

HYDROGEN SPECIATION IN LOW f_{O_2} LUNAR MELTS. M. C. McCanta¹, M. J. Krawczynski², T. L. Grove³, and S. J. Seaman⁴. ¹Department of Earth and Ocean Sciences, Tufts University, Medford MA 02155 (molly.mccanta@tufts.edu), ²Dept. of Earth, Environmental & Planetary Sciences, Case Western Reserve, Cleveland, OH 44106, ³Dept. of Earth, Atmospheric & Planetary Sciences, M.I.T., Cambridge, MA 02139, ⁴Dept. of Geosciences, University of Massachusetts, Amherst, MA 01003.

Introduction: Recent lunar samples analyses [1-3] suggest that indigenous volatiles may have been present within the Moon, following accretion, at higher levels than previously known. These higher precision measurement techniques have discovered *in situ* hydrogen and other volatiles in multiple lunar melts at levels commensurate with what is expected for the depleted terrestrial mantle (MORB source). In addition, Lunar Reconnaissance Orbiter (LRO) measurements indicate the presence of volatiles on and within the current lunar surface [e.g., 4]. These data have challenged the paradigm of a dry evolution of the Moon and established the fact that small concentrations of volatiles are present in lunar materials.

Effects of hydrogen speciation on silicate melt physical properties. The potential effect of volatiles on magmatic processes is great. The properties of silicate melts such as density [5], viscosity [6], and diffusivity of hydrogen [7] are all strong functions of the total concentration and speciation of hydrogen. Addition of small amounts of hydrogen to a magma source region induces a lowering of melting temperature [8], changes in liquid line of descent, variations in mineral composition (e.g., [9]), and variations in magma transport properties and eruption style (e.g., [7,8]). However the magnitude of these effects will to some extent be determined by the way hydrogen is speciated within the lunar melts at these low concentrations and lunar oxygen fugacities (several orders of magnitude lower than terrestrial values).

In order to determine the effects that volatiles may have on lunar magmatic properties, hydrogen speciation must be constrained. Hydrogen speciation is a function of total dissolved hydrogen content, f_{H_2} , and melt chemistry [10,11]. At low hydrogen concentrations in terrestrial settings, hydrogen is speciated mainly as OH⁻, while at higher concentrations molecular water becomes dominant (Fig. 1) [12]. [10] has showed that at low oxygen fugacities (near the iron-wüstite buffer) hydrogen can be incorporated in the melt through CH₄, and H₂ species as well.

The behavior of a melt dominated by molecular water should be different than one dominated by OH⁻; determining the ratio of coexisting hydrogen-bearing species is important in predicting potential effects on melt physical parameters as described above. Additionally, the effects of hydrogen on melt properties, such as viscosity, are most pronounced at low concen-

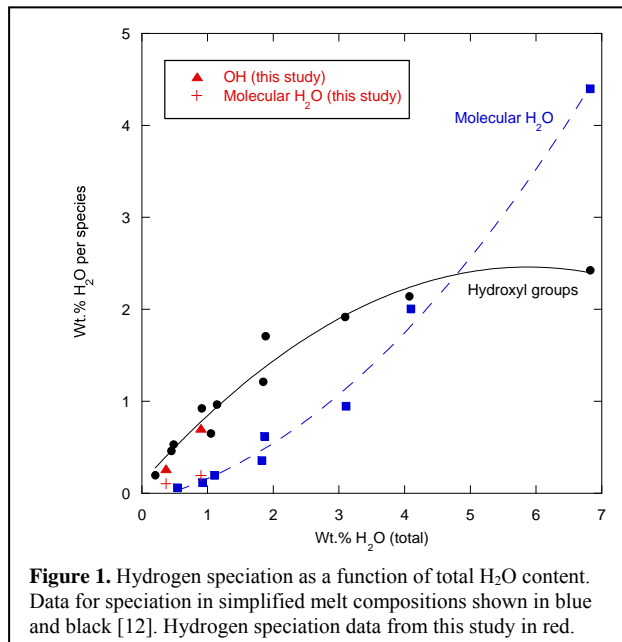


Figure 1. Hydrogen speciation as a function of total H₂O content. Data for speciation in simplified melt compositions shown in blue and black [12]. Hydrogen speciation data from this study in red.

trations [12] and the rate of change of these properties decrease as total H₂O increases. Lunar magmas now appear to have low hydrogen concentrations in the range where small uncertainties in the overall amount could have large effects on the physical properties.

