

martian surface, or further analyses of martian meteorites, is that there exist on Mars large deposits of oxalate minerals, such as  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , etc. On Earth these minerals fall at the very interface of inorganic and organic chemistry, being formed predominantly by biological processes. That they can form by purely inorganic reactions is demonstrated, however, by their presence in primitive carbonaceous chondrites [19]. If oxalates are present on Mars, this might explain the removal of  $\text{CO}_2$  from the atmosphere without the formation of observable carbonate deposits.

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**SIMULTANEOUS LABORATORY MEASUREMENTS OF  $\text{CO}_2$  AND  $\text{H}_2\text{O}$  ADSORPTION ON PALAGONITE: IMPLICATIONS FOR THE MARTIAN CLIMATE AND VOLATILE RESERVOIR.** A. P. Zent and R. Quinn, SETI Institute and NASA Ames Research Center, Moffett Field CA 94035, USA.

We are measuring the simultaneous adsorption of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on palagonite materials in order to improve the formulation of climate models for Mars. We report on the initial co-adsorption data. Models of the martian climate and volatile inventory indicate that the regolith serves as one of the primary reservoirs of outgassed volatiles and that it exchanges  $\text{H}_2\text{O}$  and  $\text{CO}_2$  with the atmosphere in response to changes in insolation associated with astronomical cycles. Physical adsorbate must exist on the surfaces of the cold particulates that constitute the regolith, and the size of that reservoir can be assessed through laboratory measurements of adsorption on terrestrial analogs. Many studies of the independent adsorption of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on Mars analogs have been made and appear in the literature [1–5]. Empirical expressions that relate the adsorptive coverage of each gas to the temperature of the soil and partial pressure have been derived based on the laboratory data. Numerical models incorporate these adsorption isotherms into climatic models, which predict how the adsorptive coverage of the regolith, and hence the pressure of each gas in the atmosphere will vary as the planet moves through its orbit [e.g., 6]. These models suggest that the regolith holds several tens to hundreds of millibars of  $\text{CO}_2$  and that during periods of high obliquity warming of the high-latitude regolith will result in desorption of the  $\text{CO}_2$ , and a consequent increase in atmospheric pressure. At lower obliquities, the caps cool, and the equator warms, forcing the desorption of several tens of millibars of  $\text{CO}_2$ , which is trapped into quasipermanent  $\text{CO}_2$  caps.

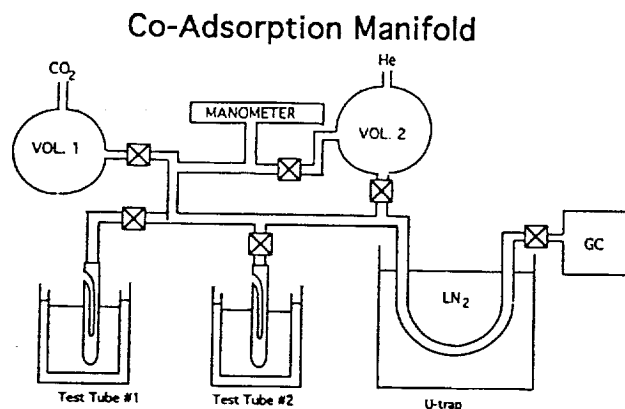


Fig. 1.

There are a number of uncertainties in these models. Extrapolating the martian orbit more than several  $10^4$  yr in either direction is difficult because of the chaotic nature of the martian orbit [7]. The extent of the regolith is unclear particularly with respect to the specific surface area of regolith materials that is in diffusive contact with the atmosphere. Finally, the adsorptive behavior of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  has always been assumed to be independent. Yet there are data that suggest that near room temperature, there is adsorptive competition between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  [8], and  $\text{H}_2\text{O}$  actively displaces  $\text{CO}_2$  from the adsorbed state. If that is the case on Mars, then current models of the  $\text{CO}_2$  inventory overestimate its size, and climate models must account for new estimates of the inventory size and the effects of  $\text{H}_2\text{O}$  on  $\text{CO}_2$  exchange. We have therefore undertaken laboratory measurement of the adsorptive competition between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  at conditions appropriate to the martian regolith in order to eliminate this uncertainty in the climate models.

