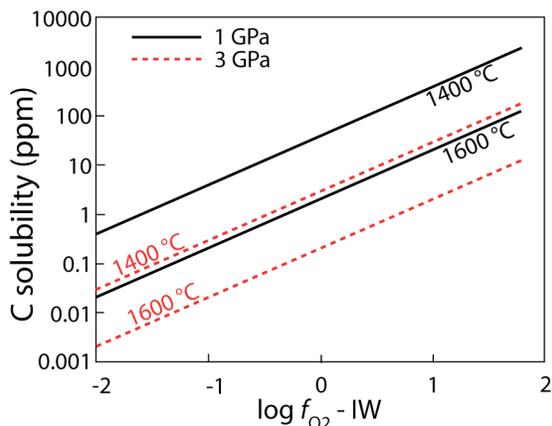


**PRELIMINARY INVESTIGATIONS OF METHANE SOLUBILITY AT REDUCED CONDITION IN A HAPLOBASALTIC LIQUID, WITH APPLICATIONS TO MAGMA OCEANS.** P. Ardia<sup>1</sup> and M.M. Hirschmann<sup>1</sup>,

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**Introduction:** Oxygen fugacity may have a critical influence on the solubility of volatile components in silicate magmas, which will in turn influence partitioning of volatiles between magma oceans and overlying atmospheres and the sequestration of volatiles in the crystallizing mantle. Experimental data suggest that carbon dissolves in mafic silicate melts chiefly as a carbonate ion [1]. However, both experimental data and thermodynamic calculations show that the solubility of carbonate in magmas becomes very low under reducing conditions, owing to graphite or diamond precipitation [2-3]. Thus, at conditions appropriate for equilibration with Fe metal, the solubility of carbon as carbonate ion is not more than a few ppm at conditions of likely for equilibration with Fe-rich metal (~IW-1 or IW-2) (Fig. 1). Under these reduced conditions, most of the carbon in the magma ocean portion of the planet would precipitate as graphite or diamond (or carbide or as an alloy with metal), possibly leading to sequestration in the solidifying mantle or core. Thus, if carbon is soluble in magma only as carbonate, then in a reduced magma ocean, much of the carbon is not volatile and is not available to be degassed into the atmosphere.



**Figure 1.** Calculated solubility of C in Hawaiian tholeiitic basalt at 1 and 3 GPa and 1400 and 1600 °C for graphite-saturated conditions as a function of oxygen fugacity based on [2,3]. For conditions similar to that in equilibrium with metallic iron alloy (~IW-1-IW-2), the C solubility is extremely low. Thus, either magma oceans will become saturated in C-rich solids (graphite, diamond, carbide, C-rich alloy), thereby limiting venting of C to the atmosphere, or other species such as CH<sub>4</sub> dominate C solubility under reduced conditions.

Experimental data show that carbon monoxide is not appreciably soluble [4]. Similarly, several experimental studies have sought, and failed to find measurable solubility of methane or related species [5,6]. Recently, Mysen et al. [7] reported up to 0.5 wt.% CH<sub>4</sub> solubility in sodium silicate melts at pressures ranging from 1 to 2.5 GPa. It is unclear why these results do not agree with previous experimental studies and it is not certain whether solubility of CH<sub>4</sub> in sim-

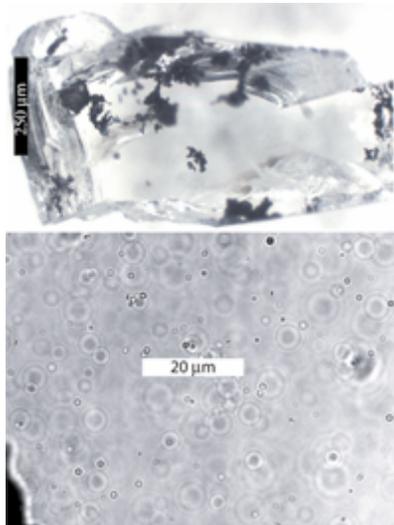
ple Na<sub>2</sub>O-SiO<sub>2</sub> melts applies to natural systems. Also, Mysen et al. [7] detected no appreciable pressure dependence to the solubility of CH<sub>4</sub> over the range of pressures investigated (1-2.5 GPa), which, to our knowledge, is distinct from the behavior of any other volatile in magmas. However, the key point is that under reducing conditions, even modest solubility of CH<sub>4</sub> or other reduced C-O-H species may exceed that of carbonate. Even if very small solubilities are found, they could well be greater than the solubility of carbonate in magma oceans close to equilibrium with metal. To better understand the role of dissolved C-O-H components in magma oceans, we conducted experiments of C-O-H fluid species under reducing conditions.

