

CARBONATE FORMATION ON MARS: IMPLICATIONS OF RECENT EXPERIMENTS.

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Summary: Could carbonate formation have reduced Martian CO₂ pressure from >1 bar to the present 7 mbar in 3-4 b.y.? Since our previous report [1], we have performed additional experiments which monitor the uptake of CO₂ by powdered basalt. Together with results from post-experimental infrared spectroscopy, these new data support the hypothesis that the kinetics and mechanism of carbonate formation under low-T and low-P(CO₂) conditions (-25°C and 100 mb) are amenable to storing significant amounts of Martian CO₂ in carbonate minerals over geologic time. This claim requires that we verify that carbonate *is* formed in our experiments, and that we support a model involving something like *log t* behavior for CO₂ uptake.

Pressure-Drop Experiments: A sensitive manometer recorded the pressure drop of CO₂ due to uptake by powdered basalt (Kilauea tholeiite, ~98% glass) for periods of days to weeks [1]. (See also [2] for details of experimental procedure.) Runs were performed at warm (~22°C) and cold (-25°C) temperatures, CO₂ pressures of 950, 100, and 34 mb, and H₂O contents equivalent to 0-5000 monolayers. Results are shown below.

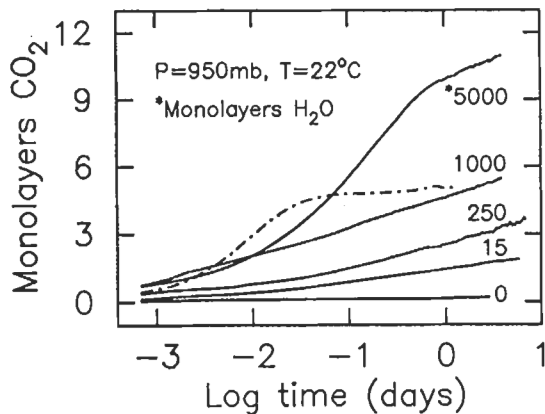


Figure 1. Pressure-drop results for crushed basalt (0.65 m²/g) under warm conditions at ~1 bar, where H₂O content (introduced at start of experiment) and CO₂ uptake (measured as a function of log *t*) are expressed in "equivalent monolayers" deposited uniformly on the surfaces. The broken curve shows the effect of CO₂ dissolution in H₂O without any sample (scaled to 5000 monolayers) and may explain rapid uptakes before ~1 day. Curves then become ~linear.

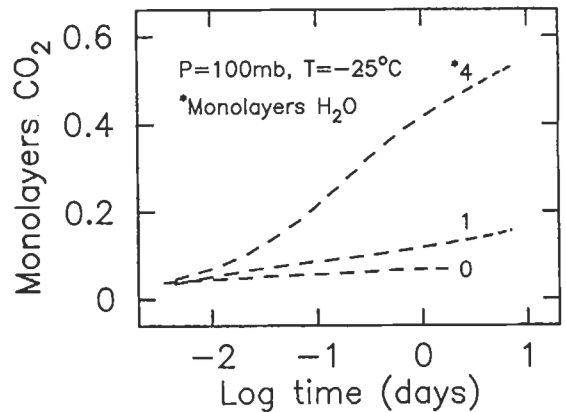


Figure 2. Basalt (1.85 m²/g) under cold conditions at 100 mb. As in Fig. 1, H₂O content varies, and similar behavior is observed. Most H₂O vapor has condensed onto grain surfaces at -25°C. A dry run (0 monolayers) shows only minor uptake after very rapid CO₂ adsorption. The two vapor experiments exhibit curves nearly linear in log *t* from ~-1 to ~-10 days, and extrapolation gives a tentative upper limit on CO₂ uptake for geologic timescales (see text).

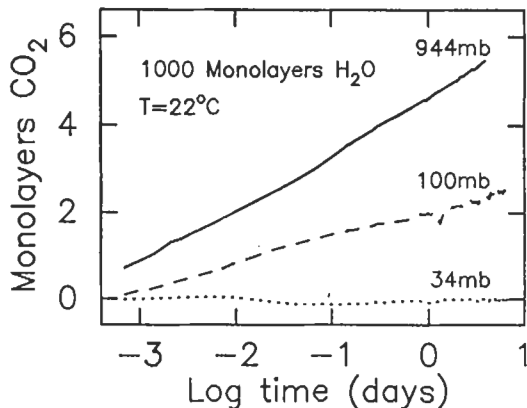


Figure 3 (left). Basalt (0.65 m²/g) under warm and damp conditions (1000 monolayers H₂O). CO₂ uptake after ~0.01 days at 100 mb is roughly half that at 944 mb. A sole experiment run at 34 mb yielded no signal (except fluctuations due to changes in lab temperature), suggesting a possible low-P limit for CO₂ uptake under these conditions. Otherwise, we see from Figs. 1-3 that T and H₂O content influence CO₂ uptake considerably more than P(CO₂). Additionally, at least ~1 monolayer H₂O appears to be necessary for any reaction to occur.