Hydrogen speciation appears correlated with f_{O_2} [10,11], however melt composition will also play a role, and experiments on lunar-relevant silicate melt compositions have not been carried out. Due to the renewed interest in hydrous magmatic processes on the Moon, an evaluation of hydrogen speciation and controls on its behavior in primitive lunar basalt compositions and under lunar-specific f_{O_2} conditions seems warranted.

Experimental and Analytical Methods: Starting compositions of high-Ti Apollo 17 orange glass and Apollo 15 green glass were synthesized from reagent grade oxides, silicates, and metals. Hydrogen was added to the experiments through addition of small amounts of deionized water added to each sample prior to insertion into the piston cylinder assembly. The sample capsules were sealed using cold compression in the piston cylinder apparatus; no welding was required to minimize water loss prior to the run. Experimental runs were completed in the MIT piston cylinder lab at temperatures and pressures necessary to be above the previously determined liquidus, with f_{O_2} conditions

controlled by the capsule material (graphite: IW+1.5 or Fe: IW-2.1 [13]) (Table 1). These values bracket the estimated oxygen fugacity of the lunar orange glass source region of IW-0.6 [14]. Run duration was 12 hours. We used a pressure-quenching technique where the piston load was dropped at the same moment the power was shut off to the experiment to minimize quench crystal formation during cooling of the experiment [15].

Hydrogen speciation has so far been quantified with Fourier transform infrared spectroscopy of doubly polished glass slices at the University of Massachusetts using a Bruker Vertex 70 spectrometer with a Hyperion 3000 microscope. The hydrogen contents in these experiments are somewhat higher than those predicted for the lunar interior, but are lower than vapor saturation, and likely representative of H speciation at f_{O_2} and pressure/temperature conditions relevant in the mare basalt source regions.

Table 1. Experimental run conditions.

	Starting Glass Composition	Container Type	P (kbar)	T (°C)
C453	Orange	Fe-metal	27	1550
C455	Green	Fe-metal	20	1550
C456	Orange	Graphite	25	1550
C457	Green	Graphite	20	1550

Results: All experimental run products contained glass + some amount of quench crystals consisting of nominally anhydrous phases (i.e., olivine). Experiments C453, C455, and C456 contained large glass pools that were of sufficient size for FTIR analysis. The quench crystals were too pervasive in C457 for analysis.

The low f_{O_2} experiments C453 and C455 contained total water concentrations of 3623-3717 and 8780-9503 ppm, respectively. In both runs OH was the dominant water species (Figs. 1,2), although molecular water was more prevalent in the orange glass run. Analyses are ongoing to characterize the water speciation in the higher f_{O_2} (graphite capsule) lunar melts.

Discussion: FTIR is most accurate for measuring the molecular water and hydroxyl species in the melt. At the low water contents in these experiments, the dominant species of these two is OH⁻. However our initial results indicate that molecular water is more stable as a hydrogen bearing melt species in lunar melts relative to their terrestrial counterparts (Fig. 2) though some of the offset at the lowest total water values may be because analytical errors associated with these measurements are high.

