

IRON REDOX SYSTEMATICS OF MARTIAN MAGMAS. S. P. Aithala¹, M. M. Hirschmann¹, M. Buss¹ ¹Dept. Earth and Env. Sci., U. Minnesota, Minneapolis, MN 55455 USA *aitha012@umn.edu*.

Introduction: The redox speciation of iron, quantified by the ratio $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ (where $\text{Fe}^{\text{T}} = \text{Fe}^{2+} + \text{Fe}^{3+}$), in magmas affects rocky planets' geochemical and petrologic diversity by influencing igneous mass transfer processes including crystallization, partial melting, degassing, ascent, and assimilation. Consequently, characterizing $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ variations in martian igneous rocks provides key insights into geochemical evolution on Mars.

Constraints on martian magma redox come from estimates of basalt oxygen fugacity (f_{O_2}) obtained by oxybarometry of martian igneous meteorites and from Mössbauer spectrometer measurements of $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratios of basalts at Gusev crater from the Spirit rover [1-3]. Recorded values of f_{O_2} span ~ 7 orders of magnitude, from 4 log units below the quartz-fayalite-magnetite (QFM) buffer in olivine-spinel-orthopyroxene assemblages up to 3 log units above QFM in ground-mass iron-titanium oxides [1-3]. Individual lithologies can display variations of f_{O_2} up to 3 orders of magnitude between early and late crystallizing phases [1-6]. These ranges are greater than those recorded by plume-derived magmas on Earth through geologic time, which span QFM-3.0 to QFM+2.0, while terrestrial interlithology f_{O_2} variation is typically less than 1 log unit [2, 3, 6, 7].

The large f_{O_2} variations between and within martian igneous lithologies may suggest significant mass transfer processes, both in formation of martian basalt sources and during their differentiation, which have not occurred on Earth. Alternatively, the large variations may indicate that martian magmas could have a greater sensitivity to f_{O_2} variation for similar mass transfer. For example, if the f_{O_2} of martian magmas are highly susceptible to small changes in $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$, then modest changes in Fe^{3+} caused by assimilation or degassing could account for the wide range of f_{O_2} recorded in martian igneous lithologies. We note that martian magmas, typically generated at reducing conditions relative to terrestrial magmas, are expected to shift more in f_{O_2} with small changes in $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ due to the logarithmic relationship between f_{O_2} and $\text{Fe}^{3+}/\text{Fe}^{2+}$. However, the degree of f_{O_2} sensitivity, as well as large shifts in f_{O_2} within oxidized lithologies are poorly understood for martian magmas. Here, we discuss the controls on $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ in magmas and share the results of our experimental campaign focused on quantitatively determining the relationship between $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ and f_{O_2} in martian magmas. We also discuss the petrologic implications of our improved understanding of martian magma redox systematics.

Iron redox in martian magmas: The relationship between $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ and f_{O_2} has been investigated

extensively, but with few exceptions [8], quantitative models formulated by previous studies are calibrated from experiments on terrestrial or synthetic melt compositions and thus may not be applicable to martian basaltic compositions [9-12]. Towards calibration of an empirical model for $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ as a function of f_{O_2} specific to martian magmas, we synthesized glasses with compositions representative of Gusev Crater basalt, Humphrey [13], at 100 kPa, 1365 °C, and f_{O_2} spanning QFM-2 – QFM+6.5 and analyzed their $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratios by room-temperature Mössbauer spectroscopy. Spectra were fit using extended Voigt based methods, with one hyperfine doublet each for Fe^{2+} and Fe^{3+} . The raw $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ ratios range from 0.12 to 0.86, but when adjusted for recoilless fraction with a correction factor of 1.2, typical for multicomponent silicate glasses [14], the range reduces to 0.10-0.72. We also conducted Fe-K α X-ray absorption near-edge structure (XANES) spectroscopy on these glasses at beamline 13-ID-E at the Advanced Photon Source at Argonne National Laboratory to characterize their pre-edge centroid energies. With these data, we develop a pre-edge centroid – $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ calibration with glass standards to facilitate future *in situ* measurements of martian glass $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$.

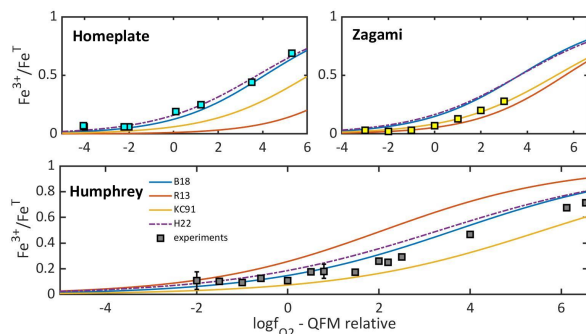


Figure 1. Measured $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ (squares) from experiments of Matzen et al. (2022; top left), Richter et al. (2013; top right), and the current study (bottom). The curves are the predictive models for $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ vs. f_{O_2} from Kress and Carmichael (1991; yellow), Richter et al. (2013; orange), Borisov et al. (2018, blue), and Hirschmann (2022; purple). Error bars in the Humphrey plot represent one s.d. and are not shown for data in which s.d. is smaller than marker size.

