Iron redox systematics in martian mantle melts and identification of primary liquids

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Many MgO-rich shergottites have olivine phenocrysts and a natural question to ask is if any of these represent primary melts from the martian mantle. To answer this requires knowledge of olivine liquid equilibrium in appropriate magma compositions. Because olivine-phyric shergottites represent either primary liquids or liquids that have been modified by fractionation or accumulation of olivine (or other phases), the equilibrium (and its K_d) 2MgO (liq) + Fe_2SiO_4 (olivine) = 2FeO (liq) + Mg_2SiO_4 (olivine), can be used to evaluate whether the olivine-bearing rocks represent liquids. Primary liquids are important to identify since they can allow estimation of compositions of martian magma source regions. If a liquid is primary, then the most magnesian olivine observed in a shergottite would be the first crystallizing olivine and in equilibrium with a liquid whose composition is the same as the bulk meteorite. Natural magmas contain iron in two oxidation states – Fe^{2+} and Fe^{3+} or FeO and Fe_2O_3. Because rocks and glass are typically analyzed for their bulk Fe content, which does not distinguish between FeO and Fe_2O_3, the Fe^{3+}/Fe^{2+} remains an unmeasured parameter for most shergottites, and igneous rocks in general. However, if the bulk composition, temperature, pressure, and fO_2 are known, the Fe^{3+}/Fe^{2+} ratio can be calculated based on experimental database (e.g. [1,2]). This approach has been applied to terrestrial and lunar lavas, as well as to Martian, and is one way to identify primitive melts from the mantles of such differentiated bodies (e.g. [3,4]). Relatively low FeO terrestrial magmas are known to have olivine/liquid $K_d = 0.30$ [5], whereas higher FeO martian magmas have higher olivine/liquid $K_d = 0.34$ to 0.39 [6,7]. The values of K_d are dependent on an understanding of redox systematics of martian liquids (high FeO) and knowledge of effect of pressure and depth range over which magma are generated. Recent studies have emphasized analytical approaches [2,8] or focused on alkali-free martian melts [7] which makes comparison difficult (and perhaps even meaningless) to more realistic alkali-bearing melts. Here we revisit olivine-melt equilibrium by applying our expression which was specifically developed for high FeO alkali-bearing martian melts. We also combine this with Matzen et al. 2022 data [7] for alkali-free melts to allow quantification of the effect of alkalis, and even low alkali melts. The expression for predicting Fe^{2+} and Fe^{3+} is $\ln(Fe^{3+}/Fe^{2+}) = a \ln fO_2 + b/T + cP/T + dX_{FeO} + eX_{Al2O3} + fX_{CaO} + gX_{Na2O} + hX_{K2O} + iX_{P2O5}$, where coefficients a through i are derived from multiple linear regression of the experimental data (**Figure 1**). This expression can also be used to calculate the change in redox state (or DFMQ) as a martian melt ascends to the surface (**Figure 2**).

Nearly 100 experimental results were compiled for olivine-liquid equilibrium in bulk compositions that are FeO > 15 wt% and limited to those >1200 °C, since we wish to apply the results to high temperature melting [9-20]. Use of the Kress and Carmichael (1991) [1] and O'Neill et al. (2018) [8] expressions developed primarily for lower FeO terrestrial liquids result in $K_d = 0.36$. Use of Righter et al. (2013) [4] and combined Righter-Matzen datasets [4,7] for higher FeO melts results in K_d in the range 0.37-0.39. If the $K_d = 0.36$, the shergottites Yamato 980459, NWA 2990, NWA 5789, Tissint, and EETA 79001 A, are all possible primary mantle melts, but the higher $K_d = 0.37$-0.39 would also allow LAR 06319/12011, NWA 6234 and 4468 to be primitive martian melts as well (**Figure 3**).

