassing was small. Nearly any terrestrial planet which has even a modestly hydrous magma ocean should experience mantle oxidation by the H<sub>2</sub> degassing mechanism, meaning that the occurrence of planetary mantles approaching QFM may be relatively common.

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