Redox systematics of martian magmas with implications for magnetite stability

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Abstract

Magnetite is commonly found at sites on Mars explored by robotic spacecraft, yet is rare in martian meteorites and in experimental studies of martian magma compositions. Iron redox systematics of the high-FeO shergottitic liquids are poorly known, yet have a fundamental control on stability of phases such as magnetite, ilmenite, and pyroxenes. We undertook experiments to constrain the $Fe^{3+}/\Sigma Fe$ in high-FeO (15–22 wt%) glasses as a function of f_{O_2}, melt P_2O_5, temperature and pressure. We also performed a series of sub-liquidus experiments between 1100 and 1000 °C and FMQ+0.5 to FMQ-1 to define magnetite stability. Run products were analyzed for Fe^{3+} and Fe^{2+} by Mössbauer spectroscopy and micro-X-ray absorption near edge structure (micro-XANES) spectroscopy. One bar liquids equilibrated at FMQ-3 to FMQ+3 show a much lower $Fe^{3+}/\Sigma Fe$ than terrestrial basalts at the same conditions. As melt P_2O_5 contents increase from 0 to 3 wt% (at fixed pressure, temperature, and f_{O_2}), $Fe^{3+}/\Sigma Fe$ decreases from 0.07 to 0.05, but this is within error on the measurements. Temperature increases between 1200 and 1500 °C cause little to no variation in $Fe^{3+}/\Sigma Fe$. Pressure increases from 1 to 4 GPa cause a 0.06 decrease in $Fe^{3+}/\Sigma Fe$. The trends with pressure and temperature are in agreement with results of previous studies. Combining our new series of data allows derivation of an expression to calculate Fe^{3+}/Fe^{2+} for high-FeO melts such as martian magmas.

$$\ln(X_{Fe^{3+}}/X_{Fe^{2+}}) = \mathbf{a}\ \ln f_{O_2} + \mathbf{b}/T + \mathbf{c}P/T + \mathbf{d}X_{FeO} + \mathbf{e}X_{Al_2O_3} + \mathbf{f}X_{CaO} + \mathbf{g}X_{Na_2O} + \mathbf{h}X_{K_2O} + \mathbf{i}X_{P_2O_5} + \mathbf{j}$$

This expression can be used to show that decompressed melts become slightly more oxidized at the surface (compared to 4 GPa). Magnetite stability is suppressed by the lower Fe^{3+}/Fe^{2+} of the high-FeO melts. Magnetite stability is a function of Fe_2O_3 and temperature and is stable ~50 °C lower than typical terrestrial basalt. Difficulty in producing magnetite as a liquidus phase in magmatic systems suggests either that many martian basalts are more oxidized than FMQ (but not represented among meteorite collections), that the titano-magnetite only forms upon cooling below ~1000 °C at FMQ, or that the magnetite has a secondary origin.

Keywords: Mars, basalt, redox, magnetite