

METHANE SOLUBILITY UNDER REDUCED CONDITIONS IN A HAPLOBASALTIC LIQUID. P. Ardia¹, A.C. Withers¹, and M.M. Hirschmann¹, ¹University of Minnesota (Dept. of Geology and Geophysics 108 Pillsbury Hall, Minneapolis, MN 55455), Richard L. Hervig², Arizona State University (School of Earth and Space Exploration, Tempe, AZ 85287).

Introduction: Oxygen fugacity has a critical influence on the solubility of volatile components in silicate magmas, which in turn influences fluxes of volatiles from planetary interiors to their atmospheres. 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, for reduced conditions such as those that may prevail in parts of the martian mantle or those relevant to early planetary conditions when Fe-metal may have been present, the solubility of carbon as carbonate ion is not more than a few ppm (~IW-1 or IW-2). If carbonate is the only C-bearing species soluble in magmas under reducing conditions then the C volatility is exceedingly low and C degassing to the atmosphere extremely limited.

Carbon monoxide, and methane are the major fluid C species at reduced conditions [4]. However, experimental data show that CO is not appreciably soluble [5]. Similarly, several experimental studies sought, and failed to find measurable solubility of methane or related species [6,7]. Recently, Mysen et al. [8] reported up to 0.5 wt.% CH₄ 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 CH₄ in simple Na₂O-SiO₂ melts applies to natural systems. Also, Mysen et al. [8] detected no appreciable pressure dependence to the solubility of CH₄ 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 CH₄ or other reduced C-O-H species could exceed that of carbonate. Even if very small solubilities are applicable, they could well be greater than the solubility of carbonate in reduced mantle environments. 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 haplobasalt composition (Di₄₀An₄₂Ab₁₈), adding 2.2 wt.% C in the form of Si₃C₁₂H₃₆ + H₂O to produce SiO₂+ CH₄ + H₂, for a total volatile content of 5 wt%. We added extra water (7 mol) in order to have the composition away from the junction C-H. Experiments were conducted in a piston cylinder apparatus at 0.7, 1.5, 2.0 and 3.0 GPa and 1400°C and experimental durations of 30 min and 1 h. To buffer oxygen fugacity, we employed a Pt double sealed capsule (3.8 and 2.0 mm external diameters) with Fe+FeO+Fe₃C+H₂O in the outer capsule, and graphite powder in the bottom of the internal capsule. The fluid composition is controlled by the external buffer, which imposes the f_{H_2} of the external assemblage, and the graphite in the internal capsule. This buffer combination is shown in Fig. 1 (by the red spot) and gives the equilibrium f_{O_2} . The inferred

oxygen fugacity is slightly lower than IW (red spot). The preliminary estimation of the equilibrium f_{O_2} is of IW -0.7 (± 0.5).

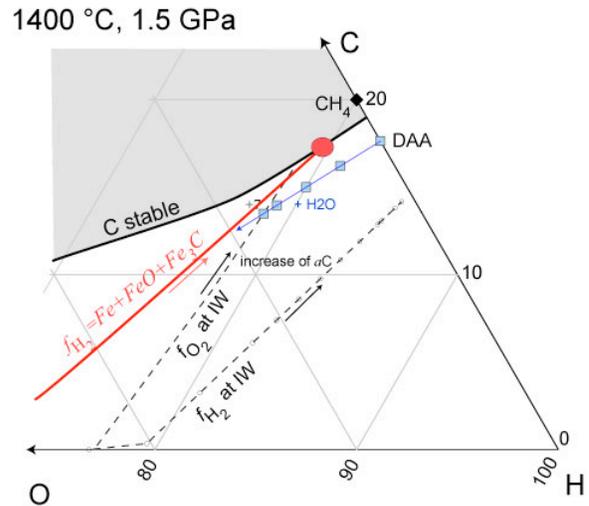


Figure 1. Calculated C-O-H fluid speciation at reduced condition (GFluid, [9]). Blue squares represent the Di₄₀An₄₂Ab₁₈ composition with water addition, the dashed line refers of the fugacities of oxygen and hydrogen in equilibrium with IW with increasing carbon activity. The red line is the f_{H_2} inferred during our experiments and crossing the C stability field recall the conditions in the internal capsule (red spot).

The experimental glasses were recovered, polished and analyzed by electron microprobe to verify major element compositions. To survey volatile 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. Double polished glasses were used for infrared spectroscopy (Bruker Tensor 37) to quantify the total dissolved water content. Dissolved C content were quantified by SIMS with the Cameca 6f instrument at the Arizona State University using Cs⁺ primary ion source with a beam current of 10 nA producing a beam diameter of ca. 50 μ m SIMS analyses, and pre-sputtering of 120 sec allowed to clean the surface of any possible C contamination. Ions counted include those of ¹²C, ¹⁷OH, ¹⁸O, ¹⁹F, and ³⁰Si, and the ¹²C/³⁰Si ratio was chosen for the quantification of C, whereas the ¹⁹F counts as indicator of contamination of the sample surface. The ¹²C/³⁰Si ratio was calibrated using synthesized glasses with various amount of dissolved C as CO₂ and H₂O (0, 0.2, 0.5 and 1.0 wt% CO₂, and H₂O from 0.17 to 1 wt%) synthesized under oxidizing conditions and previously quantified by FTIR spectroscopy. In the region of interest we could quantify the C concentration with an error of 10%. Two different blank standards were reexamined after every 5 analyses. Multiple analyses on

different days were done for each sample, to decrease the statistical error.