(text continues overleaf)

XPS (X-ray Photoelectron Spectroscopy): If pressure-drop results are due to carbonate formation and deposition, then added phases should be detectable with suitably sensitive spectroscopic or microscopic techniques. Using XPS, in which electrons generated by incident X-rays allows quantitative identification of surface elements and chemical states from binding energy spectra, we analyzed both crystals of diopside ($\text{CaMgSi}_2\text{O}_6$) and chips of the same basalt glass used as powders in pressure-drop experiments. Both were exposed for 2 to 4 weeks to a 1-bar CO_2 atmosphere saturated with H_2O vapor, and then compared with controls exposed to N_2 . Oxidized carbon, representing carbonate, would have been detected under XPS as a carbon signature shifted to higher binding energy relative to, e.g., adventitious or organic carbon. However, none was detected on either diopside or basalt, suggesting that any carbonate formation in pressure-drop experiments may be related to the surface or subsurface texture of crushed powders. We are presently using XPS to analyze powdered samples.

FTIR (Fourier Transform Infrared Spectroscopy): Infrared spectroscopy was used to test for added carbonate in experimental basalt powders. After pressure-drop runs under warm conditions at ~ 1 bar CO_2 with H_2O vapor, diopside and basalt were analyzed and compared with known carbonate spectra:

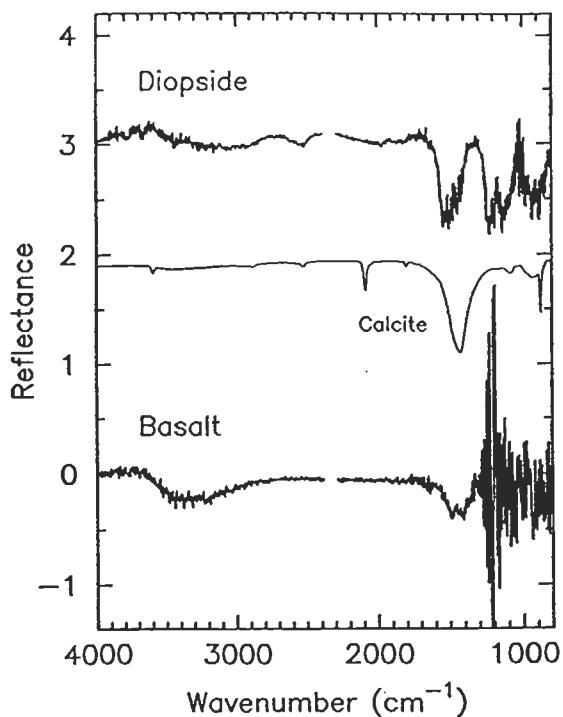


Figure 4. Ratioed spectra for basalt (corresponding to 15 monolayers H_2O on the previous page) and diopside (also warm, 1-bar, vapor conditions) are shown compared to a calcite transmission spectrum. Ratioing was done relative to control samples which were not subjected to experimental conditions (reflectance is in arbitrary units and the upper two curves are displaced for readability). Controls or dry-run powders would show flat ratioed spectra, except for noise (e.g., silicate absorptions $< 1300\text{ cm}^{-1}$), atmospheric signal (CO_2 band at 2350 cm^{-1}), and water condensation on the detector ($> 2800\text{ cm}^{-1}$). We notice prominent absorptions for both diopside and basalt (at ~ 1500 and 1450 cm^{-1}) which lie on or close to the principal calcite absorption ($\sim 1450\text{ cm}^{-1}$ or $6.9\text{ }\mu\text{m}$). There is a second absorption for diopside ($\sim 1200\text{ cm}^{-1}$) which may be due to a silicate reaction byproduct. The discrepancy between the $\sim 1500\text{ cm}^{-1}$ calcite absorption and the diopside spectrum may be due to a crystal structure other than calcite (e.g., aragonite) or to another carbonate (e.g., dolomite).

Absorptions at $\sim 1450\text{-}1500\text{ cm}^{-1}$ are very suggestive of added carbonate in both diopside and basalt. The apparent inconsistency of FTIR analysis and XPS results may be due to the difference in sampling depths of the two techniques ($\sim 1\text{ }\mu\text{m}$ for IR and $\sim 1\text{ nm}$ for XPS). Whatever is causing CO_2 to be stored in pressure-drop experiments and seen with IR may be deep enough that XPS is not seeing it at the surface of bulk samples.

Modeling and Implications for Mars: The apparent functional dependence of CO_2 uptake on $\sim \log t$ in pressure-drop experiments suggests a model for aqueous chemistry that involves reaction rate proportional to $1/t$. A diffusive process (e.g., simple non-aqueous diffusion through a reaction rind) will give reaction rate $\sim 1/t^{1/2}$. However, reaction rate $\sim 1/t$ is a natural outcome of a situation in which the source of a crucial reactant is a dissolving surface that can be encroached upon by deposition of the product. Thus, a scenario involving aqueous chemistry (perhaps as little as a monolayer of H_2O), in which reaction rate is limited by available dissolving surface (yielding cations), yields $\log t$ behavior for $P(\text{CO}_2)$ after ~ 1 day. If such a model holds, it is interesting because it is extrapolatable to geologic timescales. For example, $\log t$ is such a weak function that, for the -25°C , 100 mb, 4 monolayers H_2O case for basalt shown in Fig. 2, we can derive an upper limit for the CO_2 uptake: In 10^{12} days (3-4 b.y.), a global regolith of basalt powder 100 m in thickness will take up $\sim 10\text{-}100$ mb. The $\log t$ behavior avoids the problem of extrapolating laboratory reaction rates directly.

References: [1] Stephens S.K. et al. (1993) *LPI Tech. Rpt. 93-06, Part 1*, 46-48. [2] Stephens S.K. et al. (1992) *LPI Tech. Rpt. 92-04*, 34-36.