

EXPERIMENTAL STUDY OF THE SOLUBILITY OF CO + CO₂ IN BASALT, WITH APPLICATIONS TO EARLY ATMOSPHERE/MAGMA OCEAN EQUILIBRIA; Alison R. Pawley¹ and John R. Holloway^{1,2} (¹Dept of Chemistry and ²Dept of Geology, Arizona State University, Tempe, AZ 85287)

Primitive atmospheres formed by the degassing of impacting material during planetary accretion are proposed to have comprised between 40 and 60 mol% CO + CO₂, with CO the dominant species for a range of modelled compositions (1). Impact heating and thermal blanketing by the dense atmosphere, at pressures of up to a few hundred bars, cause melting of the planet surface and the formation of a magma ocean (2,3). In order to estimate the amount of carbon dissolved in the magma ocean, and hence the carbon content of a secondary atmosphere released on its crystallisation, data on the solubility of CO and CO₂ in basalt at low pressures are necessary. Stolper & Holloway (4) measured the solubility of CO₂-rich C-O fluids in basalt at 1200°C and 100-1500 bars. Based on estimates of initial oxygen fugacities, they assumed fluid compositions of 100% CO₂, but did not measure them directly. No previous experiments on basaltic melts have used fluids with large CO-contents. Therefore for the majority of our experiments we used CO-rich graphite-saturated C-O fluids, and for one experiment used a CO₂-rich fluid to allow a direct comparison with the results of (4). The basalt used was a MORB from the Juan de Fuca Ridge, similar in composition to that used in (4). For the graphite-saturated experiments this was dried for 2 hours at 1000°C and an oxygen fugacity of QFM-3 and enclosed in a graphite capsule, which was placed in a Pt capsule together with MgCO₃ as the fluid source. On heating during the experiment, the MgCO₃ decomposes to MgO + CO₂, and the CO₂ reacts with carbon until the equilibrium CO/CO₂ fluid composition is obtained. To obtain a CO₂-rich fluid, the sample was pre-dried for 24 hours at 1000°C and QFM+1 and contained in an Fe-saturated Pt capsule together with Ag₂C₂O₄ as the fluid source.

All experiments were conducted in a rapid-quench internally-heated pressure vessel, at conditions of 1200°C/500-1500 bars/6 hours. Final fluid compositions were measured by puncturing the capsules in a vacuum line and condensing the released CO₂ in a liquid nitrogen trap. The compositions of the graphite-saturated fluids were close to values calculated using the MRK equation of state, which were used in the subsequent calculations. Micro-FTIR spectroscopy was used to measure the concentrations of dissolved volatiles in the glasses. These were double-polished to thicknesses of 300-450 µm, and absorption spectra obtained of several spots in each sample. The only absorptions arising from vibrations involving carbon were the CO₃²⁻ ν₃ antisymmetric stretching bands. Raman spectroscopy of the glasses revealed no additional dissolved Raman-active species.

CO₃²⁻ concentrations were calculated using the Beer-Lambert Law (Fig. 1). Of all the samples, that in equilibrium with the fluid with a high CO₂-content contains the most CO₃²⁻. Thus CO₂ is more soluble than CO, and more soluble than predicted in (4). The relationship between CO and CO₂ solubilities at 1000 bars was extracted from the combined 1000 bar data and used to recalculate the solubilities at 500 and 1500 bars from the data at those pressures (Fig. 2). The close fit of the recalculated data to a linear, Henry's Law solubility model suggests that the assumption of constant ratio of CO to CO₂ solubilities with pressure (at low pressures) is valid, and hence that CO solubility, which involves an oxidation reaction, is not a very strong function of oxygen fugacity. However we emphasise that because our solubility model relies solely on CO₃²⁻ concentration measurements and we cannot distinguish between dissolved CO and CO₂, we should not exclude the possibility that there are species additional to CO₃²⁻ dissolved in the melt, and that the ratio of CO to CO₂ solubility varies with pressure. But even if our data can only be used to predict dissolved CO₃²⁻ concentrations as a function of pressure and oxygen fugacity, these predictions may usefully be applied to the interpretation of solubilities in natural basaltic glasses, for which the same technique is usually used to measure only total dissolved CO₃²⁻.

Our results imply that the fluids in Stolper & Holloway's experiments (4) were CO₂-CO mixtures, not pure CO₂, and we calculate them to contain 30-50% CO at 500-1500 bars, corresponding to oxygen fugacities of QFM-2.0 to QFM-2.7.

