CO$_2$ SOLUBILITY IN MARTIAN BASALTS AND APPLICATIONS TO ATMOSPHERIC EVOLUTION.

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Introduction: A strong early Martian greenhouse atmosphere is required to account for evidence of liquid water on the surface of Mars [e.g. 1]. Many models of Mars' atmospheric evolution incorporate magmatic outgassing fluxes of CO_2 based on analogy to terrestrial magmas [2-5]. Here we investigate the solubility of carbon dioxide in Martian analogue basaltic melts at 2.0 GPa to constrain this important variable.

Experiments: The starting material was a synthetic basalt composition obtained from Justin Filiberto at the LPI based on surface measurements of the Adirondack-class basalt "Humphrey" by the Spirit rover (see Table 1). Carbon dioxide was added as silver oxalate, $Ag_2(CO_2)_2$.

Table 1. Starting composition compared to published compositions of Humphrey Martian basalt (reported in wt.%)

	Gellert et al. [6]	McSween et al. [7]	Experimental glass composition
SiO$_2$	46.96	46.49	46.91
TiO$_2$	0.56	0.59	0.53
Al$_2$O$_3$	10.93	10.55	10.52
FeO$_T$	19.23	18.95	19.87
MnO	0.42	0.43	0.38
MgO	10.65	10.82	10.79
CaO	8.02	8.26	7.99
Na$_2$O	2.56	2.38	2.40
K$_2$O	0.10	0.09	0.11
P$_2$O$_5$	0.57	0.60	0.52
FeS	0.00	0.84	0.00
Total	100.00	100.00	100.00

FeO$_T$ = total iron (Fe$_2$O$_3$ + FeO).
Compositions are calculated Cr-free and normalized.

Experiments were performed in Pt capsules presaturated with Fe by 24-hour equilibration with molten MORB basalt at 1250 ºC in a CO-CO$_2$ atmosphere adjusted to an fO$_2$ near QFM -2.5. Experiments at 2 GPa and 1400-1600 °C were performed in a half-inch, end-load piston cylinder apparatus under hot piston-in conditions. Apart from drying the MgO spacers overnight, no other steps were taken to ensure a nominally anhydrous charge.

After the run, capsules were sectioned with a 50-µm tungsten wire saw. Run products consist of glass coexisting with spherical voids inferred as remnants of CO_2 vapor bubbles present during the experiment (see Fig. 1). One half was polished and mounted for compositional analysis with the JEOL JXA8900R Super Probe. Glass chips from second half were doubly polished and analyzed for CO_3^{2-} with a Nicolet II Magna-IR FTIR.
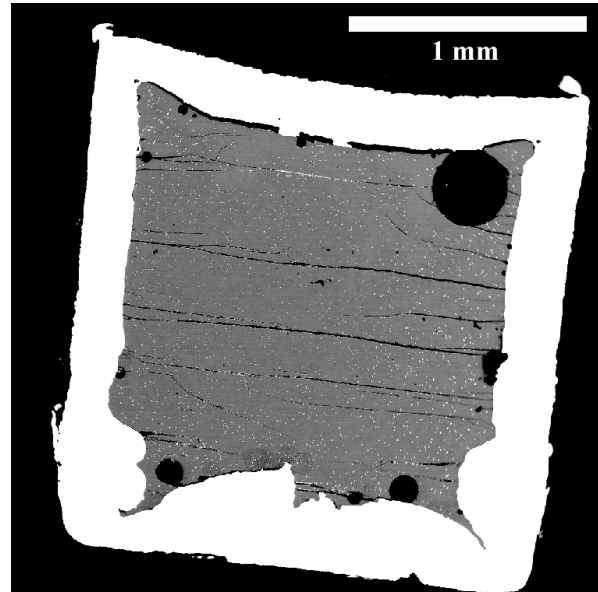

Figure 1. Electron backscatter image of experimental capsule run at 1450°C, 2 GPa, showing glass coexisting with vapor bubbles demonstrating saturation with CO_2 vapor. Bright flecks in glass are Ag metal.

Results: Electron microprobe analyses of the run products showed that homogeneous glass was quenched in all experiments run at 2 GPa and 1400-1600°C, with only the 1400°C experiment showing incomplete melting. Glass compositions showed little iron-loss during the 30 minute runs and had Mg # between 47.5-49.0 compared to the original of 49.2.

FTIR spectra were collected from glass chips of all experimental runs. All spectra show doublets at 1415 cm^{-1}, as expected from CO_2 dissolution as CO_3^{2-} in basaltic melts. As expected for mafic silicate melts [16], molecular CO_2 concentrations were negligible. CO_2 solubility (reported in wt.%) is plotted against temperature in Figure 2.

