S27-91 ABS. ONLY

N94-35475

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SIMULTANEOUS ADSORPTION OF CO_2 AND H_2O UNDER MARS-LIKE CONDITIONS AND APPLICATION TO THE EVOLUTION OF THE MARTIAN CLIMATE

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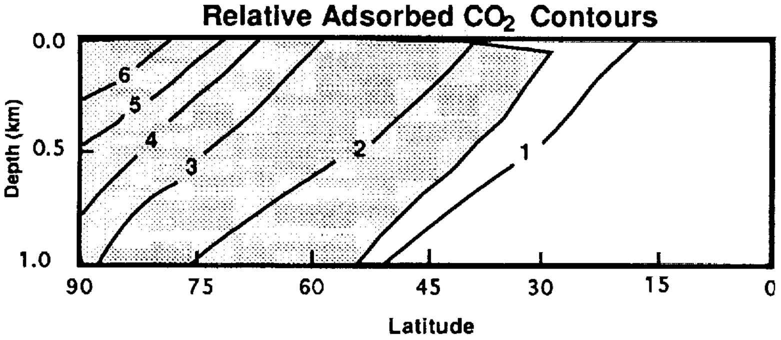
The martian regolith is the most substantial volatile reservoir on the planet (1-2); it holds CO_2 as adsorbate, and can exchange that CO_2 with the atmosphere-cap system over timescales of 10^5 to 10^6 years. The climatic response to insolation changes caused by obliquity and eccentricity variations depends in part on the total reservoir of adsorbed CO_2. 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 CO_2 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 CO_2 inventory is that which satisfies a) adsorptive equilibrium, b) observed atmospheric pressure, and c) no permanent CO_2 caps. Atmospheric pressure history over an obliquity cycle can be found by re-calculating the thermal gradient at each obliquity, and balancing the CO_2. 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 CO_2 is recalculated in accord with the new atmospheric pressure, and the remainder of the CO_2 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 CO_2 inventory is wrong, and the climate history is wrong.

There is laboratory evidence that H_2O poisons the CO_2 adsorptive capacity of most materials (4). No consideration of CO_2 - H_2O co-adsorption was given in previous estimates of the martian CO_2 inventory, although H_2O is present in the vapor phase, and so as adsorbate, throughout the regolith.

If CO_2 is substantially displaced from martian materials by H_2O, 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 CO_2 relative concentrations. The stippled area is the domain within which R_H is near unity, and the monolayer coverage of adsorbent surfaces by H_2O is highest. Over 83% of the total CO_2 inventory is adsorbed in the



domain in which the H_2O abundance is highest. The potential effect of adsorptive competition by H_2O may be then to decrease estimates of the total exchangeable CO_2 inventory by a factor of 6.

To test the effects of H_2O on the CO_2 adsorptive capacity of the martian regolith, we measured co-adsorption of H_2O and CO_2 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.. CO_2 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 H_2O in the manifold, and temperature of the soil, by cryogenic baths. The temperature of the soil is always greater than the temperature of the H_2O 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 H_2O; the GC was not used. We used these CO_2 isotherms to calculate a BET area of 94.8 m^2/g for the palagonite.

At T_{soil} = 210 K, we found no significant displacement of CO_2 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 H_2O adsorb.

At higher temperatures, (T_{soil} = 242 K) the water poisons CO_2 adsorption at lower R_H. We measured co-adsorption isotherms at $R_H = 9.3\mathrm{x}10^{-3}$ 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 CO_2 as a function of its partial pressure and the measured adsorptive coverage of H_2O. (The adsorption of H_2O is assumed to be independent of the partial pressure of CO_2).

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

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

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 $\alpha = 1.002\mathrm{x}10^{17}$ 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 H_2O co-adsorption will be to displace a substantial fraction of the CO_2 previously thought to be adsorbed in the high-latitude regolith. As a consequence, the total CO_2 inventory must be revised downward. More quantitative predictions await highest R_H data, and will be presented at the meeting.

References

(1) Toon et al., *Icarus*, **44**, 552-607, 1980; (2). Kieffer and Zent, *Mars*, 1180-1218, 1992; (3) Fanale et al, *Icarus*, **50**, 381-407,1982; (4) Carter and Husian, *Chem Eng. Sci.* **29**, 267-273, 1974