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We have also used our model to calculate the CO₃²⁻ content of a basaltic magma ocean in equilibrium with a primitive atmosphere at 1200°C and low pressures (Table 1, Fig. 3). Making use of available data on the solubility of H₂O in basalt (5), we calculate that weight ratios of dissolved CO₂ to dissolved H₂O in the magma ocean vary from 0.001-0.003 at 50 bars to 0.003-0.006 at 200 bars. These values are two orders of magnitude less than the present-day ratio of CO₂ in the earth's crust to H₂O in the oceans + crust. The very low C/H ratio in the magma ocean therefore poses severe mass balance problems for the thick atmosphere-magma ocean model for the formation of terrestrial planets, unless significant amounts of carbon in the thick atmosphere are retained at the end of accretion and converted into carbonate sediments.

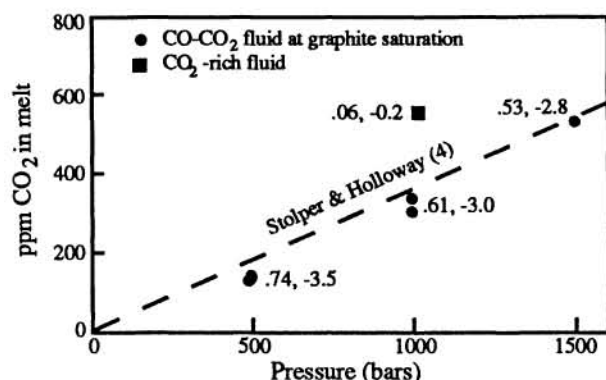


Fig.1. Dissolved CO₃²⁻ contents of glasses, expressed as ppm CO₂, versus P. Numbers are mole fractions of CO in the fluid and oxygen fugacities relative to QFM. Dashed line is modelled CO₂ solubility curve of Stolper & Holloway (4).

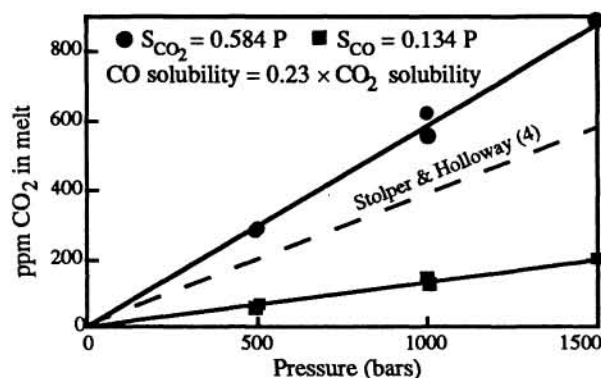


Fig.2. CO-CO₂ solubility data, recalculated as CO and CO₂ solubilities, as a function of P.

Table 1. Modelled primitive atmosphere compositions at 1200°C, 50-200 bars, and with H/C ratios spanning the probable range in the accreting material. Accreting material compositions were based on those of carbonaceous chondrites and unequilibrated ordinary chondrites.

	H/C = 0.75	H/C = 1.5
CO	.48	.33
CO ₂	.10	.07
H ₂ O	.13	.19
H ₂	.28	.39

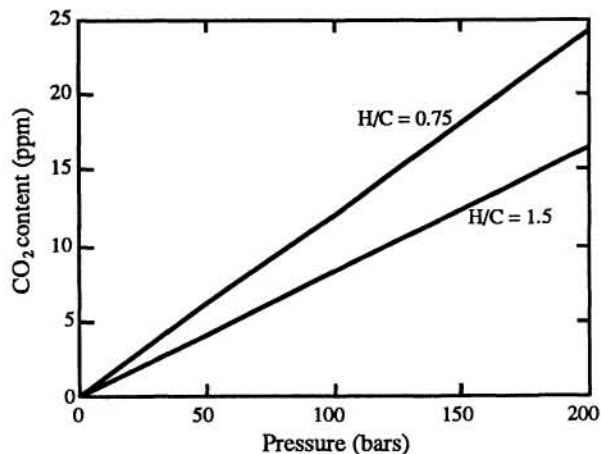


Fig.3. Total dissolved CO₃²⁻, expressed as ppm CO₂, versus P for a basaltic magma ocean in equilibrium with the two atmosphere compositions listed in Table 1.

References:

- (1) Holloway J.R. (1988) *Lunar Planet. Sci. Conf.*, XIX, 499-500.
- (2) Matsui T. and Abe Y. (1986) *Nature*, **319**, 303-305.
- (3) Zahnle K.J., Kasting J.F. and Pollack J.B. (1988) *Icarus*, **74**, 62-97.
- (4) Stolper E. and Holloway J.R. (1988) *Earth Planet. Sci. Lett.*, **87**, 397-408.
- (5) Hamilton D.L., Burnham C.W. and Osborn E.F. (1964) *Jour. Petrol.*, **5**, 21-39.