Results: Quenched capsules were sectioned along the capsule axis using a W wire saw. The recovered half capsule was at first examined optically to verify the persistence of the buffer assemblage. Afterwards, the internal glass was doubly polished and prepared for microscopy and spectroscopic analyses. The quenched glasses are transparent and contain equilibrium bubbles from 50 to 250 μm in diameter, and graphite is accumulated on the lower side of the capsule as was added to infer the desired $f\text{O}_2$. The bubbles are clear or show dark solid deposits as coating around the bubble or accumulated in the lower side of the bubble as precipitates upon quenching.

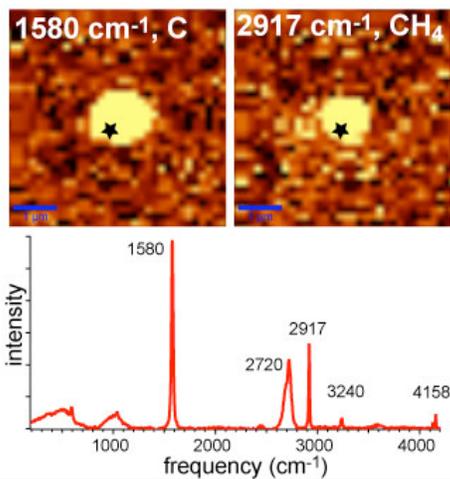


Figure 2. Raman scan of exp. at 2.0 GPa, 1400°C, 30 min highlighting the $\sim 1580\text{ cm}^{-1}$ peak indicative of C, and the 2917 peak of CH_4 . The C is present as a film on the bubble walls and is believed to be a quench feature. Spectra of the bubble (star) is shown along the bottom. Scans are $5 \times 5\ \mu\text{m}$

Raman spectroscopy of the bubble and precipitates reveals peaks at ~ 1350 , ~ 1580 , ~ 2450 , and 2720 cm^{-1} , consistent with C-deposits (possible C nanofibres). Sharp intense peaks at 2920 and 4150 cm^{-1} are consistent with methane and H_2 (Fig. 2) volatiles. The CH_4 - H_2 species are more concentrated in the central part of the bubble, and the C deposits occupy the periphery (Fig. 2). The C rich precipitates are interpreted as quench features. No differences are observed between 30 min and 1 h experiments.

Raman analyses of glasses indicate dissolved CH_4 , H_2O and H_2 , with peak assignments of 2920 cm^{-1} for CH_4 , the 4150 cm^{-1} for the H_2 and the broad water band around 3600 cm^{-1} . CH_4 absorbances at 3.0 GPa are approximately twice as great as at 1.5 GPa.

The C quantification by SIMS allows estimation of the dissolved C content of graphite-saturated basaltic magmas under reduced conditions. Results at 1400°C indicate an increase of the dissolved carbon content from 70 ppm at 0.7 GPa to 370 ppm at 3.0 GPa (Fig. 3). These are ca. 1 order of magnitude higher than the dissolved C as carbonate at IW -1, indicating that methane, rather than carbonate dominates volatile carbon in reduced magmas. However, measured CH_4

solubilities are dramatically lower than those reported by Mysen [8] for $\text{Na}_2\text{O-SiO}_2$ liquids at comparable pressures.

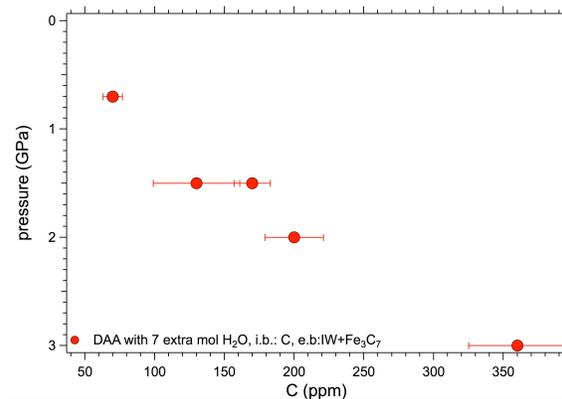


Figure 3. SIMS determinations of C content of haplobasaltic glasses saturated in C near IW-0.7 as a function of pressure. Error bars are calculated as st.dev. of the multiple analyses of each sample and each symbol correspond to a different experiment.

Discussion The experiments clearly document that reduced CH_4 and possible CH_3 species are soluble in mafic magmas, indicating an increase in solubility with pressure. Methane solubility exceeds that of carbonate at reducing conditions relevant to magmas from reduced planetary mantles that are 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.

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] Holloway J. R. (1981) *Adv. Phys. Geochem. 1*, 273-293. [5] Pan V. et al. (1991) *GCA* 55, 1587-1595. [6] Taylor, W.R. and Green, D.H. (1987) *Geochem. Soc. Spec. Pub. 1* 121-138. [7] Kadik, A. et al. (2004) *J. Petrol.* 45, 1297-1310. [8] Mysen, B.O. et al. (2009) *GCA* 73, 1696-1710. [9] Zhang and Duan (2009) *GCA* 73, 2089-2102.