The Effect of Fe on OH⁻ Content 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. E-mail: withe012 at umn.edu).

Introduction: The concentration of H_2O 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 H_2O inventory similar to 0.06-0.27 terrestrial oceans [4]. If all of this H_2O were incorporated into the mantle, the Martian mantle would initially have 200-1000 ppm H_2O, which is consistent with the bulk H_2O mantle concentration (288 ppm) estimated by Lodders and Fegley [8], but considerably more than the 36 ppm value favored by Dreibus and Wanke [1]. Estimates of the fraction of this original H_2O remaining in the mantle at the present time range from 50 to 95% [8,4]. Determination of solubilities and mineral/melt partition coefficients of H_2O for Martian magmas and minerals may constrain H_2O 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 SiO_2 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/Si =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 H_2O using SIMS calibrated against FTIR measurements of mineral standards [11,12]. Mineral H_2O concentrations were determined from $^{16}O^1H/^{30}Si$ 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 H_2O). 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 $K_D^{Fe\text{-}Mg}$ between olivine and opx are consistent with equilibrium values [13].
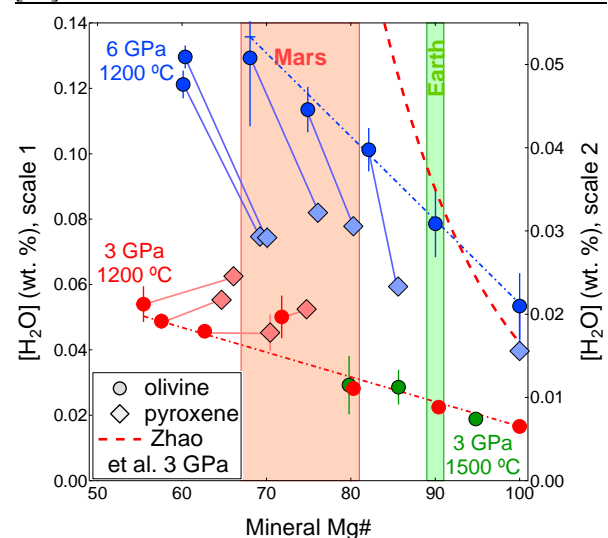

Fig. 1: Experimentally determined H_2O storage capacity in olivine and opx measured using SIMS, as a function of mineral Mg #. Absolute values are subject to considerable uncertainty owing to difficulty in establishing independent measurements of mineral standards. The left axis is based on mineral-specific FTIR analyses of standards [14,15] and applies to olivine and opx. The right axis shows an alternative scale for olivine, resulting from application of a general calibration [16] in FTIR measurements of olivine standards. Results in text are given by scale 1. Data are averages of up to 8 analyses. Solid lines connect olivine and opx analyses from the same experiment, and dot-dashed lines are linear fits to olivine data. The dashed line shows predicted concentration of H_2O in olivine based on 0.3 GPa data [17]. Ranges of Mg# expected for olivine of Martian and Earth mantles are shown as shaded regions.

$D_{H2O}^{ol/opx}$ increases from 0.93 at 3 GPa to 1.6 at 6 GPa, which is consistent with previous measurements of pressure dependence of H_2O in olivine and opx [18, 19]

Discussion: H_2O storage capacities in olivine at 3 and 6 GPa increase linearly with Fe content. This is in contrast to solubilities of H_2O measured at 300 MPa under oxidizing (Ni-NiO) conditions [17], which indicate that H_2O 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 H_2O 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 $D_H^{ol/liq}$ [20] H_2O will be slightly more compatible during mantle melting on Mars ($D_H^{ol/liq}$=0.01) as compared to Earth ($D_H^{ol/liq}$=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 $D_H^{ol/liq}$ for Mg# 75 would be ≈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 ($D_K^{ol/liq}$=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.

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