**Methods:** We investigated the solubility of C-O-H fluids in a model basalt composition (Di<sub>40</sub>An<sub>42</sub>Ab<sub>18</sub>), adding 1 wt.% C in the form of Si<sub>5</sub>C<sub>12</sub>H<sub>36</sub> + H<sub>2</sub>O to produce SiO<sub>2</sub> + CH<sub>4</sub> + H<sub>2</sub>. We also added 0.5 wt.% V<sub>2</sub>O<sub>5</sub> to monitor oxygen fugacity. Experiments were conducted in a piston cylinder apparatus at 1.5-2.5 GPa and 1450-1515 °C and experimental durations from 5 min to 6 h. To buffer oxygen fugacity, we employed a Pt double capsule with Fe+FeO+H<sub>2</sub>O in the outer capsule. The experimental glasses were analyzed by electron microprobe to verify major element compositions. To observe qualitative volatile concentrations and speciation, we employed Raman spectroscopy, using a Witec confocal Raman spectrometer, an Argon ion laser with 514.5 nm excitation, power up to 540 mW and an optical resolution of 250x500 nm. Preliminary quantitative analyses of C have been conducted using Rutherford backscattering (RBS). Verification of the oxidation state of the glasses via V XANES oxybarometry [8] is planned.

**Results:** Glasses quenched from 30 min experiments are transparent and contain equilibrium bubbles from 10 to 250 μm in diameter as well as dendritic black precipitates (Figure 2). Raman spectroscopy of the precipitates reveals peaks at ~1350 cm<sup>-1</sup>, ~1600 cm<sup>-1</sup>, ~2450 cm<sup>-1</sup>, and 2700 cm<sup>-1</sup>, consistent with C-nanotubes or fibers. A second population of bubbles, 1-2 μm in diameter are homogeneously distributed throughout the charge together with μm-sized black precipitates (Fig. 2). These are interpreted as quench features. Glasses quenched from 2-6 hour experiments show increasing growth of equilibrium bubbles (up to 1 mm) and segregation of these bubbles to the top of the capsule, with corresponding segregation of the carbon nanofibers to the capsule top. The longer experiments lack quench bubbles, but quench precipitates persist. The addition of 3 wt.% water to the starting material results in clear glass with a smaller number of C nanofibers.

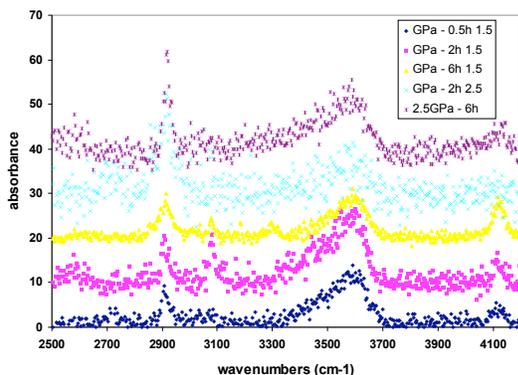
The quench bubbles contain chiefly of CH<sub>4</sub> (~2900 cm<sup>-1</sup>) with a smaller amount of a CH<sub>3</sub><sup>-</sup> species (~3070 cm<sup>-1</sup>) and are seemingly devoid of water or H<sub>2</sub>. Analyses of glasses indicate dissolved CH<sub>4</sub>, H<sub>2</sub>O and H<sub>2</sub> (Figure 3) and in longer duration experiments (2, 6 h), dissolved CH<sub>3</sub><sup>-</sup>. With time, the relative peak heights of CH<sub>4</sub> change little, that of H<sub>2</sub> increases slightly, OH<sup>-</sup> increases noticeably and H<sub>2</sub>O slightly

