UNUSUAL IRON REDOX SYSTEMATICS OF MARTIAN MAGMAS.

L. Danielson[1], K. Righter[2], K. Pando[1], R.V. Morris[2], T. Graff[1], D. Agresti[3], A. Martin[2], S. Sutton[4], M. Newville[4], A. Lanzirotti[4]. [1]ESCG, Houston, 77058, lisa.r.danielson@nasa.gov, [2]NASA/JSC, [3]University of Alabama at Birmingham, [4]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] proposed 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 stabilities 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 determine the FeO and Fe_2O_3 contents of super- and sub-liquidus glasses from a shergottite bulk composition at 1 bar to 4 GPa, and variable fO_2. Second, we document the stability of magnetite with temperature and fO_2 in a shergottite bulk composition.

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: This series was carried out between FMQ–3 and FMQ+3 at 1300 °C and will constrain the variation of Fe^{3+}/Fe(tot) for a martian basaltic melt over a large fO_2 range.

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 (FMQ+0.5, FMQ, FMQ-0.5, and FMQ-1). These experiments were carried out to supplement previous work [2,3] 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 1 bar experimental glasses (series A) were made using Mössbauer spectroscopy at NASA-JSC[10,11]. Measurements of Fe^{3+} and Fe^{2+} in glasses from high pressure glasses and samples that are a mixture of crystal and glass (series B and C) 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 [12]). Fe-bearing glasses analyzed independently using Mössbauer spectroscopy were 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 smaller area high pressure glasses, and also samples with mineral – melt mixtures.

Terrestrial magmatic constraints: The variation of Fe^{3+}/Fe(tot) in silicate melts of a wide range of terrestrial compositions has been well studied, but these melts typically have Al_2O_3 between 10 and 20 wt% and FeO up to 15 wt% [5, 13-15] compared to lower Al_2O_3 and higher FeO shergottites, suggesting that any calibrations for terrestrial magmas must be extrapolated to compositions well outside the calibration database. The only experiments done at very high FeO contents are those from simple systems and carried out in air [5]. Indeed, when such terrestrial calibrations are applied to the few existing data for martian melt compositions, the mismatch is significant (**Fig. 1**), espe-

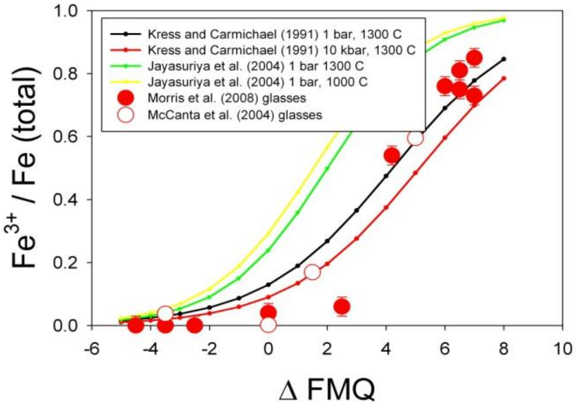

Figure 1: Fe^{3+}/Fe(tot) calculated for a Zagami-like shergottite using the expressions of [5] and [16] along with data for FeO-rich glasses from [1], [17].

cially in the Mars-relevant region between FMQ-2 and FMQ+2. A few martian melts have low Fe^{3+}/Fe(tot) at fO_2s where in terrestrial systems they would have values well over 0.2 [1], whereas others [17] are higher (**Fig. 1**). We aim to address this inconsistency with our new experiments in series A.

Many previous experiments define magnetite stability in terrestrial melt compositions (**Fig. 2**). Magnetite becomes stable at higher FeO content of silicate melts as Fe^{3+}/Fe(tot) decreases. 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. We will also test this with experiments in series C.

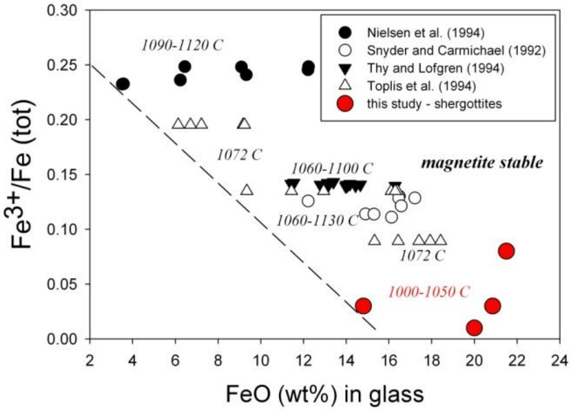

Figure 2: Literature experiments defining the stability of magnetite in basaltic systems ([4, 18-20]) and Fe^{3+}/Fe(tot) calculated using [5], along with XANES measurements on glasses coexisting with magnetite in this study.

