

SOLUBILITY OF C-O-H VOLATILES IN GRAPHITE-SATURATED MARTIAN BASALTS. B. D. Stanley and M. M. Hirschmann, Dept. of Earth Sciences, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, MN, 55455 (stan0525@umn.edu).

Introduction: Evidence for standing liquid water on the ancient Martian surface [e.g. 1] requires the presence of a thick greenhouse atmosphere not present on Mars today. Yet there remains considerable uncertainty as to how this greenhouse was created and maintained, and how it evolved to the current thin, modern atmosphere. A key constraint in Martian atmospheric evolution is the source region conditions of magma melting. The stable phase of carbon in a reduced Martian mantle is likely to be graphite [2]. In graphite-saturated silicate melts Holloway et al. [3, 4] showed that oxygen fugacity (f_{O_2}) is related to CO_2 solubility, as an order of magnitude increase in f_{O_2} changes the amount of CO_2 dissolved in the melt by one order of magnitude. A reduced, graphite-saturated Martian mantle is likely to have insignificant dissolved CO_2 , making it implausible for an early greenhouse atmosphere to be primarily CO_2 . This study investigates the extraction of C-O-H volatiles from the Martian mantle by determining the concentrations these volatiles as a function of f_{O_2} in graphite-saturated melts of Martian composition.

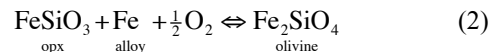
Experiments: Experiments were performed using Pt-graphite double capsules in a half-inch, end-load piston cylinder apparatus under hot piston-in conditions. To crystallize all desired phases, experiments were run for 24 h at 1.0 GPa and 1340-1355 °C. Apart from drying the MgO spacers overnight, no other steps were taken to ensure a nominally anhydrous charge.

Starting materials were created to produce appropriate model Martian liquid and mineral phase compositions (Fig. 1). In an effort to crystallize olivine and pyroxene along with a melt phase we added 15 wt.% of Martian composition olivine and pigeonite (compositions from [5]) to our Humphrey basalt composition (see [6] for more details on Humphrey). To investigate the effect of f_{O_2} , we added variable amounts of reduced and oxidized Humphrey basalt, thereby varying the ratios of Fe_2O_3/FeO in the silicate mix. No CO_2 was added to these starting materials. Graphite-saturated melts beginning with high Fe_2O_3 yield CO_2 -bearing liquids, owing to the reaction



[3, 4]. At the low oxygen fugacities imposed by graphite saturation virtually all the Fe_2O_3 will convert to FeO [7].

A $\sim 1 \mu m$ long piece of Pt wire was added to each experiment. These become FePt alloys during the experiment allowing *a posteriori* evaluation of f_{O_2} through thermodynamic analysis of the equilibrium reaction between FePt alloy, olivine, and orthopyroxene



using measured compositions of the phases and thermodynamic models for FePt alloy, orthopyroxene, and olivine [8].

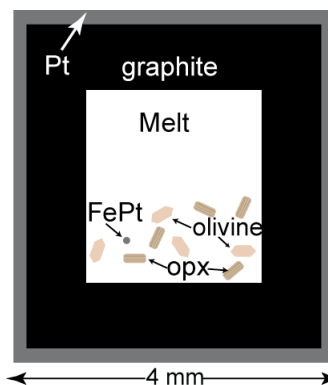


Figure 1. Cartoon of the capsule design of the project.

After the experiment, capsules were sectioned with a 50 μm diameter tungsten wire saw. Experiment products consist of glass, orthopyroxene, olivine, and FePt alloys (Fig. 2). One half was polished and mounted for compositional analysis with the JEOL JXA8900R electron microprobe at UMN. The other half of each experiment was double polished to a thickness of less than 150 μm and analyzed for CO_3^{2-} using a Bruker Tensor 37 FTIR bench and Hyperion 2000 microscope at the UMN Experimental Petrology Laboratory.

Results: Electron microprobe analyses of FePt alloys and coexisting silicates indicated little variation in f_{O_2} with changes in the amounts of reduced and oxidized Humphrey (see Fig. 3). All produced conditions similar to CCO. We surmise that even the reduced mixture had a Fe^{3+}/Fe^T ratio comparable to that in equilibrium at CCO, and so all produced conditions similar to that buffer. When 2.5 wt.% Fe metal was added to the starting material the f_{O_2} dropped almost an order of magnitude. Examination of the charge showed no visible Fe metal.

FTIR analyses of experimental glasses indicates CO_2 dissolved only as CO_3^{2-} , as expected for mafic silicate glasses [9]. Measured CO_2 solubilities are plotted versus $f\text{O}_2$ (relative to the iron-wüstite buffer, IW) in Fig. 3. In these preliminary results, $f\text{O}_2$ is analyzed after the experiment by measuring the Fe content of the glass and applying the FePt alloy model of Medard et al. [10].