decreases. For the H<sub>2</sub>O-added experiments, quench bubbles have two distinct compositions indicating the presence of CH<sub>4</sub>, CH<sub>3</sub><sup>-</sup> and H<sub>2</sub> or just H<sub>2</sub>O. The glass has dissolved water and CH<sub>3</sub><sup>-</sup> and minor amounts of CH<sub>4</sub> and H<sub>2</sub>. Preliminary RBS analyses of a single experiment at 1.5 GPa and 1450 °C suggest a total (CH<sub>4</sub>+CH<sub>3</sub>) solubility of 0.21 wt.%.



**Figure 2.** Optical photograph (top) and micrograph (bottom) of glass fragment experimental charge quenched from 1450°C and 1.5 GPa for 2 h. Dark precipitates (top image) correspond to segregations of carbon nanofibers. The lower image shows the quench dendritic black precipitates. They appear similar to bubbles, but a closer inspection reveals nanofiber textures.

The changes in dissolved volatiles and in the occurrence of quench bubbles suggest that the oxygen fugacity in the melt evolves as the IW buffer is imposed gradually on the inner capsule. These changes result in evolving vapor composition and dissolved volatile speciation and concentrations. The carbon nanofibers indicate that the charges are close to graphite saturation.



**Figure 3.** Raman spectra of haplobasaltic glasses quenched from 1.5 and 2.5 GPa, showing absorbances of CH<sub>4</sub> (2900 cm<sup>-1</sup>), CH<sub>3</sub> (3035 cm<sup>-1</sup>), OH<sup>-</sup> (3600 cm<sup>-1</sup>), and H<sub>2</sub> (4100 cm<sup>-1</sup>) species dissolved in glass. Note that CH<sub>4</sub> absorbances at 2.5 GPa are approximately twice as great as at 1.5 GPa.

**Discussion** The experiments clearly document that reduced CH<sub>4</sub>+CH<sub>3</sub> species are soluble in mafic magmas. Though more work is required to quantify these solubilities and to document equilibrium between vapor, melt and the external *f*O<sub>2</sub> buffer, it is highly probable that methane solubility exceeds that of carbonate at reducing conditions relevant to magma oceans close to equilibrium with metal. Thus, solubilities of reduced carbon species in magma oceans may well control the exchange of carbon between magma oceans and early atmospheres if the shallow magma ocean is reduced. However, they may also control this exchange even if the shallow portions of the magma ocean are comparatively oxidized [9], so long as the deeper parts of the magma ocean are reduced. Equilibration between the atmosphere and the shallow magma ocean would implant small amounts of carbon into the magma. Convection could then deliver that magma to the deeper parts of the magma ocean, where auto-reduction owing to self-compression would then cause precipitation of a C-rich solid (graphite, diamond, carbide, or alloy). This could work as a carbon pump, sequestering C from the atmosphere into the deep parts of the mantle, even if the absolute solubilities of C in the magma are low. Evaluation of the efficacy of this process requires further quantitative characterization of the solubility of reduced C species in magmas.

**References:** [1] Blank and Brooker (1994) *Rev. Mineral.* 30, 157-186. [2] Holloway J. R. et al. (1992) *Eur J Mineral.* 4, 105-114. [3] Hirschmann M. M., and Withers A. C. (2008) *EPSL*, 270, 147-15 [4] Pan V. et al. (1991) *GCA*, 55, 1587-1595. [5] Taylor, W.R. and Green, D.H. (1987) *Geochem. Soc. Spec. Pub. 1* 121-138. [6] Kadik, A. et al. (2004) *J. Petrol.* 45, 1297-1310. [7] Mysen, B.O. et al. (2009) *GCA* 73, 1696-1710. [8] Sutton, S.R. et al. (2005) *GCA* 69, 2333-2348. [9] Hirschmann, M.M. (2010) *LPSC this meeting*.