CARBONATES ON MARS: EXPERIMENTAL RESULTS.

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Summary: Experiments exposing crushed basalt glass to carbon dioxide and water vapor at conditions similar to those at the past and present surface of Mars ($T = 245\text{-}300$ K, $P(CO_2) = 7$ mb-1 bar, and $P(H_2O)$ equivalent to the vapor pressure of H_2O at this T) consistently yield continued uptake of CO_2 for $t \sim 0.5\text{-}100$ days. Direct correlation of these results with absorption strengths near 7 μm in reflectance spectra of experimental samples supports the conclusion that carbonates can form on Mars. Rates of carbonate formation correspond to 0.01-1 monolayer per unit of $\log_{10}t$ and are faster for greater H_2O abundances. The logarithmic rate is consistent with declining accessibility of chemisorption sites and allows a finite limit to be put on total carbonate formed over geologic time. For a global layer of basalt powder, only a high specific surface area (>1 m^2/g), a thick regolith (>100 m), or plentiful H_2O vapor (equivalent to films >5 monolayers thick) allow total $P(CO_2)$ stored as carbonate to exceed ~10-100 mb. Unless very wet conditions once existed, or unless diffusive transport of CO_2 and H_2O through a rind becomes significant over geologic timescales, carbonate formation probably could not have removed an early, dense CO_2 atmosphere.

Experiments (basalt glass): A sensitive manometer recorded the change in CO_2 pressure due to adsorption and reaction with powdered basalt (Kilauea tholeiite, ~98% glass, surface area ~ 1-10 m^2/g) (e.g., [1], described in detail in [2]). Designed to confirm findings of Booth and Kieffer (1978) [3], these experiments showed (*Figures 1 and 2*) that CO_2 is stored at diminishing (but greater than zero) rates as available chemisorption sites are progressively utilized. Logarithmic kinetics are suggested by power-law fits to data, in which $dP(CO_2)/dt \sim t^{-B}$ yields $B = 0.85 \pm 0.2$. Transitions to linear behavior with log t after $t_o \sim 0.5$ days (*Figure 1*) supports a model in which $P(t) = C + D \log(t/t_o+1)$. (Parabolic rates cannot be excluded as important on geologic timescales if the coefficient in front of $t^{1/2}$ is small but finite.)

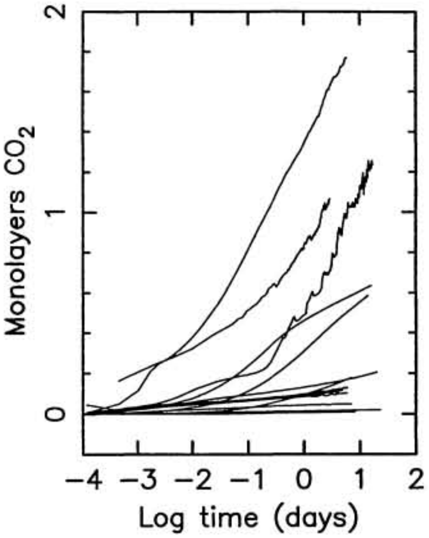

Figure 1. *Gas uptake, expressed as equivalent monolayers of CO_2 deposited uniformly on powder surfaces, versus log (base 10) of time since start of experiments. Two curves with steepest uptake rates are for* warm *(295 K) conditions: $P(CO_2)$ = 1 bar (upper) and 100 mb (lower). Other curves are for* cold *(~250 K) conditions: $P(CO_2)$ = 7 mb-1 bar (steepest is for 1 bar). Two lowest curves are for powder pretreated with weak acid. H_2O was introduced as* vapor *in all experiments shown: equivalent content ≤ 5 monolayers (see also Figure 2).*

For $t \leq 0.5$ days, CO_2 uptake is rapid, suggesting chemisorption or reaction at decreasingly available adsorption sites. At later times, growth rates are nearly logarithmic ($P \sim \log t$); continued reaction is limited only by accessibility of unreacted surface [4]. Parabolic rates ($P \sim t^{1/2}$), where reaction is limited by diffusion through a product layer, are not observed.