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 (**Fig. 3**). The effect of temperature does not change this significantly, and the effect of pressure (up to 4 GPa) is similar to that documented in other FeO-bearing terrestrial melts [5,21]. The role of phosphorus (P) in FeO-bearing silicate melts is important to define [22]. 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 [22]. 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 small, causing a change in Fe^{3+}/Fe(tot) of only 0.03 across 3 wt% P_2O_5. In the subliquidus series C experiments, we found that magnetite is only stable at <1025 ºC and FMQ-1. This is ~100 ºC lower than in terrestrial systems at comparable fO_2. High FeO melts will stabilize magnetite at lower Fe^{3+}/Fe(tot) but at higher FeO (tot), as suggested by trends defined by terrestrial studies (**Fig. 2**).

Implications: Fe^{3+}/Fe(tot) in shergottites remain significantly lower than in lower FeO terrestrial basalt. This is consistent with the smaller stability field for magnetite, and indicates low Fe^{3+}/Fe(tot) in martian melts will have important controls on phase equilibria.

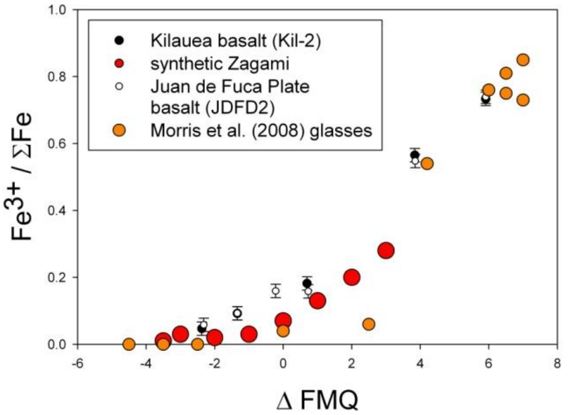

Figure 3: New results for glasses measured using Mössbauer spectroscopy illustrating that the shergottite composition remains low relative to terrestrial basalts such as mid ocean ridge (JDFD2) and Hawaiian (Kil-2) basalts (from [5]). One glass from [1] may be anomalously low.

In future experiments the effect of dissolved water will be explored – hydrous conditions could increase ferric/ferrous and thus expand the magnetite stability field [23]. 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.

References: [1] Morris, R.V. et al. (2008) JGR 113, 2008JE003201; [2] Stolper, E. and McSween, H.Y. (1979) GCA 43, 1475-1498; [3] McCoy, T.J. and Lofgren, G.E. (1999) EPSL 173, 397-411; [4] Toplis, M.J. et al. (1994) GCA 58, 797-810; [5] Kress, V.C. and Carmichael, I.S.E. (1991) CMP 108, 82-92; [6] Righter, K. et al. (2009) EPSL 288, 235-243; [7] Righter, K. et al. (2008) Nature Geosc. 1, 321-323; [8] O'Neill, H.St.C. (1986) Amer. Mineral. 71, 1007-1010; [9] Taylor, J.R. et al. (1992) Amer. Mineral. 77, 284-295; [10] Klingelhofer, G, et al. (2002) Hyperfine Inter. 144/145, 371-379. [11] Agresti, D.G. and Gerakines, P.A. (2009) Hyperfine Inter. 188, 113-120. [12] Bajt, S. et al. (1994) *GCA 58*, 5209-5214; [13] Kress, V.C. and Carmichael, I.S.E. (1988) *Amer. Mineral.* 73, 1267-1274; [14] Kilinc, A. et al. (1983) CMP 83, 136-145; [15] Sack, R.O. et al. (1980) CMP 75, 369−376; [16] Jayasuriya, K.D. et al. (2004) Amer. Mineral. 89, 1597-1609; [17] McCanta, M.C. et al. (2004) Amer. Mineral. *89*, 1685–1693; [18] Nielsen, R.L. et al. (1994) Chem. Geol. 117, 167-191; [19] Snyder, D.A. and Carmichael, I.S.E. (1992) GCA 56, 303-318; [20] Thy, P. and Lofgren, G.E. (1994) CMP 116, 340-351; [21] Mysen, B.O. and Virgo, D (1985) Phys. Chem. Mineral. 12, 191-200; [22] Horng, W.-S. et al. (1999) GCA 63, 2419-2428; [23] Minitti, M. and Rutherford, M.J. (2000) GCA 64, 2535-2547.