

## EXPERIMENTAL INVESTIGATION OF CO<sub>2</sub> SOLUBILITY IN PRIMITIVE MARTIAN BASALTS SIMILAR TO YAMATO 980459 AND IMPLICATIONS FOR MARTIAN ATMOSPHERIC EVOLUTION.

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**Introduction:** Several lines of evidence suggest that liquid water flowed at the Martian surface during parts of the late Noachian and early Hesperian epochs [1], requiring a greenhouse atmosphere during this period. It remains unclear how this greenhouse was created and how it evolved to the modern thin atmosphere. One possibility is a CO<sub>2</sub> greenhouse produced by volcanic outgassing during the formation of the Tharsis plateau [1]. Early estimates based on terrestrial magmas suggested this as a possibility [2], but these did not account for the diminished solubility of CO<sub>2</sub> in basalts derived from the reduced source regions of Martian basalts [3]. They also did not account for potential influences on solubility from compositional differences between Martian and terrestrial lavas.

Greenhouse conditions on Mars may have coincided with the emplacement of the giant Tharsis magmatic province [4]. One possibility is that comparatively hot primitive magmas could have enhanced CO<sub>2</sub> solubility. Although the composition of Tharsis magmas are unknown, the plume hypothesis is consistent with comparatively hot temperatures [5]. Consequently, as a model for Tharsis lavas, we investigated carbonate solubility in a synthetic melt based on the shergottite meteorite Yamato 980459 (Y 980459). Y 980459 is a primitive (19 wt.% MgO) picrite thought to be derived from near-primary liquid with a source temperature near 1540°C [6].

**Methods:** We employed a synthetic mixture similar in composition to Martian meteorite Y 980459 [6], which was derived from a mixture of oxides and carbonates, and additionally had 5 wt.% CO<sub>2</sub> added as calcium and sodium carbonate. The material was homogenized under ethanol in an agate mortar.

Experiments were performed in 2 mm Pt capsules that were iron-presaturated to prevent iron loss from the starting material during the experiment. Presaturation was performed by packing capsules with a basalt powder and then heating them in a gas-mixing furnace for 24 hours at 1250 °C under a CO-CO<sub>2</sub> atmosphere adjusted to an oxygen fugacity ca. QFM -4. The basaltic glass was then removed from the treated capsules by immersion in warm hydrofluoric (HF) acid for several days. Two batches of capsules were made; one was presaturated with a MORB composition [7], while the other was presaturated with the synthetic Y 980459 analog. The presaturation material did not noticeably

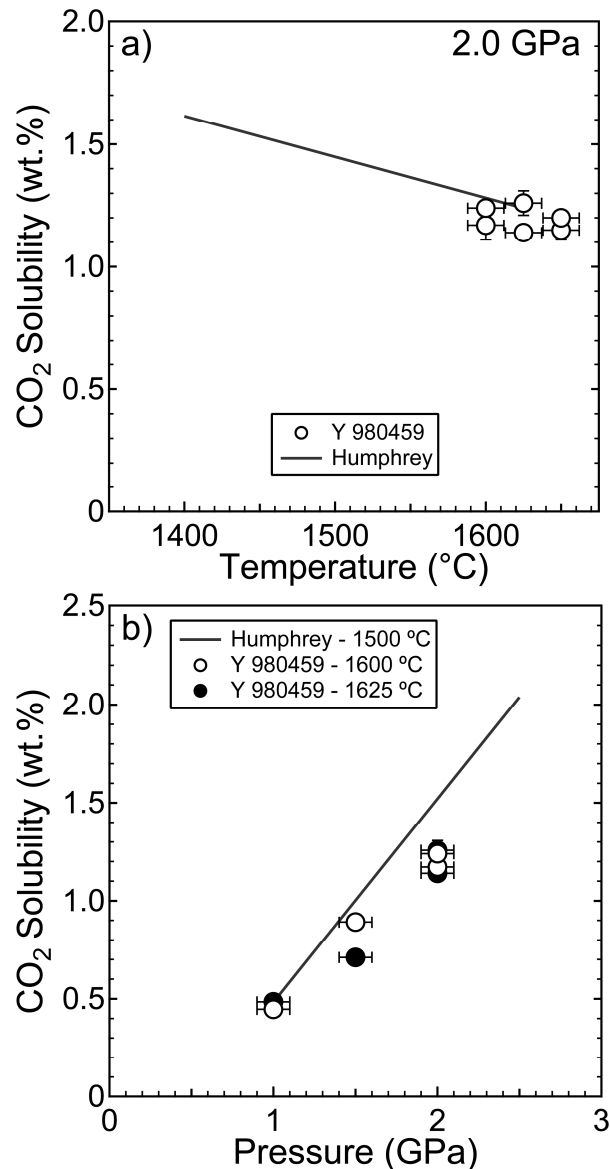
affect iron loss during the experiments (major element composition analyzed using the JEOL JXA8900R electron microprobe at the UMN).

Experiments were performed in a half-inch end-loaded piston-cylinder apparatus under hot piston-in conditions. Pressures ranged from 1.0-2.0 GPa and temperatures from 1600-1650 °C. The narrow temperature range was necessary owing to the starting material's high melting point and the comparatively low melting point of the capsules. A run duration of 30 minutes prevented significant hydrogen gain or iron loss over the experiment, confirmed by electron microprobe analysis.