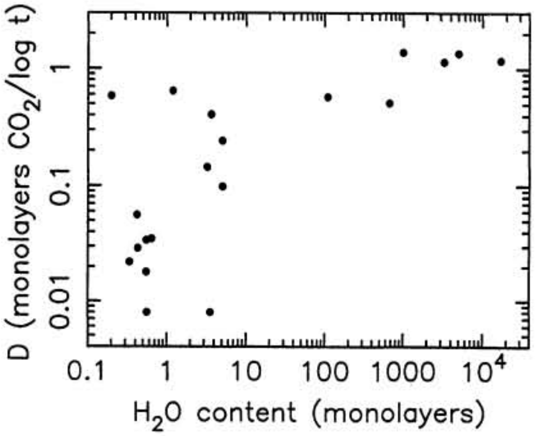

Figure 2. *Reaction rates per log time for* vapor *experiments in Figure 1, plus rates for experiments with* liquid *water (1-5 ml of H_2O introduced for each 1-5 g of powder, under* warm *conditions), as a function of equivalent H_2O content. Two points at upper left are for* warm/vapor *experiments; two lowest points represent acid-treated powder.*

The log-log plot shows a clear correlation between reaction rate and availability of H_2O. Temperature and $P(CO_2)$ also have an effect, but less than H_2O content. Experiments with monomineralic powders give different quantitative results, but similar qualitative behavior. Declining rates for H_2O content < 1 monolayer suggest that a thin film of adsorbed water may be necessary for reaction. Logarithmic rates give upper limits on atmospheric loss and carbonate formation when extrapolated to geologic timescales on Mars (see text).

Infrared Spectroscopy: Reflectance spectroscopy of experimental powders, at 6000-600 cm^{-1} (1.7-16.7 μm), led to the identification of absorptions near 7 μm due to vibrations within the carbonate (CO$_3^{-2}$) ion (*Figure 3*). Small amounts of added carbonate (~0.1 wt%) were determined to be detectable with this technique. Spectra of carbonate reference powders, greater absorptions for powders exposed to more H$_2$O, and positive correlation with modeled logarithmic CO$_2$ uptake rates (*Figure 4*) all support the conclusion that carbonates formed in experimental samples.

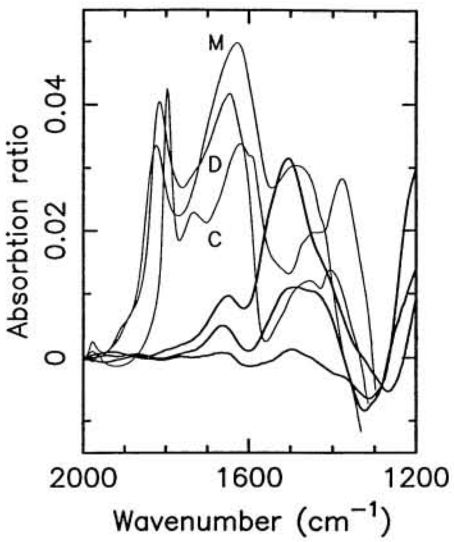

Figure 3. *Ratioed spectra (thick lines) for representative experiments whose results are plotted in Figures 1 and 2. Ratios are intensities of reflection signals (plotted as absorptions) for experimental basalt powders divided by intensities of signals for starting powders, at each wavenumber. Equivalent wavelength range is 5.0-8.3 μm. Controls (e.g., a starting powder ratioed to another sample of itself) would give nearly flat ratioed spectra, aside from noise and atmospheric signal.*

Spectra for carbonate powders ratioed to starting basalt powder are also shown (thin lines). C *is calcite, CaCO$_3$;* M *is magnesite, MgCO$_3$;* and D *is dolomite, CaMg(CO$_3$)$_2$. These spectra are scaled for comparison to experimental results. They are similar to reflectance spectra published by Salisbury et al. (1991) [5]. All ratioed spectra are set to 0 at 2000 cm^{-1}, to account for systematic offsets due to grain-size effects, etc.*

