

EXPERIMENTAL INVESTIGATION OF CO₂ SOLUBILITY IN MARTIAN BASALTS WITH VARIED OXIDATION STATE AND APPLICATIONS TO MARTIAN ATMOSPHERIC EVOLUTION.

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Introduction: The evidence for stable liquid water on the surface of Mars early in its history [e.g. 1] requires the presence of a much stronger greenhouse atmosphere in the past relative to the current atmosphere. Existing models of Martian atmospheric evolution incorporate magmatic outgassing fluxes of CO₂ based on studies of terrestrial magmas [2-5]. This study investigates the solubility of CO₂ in basalts of Martian composition at varying oxygen fugacities (fO_2) and conditions of possible partial melt generation in the mantle in order to construct more realistic models of the evolution of the Martian atmosphere.

Experiments: Experiments were performed on a synthetic starting material similar to measurements by the Spirit rover of the Gusev Crater basalt “Humphrey”, see [6] for details. For some experiments the starting material was reduced for 12 hours in a CO-CO₂ atmosphere adjusted to an fO_2 near QFM -1. The oxidation state of the two starting materials was determined by Mössbauer spectroscopy at the University of Minnesota (UMN) Institute for Rock Magnetism. The iron in the oxidized starting material contained 82.5% Fe³⁺ and 17.5% Fe²⁺, while the reduced starting material contained 100% Fe²⁺. The oxygen fugacities prevailing in the experiments will be determined by V oxybarometry [7] using micro-XANES (X-ray Absorption Near-Edge Structure) spectroscopy, at the Advanced Photon Source, Argonne National Laboratory. Carbon dioxide was added to both starting materials as silver oxalate, Ag₂(CO₂)₂.

We investigated conditions of 1400-1625°C and 1.0-2.5 GPa using two different capsule designs (Fig. 1) in a half-inch, end-loaded piston cylinder apparatus under hot piston-in conditions. To minimize iron loss, most of the experiments presented here were run in 2 mm iron-presaturated Pt capsules that were equilibrated for 24 hours with MORB glass in a CO-CO₂ atmosphere at an fO_2 near QFM -2.9. To investigate the effect of graphite saturation, experiments were also run in 4 mm Pt-graphite double capsules. Experiments with Pt-Fe doped capsules lasted 30 minutes, and the Pt-graphite experiments were heated for 6 hours to allow for textures amenable to FTIR analysis, as shorter experiments were marred by graphite precipitates distributed throughout quenched glass. The experiments conducted in Pt-graphite capsules are assumed to approximate conditions close to the CCO

(graphite-CO-CO₂) buffer [8], though verification via V oxybarometry is required.

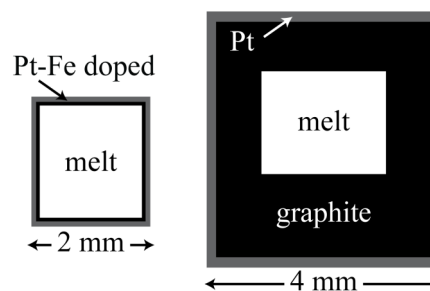


Figure 1. Cartoon of the capsule design of the two projects.

The major element composition of experimental glasses was analyzed using the JEOL JXA8900R electron microprobe at the UMN. Small glass chips from each run were double polished to a thickness of less than 30 μm and analyzed for CO₃²⁻ using a Bruker Tensor 37 FTIR bench and Hyperion 2000 microscope at the UMN Experimental Petrology Laboratory.

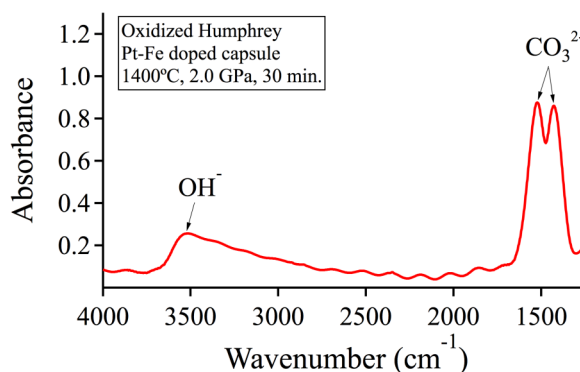


Figure 2. Sample FTIR spectra showing the carbonate doublet at 1525 and 1425 cm⁻¹ that appears in all spectra.

