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# Early Atmosphere/Magma Ocean Equilibria: Constraints from the Experimental Determination of Nitrogen, Ammonia, and Carbon Monoxide

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John R. Holloway

Arizona State University
Departments of Chemistry and Geology
Tempe, Arizona 85287-1604

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## SUMMARY

CO Solubility in Basaltic Melt at Low Pressures

Primitive atmospheres are proposed to have been carbon-bearing and reducing. Carbon monoxide can be a significant component of such fluids, and a determination of its solubility in a coexisting basaltic magma ocean is therefore desirable. Although previous studies have aimed to determine CO solubility in basalt, none have measured it directly, and the low CO contents of the experimental fluids have led to large uncertainties in the solubility estimates. In this study we have therefore used a fluid of high CO content and measured its solubility directly using Fourier Transform Infrared (FTIR) spectroscopy.

Equilibrium calculations using the modified redlich-Kwong (MRK) equation of state indicate that the highest CO contents in pure C-O fluids are fixed by the graphite saturation surface, and the mole fraction of CO ($X_{CO}$) increases as the pressure decreases and as the oxygen fugacity ($f_{O_2}$) decreases. We therefore used low pressures of 500-1500 bars for these experiments, a temperature of 1200°C, and graphite-saturated C-O fluids.

The basalt used was a MORB from the Juan de Fuca Ridge. The experimental conditions were obtained by enclosing the powdered sample in a graphite capsule within a sealed platinum capsule. $MgCO_3$ was used as the fluid source. On heating it breaks down to $MgO + CO_2$ fluid composition is obtained.

The experiments were conducted in a Rapid Quench Pressure Vessel, a vertical internally-heated argon gas pressure vessel, in which the sample is suspended from a Pt quenchwire within the furnace hot-spot, and its temperature monitored using an array of 4 thermocouples. Experiments last for 6 hours, after which the quenchwire is fused and the sample falls to the bottom of the vessel and is quenched to a glass.

Fluid compositions at the end of the experiment (assumed to be the same as those in equilibrium with the melt at pressure and temperature) were measured by puncturing the capsule in a vacuum line and determining the ratio of total gas pressure ($CO + CO_2$) to the pressure of CO after condensing the $CO_2$ in a liquid nitrogen trap. They were close to the values calculated using the MRK equation of state. The latter values were used in the subsequent calculations.

The glass samples were double-polished to thicknesses of 300-450 μm. Optical examination revealed them to be clear and crystal-free, and the disatribution of vesicles suggested that convection had occurred during the experiment, enhancing the equilibration process. Transmission micro-FTIR spectra were then taken of several spots in each sample, using the Digilab FTS-40 instrument in Dr. P. McMillan's laboratory at Arizona State University. In all samples the only vibrations arising from dissolved volatile species in the glasses were $CO_3^{2-}$ antisymmetric stretching vibrations ($OH^-$ stretching bands representing < 10 ppm $H_2O$ were present in some spectra). A preliminary Raman Spectroscopic study did not reveal any additional vibrations.
$CO_3^{2-}$ concentrations were calculated using the Beer-Lambert Law, and are shown in Figure 1 together with the calculated CO contents of the fluids in equilibrium with the melts, and the calculated oxygen fugacities relative to QFM. Also shown are the $CO_2$ solubility data of Stolper & Holloway (1988), obtained at 1200°C on a MORB of similar composition as that used in this study, and measured using FTIR spectroscopy. Both sets of data are plotted as the $CO_2$ equivalent of the dissolved $CO_3^{2-}$. The experiments of Stolper & Holloway were conducted using C-O fluids more oxidising than those used in

this study. Fluid compositions were not measured, but were assumed to be pure $CO_2$. We believe, however, that the fluids may have contained significant CO, due to the small amounts of $CO_2$ added to the experimental charge and relatively reduced nature of the starting material. We therefore performed a further ecperiment at 1000 bars, 1200°C, using a fluid of high $CO_2$ content, which we measured to be 94% $CO_2$, 6% CO; in contrast to the graphite-saturated fluid composition of 39% $CO_2$, 61% CO. The $CO_3^{2-}$ concentrations of these two samples were 556 ppm and 309 ppm $CO_2$ respectively. Thus $CO_2$ is more soluble than CO, and the results of the two experiments at 1000 bars can be combined to give the individual solubilities of $CO_2$ and CO. The relationship $S_{CO} = 0.23\ S_{CO_2}$ is obtained, where $S_{CO}$ and $S_{CO_2}$ are the solubilities of CO and $CO_2$ respectively. This relationship may be used to extract $S_{CO}$ and $S_{CO_2}$ at 500 and 1500 bars from the total dissolved carbonate at those pressures. All values lie on straight lines through the origin, indicating that CO and $CO_2$ solubilities at low pressures obey Henry's Law. The modelled $CO_2$ solubility of Stolper & Holloway (1988) lies between $S_{CO}$ and $S_{CO_2}$ of this study, implying that their fluids were indeed mixtures of CO and $CO_2$. We have used our model to calculate their fluid compositions and hence the oxygen fugacities of their experiments, and calculate significant CO contents and relatively low oxygen fugacities, in accord with our preliminary hypothesis.

## PUBLICATIONS

The effect of oxygen fugacity on the solubility of carbon-oxygen fluids in basaltic melt, A. R. Pawley, J. R. Holloway, P. F. McMillan, *Earth and Planetary Science Letters*, 1992, in press.