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Iron redox systematics of martian magmas. K. Righter[1], L. Danielson[1], A. Martin[1], K. Pando[1], S. Sutton[2], M. Newville[2]; [1] NASA/JSC, [2] Univ. Chicago, GSECARS.

Introduction:

Martian magmas are known to be FeO-rich and the dominant FeO-bearing mineral at many sites visited by the Mars Exploration rovers (MER) is magnetite [1]. Morris et al. [1] propose that the magnetite appears to be igneous in origin, rather than of secondary origin. However, magnetite is not typically found in experimental studies of martian magmatic rocks [2,3]. Magnetite stability in terrestrial magmas is well understood, as are the stability of FeO and Fe_2O_3 in terrestrial magmas [4,5]. In order to better understand the variation of FeO and Fe_2O_3, and the stability of magnetite (and other FeO-bearing phases) in martian magmas we have undertaken an experimental study with two emphases. First we document the stability of magnetite with temperature and fO_2 in a shergottite bulk composition. Second, we determine the FeO and Fe_2O_3 contents of the same shergottite bulk composition at 1 bar and variable fO_2 at 1250 ºC, and at variable pressure. These two goals will help define not only magnetite stability, but pyroxene-melt equilibria that are also dependent upon fO_2.

Experimental and analytical techniques:

A synthetic basaltic shergottite composition, similar to the bulk composition of Zagami, was prepared from high purity oxides, and homogenized by repeated fusion and grinding. Some experiments (series A and C) were carried out at 1 bar in gas mixing furnaces controlled by CO-CO_2 mixtures and equilibrated at 1300 °C. High pressure experiments (Series B) were carried out in piston cylinder and multi-anvil apparatuses at NASA-JSC [6,7].

Series A: was carried out on the shergottite composition between FMQ – 3 and FMQ + 3, at 1300 ºC. This series is meant to constrain the variation of Fe^{3+}/Fe(tot) for a martian composition over a large fO_2 range, and will serve as a baseline for understanding any variation we find in iron redox ratio for samples equilibrated at higher pressure and volatile contents.

Series B: Several kinds of experiments were carried out at higher pressures in a piston cylinder and multi-anvil apparatus. Some experiments were completed in molybdenum capsules, which buffer fO_2 at the Mo-MoO_2 buffer, near IW [8]. Other experiments were carried out in graphite capsules with fO_2 monitored by Co-(CoMg)O sliding sensor [9]; these equilibrated at FMQ-2 [6]. These experiments were designed to define the effect of pressure on the Fe^{3+}/Fe(tot) in the shergottite.

Series C: The last series of experiments was carried out at 1 bar, at subliquidus conditions to help define magnetite stability. Several experiments were carried out at FMQ -1 and variable temperature. Others were carried out at fixed temperature (1050 °C) and variable fO_2 from FMQ+0.5, FMQ, FMQ-0.5, FMQ-1. These experiments were carried out to supplement previous work [4,5] at these relatively low temperatures where magnetite may or may not be stable.

Run products were analyzed by electron microprobe for major and minor elements using standard approaches (e.g., [6]). Measurements of Fe^{3+} and Fe^{2+} in the experimental glasses were made using micro-XANES (X-ray absorption near edge structure) at the Advanced Photon Source (Argonne National Lab). A monochromatic X-ray beam from a Si(111) double crystal monochromator was focused onto the sample and the fluorescent X-ray yield was plotted as a function of incident X-ray energy (more detail can be found in [10]). Fe-bearing glasses are used to calibrate valence vs. centroid energy (area-weighted average energy of the pre-edge peaks). XANES has the advantage of good spatial resolution – an important capability when analyzing high pressure glasses, and also samples with mineral – melt mixtures.

Terrestrial magmatic constraints

The variation of Fe^{3+}/Fe(tot) in silicate melts has been well studied for terrestrial magmatic rocks, which typically have Al_2O_3 between 10 and 20 wt% and FeO up to 15 wt% [5, 11-13]. However, shergottites contain lower Al_2O_3 contents and higher FeO contents [14], suggesting that any calibrations for terrestrial magmas must be extrapolated to compositions well outside the calibration database (Fig. 1). The only experiments done at very high FeO contents are those from simple systems and carried out in air (Fig. 1). Indeed, when such

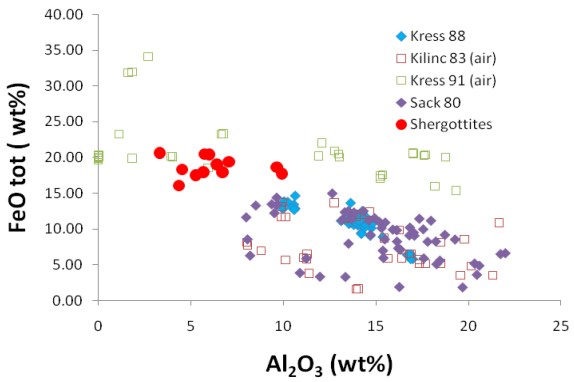

Figure 1: FeO (total) vs. Al_2O_3 for experimental data used to predict the Fe^{3+}/Fe^{2+} in terrestrial basalt. Data (from [5, 11-13]; shergottites data from Lodders 1998 compilation, [14]) do not overlap with shergottite compositions.