Features in experimental ratioed spectra are interpreted as absorptions by reaction products; their position at ~7 μm is consistent with the presence of additional carbonate. Absorptions supporting this conclusion occur prominently at ~1500-1400 cm^{-1}; there is a weaker but consistent feature at ~1650 cm^{-1}. Both are also present in the three carbonate spectra. The absence of other experimental peaks diagnostic of carbonates, e.g., ~1800 cm^{-1}, may be due to the different nature of carbonate reaction product (presumably on surfaces of basalt grains) and powdered carbonate. Interpretation of absorptions at the right edge of experimental plots is complicated by the presence of strong silicate absorptions <1300 cm^{-1} (although silicates are possible reaction products).

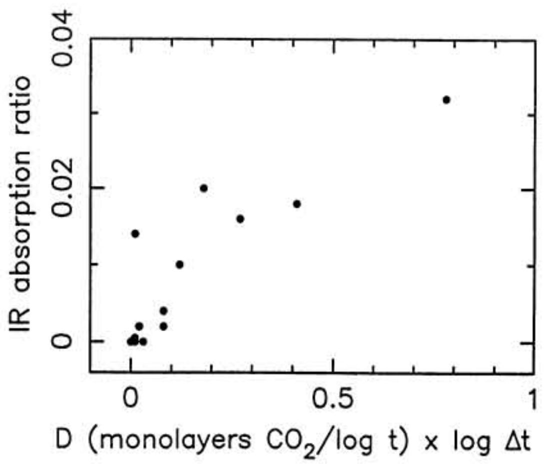

Figure 4. *Correlation of infrared absorption ratios (for largest observed peaks, ~1500-1400 cm^{-1}) with expected thicknesses of reaction product inferred from experimental results. The rate D from Figure 2 is multiplied by log Δt, where Δt (2-23 days) is duration of experimental temperature and pressure. The point with ratio = 0.014 is for an experiment on acid-treated basalt. Results for the other acid-treated powder are not shown, since its spectrum has not yet been measured.*

There is a clear positive correlation between experimental CO$_2$ uptake and strength of IR absorption in resulting powders. Although the significance of weaker (but non-zero) results for acid-treated basalt powder is presently uncertain, agreement between the two sets of results strengthens the conclusion that carbonates were produced in pressure-drop experiments.

Application to Mars: Rates of carbonate formation measured in experiments with H$_2$O vapor, when applied to models of atmospheric evolution on Mars [6-10], may be insignificant compared to other mechanisms of CO$_2$ loss. It may be that substantial carbonates only formed in very wet conditions, or in low-T hydrothermal systems (e.g., [11]).

References: [1] Stephens S.K. et al. (1994) *Lunar Planet. Sci. Abs. XXV*, 1343-1344. [2] Stephens S.K. (1995) Caltech PhD thesis, in prep. [3] Booth M.C. and H.H. Kieffer (1978) *JGR*, *83*, 1809-1815. [4] Landsberg P.T. (1955) *J. Chem. Phys.*, *23*, 1079-1087. [5] Salisbury J.W. et al. (1991) *Infrared (2.1-25 μm) Spectra of Minerals*, Johns Hopkins Univ. Press, Baltimore, 267 pp. [6] Pollack J.B. et al. (1987) *Icarus*, *71*, 203-224. [7] Kahn R. (1985) *Icarus*, *62*, 175-190. [8] Haberle R.M. et al. (1994) *Icarus*, *109*, 102-120. [9] Fanale F.P. and J.R. Salvail (1994) *Icarus*, *111*, 305-316. [10] Pepin R.O. (1994) *Icarus*, *111*, 289-304. [11] Romanek C.S. et al. (1994) *Nature*, *372*, 655-657.