The Effect of Fe on OHContent of Olivine: Implications for Extraction of H2O from the Martian Mantle. A. C. Withers, M. M. Hirschmann and T. J. Tenner, University of Minnesota, Dept. of Geology and Geophysics. Email: withe012@umn.edu.

Introduction: The concentration of H2O in the Martian mantle is of importance to understanding the dynamics of convection, the spatial and temporal occurrence of partial melting, and the history of volatile fluxes from the interior to the surface, but is subject to considerable uncertainty and vigorous debate [1-6]. Simulation of the cosmochemical and accretionary origin of Mars suggests an initial H2O inventory similar to 0.06-0.27 terrestrial oceans [4]. If all of this H2O were incorporated into the mantle, the Martian mantle would initially have 200-1000 ppm H2O, which is consistent with the bulk H2O mantle concentration (288 ppm) estimated by Lodders and Fegley [8], but considerably more than the 36 ppm value favored by Dreybus and Wanke [1]. Estimates of the fraction of this original H2O remaining in the mantle at the present time range from 50 to 95% [8,4]. Determination of solubilities and mineral/melt partition coefficients of H2O for Martian magmas and minerals may constrain H2O concentrations in the Martian mantle by allowing analogies to non-volatile species such as K and REE, as has been done for Earth's mantle [9,10].

Experimental and Analytical Methods: Starting materials consisted of mixtures of MgO, MgOH, FeO and SiO2 such that the bulk composition in each experiment was equivalent to 90% olivine + 10% pyroxene, with Mg# (100*Mg/[Mg+Fe]) ranging from 50 to 100, and H/Sl = 1. Experiments were run at 3 GPa and 1200-1500 °C in a piston cylinder and at 6 GPa and 1200 °C in a multi-anvil apparatus. Starting materials were sealed in 2 mm AuPd capsules that, in the case of the 3 GPa/1200 °C experiments, were embedded in FeO within an outer capsule of Fe. Run duration was 6 h at 1200 °C and 3 h at 1500 °C.

Run products were analysed for H2O using SIMS calibrated against FTIR measurements of mineral standards [11,12]. Mineral H2O concentrations were determined from 16O/1H-30Si mass ratios by means of mineral specific calibration curves that were determined at the time of analysis. Raman analysis of areas probed by SIMS verified homogeneity of the phases analysed, and mineral compositions were measured using electron microprobe.

Results: Run products consist of olivine crystals (≤300 μm in diameter), orthopyroxene (≤40 μm) and quenched liquid (fine grained, elongate exsolved crystals interspersed with H2O). Experiments with bulk Mg# ≤ 60 contain Fe intergrown with opx and olivine at the lower end of the capsule. Olivine Mg# varies from 55 to 100, and measurements of KDFe-Mg between olivine and opx are consistent with equilibrium values [13].

Discussion: H2O storage capacities in olivine at 3 and 6 GPa increase linearly with Fe content. This is in contrast to solubilities of H2O measured at 300 MPa under oxidizing (Ni-NiO) conditions [17], which indicate that H2O solubility increases exponentially with decreasing Mg# (Fig. 1). The experimental results indicate that under reducing conditions, Fe content has only modest effect on the energetics of OH substitution in olivine and orthopyroxene, the principal Martian mantle minerals. The enhanced solubility of H2O in olivine relevant to the Martian mantle (Mg# 67-81) compared to its terrestrial equivalent (Mg# 89-91) amounts to a factor of approximately 1.5. Considering
that changes in olivine storage capacity can be related directly to variations in $D_{H_2O}^{\text{ol/liquid}}$ [20] $H_2O$ will be slightly more compatible during mantle melting on Mars ($D_{H_2O}^{\text{ol/liquid}}=0.01$) as compared to Earth ($D_{H_2O}^{\text{ol/liquid}}=0.006-0.009; [21,11]$), and as on Earth, will behave similarly to Ce. If the Zhao et al. [17] exponential relationship were to hold, the predicted applicable value of $D_{H_2O}^{\text{ol/liquid}}$ for Mg# 75 would be $\approx 0.03$, more similar to Nd. Considering inferences that about half the K on Mars remains in the mantle [22] and that K is more incompatible than $H_2O$ during Martian mantle melting ($D_{K}^{\text{ol/liquid}}=0.001; [23]$), this argues that a similar proportion of Martian $H_2O$ remains in the mantle. Assuming that melt fractions generated during melting responsible for the majority of Martian crust exceed 1%, fractionations between $H_2O$ and K must have been negligible, and so our results are not consistent with simulations that suggest that 90-95% of Mars’ water remains in the mantle [8]. If, as suggested by dynamical accretion simulations [4], Mars’ original water budget amounted to 0.06 to 0.27 terrestrial oceans, then the minimum $H_2O$ content of the present-day Martian mantle should be 100 ppm $H_2O$, similar to that of Earth’s upper mantle, and the maximum is approximately 500 ppm $H_2O$, similar to the source regions of Earth’s oceanic island basalts.