THE SPECTRA OF CHEMISORBED CO₂ ON MARS ANALOG MATERIALS, A. P. Zent, SETI Institute and NASA Ames Research Center, Moffett Field, Ca 94035, T. L. Roush, San Francisco State University, San Francisco, Ca 94132 and NASA Ames Research Center, Moffett Field, 94035.

Introduction: The goal of this work is to estimate the possible reservoir of CO₂ that has been removed to a quasi-stable reservoir on the martian surface by chemisorption, and to estimate the spectral effects of chemisorbed CO₂ in remotely sensed martian spectra. Our approach is to search for infrared spectral bands that result from chemisorption of CO₂ molecules onto Mars-like materials.

A persistent problem with understanding the climatic history of Mars is that the total amount of CO₂ that appeared in the early martian atmosphere, and consequent surface temperatures, are unknown [1]. It appears now that a CO₂ greenhouse may not be an adequate greenhouse mechanism under any circumstances [2]; however, if significant amounts of CO₂ were present and responsible for elevated surface temperatures, then most of that CO₂ must still be in the near-surface environment since there is no escape mechanism that will remove it after the decline of channeling. The only reservoir that is reasonable is carbonate, and there are various remote sensing techniques which can be used to search for that carbonate [3]. We are investigating CO₂ chemisorption as a permanent CO₂ sink, and to aid in interpretation of remotely-sensed IR spectra of Mars.

A common effect reported in CO₂ adsorption studies is the formation of a layer of carbonate or bicarbonate anions on adsorbents that have OH⁻ groups available on their surfaces [4]. The process responsible for this reaction is chemisorption. Chemisorption is distinguished from physical adsorption in that there is a transfer of electrons between species, and the formation of a chemical bond. The heat of chemisorption is typically of the same order as heats of chemical reaction (i.e. a few hundred to a few thousand kJ/mole), as opposed to heats of physical adsorption (a few kJ per mole). A predictable consequence if that chemisorption is an activated process, that is promoted by an increase in temperature - quite the opposite of physical adsorption. Chemisorption is not reversible in the sense that physical adsorption is.

Experiment: We selected montmorillonite as the initial analog material because we wanted to maximize the probability of identifying carbonates and bicarbonates. Inorganic hydroxyl groups occur on phyllosilicates, amorphous silicates, metal oxides, oxyhydroxides, and hydroxides; it is the most abundant and reactive surface functional group on the periphery of terrestrial silicates [4]. Montmorillonite has a very high specific area and hence among the highest abundance of surface hydroxyls per unit mass of commonly available materials. We also selected CaO and CaOH as reference materials because they have been reported in the literature to form carbonate and bicarbonate ions by CO₂ chemisorption within minutes [5].

Sample preparation was accomplished by sealing powdered samples in serum vials and purging the head space with CO₂ at 10⁶ Pa, at a flow rate of 4 ml min⁻¹ for approximately 24 hours. Controls were sealed at the same time as the samples but not exposed to CO₂. Controls and samples were simultaneously warmed slightly to about 320 K to maximize chemisorption and minimize physical adsorption. After 24 hours, the powders were removed from the serum vials and 0.2 mg were mixed with approximately 200 mg of KBr and pressed into pellets. The pellets were placed in the spectrometer, which was purged with dry nitrogen gas. Nitrogen purge throughout data acquisition further reduces the abundance of physically adsorbed CO₂ as well as other species.

Transmission spectra were acquired from 400 to 4000 cm⁻¹ with a resolution of 1 cm⁻¹. The data for each sample were ratioed against their respective controls, and the result plotted in Figure 1. Differences in the thickness and weight percent of sample and control (Table 1) cause some of the spectral changes to appear as maxima, and others to appear as minima.

Montmorillonite: The silicate fundamental was saturated in the reference spectrum, so the
CHEMISORBED CO$_2$: Zent, A.P. and Roush, T.L.

ratio spectrum in the vicinity of 1000 cm$^{-1}$ is not useful. There was no evidence when comparing the reference and sample spectra that any new bands appeared due to the sample preparation. A ratio of the sample and reference spectra also fails to reveal any new bands. A specific search for carbonate bands at 1415, 1063, 879 and 680 cm$^{-1}$ did not reveal any new bands. No evidence of carbonate or bicarbonate formation was detected. In order to assess the efficacy of this technique for detection of carbonate, we compared the results of the montmorillonite spectra to CaO and CaOH.

CaO: The sample/reference ratio shows definite peaks at 862, 1069 and 1412 - 1475 cm$^{-1}$, which are all consistent with carbonate [5].

CaOH: There were pronounced effects on the CaOH spectrum caused by exposure to CO$_2$. In addition, during purge the inside of the serum vial was observed to be covered with a condensate. There are reports in the literature that CO$_2$ adsorption by La(OH)$_3$ caused the formation of water by displacing structural OH from the adsorbent [5]. It was also noted in the CaOH spectra that the 3640 cm$^{-1}$ band was considerably shallower in the sample spectrum than in the reference spectrum, and that no corresponding decrease in the accompanying 3420 cm$^{-1}$ band was observed. Although the masses of sample and reference differ too much to assert positively that the surface OH groups were altered, by addition of CO$_2$ to the headspace the available data are consistent with that hypothesis. We identified bands at 860 and 1070 cm$^{-1}$ and a saturated band at 1400 - 1500 cm$^{-1}$ that correspond in general to carbonates. An additional band was identified near 717 cm$^{-1}$, its doublet nature, and the doublet nature of the 860 cm$^{-1}$ band all suggest a carbonate structure with lower symmetry than calcite and are consistent with an interpretation of the presence of bicarbonate [6]. Three additional bands are observed at 1791, 2522, and a complex between 2850 and 3000 cm$^{-1}$. We tentatively ascribe the first two features to combination modes [7]. The complex feature occurs in the region of the C-H stretching fundamental, so its source remains uncertain at this time.

Summary: Exposure to 100 kPa of CO$_2$ for 24 hours at 50°C produced easily detectable amounts of chemisorbed carbonate and possible bicarbonate ion on the surface of CaO and particularly CaOH. There was no spectral evidence for the formation of either carbonate or bicarbonate upon exposure of montmorillonite to the same conditions, and there is not yet evidence that significant amounts of CO$_2$ could be stored irreversibly as carbonate or bicarbonate, nor is there any reason to suspect that infrared studies of the martian regolith must account for chemisorbed CO$_2$.


Table 1 - Weight Percent of 200 mg KBr Pellet

<table>
<thead>
<tr>
<th>Montmorillonite</th>
<th>Reference</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>0.19%</td>
<td>0.74%</td>
</tr>
<tr>
<td>CaOH</td>
<td>0.58%</td>
<td>0.87%</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>0.59%</td>
<td>0.88%</td>
</tr>
</tbody>
</table>

Figure 1. Ratio of sample to control spectra with tentative band identifications.