IGNEOUS SPINEL CHEMISTRY AS A FUNCTION OF TEMPERATURE AND OXYGEN FUGACITY IN MARTIAN MELTS. P. V. Burger1, C. K. Shearer1, J. J. Papike1, A. S. Bell1 and N. Muttik2. 1Institute of Meteoritics, Department of Earth and Planetary Science, University of New Mexico, Albuquerque, New Mexico 87131 (pvburger@unm.edu), 2Institute for Advanced Materials, Louisiana State University, Baton Rouge, Louisiana 70803

Introduction: Using a variety of empirical and experimental methods, studies of martian basaltic meteorites have collectively estimated that the redox conditions during crystallization range from IW-1 to FMQ+4 [e.g. 1-4]. Previous studies have demonstrated that the fO2 of crystallization determined for the shergottites shows a clear correlation with various geochemical characteristics (i.e., REE, εNd, etc.). This being the case, an understanding of the fO2 of crystallization not only provides a window into the nature of the martian mantle and crust, but also increases our understanding of the petrologic linkages among the shergottites.

Determining the fO2 of martian meteorites relies on various methods including examining mineral assemblages and chemistries, as well as direct measurement of multivalent cations in minerals hosted in martian basalts (e.g., Cr2+,Cr3+, V3+, V4+, V5+ in olivine, spinel, and pyroxene) using techniques such as X-ray absorption near edge structure (XANES). While analytical techniques such as XANES are quite powerful, they are not widely available. XANES is also complicated by other difficulties such as non-standardized data reduction schemes, and x-ray anisotropy. McKay et al. [5] demonstrated a simpler method for estimating the fO2 of a martian basalt is to examine the major element chemistry of the spinel phase as its magnetite component directly correlates with the fO2 of crystallization.

In this study, we expand on the original experiments of McKay et al. [5], who compared the spinel chemistry of martian basalt Yamato 980459 (Y98) to those found in Y98 analog experiments, crystallized at fO2s of IW+1 and FMQ. This study improves on those results, as it examines the changes in spinel chemistry over a wider range of fO2 (IW-1 to FMQ+2), at more discreet intervals, as well as the extent to which the chemistry of spinels changes with the crystallization temperature.

Experimental and Analytical Approach: A series of 1 atmosphere equilibrium experiments on Y98 bulk compositions were performed in Deltech furnaces at the Johnson Space Center and the Institute of Meteoritics (IOM-UNM) at the University of New Mexico. Several overlapping experiments were carried out at both labs to confirm reproducibility. Temperatures of the experiments ranged from 1000°C to 1450°C; the experiments addressed in this abstract are from the 1200 and 1300°C series. The experiments were carried out at fO2s ranging from IW-1 to FMQ+2. Oxygen fugacities were controlled using CO-CO2 gas mixtures and sample wire loop compositions were changed to accommodate experiments at different fO2. Experimental charges were heated above the liquidus to 1470°C and rapidly dropped down to the final experimental temperature. At the conclusion of the experiment, charges were drop quenched into water. Epoxy mounts of the experiments were initially examined using backscattered electron imaging on the JEOL JXA-8200 at UNM. Quantitative point analyses were conducted on oxide phases using the EMP. These analyses occurred at an accelerating voltage of 15 kV, a beam current of 20 nA, and a spot size from 1-3 µm. Calibration was achieved using a series of Taylor & Co. Electron Microprobe Standards, as well as in-house mineral standards. Ferric Fe was determined by difference, using the methodology of [6].

Results & Discussion: As was previously noted by McKay et al. [5], for Y98 compositions, there is a strong correlation of spinel chemistry with fO2. Specif-
ically, the magnetite component of the spinels systematically increases with increasing $fO_2$, as the concentration of Fe$^{3+}$ increases in the melt. In the 1200°C experiments (Fig. 1), the magnetite component of the spinels jumps from an average of 1.5 mol.% at IW-1 to 24.7 mol.% at FMQ+2. It is worth mentioning that in the highest $fO_2$ experiments, (i.e., FMQ+1 and FMQ+2), the spinel compositions overlap. Spinels from experiments crystallized at 1300°C show exactly the same behavior (Fig. 2), though the average magnetite abundance at FMQ+2 is 25.5 mol.%. As was suggested by Papike [7], magnetite represents a change in the crystal structure, from that of “normal” to “inverse” spinel. While a normal spinel may contain some isolated inverse domains, there appears to be an upper limit to the concentration of these domains at these temperatures. This suite of experiments suggests that the limit is ∼25 mol. % magnetite in a Y98 composition melt. End-member magnetite was not observed in any of the experiments. It should be mentioned too, that the concentration of magnetite in spinels from natural Y98 [5] overlaps with the ratios measured in our 1300°C, IW+1 experiments (Fig. 2), which is in agreement with other, independently determined $fO_2$ estimates for Y98 [8,9].

Another interesting aspect of the spinel chemistry is the ratio of divalent Fe to Mg. The largest shifts in this ratio are observed between spinels crystallized at different temperatures, at the same $fO_2$. (Fig. 2). In spinels crystallized at 1300°C and IW+1, the average Fe$^{2+}$(Fe$^{2+}$ + Mg) is 0.58, while at 1200°C, this ratio is 0.66. Similarly, at an $fO_2$ of FMQ+2 and 1300°C, the average Fe$^{2+}$(Fe$^{2+}$ + Mg) is 0.50, while at 1200°C, this ratio is 0.63. The 1200°C set of experiments demonstrate that $fO_2$ plays a role in determining this ratio as well, though to a lesser extent (Fig. 1). The lowest $fO_2$ experiment has the highest Fe$^{2+}$(Fe$^{2+}$ + Mg), ~0.68 at IW-1. At the most oxidizing conditions (FMQ+2), this ratio decreases to ~0.63. The effect of temperature on the Fe to Mg ratio at constant $fO_2$ parallels observations typically made in olivine and pyroxene, where this ratio (typically reported as Mg#) is used as a differentiation index. Magnesium-rich grains crystallize early, and in lower temperature experiments, the equilibrium phases become progressively enriched in Fe$^{2+}$. Temperature is not alone in modifying the Fe$^{2+}$(Fe$^{2+}$ + Mg) ratio in equilibrium spinels, however. While more subtle, the Fe$^{2+}$(Fe$^{2+}$ + Mg) becomes progressively lower with increasing oxidation as Fe$^{3+}$ increases at the expense of Fe$^{2+}$ in the melt.

Conclusions: Spinel contains ubiquitous in primitive basaltic compositions and are sensitive indicators of evolving melt chemistry. The Fe$^{2+}$(Fe$^{2+}$ + Mg) ratio of a given spinel is influenced by both temperature and $fO_2$, therefore, if it is to be used as a differentiation index, more information is generally needed. The usefulness of spinels, however, is the ratio of its components, with the magnetite component acting as a robust indicator of $fO_2$ during crystallization. This remains true up to ~FMQ, at which point the capacity of a spinel to incorporate additional inverse domains is exhausted. This likely explains why the magnetite concentration of spinels in the 1200°C experiments at FMQ+1 and FMQ+2 overlap, and why no end-member magnetite is found in any of the experiments.

The documentation of near-end-member magnetite in other martian meteorites, such as NWA 8159 (an augite basalt) [10] and igneous clasts in NWA 7034 may be related to a drastically different parental melt composition, or may not be igneous in origin at all.