The experimental apparatus is shown schematically in Fig. 1. The manifold and sample are baked out overnight and we then fill volume 2 to a known pressure with He and expand into the sample to estimate the dead volume in the system. The sample is cryogenically cooled to a preselected temperature,  $T_1$ . Doubly distilled water in test tube #2 is cryogenically cooled to temperature  $T_2$ . We maintain  $T_2 > T_1$  in order to keep the relative humidity in the soil chamber well below unity.  $T_1$  and  $T_2$  are constantly monitored. To acquire a data point, we fill volume 1 with a known pressure of  $\text{CO}_2$  and

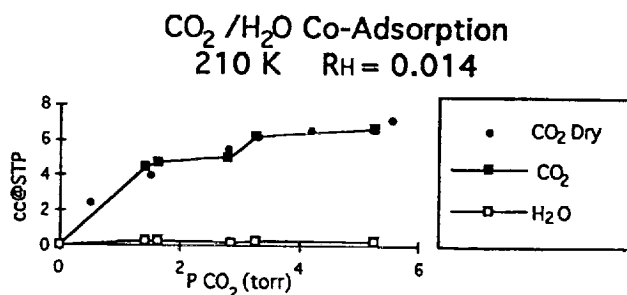


Fig. 2.

expand it into the sample chamber along with the H<sub>2</sub>O vapor buffered at T<sub>2</sub>. Equilibration to within the precision of our data analysis typically requires on the order of 6 hr. We have made several estimates of this timescale by varying the equilibration period and comparing analyses of several points. After equilibration, we isolate the soil sample and heat it to approximately 50°C while opening the head space to an LN<sub>2</sub> trap. After 5 hr, the U trap is isolated, removed from the manifold, and attached to a gas chromatograph. The U trap is heated to desorb gas on the interior walls and injections are made. Occasionally, a second injection is done and compared to the first, in order to disprove the possibility that substantial amounts of H<sub>2</sub>O are adsorbed onto the warm walls of the U trap. We do not find evidence of significant H<sub>2</sub>O adsorption in the warm trap. The data are discarded if any N<sub>2</sub> peaks appear in the chromatogram, indicating a leak in the manifold. While the U trap is attached to the GC, the sample is baked out under vacuum at 50°C for 16 hr. Since each data point is independently acquired, the spread about a smooth isotherm is a measure of the random error in the technique. The dry CO<sub>2</sub> isotherm is acquired by simply measuring the pressure drop of CO<sub>2</sub> over the soil and is an independent technique.

All data acquired to date are at 210 K, and low relative humidity ( $R_H = 0.014$ ). We have found, contrary to our expectations, that CO<sub>2</sub> is not substantially displaced by adsorbed H<sub>2</sub>O (see Fig. 2) relative

to its adsorptive coverage from a dry atmosphere. We are currently performing adsorption curves at T = 210 K and  $R_H \approx 50\%$  (relative to ice) in order to assess the capability of H<sub>2</sub>O to displace adsorbed CO<sub>2</sub>. We are continuing data acquisition, and will move to higher temperature isotherms.

Interpretation of the new data, insofar as conclusions can be drawn from such a limited set, is uncomplicated, since these data support the assumptions of independent adsorptive behavior that have already been published in the literature. We believe that at higher temperatures, H<sub>2</sub>O will compete more effectively for adsorption sites than it does at low temperatures, requiring some modification of the climate models. At low temperatures and relative humidity, however, such as in the winter hemisphere or during periods of low obliquity when most H<sub>2</sub>O may be cold trapped at quasipermanent CO<sub>2</sub> caps, there is no indication in the data that substantial modification of the current models is required.

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