One example of a homogeneous equilibrium reaction controlling the melt hydrogen species and f_{O_2} is:

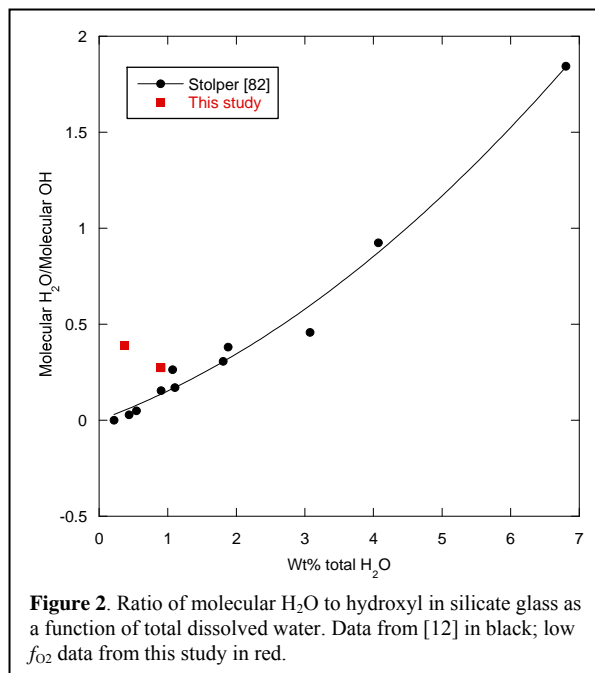
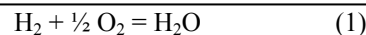


Figure 2. Ratio of molecular H₂O to hydroxyl in silicate glass as a function of total dissolved water. Data from [12] in black; low f_{O_2} data from this study in red.



and controlled by the equilibrium constant

$$K = f_{H_2O}/f_{H_2}f_{O_2}^{0.5} \quad (2)$$

This relationship can be used to calculate the melt f_{H_2} utilizing a K value of 10^5 at $T=1300^\circ\text{C}$ [16], the experimental f_{O_2} ($\sim 10^{-10}$ bars), and f_{H_2O} determined by the measured water contents. This results in a f_{H_2} between 1 and 50 bars. If we carry out the calculation over a range of f_{H_2O} , we see that under these low f_{O_2} conditions f_{H_2} and f_{H_2O} are equal. This is similar to the findings of [17] who suggest that f_{H_2} must be $\geq f_{H_2O}$ under low f_{O_2} , high temperature conditions.

Future Work: To better constrain the relationship between hydrogen speciation and f_{O_2} , the higher f_{O_2} orange glass graphite capsule experiment (C456) will be analyzed for hydrogen speciation. Additional graphite runs are planned for the green glass composition as well. Resolution of carbon speciation (i.e., CH₄, CO₂) in these experiments is on-going.

References: [1] Saal et al. (2008) *Nature* 454, 192-195. [2] Hauri et al. (2011) *Science* 333, 213-25. [3] McCubbin et al. (2010) *Am.Min.* 95, 1141-1150. [4] Mitrofanov et al. (2010) *Science* 330, 483-486. [5] Ochs & Lange (1999) *Science* 283, 1314-1317. [6] Bottinga & Weill (1970) *Am.J.Sci.* 269, 169-182. [7] Zhang & Behrens (2000) *Chem.Geol.* 169, 243-262. [8] Hirth & Kohlstedt (1996) *EPSL* 144, 93-108. [9] Goldsmith (1982) *Am.Min.* 67, 653-675. [10] Mysen and Yamashita (2010) *GCA* 74, 4577-4588. [11] Mysen et al. (2011) *GCA* 75, 6183-6199. [12] Stolper (1982). *GCA* 46, 2609-2620. [13] Krawczynski and Grove (2012) *GCA* 79, 1-19. [14] Sato (1979) *PLPSC* 10, 311-325. [15] Putirka et al. (1996). *CMP* 123, 92-108. [16] Wagman et al. (1945) *J.Res.Natl.Bur.Stand.* 34, 143-161. [17] Elkins-Tanton and Grove (2011) *EPSL* 307, 173-179.