THE SOLUBILITY AND SPECIATION OF CARBON IN LUNAR PICRITIC MAGMAS. D. T. Wetzel[1], S. D. Jacobsen[2], M. J. Rutherford[1], E. H. Hauri[3], and A. E. Saal[1], [1]Dept. of Geological Sciences, Brown University, Providence RI 02912 (Diane_Wetzel@brown.edu) , [2]Dept. of Earth and Planetary Sciences, Northwestern University, Evanston, IL 60208 (steven@earth.northwestern.edu), [3]DTM Carnegie Institute of Washington, DC 20015 (hauri@DTM.ciw.edu).
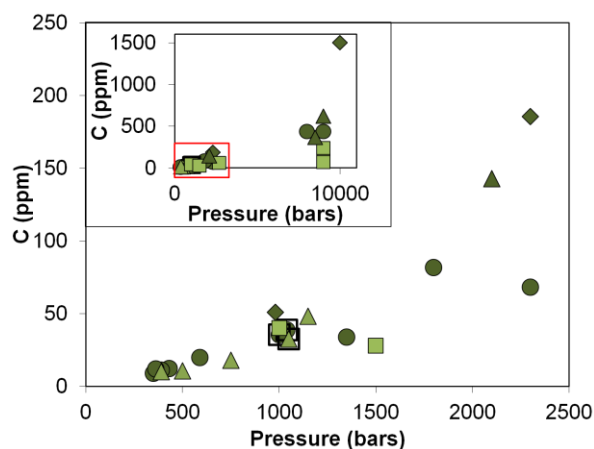
Introduction: In the absence of hydrogen, carbon is likely responsible for generating the gas phase that drove lunar fire-fountain eruptions [1,2]. A CO-rich gas phase is thought to be generated by the oxidation of C coupled by Fe reduction in lunar magmas, supported by the discovery of Fe-metal in natural samples [3]. Recent experiments confirm that C forms a CO-rich gas phase in lunar picritic magmas at 40 MPa (~8.5km) [4]. Recently, however, Saal et al. [6] identified indigenous H, F, Cl, and S in a range of picritic glass compositions. Concentrations were found as residual diffusion-loss profiles in the lunar beads, which led to estimates for initial lunar volatile abundances. The discovery of H in the lunar beads requires a study of how H may alter the composition of the gas phase. Our study was designed to determine the solubility and speciation of carbon in H-bearing, graphite-saturated picritic lunar magmas, and the effect of H on the initial gas phase generated in these magmas at liquidus temperatures.

Experimental and analytical methods: Experiments on synthetic A15 green glass compositions were carried out in an IHPV at Brown University. Samples were run with excess graphite in sealed Pt tubes as described by [4]. A set of experiments were buffered by adding Fe metal or $Fe_{80}Ni_{20}$ metal to the starting material. The rest of the experiments were buffered by graphite (fO_2~IW-1.5 to IW+1.5 for P=0.4-10 kbars). The metal bearing experiments are more reduced compared to the graphite buffered experiments at high pressures (8-10 kbars). Temperatures were held at 1465°C, or ~15°C above the green glass liquidus T, at lower pressures and 1500°C for higher pressures (>8 kbars). Pressures ranged from 0.4-10 kbars. Samples were quenched to a glass and analyzed by EMP, SIMS, XANES, FTIR, and Raman spectroscopy.

Results: Volatile abundances were determined by SIMS for all glass samples. Carbon concentrations ranged from 10-1500ppm and correlated with pressure (Fig. 1). The reduced samples (Fe metal buffer) contained up to 240ppm C while more oxidized samples (graphite only buffer and $Fe_{80}Ni_{20}$ metal) contained between 440 and 1500ppm C, depending on the amount of dissolved H_2O.

Raman and FTIR spectroscopy indicates the presence of several C and H species (Fig. 2 and 3). As seen by peaks at ~1430 and 1530 cm^{-1} in FTIR, oxidized

samples contain carbonate, whereas the reduced samples do not. All samples have O-H peaks at 3550 cm^{-1} in both FTIR and Raman. Reduced samples analyzed by Raman have peaks associated with C species located at 2110, 2900, and possibly 3270 cm^{-1}. Oxidized samples do not have C peaks in Raman. GG-14 is the only sample to contain H_2 (4110 cm^{-1}).

Fig. 1. SIMS carbon concentrations measured for the glasses show a positive correlation with pressure. The inset graph shows the full range of data. The green circles are experiments buffered by graphite. The green triangles are experiments buffered by $Fe_{80}Ni_{20}$ metal and the light green squares are buffered by Fe metal. The light green triangles are experiments with dried graphite (minimal H), diamonds are run with 1-2 wt% added H_2O, and the black square outlines are reversals.

