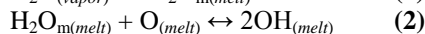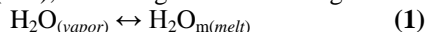SOLUBILITY AND DIFFUSIVITY OF H-BEARING SPECIES IN LUNAR BASALTIC MELTS. M. New-combe*[1], A. Brett[2], J. R. Beckett[1], M. B. Baker[1], S. Newman[1], and E. M. Stolper[1] [1]California Institute of Technology, Pasadena, CA 91125 USA [2]University of Cambridge, Cambridge, CB2 3EQ, UK *megan@gps.caltech.edu

Introduction: We have measured the solubility and diffusivity of water in silicate melts similar in composition to lunar magmas under conditions similar to those thought to exist on the Moon. Such measurements provide constraints on the conditions of generation and degassing of water-bearing lunar magmas [e.g. 1,2]. Despite extensive work on intermediate and silicic melts, measurements of water solubility, speciation, and diffusivity at low pressures are limited for basaltic melts [3,4], and essentially nothing is known for melts similar in composition to lunar basalts.

Speciation of "water" in lunar basalt: A silicate melt in equilibrium with a water-bearing vapor will dissolve water as molecular water (H_2O_m) and hydroxyl groups (OH), according to the following reactions [5]:

$$H_2O_{(vapor)} \leftrightarrow H_2O_{m(melt)} \qquad \textbf{(1)}$$
$$H_2O_{m(melt)} + O_{(melt)} \leftrightarrow 2OH_{(melt)} \qquad \textbf{(2)}$$

Reactions (1) and (2) can be combined to one governed by the following equilibrium constant (square brackets indicate concentration):

$$K_{eq}^{OH} \propto \frac{[OH_{(melt)}]^2}{pH_2O_{(vapor)} \cdot [O_{(melt)}]} \qquad \textbf{(3)}$$

If the concentration of reactive oxygens in the melt, $[O_{(melt)}]$, is ~constant, then at low pressures the concentration of hydroxyl groups in vapor-saturated melt is expected to be proportional to the square root of the partial pressure of water in the coexisting vapor:

$$[OH_{(melt)}] \propto \sqrt{pH_2O_{(vapor)}} \qquad \textbf{(4)}$$

$H_2O_{m(melt)}$ only becomes significant above ~0.5 wt. % total dissolved water [5], so at the low total dissolved water contents thought to be relevant to lunar basalts (<0.1–0.2 wt% [1, 2]), OH is the dominant dissolved species and thus eqn. (4) is expected to describe fully the solubility of water in lunar basaltic melts.

Here, we demonstrate the validity of eqn. (4) for a haplobasaltic melt and for a synthetic lunar basaltic melt over a range of pO_2 (from 10^{-13} to 10^{-7} atm) and pH_2/pH_2O (from 0.01 to 24), and we determine the constant of proportionality for this equation for both melt compositions. We also report a value for D_{water}^* (the apparent diffusion coefficient for total water [6]) at 1350°C and a pO_2 of IW+1.

Methods: *Solubility experiments:* We equilibrated a synthetic Apollo 15 yellow glass composition (AY) [7] and the 1-atm eutectic composition for the anorthite-diopside join ($An_{36}Di_{64}$) (AD) with flowing H_2-CO_2 gas mixtures at 1350°C and 1-atm total pressure

(P_{tot}). Concentrations of OH in quenched experimental glasses were measured by FTIR.

The initial H_2/CO_2 ratio of the gas mixture (R), fixes its equilibrium pH_2O, pO_2, pCO_2, and pH_2 in the furnace (Fig. 1); each of the two melt compositions was equilibrated with gas over a range of H_2/CO_2 ratios, and therefore over a range of pH_2O, pH_2, and pO_2. With decreasing R, pH_2 decreases monotonically, pCO_2 increases monotonically, and pH_2O shows a maximum at IW+0.3 (Fig. 1). Therefore, for any value of pH_2O (except at the maximum), there are 2 possible values of pH_2. We can exploit this feature of the system to determine the dependence (if any) of water solubility (and diffusivity; see below) on pH_2 and pO_2.
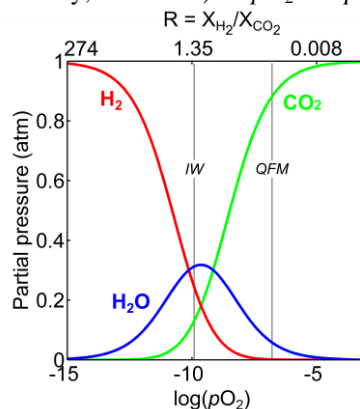

Fig. 1. Partial pressures of H_2, CO_2 and H_2O in vapor as functions of $\log(pO_2)$ at 1350°C and P_{tot}=1 atm. Top axis: R is the ratio of mole fractions of H_2 and CO_2 in the introduced gas mixture. Gray vertical lines are buffers (IW = iron-wüstite; QFM = quartz-fayalite-magnetite).

Diffusion experiments: OH concentration gradients were generated in a three-stage process: (1) AD melt in a 3.6 mm ID Pt crucible was fused at 1350°C and IW+1 for 70 hrs using a CO-CO₂ gas mixture. Charges equilibrated in this way contain <50 ppm water (as measured by FTIR). (2) With the sample still hanging in the furnace, the gas mixture was switched to a H_2-CO_2 mixture at IW+1, which fixed pH_2O and pH_2 (see Fig. 1). (3) After exposure to the H_2-CO_2 gas for 10 min (which generated a ~10^3 μm diffusion profile), the sample was quenched in deionized H_2O. The diffusively generated concentration gradient in the quenched glass was measured by FTIR.

