Oxygen Fugacity of the Upper Mantle of Mars. Evidence from the Partitioning Behavior of Vanadium in Y980459 (Y98) and other Olivine-Phyric Shergottites.

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Introduction: Previous studies[1,2,3,4] have demonstrated that the f_{O2} in martian shergottites varies by at least 3 log units and is correlated with geochemical parameters such as LREE/HREE, initial $^{87}Sr/^{86}Sr$, and initial ε_{Nd}. These correlations have been interpreted to indicate the presence of reduced, incompatible element-depleted and oxidized, incompatible element-enriched reservoirs that were produced during early stages of martian differentiation ($\approx$ 4.5 Ga) [1,2,3,4,5,6]. Martian basaltic magmatism represented by the shergottites is thought to represent mixing between these two reservoirs. The behavior of V in the shergottites may provide an independent means of evaluating the f_{O2} conditions under which they crystallized. The valence state of vanadium (V^{2+}, V^{3+}, V^{4+}, V^{5+}) is highly sensitive to variations in redox conditions of basaltic magmas. Differences in valence state will influence its partitioning behavior between mineral phases and basaltic liquid. Using partitioning behavior of V between olivine and basaltic liquid precisely calibrated for martian basalts, we determined the redox state of primitive (olivine-rich, high Mg#) martian basalts near their liquidus. The combination of oxidation state and incompatible element characteristics determined from early olivine indicates that correlations between f_{O2} and other geochemical characteristics observed in many martian basalts is also a fundamental characteristic of these primitive magmas. However, our data does not exhibit the range of f_{O2} observed in these previous studies. We conclude that the f_{O2} for the martian upper mantle is approximately IW+1 and is incompatible-element depleted. It seems most likely (although clearly open to interpretation) that these mantle-derived magmas assimilated a more oxidizing (>IW+3), incompatible-element enriched, lower crustal component as they ponded at the base of the martian crust.

Rationale and Analytical Approach: In magmatic systems V occurs in several valence states: V^{5+} (0.54Å), V^{4+} (0.59Å), V^{3+} (0.64 Å), and perhaps even V^{2+} (0.79 Å) [7]. V^{5+} occurs in highly oxidizing environments on Earth, whereas V^{2+} may occur in highly reducing environments of the Moon and the early solar system (more reducing than IW-1). V^{3+} and V^{4+} are the dominant cations between the QFM buffer and IW-1. Within this range, the ratio of V^{4+}/V^{3+} in the magma is dependent upon f_{O2} and decreases with increasing reduction. A companion paper explores these variations with micro-XANES [8]. The partitioning behavior of V between olivine and basaltic melt is due to differences in charge and ionic radii of the V cation. For example, V^{3+} will be preferred in the M1-M2 octahedral sites in olivine relative to V^{4+}[9]. We calibrated the relationship between f_{O2} and $D_V^{olivine/melt}$ at several different f_{O2} conditions in the 1 atmosphere gas-mixing furnaces at NASA JSC. The starting composition was equivalent to the most primitive martian basalt composition yet documented (Y98) and doped with approximately 1500 ppm V. The mixtures were held above the liquidus at 1500°C before being lowered to temperatures just below the liquidus at temperatures of 1375-1380°C and 1320°C. The charges were then drop quenched in equilibrium at imposed f_{O2} conditions of IW-1, IW+1 and IW+3.5 (=QFM). Olivine-phyric martian basalts NWA1110, SaU005, DaG476, and Y98 were analyzed in this study. These four shergottites have been previously studied [2,3,4]. In addition to these four martian basalts, we also analyzed two basalts from basaltic systems with well defined f_{O2}: an Apollo 12 olivine basalt, that crystallized at an f_{O2} of IW-1 and a terrestrial basalt from the Makaopuhi lava lake that crystallized at 1145˚C and an f_{O2} of IW+3.65 (=FMQ+0.15). Vanadium and a suite of trace elements were analyzed (Sc, Cr, Ti, Mn, Co, Ni, and Y) using the Cameca 4f ims ion microprobe housed in the Institute of Meteoritics at UNM. The $D_V^{olivine/melt}$ in the experimental charges were calculated by the ratio of [measured $V_{olivine}$/measured V_{melt}], while the distribution coefficients between olivine and melt in the olivine-phyric shergottites, lunar basalt, and terrestrial basalt were calculated by the ratio of [measured $V_{early\ olivine}$/measured $V_{whole\ rock\ or\ associated\ glass}$]. In the later calculation, as the whole rock value deviates from a melt composition due to the accumulation of olivine or other phases the [measured $V_{early\ olivine}$/measured $V_{whole\ rock}$] deviates from the true $D_V^{olivine/melt}$. The extent of this deviation can be estimated based on the K_D Fe^{2+}-Mg between olivine and the whole rock. Of the martian basalts, Y98 provided the best estimates of f_{O2}.

