EVALUATING THE REDOX EVOLUTION OF MARTIAN MAGMAS. S. P. Aithala\textsuperscript{1} and M. M. Hirschmann\textsuperscript{1}, Dept. of Earth and Env. Sci., U. Minnesota, Minneapolis, MN 55455 USA aitha012@umn.edu.

Introduction: The influence of oxygen fugacity ($f_{O2}$) on igneous processes including crystallization, partial melting, degassing, ascent, and assimilation has long been a subject of interest in planetary geology as its consequences include planetary habitability and petrologic diversity. We seek to better understand the martian interior and its magmatic history by characterizing the processes that produced the rocks in the martian rock record.

Variations in terrestrial basalt $f_{O2}$ span from QFM-3 to QFM+3 and are linked to plate tectonics and associated interactions between surface-materials and mantle [1]. Somewhat surprisingly, martian basalt $f_{O2}$ variation is even greater, ranging from QFM-4 to QFM+3 [2, 3], despite Mars not having plate tectonics. In addition, some martian magmas undergo extents of assimilation, modifying melt with open system processes, like degassing or partial melting, degassing, ascent, and assimilation has extents at which these processes occurred lack quantitative constraints without models that link magma partitioning. In the future, we intend on developing a martian-specific parameterization that interrelates mineral-melt $f_{O2}$ evolution not documented in terrestrial analogs, with $f_{O2}$ recorded in early crystallized olivine-orthopyroxene-spinel and late crystallized iron-titanium oxide assemblages varying by up to three log units in the same rock [4, 5]. Workers rationalize $f_{O2}$ shifts within martian lithologies as evidence for martian magmas having undergone unbuffered crystallization with open system processes, like degassing or assimilation, modifying melt $f_{O2}$ [3, 5-7]. However, the extents at which these processes occurred lack quantitative constraints without models that link magma $f_{O2}$ to mass transfer as a function of Fe\textsuperscript{3+}/Fe\textsuperscript{2+}.

We are currently developing this model by conducting superliquidus experiments on Gusev Crater basalt, Humphrey [8] and a basaltic-trachyandesite clast from NWA 7034 [9] at controlled $f_{O2}$ and 100 kPa and measuring their Fe\textsuperscript{3+}/Fe\textsuperscript{2+} with 293 K Mossbauer spectroscopy [10]. So far, our data unveil two conclusions that help us better interpret the $f_{O2}$ span recorded by martian magmas (Fig. 1):

1. At reducing conditions relevant to martian magmas, small changes in Fe\textsuperscript{3+}/Fe\textsuperscript{2+} generate large changes in $f_{O2}$.

2. Available models that interrelate Fe\textsuperscript{3+}/Fe\textsuperscript{2+} - $f_{O2}$ - T - X for terrestrial magmas (e.g. [11, 12]) typically overestimate $f_{O2}$ at a given Fe\textsuperscript{3+}/Fe\textsuperscript{2+} in martian magmas.

With both conclusions suggesting that changes in martian magmatic Fe\textsuperscript{3+}/Fe\textsuperscript{2+} lead to comparatively large shifts in $f_{O2}$, we hypothesize that auto-oxidation of martian magmas, driven by the enrichment of Fe\textsuperscript{3+} in the melt by the preferential incorporation of Fe\textsuperscript{2+} in olivine and pyroxene, could play a larger role in $f_{O2}$ variation in martian magmas than previously thought. To test this hypothesis, we utilized Rhyolite-MELTS [13] to model how Fe\textsuperscript{3+}/Fe\textsuperscript{2+} evolves during the crystallization of Tissint, an olivine-phyric, depleted shergottite that underwent a 2.1±0.5 log unit increase in $f_{O2}$ throughout its crystallization history [4].

