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SIMULTANEOUS ADSORPTION OF CO₂ AND H₂O UNDER MARS-LIKE CONDITIONS AND APPLICATION TO THE EVOLUTION OF THE MARTIAN CLIMATE

Aaron P. Zent, Richard Quinn, SETI Institute and NASA Ames Research Center, Moffett Field CA, 94035.

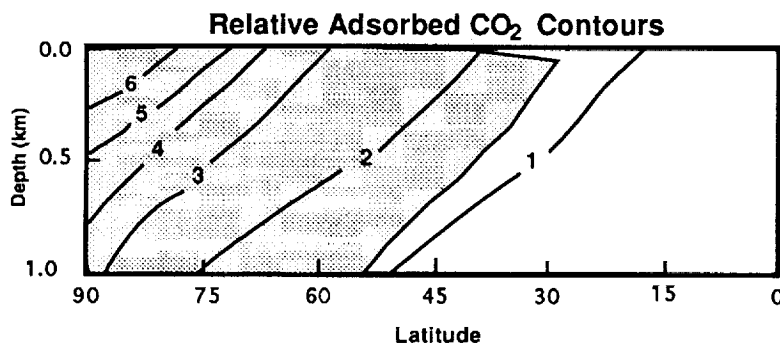
The martian regolith is the most substantial volatile reservoir on the planet (1-2); it holds CO₂ as adsorbate, and can exchange that CO₂ with the atmosphere-cap system over timescales of 10⁵ to 10⁶ years. The climatic response to insolation changes caused by obliquity and eccentricity variations depends in part on the total reservoir of adsorbed CO₂. Previous estimates of the adsorbate inventory have been made by measuring the adsorptive behavior of one or more Mars-analog materials, and deriving an empirical equation that described that adsorption as a function of the partial pressure of CO₂ and the temperature of the regolith.

One can solve the heat diffusion equation for annually averaged conditions and determine the temperature profile to any depth of interest. The current CO₂ inventory is that which satisfies a) adsorptive equilibrium, b) observed atmospheric pressure, and c) no permanent CO₂ caps. Atmospheric pressure history over an obliquity cycle can be found by re-calculating the thermal gradient at each obliquity, and balancing the CO₂. If the atmospheric pressure exceeds the vapor pressure at the poles, permanent caps are assumed to exist, and they fix the atmospheric pressure. The adsorbed CO₂ is recalculated in accord with the new atmospheric pressure, and the remainder of the CO₂ is assumed to be in quasi-permanent polar caps (3).

An important assumption has to do with the applicability of the laboratory measurements to the martian regolith. If the assumed adsorption isotherms are wrong, then the CO₂ inventory is wrong, and the climate history is wrong.

There is laboratory evidence that H₂O poisons the CO₂ adsorptive capacity of most materials (4). No consideration of CO₂ - H₂O co-adsorption was given in previous estimates of the martian CO₂ inventory, although H₂O is present in the vapor phase, and so as adsorbate, throughout the regolith.

If CO₂ is substantially displaced from martian materials by H₂O, then the current estimates of the adsorptive capacity of the regolith must be too high. The martian regolith is at or near 100% relative humidity (R_H) throughout the latitude-depth domain in which ground ice is stable. Figure 1 shows a hemispheric map of the subsurface, contoured with predicted adsorbed CO₂



relative concentrations. The stippled area is the domain within which R_H is near unity, and the monolayer coverage of adsorbent surfaces by H₂O is highest. Over 83% of the total CO₂ inventory is adsorbed in the

domain in which the H₂O abundance is highest. The potential effect of adsorptive competition by H₂O may be then to decrease estimates of the total exchangeable CO₂ inventory by a factor of 6.

To test the effects of H₂O on the CO₂ adsorptive capacity of the martian regolith, we measured co-adsorption of H₂O and CO₂ under conditions appropriate to the martian regolith. We constructed a manifold that allows us to control partial pressures, and the temperature of the soil sample. We use Mauna Kea palagonite as our Mars analog material, and evacuate it at 120° C overnight. CO₂ is 99.999%; the pressure is measured by a capacitance manometer. Doubly distilled water is placed in a reservoir in the manifold and evacuated briefly under vacuum to remove dissolved gases.

We control the partial pressure of the H₂O in the manifold, and temperature of the soil, by cryogenic baths. The temperature of the soil is always greater than the temperature of the H₂O ice in order to keep the relative humidity in the soil chamber below unity.

We analyze the adsorbed gases by gas chromatograph (GC); the GC is calibrated every few days for the partial pressure ranges of interest. In all cases, we first measured zero relative humidity isotherms by pressure drop in order to establish a baseline against which to compare the effects of H₂O; the GC was not used. We used these CO₂ isotherms to calculate a BET area of 94.8 m²/g for the palagonite.

At T_{soil} = 210 K, we found no significant displacement of CO₂ from its R_H = 0 coverage during experiments at R_H = 0.013 and R_H = 0.47; displacement is anticipated at higher R_H, where closer to 0.5 monolayers of H₂O adsorb.

At higher temperatures, (T_{soil} = 242 K) the water poisons CO₂ adsorption at lower R_H. We measured co-adsorption isotherms at R_H = 9.3×10⁻³ and 0.38, and found up to 30% displacement from the zero relative humidity isotherm.

One can derive the following Langmuir isotherm describing the monolayer coverage of CO₂ as a function of its partial pressure and the measured adsorptive coverage of H₂O. (The adsorption of H₂O is assumed to be independent of the partial pressure of CO₂).

This equation can be fit to the data for α and β

$$\theta_c = \frac{a(\alpha T^{-\beta})P_{CO_2}}{(1 + a(\alpha T^{-\beta})P_{CO_2})} \quad 1$$

where a is defined as $(1 - \theta_h)$, where θ_h is the fractional monolayer coverage of water. A least-squares fit to a linearized form of this equation yields $\alpha = 1.002 \times 10^{17}$ and $\beta = -8.635$. These parameters can be expected to change as additional data, particularly at high R_H, are acquired.

Application of this equation to the martian regolith suggests that the effect of H₂O co-adsorption will be to displace a substantial fraction of the CO₂ previously thought to be adsorbed in the high-latitude regolith. As a consequence, the total CO₂ inventory must be revised downward. More quantitative predictions await highest R_H data, and will be presented at the meeting.

References

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- (2) Kieffer and Zent, *Mars*, 1180-1218, 1992;
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- (4) Carter and Husian, *Chem Eng. Sci.* 29, 267-273, 1974