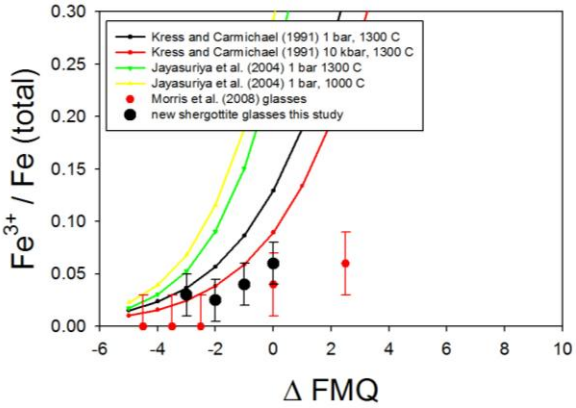

Figure 2: Fe^{3+}/Fe(tot) vs ΔFMQ calculated for a Zagami-like shergottite using the expressions of [5] Kress and Carmichael, 1991 and [15] Jayasuriya et al., 2004, along with data for FeO-rich glasses from [1] Morris et al., 2008, and our new data at FMQ to FMQ-3.

terrestrial calibrations are applied to the few existing data for martian melt compositions, the mismatch is significant (Fig. 2; [5,15]). The Fe^{3+}/Fe(tot) for a few martian melts stays low even at fO_2s where in terrestrial systems they would have values well over 0.2 (Fig. 2). This is a feature which we will try to verify with our new experiments.

Many experiments have been performed and published which define magnetite stability in terrestrial melt compositions (Fig. 3). The conditions at which magnetite becomes stable show a trend of increasing FeO content of silicate melt with decreasing Fe^{3+}/Fe(tot). This suggests that martian silicate melts with FeO contents of ~ 20 wt%, may be able to saturate or stabilize magnetite at Fe^{3+}/Fe(tot) values as low as 0.05.

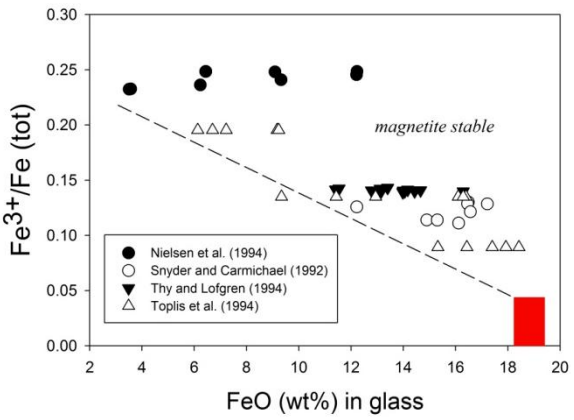

Figure 3: Literature experiments defining the stability of magnetite in basaltic systems ([4, 16-18]). Red box is the range of FeO contents for shergottites, showing that magnetite may be stable with Fe^{3+}/Fe(tot) values as low as 0.05.

Our new results:

Our new results for shergottite glasses indicate that the Fe^{3+}/Fe(tot) remains as low as 0.05 even at FMQ+2. The effect of pressure does not change this significantly, although we have only 1 GPa data so far and will expand to higher pressures near 4 GPa, as might be possible in the martian crust and mantle.

The role of phosphorus (P) in FeO-bearing silicate melts is important to define [19]. In terrestrial systems, there can be Fe^{3+}-P^{5+} complexing that can affect the overall Fe^{3+}/Fe(tot) ratios independently of fO_2 [19]. Therefore, we carried out a series of experiments with variable P_2O_5 contents. For this shergottite composition, the effect of P_2O_5 is very small, causing a change in Fe^{3+}/Fe(tot) of only 0.01 across 3 wt% P_2O_5.

In the subliquidus series experiments, we found that magnetite is only stable at 1000 ºC and FMQ-1. This is a significantly lower temperature than many 1 bar terrestrial samples, where magnetite stability is between 1050 and 1100 °C. Future analyses will measure the Fe^{3+}/Fe(tot) in glasses co-existing with magnetite in these experiments and others at higher fO_2.

Implications:

Low ferric/ferrous ratios in shergottites are consistent with the smaller stability field for magnetite. In future experiments, the effect of dissolved water will be explored – hydrous conditions could increase ferric/ferrous and thus expand the magnetite stability field. If the commonly observed surficial magnetite (e.g., at MER sites) is igneous in origin, it likely originates from more evolved (fractionated) or more oxidized magmas which are not necessarily represented in the meteorite collections.

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