Discussions and Applications: Conventional and trace element oxybarometry of SNC meteorites suggest that the oxygen fugacity of much of the Martian mantle is reducing and within 1 order of magnitude of the iron-wustite (IW) buffer [e.g. 8, 9]. Consequently, carbon is likely stored as graphite [3]. Following Holloway [10], the solubility of dissolved CO_2 in graphite-bearing basaltic magmas depends only on oxygen fugacity:

$$X_{CO_3^{2-}}^{melt} = \frac{K_I K_{II} fO_2}{1 + K_I K_{II} fO_2} \qquad (1)$$

provided that values for two equilibrium constants, K_I and K_{II} are known. K_{II} is simple graphite oxidation and K_I represents the solubility of CO_2 in basaltic magma of the appropriate composition. Hirschmann and Withers [3] applied Eqn. 1 to estimate the time-integrated magmatic fluxes of CO_2 to the Martian atmosphere, using values of K_I determined experimentally for Hawaiian olivine tholeiitic basalt [11].
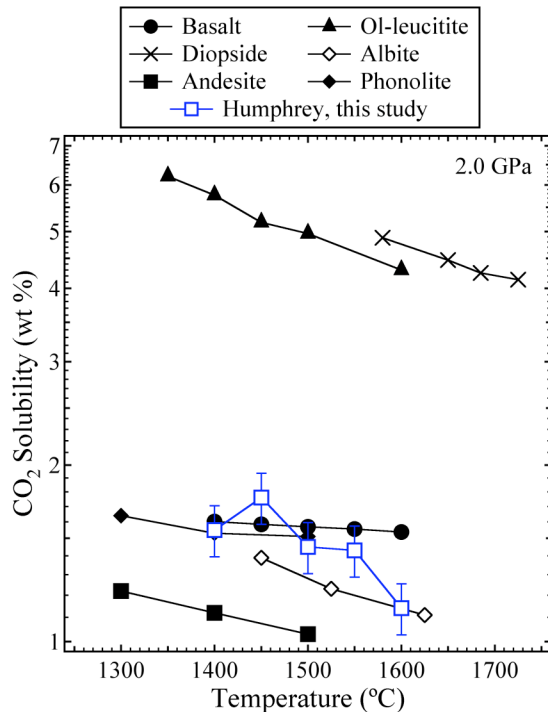

Figure 2. Experimentally determined CO_2 solubilities vs. temperature at 2 GPa for Humphrey basalt [this study] relative to determinations on several terrestrial compositions. After [12]. Data from: Hawaiian olivine tholeiitic basalt (extrapolated from 1.5 GPa experiments [11] using the thermodynamic parameterization of [11]); diopside - [13]; andesite and phonolite - [14]; ol-leucitite - [15]; albite - [16].

At the time, it was not known whether similar values would apply for Martian basalts. As shown in Figure 2, our new experimental data give CO_2 solubilities that are nearly identical to the extrapolated Hawaiian olivine tholeiitic basalt [11] used in the Holloway calibrations [10], except at 1600 °C. The discrepancy at 1600 °C may indicate a different temperature dependence to the solubility for the two compositions, and this requires further experimental investigation, but provisionally the solubilities are taken to be within uncertainty of each other. Consequently, calculation for dissolved magmatic CO_2 for Martian basalts using Humphrey basalt or Hawaiian olivine tholeiite may not be distinguishable.

Figure 3 compares calculated time-integrated Martian magmatic fluxes of CO_2 calculated from Eqn. 1, using appropriate CO_2 solubility relations and parameterized Martian magmatism through time [3] at conditions ranging from IW to IW+1 and for temperatures and pressures appropriate for partial melting in Martian basalt source regions [17, 18]. The resulting cumulative CO_2 outgassed ranges from 40 mbar to 1.4 bars, but the larger numbers are found only for comparatively oxidizing conditions and for high temperature (1540 °C) melting. Therefore, the magmatic supply of CO_2 to the Martian atmosphere may not have been sufficient to create a strong greenhouse without contributions from other volatile components.
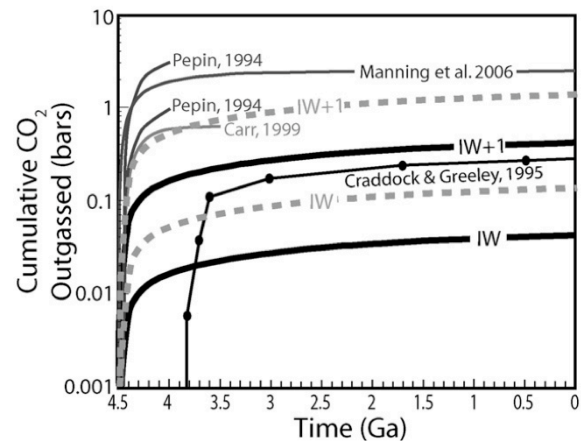

Figure 3. Calculated magmatic outgassing of CO_2 from the Martian mantle from 4.5 Ga to present. Solid curves are calculated production models from mantle oxygen fugacities of IW and IW+1 at 1320°C, 1.2 GPa ([17], black curves) and 1540°C, 1.2 GPa ([18], grey curves). Other curves are magmatic outgassing fluxes from previous atmospheric evolution models: [2, 4, 5, 19]

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