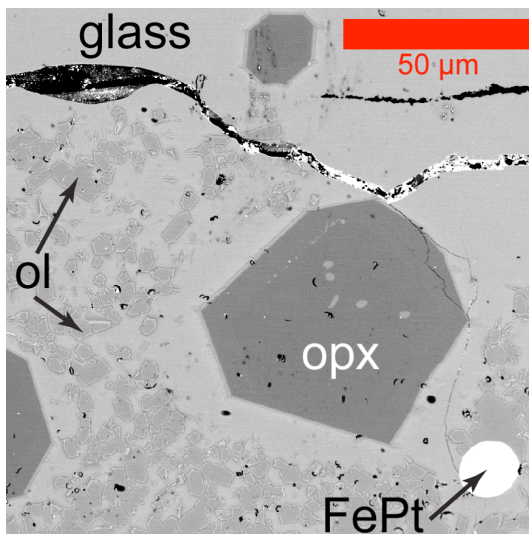


Figure 2. Back-scattered electron (BSE) image of B379 (1355 °C, 1.0 GPa, 50-50 mixture of oxidized and reduced Humphrey basalt in the starting material).

Discussions and Applications: Our preliminary results show that the CO_2 solubility in synthetic Humphrey basalt follows the relationship between $f\text{O}_2$ and CO_2 solubility predicted by Holloway et al [3, 4](Fig. 3, red line). These experiments give direct experimental evidence of the concentrations of CO_2 dissolved in graphite-saturated Martian magmas at low $f\text{O}_2$.

These results are in agreement with previous estimates by the authors [6]. In a reduced, graphite-bearing Martian mantle representative basalts have CO_2 contents of 54 ppm at IW, and 540 ppm at one order of magnitude above IW (IW+1) at conditions similar to experiments (1340 °C, 1.0 GPa)(Fig. 3). For expected magmatic fluxes over the last 4.5 Ga of Martian history [2], magmas similar to Humphrey (melting at predicted source region conditions of 1350 °C and 1.2 GPa) would only produce 0.03 and 0.26 bars from sources at IW and IW+1 respectively. Therefore the Martian mantle is likely incapable of degassing sufficient CO_2 to sustain a thick greenhouse atmosphere in the Late Noachian. Therefore, models of Martian atmospheric evolution considering only the greenhouse

effects of CO_2 should be reexamined and additional volatiles such as SO_2 and CH_4 should be considered.

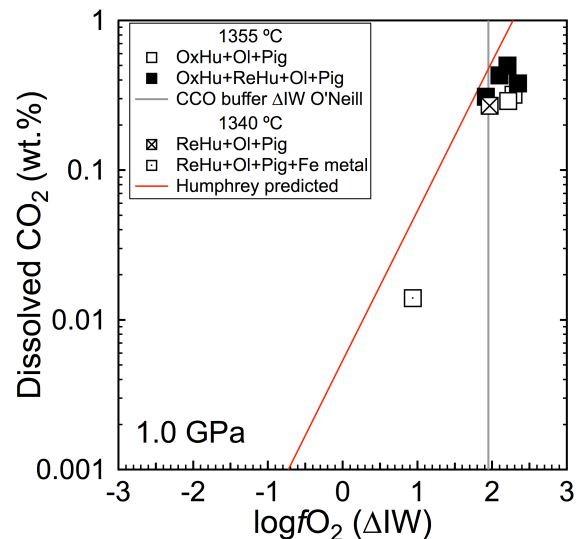


Figure 3. Plot of $\log f\text{O}_2$, relative to IW ([11] with pressure term from [12]), versus dissolved CO_2 after the experiment. Data from experiments is listed with the components mixed to create the starting material: OxHu – oxidized Humphrey basalt; ReHu – reduced Humphrey basalt; Ol – olivine; Pig – pigeonite. Olivine and pigeonite compositions are from phase equilibria experiments on Humphrey composition [5]. The Humphrey predicted line is the $\log f\text{O}_2$ versus CO_2 solubility line predicted for graphite-saturated Humphrey melts using fitting parameters from [6] at 1340 °C and 1.0 GPa. The CCO buffer [13] is plotted at 1355 °C, 1.0 GPa for reference.

References: [1] Grant J.A. et al. (2011) *Icarus*, 212, 110-122. [2] Hirschmann M.M. and Withers A.C. (2008) *Earth Planet. Sc. Lett.*, 270, 147-155. [3] Holloway J.R. (1998) *Chem. Geol.*, 147, 89-97. [4] Holloway J.R. et al. (1992) *Eur. J. Mineral.*, 4, 105-114. [5] Filiberto J. et al. (2008) *Meteorit. Planet. Sci.*, 43, 1137-1146. [6] Stanley B.D. et al. (2011) *Geochim. Cosmochim. Acta*, 75, 5987-6003. [7] Kress V.C. and Carmichael I.S.E. (1991) *Contrib. Mineral. Petr.*, 102, 82-92. [8] Kessel R. et al. (2001) *Am. Mineral.*, 86, 1003-1014. [9] Blank J.G. and Brooker R.A. (1994) in *Volatiles in Magmas*, pp. 157-186. [10] Médard E. et al. (2008) *Am. Mineral.*, 93, 1838-1844. [11] O'Neill H.S.C. (1988) *Am. Mineral.*, 73, 470-486. [12] Huebner J.S. (1971) in *Research Techniques for High Pressure and High Temperature*, pp. 123-177. [13] Frost D.J. and Wood B.J. (1997) *Geochim. Cosmochim. Acta*, 61, 1565-1574.