Results: Electron microprobe analyses showed all runs produced homogeneous glasses with little iron loss except in experiments with reduced starting mixtures, which had a Mg# near 52 compared to the original of 49.2. FTIR analyses of experimental glasses indicates CO₂ dissolved only as CO₃²⁻ (Fig. 2), as expected for mafic silicate glasses [9]. Measured CO₂ solubilities are plotted versus temperature (Fig. 3a) and pressure (Fig. 3b).

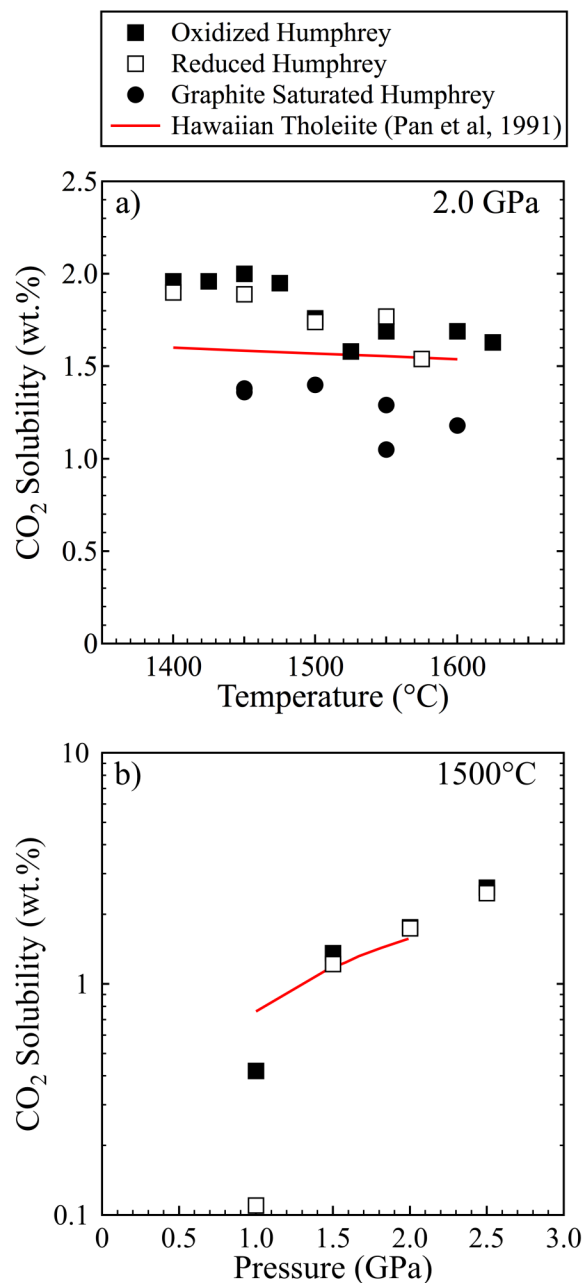


Figure 3. a) Plot of CO₂ solubility versus temperature at 2.0 GPa for experimental Humphrey basalt (square – Pt-Fe doped capsule; circle – Pt-graphite capsule) and model of Hawaiian Tholeiite from [10] (red line); b) Plot of CO₂ solubility versus pressure at 1500°C, the 2.0 GPa oxidized and reduced Humphrey data points are overlapping (symbols same as Fig. 3a).

Discussion and Application: Our results show that the CO₂ solubility in synthetic Humphrey basalt does not depend on the oxidation state of the iron, thereby confirming the assertion of Brooker [11] that Fe²⁺ and Fe³⁺ have similar influence on CO₂ solubility in mafic silicate melts.

Measured CO₂ solubilities for graphite-free experiments are approximately 20% higher than that for Hawaiian tholeiite [10] (Fig. 3). Graphite-saturated experiments are similar to those expected for graphite-saturated Hawaiian tholeiite at CCO as predicted by the thermodynamic model of Holloway [12]. This is owing to the diminished fugacity of CO₂ under reducing conditions in the presence of graphite. Extrapolation of this model, as described in [5], to more reducing conditions appropriate for partial melting of a graphite-bearing Martian mantle (iron-wüstite \pm one log unit or IW \pm 1 [13]) indicates that Gusev Crater basalts can have no greater than 0.1 wt.% CO₂ dissolved as carbonate for the Martian mantle at IW+1 and possibly as little as 10 ppm CO₂ at IW-1 [5]. Further experiments are required to document dissolved C contents and speciation under these more reducing conditions. However, the experimental data to date corroborate the conclusion [5] that volcanogenic fluxes of CO₂ to the atmosphere have been limited throughout Martian history, and suggests that CO₂ may not be the principal greenhouse agent. Therefore, other volatiles such as SO₂ or CH₄ may be required, either as chief greenhouse agents or in combination with CO₂.

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