Model setup: We initialized Rhyolite-MELTS with the parental magma composition of Tissint [4] above its liquidus at 1400 °C and 1 bar. We conducted two model runs where Fe\textsuperscript{3+}/Fe\textsuperscript{2+} was set to 0.028 and 0.02. We selected a Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio of 0.028 to resemble the Fe\textsuperscript{3+}/Fe\textsuperscript{2+} determined by the Kress and Carmichael (1991) model at Tissint’s early $f_{O2}$ estimate of QFM-3.24 [4], while the Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio of 0.02 was selected to reflect our finding of Kress and Carmichael (1991) overpredicting Fe\textsuperscript{3+}/Fe\textsuperscript{2+} in martian magmas at a given $f_{O2}$. However, in unbuffered systems, Rhyolite-MELTS calculates $f_{O2}$ from the melt Fe\textsuperscript{3+}/Fe\textsuperscript{2+} using Kress and Carmichael (1991) so changing the initial Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio alters the $f_{O2}$ which Rhyolite-MELTS uses to calculate mineral stability and Fe\textsuperscript{3+}-Fe\textsuperscript{2+} mineral-melt partitioning. In the future, we intend on developing a martian-specific parameterization that interrelates Fe\textsuperscript{3+}/Fe\textsuperscript{2+} - $f_{O2}$ - T - X to allow for accurate modelling of Fe\textsuperscript{3+}/Fe\textsuperscript{2+} and $f_{O2}$ during crystallization.

![Figure 1. Measurements of Fe\textsuperscript{3+}/Fe\textsuperscript{2+} vs. $f_{O2}$ (relative to QFM) from 100 kPa gas-mixing furnace experiments at 1365 °C on Humphrey (black) and NWA 7034 basaltic-trachyandesite (red) plotted against Fe\textsuperscript{3+}/Fe\textsuperscript{2+} - $f_{O2}$ - T - X parameterizations from Borisov et al. (2018; solid) and Kress and Carmichael (1991; dashed). Note that the Borisov18 curves for Humphrey and NWA 7034 overlap.](image-url)
Figure 2. Rhyolite-MELTS model results tracking the evolution of a) melt Fe³⁺/Fe⁴⁺ and b) log\(f_{O_2}\) with temperature for model runs with initial Fe³⁺/Fe⁴⁺ = 0.028 (black) and 0.02 (red). In b), gray contours are 1 log unit intervals relative to QFM, and the black and red shaded boxes represent Tissint’s recorded \(f_{O_2}\) evolution of ΔQFM = 2.1 ± 0.5 from liquid to groundmass compared to the initial \(f_{O_2}\) of the model runs.

**Crystallization Results:** The models proceeded from 1400 to ~1110 °C and reached ~85% crystallization, after which the modeled mineral and melt chemistry evolved to unrealistic compositions. Fe³⁺/Fe⁴⁺ evolved from 0.028 to 0.091 and from 0.02 to 0.075 for the two models. The absolute increase in Fe³⁺/Fe⁴⁺ is greater for the melt with initial Fe³⁺/Fe⁴⁺ of 0.028 but the relative increase in Fe³⁺/Fe⁴⁺ is greater for the melt with initial Fe³⁺/Fe⁴⁺ of 0.02 (Fig. 2a). In both models, the latter stages of crystallization following plagioclase saturation, from 1140 °C to 1110 °C, result in more pronounced melt Fe³⁺/Fe⁴⁺ increases as the fraction of crystallization per increment of cooling increases and therefore the modal percentage of ferrous minerals grows rapidly. The crystallizing assemblages evolved from QFM-3.24 to QFM-1.04 and from QFM-4.02 to QFM-1.59 for the initially more oxidized and more reduced melts, respectively and both underwent a ΔQFM (i.e., the change in \(f_{O_2}\) with respect to QFM at the initial and final T) similar to Tissint’s \(f_{O_2}\) evolution of ΔQFM = 2.1 ± 0.5.

**Discussion:** Although existing thermodynamic models do not fully capture martian magma Fe³⁺/Fe⁴⁺ – \(f_{O_2}\) – T – X interrelations, they indicate that unbuffered closed-system magmatic crystallization can produce significant \(f_{O_2}\) shifts. As martian magmas modify \(f_{O_2}\) more readily with changes in melt Fe³⁺/Fe⁴⁺ than predicted by Kress and Carmichael (1991) or other extant models, we expect that the \(f_{O_2}\) shifts calculated by Rhyolite-MELTS are underestimate of how natural martian magmatic systems evolve. These results suggest that closed system crystallization of martian magmas can account for a greater extent of oxidation than previously believed.


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