Results: We compare our 100 kPa Humphrey data to existing parameterizations of $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ vs. f_{O_2} and compare these to $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ measurements of synthetic martian glasses representative of surface basalt, Homeplate [15] and basaltic shergottite, Zagami [8] (Fig. 1). When compared to the $\text{Fe}^{3+}/\text{Fe}^{\text{T}} - f_{\text{O}_2}$ models of Kress and Carmichael (1991), Borisov et al. (2018), Hirschmann (2022), and Richter et al. (2013), we find that the experimental data for Humphrey and

Homeplate are well-reproduced by the parameterizations of Hirschmann (2022) and Borisov et al. (2018). However, the experiments on Zagami are better predicted by the parametrizations of Kress and Carmichael (1991) and Righter et al. (2013). The lack of agreement between the Righter et al. (2013) model and measurements on Homeplate and Humphrey is peculiar given that the Righter et al. (2013) model is calibrated specifically for martian magmas. The lack of agreement amongst the experimental datasets further highlights the need for a more comprehensive parameterization applicable to martian compositions.

We find the relationship between pre-edge centroid energy and $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ is similar between martian and terrestrial basaltic glasses up to 50% $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ (Fig. 2). The agreement between these data suggest that $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ can be measured *in situ* in martian basaltic glasses using the established Fe-K α XANES calibration developed by Cottrell et al. (2009).

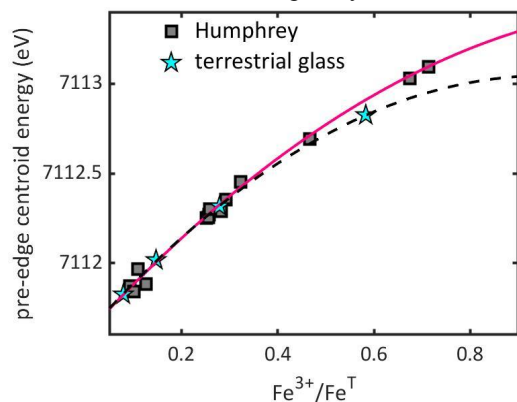
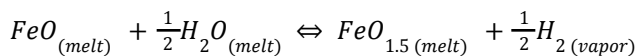


Figure 2. XANES pre-edge centroid energy of Humphrey glasses and terrestrial glasses (Smithsonian standards synthesized by [17] with $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ from [18]), measured in the same beamline session, plotted against $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$. Pink and dashed curves are quadratic fits to Humphrey and terrestrial glass data, respectively.

Discussion: There are two prevailing interpretations of redox heterogeneity in martian basalts. One model, based on a correlation between La/Yb ratios and f_{O_2} measured by ferrous-ferric mineral equilibria oxybarometry, suggests that variably oxidized martian basalts are derived from heterogeneous, depleted and enriched mantle sources [2, 19]. The competing interpretation of redox heterogeneity in martian basalts, which is predicated on the poor correlation between La/Yb ratios in basalts and f_{O_2} measured by V-in-olivine oxybarometry, argues for basalt sources that are uniform in f_{O_2} [3] independent of. This model attributes f_{O_2} variance recorded in martian basalts to shallow processes including degassing and assimilation [3]. As the Borisov et al. (2018) model best reproduces $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ of martian magmas, we use it to quantify the mass transfer required to explain the wide range of f_{O_2} recorded in early-crystallized mineral phases of

shergottites from a homogenous mantle source. We consider an aliquot of Humphrey generated at QFM-4, and investigate how shallow degassing of H_2 , by the reaction:



or Cl_2 by the reaction:



could result in its oxidation to QFM-2. Per the Borisov et al. (2018) model, oxidation of Humphrey from QFM-4 to QFM-2 requires an increase in $\text{Fe}^{3+}/\text{Fe}^{\text{T}}$ from 0.024 to 0.059 which can be caused by the degassing of ~88 ppm H_2 or ~20 wt% Cl_2 . The large magnitude of Cl_2 degassing required disqualifies it from being a primary process to oxidize Humphrey but H_2 degassing or a combination of H_2 and Cl_2 degassing are capable of increasing f_{O_2} by multiple orders of magnitude [20–22]. We demonstrate that martian magmas spanning the f_{O_2} range observed in shergottites can be explained by identical, reduced magmas having undergone various extents of degassing, lending credence to the homogenous mantle model.

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