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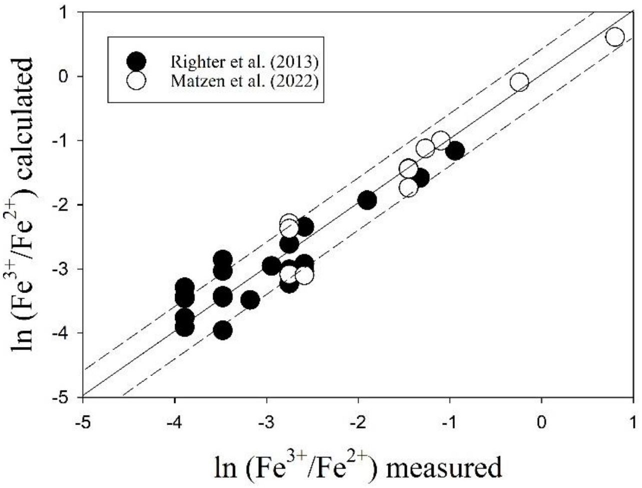

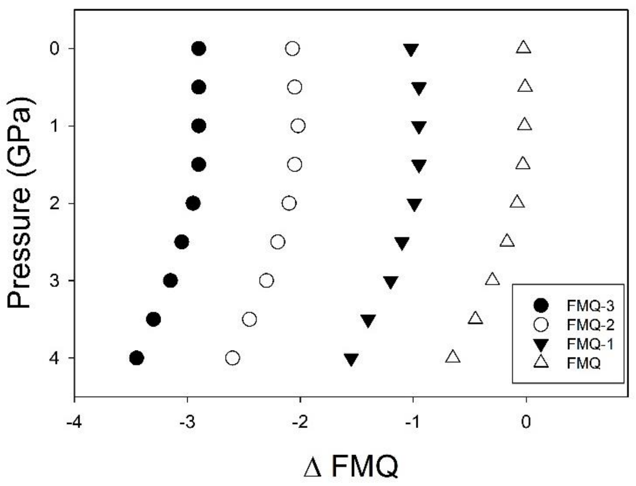

Figure 1: comparison of ln(Fe^{3+}/Fe^{2+}) calculated versus measured with the combined Righter et al. (2013) and Matzen et al. (2022) datasets. Dashed lines are 1 sigma error on the regression.

Figure 2: Calculated oxidation of martian mantle liquids upon decompression and ascent. The change is small and less than one log fO_2 unit between FMQ-3 and FMQ, with much of the effect occurring at high pressures. Shallow decompression will lead to little or no change.

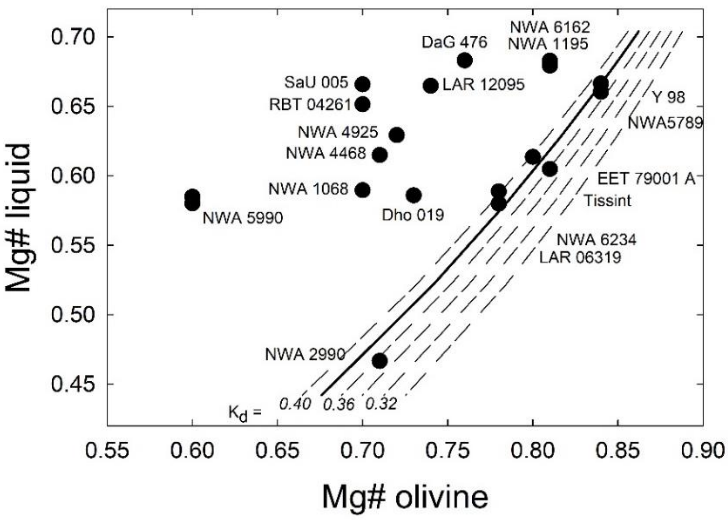

Figure 3: Mg# of olivine and liquids in equilibrium, calculated assuming specific values for the olivine-liquid (Mg-Fe) K_d (dashed lines). The value of K_d appropriate for martian liquids is higher than that for terrestrial compositions (0.30). Previous work has suggested values of 0.35-0.36, but application of our expression for Fe^{3+}/Fe^{2+} equilibrium results in K_d ~ 0.38 (heavy solid line). Several olivine-phyric shergottites fall along or near this line suggesting they could be liquid compositions: Yamato-980459, NWA 5789, EET 79001 (lithology A), Tissint, NWA 6234, LAR 06319, NWA 2990. Even LAR 06319 and NWA 6234 have high olivine modal % and adjustment to the Mg# liquid is necessary, these two compositions are still potential liquids. Data for meteorites from references in [21].