Results: Olivine was the first phase to crystallize in all the experiments followed by chromite in all runs at f_{O2} at IW+1 to more oxidizing conditions. The Fe-Mg $K_d^{olivine/melt}$ for all experimental charges is between 0.30 and 0.33, which indicates that olivine is in equilibrium with the melt in all of these experiments. The relationship between f_{O2} and distribution of V between olivine and melt was calibrated through these experimental

charges (Fig. 1). The $D_V^{olivine/melt}$ increases from approximately 0.055 at IW+3.5 (=QFM) to approximately 0.5 at IW-1 and is similar to the range observed in other studies [10]. $D_V^{olivine/melt}$ appears not to be sensitive to slight differences in temperatures (55 to 60°C) just below the liquidus. The $D_V^{olivine/melt}$ for the same f_{O2} is identical within analytical uncertainty. The slope between $D_V^{olivine/melt}$ and f_{O2} changes more abruptly at conditions more reducing than IW+1 (Fig. 2). This is a function of either a non-linear decrease in the V^{4+}/V^{3+} ratio at low f_{O2} or the effect of V^{5+} or V^{2+} on partitioning. Vanadium in the olivine from the martian, terrestrial, and lunar basalts exhibit distinct variations from the core to rim. In the basalts that closely approach liquid compositions and the Fe-Mg $K_d^{olivine/melt}$ indicates that olivine is in equilibrium with that melt (Y98, 12009, Makaopuhi), the V increases and the Ni decreases from core to rim (Fig. 2). In the coarser-grained olivine-phyric shergottites with Fe-Mg $K_d^{olivine/melt}$ that appears to deviate from equilibrium (SaU005, NWA1110, DaG489), both V and Ni decrease from core to rim (Fig. 2). Using the measured ($V_{early olivine}$/measured $V_{whole rock}$) and the experimentally determined relationship between $D_V^{olivine/melt}$ and f_{O2}, the calculated f_{O2} conditions under which these earliest olivines crystallized (near the liquidus and prior to the crystallization of other phases) for these near-primary martian magmas range from approximately IW+0.7 to IW+2.1 (Fig. 3). In addition, the earliest olivines exhibit a range of incompatible element characteristics as illustrated by the concentration of Y. In the more reduced shergottites, Y is approximately 100 ppb in the earliest olivine, whereas in the more oxidized shergottites the earliest olivine has 15 times more Y (Fig. 3).

Discussion: The real advantages of this approach are that (1) the f_{O2} for olivine-phyric shergottites is estimated for conditions just 10-50°C below the liquidus, (2) the f_{O2} and incompatible element characteristics of the basalt can be estimated from a single, early liquidus phase, and (3) the calibration is applicable to olivine-phyric shergottite compositions and a range of near-liquidus T (1380-1320°C). The interpretation of these data indicates that the sources for the "depleted" olivine-phyric shergottites are at an f_{O2} of approximately IW+1 and that the f_{O2} of the martian mantle may range from IW+1 (shallow) to IW-1 (deep). It is these basaltic magmas that more closely represent primary martian basalts. Assimilation of the lower martian crust to produce the "enriched" shergottites is more consistent with the conclusion from isotopic data that the shergottites represent mixing of components from two distinctly different reservoirs that were formed during initial martian differentiation at 4.5 Ga. This is clearly not a unique interpretation of these data. However, if true, the "enriched" olivine-phyric basalts

do not approach primary melt compositions and should not be inverted to estimate the character of the martian mantle.

References: [1] Herd et al. (2002) *GCA* 66, 2025-2036. [2] Herd (2003) *MAPS* 38, 1993-1805. [3] Wadhwa [2001] *Science*, 292, 1527-1530. [4] Goodrich et al. [2003] *MAPS* 38, 1773-1792. [5] Shih et al. (1993) *GCA* 46, 2323-2344. [6] Borg et al. (1997) *GCA* 61, 4915-4931.[7] Sutton et al. (2005) GCA 69, 2333-2348. [8] Karner et al. (2006) LPSC XXXVII. [9] Papike et al. (2005) Am. Min. 90, 277-290. [10] Canel and Fedortchouk (2001) Can. Min.. 39, 319-330.

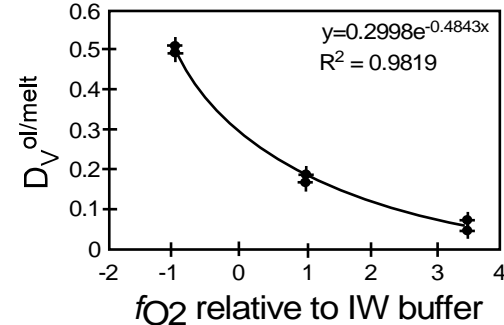Fig. 1. Relationship between $D_V^{olivine/melt}$ and f_{O2}
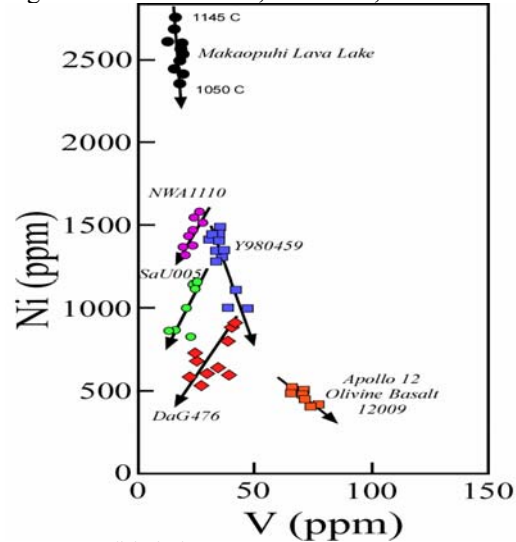

Fig. 2. V-Ni in martian, terrestrial, and lunar olivine.

Fig 3. $D_V^{olivine/melt}$ vs. Y in martian basalts.