The experimental assembly consisted of BaCO<sub>3</sub> sleeves surrounding straight graphite heaters and internal spacers of crushable MgO. Temperatures were measured and controlled with a W<sub>97</sub>Re<sub>3</sub>-W<sub>75</sub>Re<sub>25</sub> (Type D) thermocouple placed above the capsule. There is a pressure correction of -0.2 GPa for this assembly, and *P-T* uncertainties are ± 0.1 GPa and ± 12 °C respectively [8]. Experiments were quenched by turning off the power to the piston-cylinder.

Recovered capsules were sectioned using a 50 µm diameter tungsten wire saw. One half was polished for compositional analysis by ion microprobe, using diamond lapping films (15-1 µm). Loose chips of the remaining half were doubly polished to thicknesses between 20 and 80 µm for volatile analysis by Fourier transform infrared spectroscopy (FTIR) using a Bruker Tensor 37 FTIR bench and Hyperion 2000 microscope at the UMN Experimental Petrology Laboratory. The integrated molar absorptivity and density values of glassy Humphrey basalt [9] were used for volatile concentration calculations.

**Results:** Analyzed samples contained little to no crystals and contained bubbles, proving CO<sub>2</sub> saturation in the melt. In all cases, the portion of the charge used for FTIR was a homogeneous glass. CO<sub>2</sub> contents ranged from 0.45-1.26 wt.%. Measured CO<sub>2</sub> solubilities are plotted versus temperature in Fig. 1a, where they compare favorably to the solubilities measured for a synthetic basalt with the composition of Humphrey, a basalt from Gusev Crater [9] (Fig. 1a). Solubilities increase with increasing pressure (Fig. 1b) along a trend that is similar to but slightly lower than that measured for Humphrey.

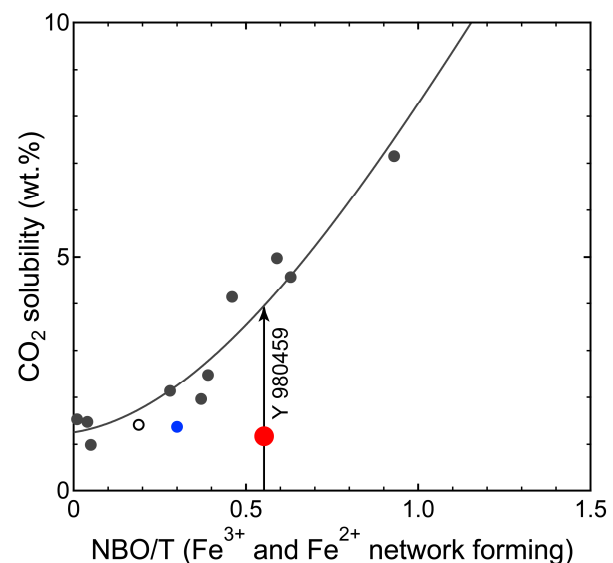


**Figure 1.** a) Plot of CO<sub>2</sub> solubility versus temperature at 2.0 GPa for experimental Y 980459 (circles) and Humphrey basalt (line, [9]); b) Plot of CO<sub>2</sub> solubility versus pressure for experimental Y 980459 at 1600°C (empty circles) and 1625°C (filled circles) and Humphrey at 1500°C (line, [9]).

**Discussion:** The similarity in CO<sub>2</sub> solubility for Y 980459 and Humphrey [9] (Fig. 1) was a surprise, as we anticipated greater solubility in the more primitive and less polymerized Y 980459. This expectation was based on the correlations between solubility and melt polymerization recognized previously [10] (Fig. 2). However, these correlations were based chiefly on depolymerized melts rich in alkalis or CaO, and our results suggest that MgO and FeO enrichment do not have the same influence on solubility.

The similarities in CO<sub>2</sub> solubility between Humphrey and Y 980459 indicate that precise information

about the composition of Martian basalts is not required to gain an accurate estimate of their capacity to vent volcanogenic CO<sub>2</sub> to the Martian atmosphere. Taking into account the volume of Tharsis magmatism [4], the entire Tharsis event could have contributed no more than 30-300 mbars of CO<sub>2</sub> to the Martian atmosphere (assuming source oxygen fugacities of IW and IW+1, respectively). This is far short of the 2 bars of CO<sub>2</sub> thought to be required to stabilize an equable climate in the late Noachian/Early Hesperian. Thus, unless the source of Tharsis magmatism was anomalously oxidized compared to Martian mantle sources (i.e., ~IW+2), additional volatiles such as SO<sub>2</sub> and CH<sub>4</sub> are required for a volcanogenic greenhouse.



**Figure 2.** Plot of experimentally determined CO<sub>2</sub> solubility versus calculated NBO/T at 2 GPa and 1500-1650 °C, a measure of melt polymerization. Grey circles are values used in calibration of curve. Empty and blue circles are, respectively, reduced and oxidized Humphrey basalt [9]. Experimental Y 980459 CO<sub>2</sub> solubility marked by red circle. After [10].

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