Discussion and Conclusions: Analyses of the natural lunar samples [3] and our experimental green glasses suggest the formation of a CO-rich gas phase via C-oxidation at P< 40 MPa due to Fe metal present in these melts. However, the speciation of C in picritic melts depends on fO_2. With hydrogen present, Raman spectroscopy indicates C-H species are dissolved in the reduced (Fe-metal) melts (peaks at 2900 and 3270 cm^{-1}). The reduced melts also contain a Raman peak at 2110 cm^{-1}, which is either due to molecular C-O or a metal ligand C-O species such as Fe-carbonyl. The more oxidized samples contain carbonate, as seen by the carbonate doublets in FTIR. Both FTIR and Raman

indicate that most of the hydrogen seems to be speciated as O-H in all.

The carbon abundance is dependent on pressure as well as fO_2. Carbon dissolved in the melt increases with increasing pressure, independent of fO_2. However, as seen by the high pressure experiments, the oxidized melts can have between 2-8 times more C dissolved than reduced melts. A relationship between amount of dissolved carbonate and water may also be possible as seen by the range of 440 and 1500 ppm C corresponding to increased water content.

The determination of C species in the melts is important for considering the composition of the first gas phase produced. If decompression-induced CH-gas saturation is reached at pressures greater than 40 MPa, methane could produce the first gas phase. These results are consistent with experiments on Na-silicate [7,8] and haplobasaltic [9] melts that indicate CH_4 dissolved in melts at $fO_2 \sim IW-1$. However, more oxidizing conditions will result in the degassing CO/CO_2 and possibly H_2O if decompressed enough. More oxidizing experiments on Na-silicate [8] and haplobasaltic[10] melts contain carbonate and are also consistent with this possible first gas phase. At reducing conditions, thermodynamic models [11] predict a CH_4- and H_2-rich gas phase in equilibrium with a melt at higher pressures and CO-rich gas phase at lower pressures (near 40 MPa C oxidation reaction).
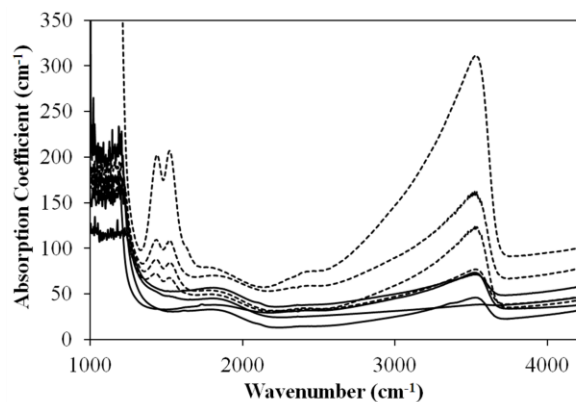
Fig. 2.   FTIR spectra of oxidized (gray dashed lines) and reduced (black solid lines) high pressure (8-10 kbars) glass samples with 1 low pressure (1.5 kbar) sample. All samples have O-H peak at 3550 cm^{-1}. Only oxidized glasses contain carbonate, as seen by the carbonate doublet at ~1430 and 1530 cm^{-1}.
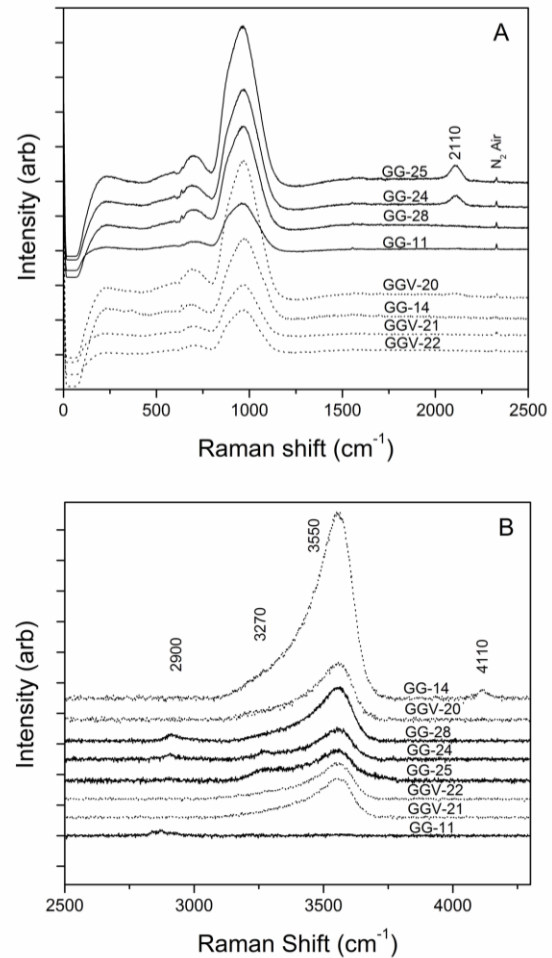
Fig. 3.   Raman spectra obtained for the same oxidized (gray dashed lines) and reduced (black solid lines) glass samples as in Fig. 2. All samples were quenched at 8-9 kbars except GG-14 (10 kbars) and GG-11 (1.5 kbars). The low wavenumber region (A) contains C-O peak at 2110 cm^{-1}. The high wavenumber region (B) contains O-H peak at 3550 cm^{-1}, C-H peaks at 2900 and 3270 cm^{-1}, and H_2 peak at 4110 cm^{-1}.

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