Results: *Solubility experiments:* We conducted 10 experiments on AD (IW–2.3 to IW+3.4) and 7 experiments on AY (IW–3.0 to IW+3.0). OH was the only dissolved species detected in the quenched glasses,

although we looked for molecular H_2O (by FTIR) and H_2 (by FTIR and Raman). As predicted by eqn. (4), the concentrations of OH dissolved in both the AY and AD melts were proportional to $pH_2O^{1/2}$. Best fits to our data are

$$[OH_{AD}](ppm) = (685 \pm 13)\sqrt{pH_2O_{vapor}(atm)} \quad \textbf{(5)}$$

$$[OH_{AY}](ppm) = (691 \pm 15)\sqrt{pH_2O_{vapor}(atm)} \quad \textbf{(6)}$$

The fact that the proportionality constants are the same within error for AD and AY confirms that the solubility of water is not strongly dependent on melt composition. Moreover, the amount of dissolved OH depends only on pH_2O and is independent of pH_2 and pO_2 across the significant experimental range.

Diffusion experiment: Assuming D^*_{water} to be constant, we used equation (3.13) from [8] to fit the concentration profile from the single diffusion experiment reported here. This yielded a best-fit value for D^*_{water} for the AD melt at 1350°C and IW+1 of $2.2(\pm 0.4) \times 10^{-10}$ m^2/s.

Discussion: *Solubility:* Eqn. (6) can be used to determine pH_2O of vapor in equilibrium with lunar glasses and melt inclusions [1,2] at 1350°C. For example, a melt containing ~1400 ppm water (as observed in melt inclusions by [2]) would imply pH_2O ~4 atm. Assuming pO_2=IW−1 for lunar magmas [9], we can use the gas-phase reaction $H_2 + 0.5O_2 = H_2O$ and data of [10] to estimate pH_2 ~11 atm for this vapor. We can thus place a lower limit of ~15 atm on the entrapment pressure of lunar melt inclusions; the actual entrapment pressure will be higher if the entrapped melt was not vapor-saturated or (as is likely) other gaseous species (e.g, C- and S-bearing species) have significant partial pressures.

Diffusivity: D^*_{water} is known to be a strong function of the total dissolved water content of silicate melts at water contents above 0.1 wt% (e.g. [4,6]). Extrapolations of proposed functional forms for this concentration dependence for basaltic melts are compared with our result for AD melt in Fig. 2. Note that at water concentrations from 0.5–3 wt%, these functional forms for D^*_{water} are similar [4], but they diverge at low concentrations (Fig. 2). Under oxidized conditions (i.e., water dissolved only as water molecules and hydroxyl), [6] proposed that the concentration dependence of water diffusivity reflects low concentrations of mobile dissolved water molecules that react via eqn. (2) to produce immobile OH groups. Under the reducing conditions relevant to lunar petrogenesis, highly mobile, low-concentration, dissolved H_2 molecules could react via an oxidation-reduction reaction to generate immobile OH groups [12]. Or mobility and reactions

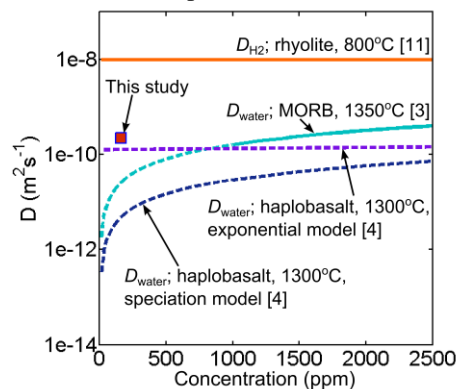among all three components could contribute to the observed concentration profiles in OH.

Fig. 2. Comparison of existing models of water and H_2 diffusivity with D^*_{water} determined in this study. Exponential and speciation model are taken from [4] and are fits to a haplobasalt experiment run at 1300°C. D^*_{water} from Zhang and Stolper [3] is based on fits of the speciation model to diffusive profiles in MORB (calculated at 1350°C). Dashed curves are extrapolations from fits to higher water concentration experiments. H_2 diffusivity from Gaillard et al [13] is a lower bound measured at 800°C in rhyolitic melt .

D^*_{water} determined in this study is ~10^1-10^2 times greater than D^*_{water} predicted by extrapolations of the speciation model that assumes mobile H_2O molecules (with constant D_{H2Om}) and immobile OH groups (Fig. 2). Possible explanations include: (1) The assumption of the speciation model that D_{OH}=0 may be incorrect, and the value of D^*_{water} as water concentration approaches zero would then reflect the mobility of OH [11]. (2) Rapid diffusion of small concentrations of dissolved H_2 followed by reaction of this H_2 with oxygen in the melt to form OH groups could lead to significant increases in D^*_{water} under highly reducing conditions [14]. However, the very low dissolved H_2 contents expected in experiments under the conditions of our experiment would likely require a value of D_{H2} much greater than currently available estimates [13]. Also, the absence of obvious species to react with dissolved H_2 in the Fe-free AD composition to generate OH argues against this. (3) The difference may reflect a strong temperature or compositional dependence of D^*_{water} at very low total water contents.

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