THE ADSORPTION OF GASES ONTO REFRACTORY MATERIALS: CO_2 ONTO CLAYS AND THEIR RELEVANCE TO THE ICY GALILEAN SATELLITES C. A. Hibbitts, Sean Hagaman, A. Greenspon, JHU-APL, Laurel, Md. 20723 karl.hibbitts@jhuapl.edu

Introduction: Volatiles are of interest in part because of their potential role in the formation of life or as markers of life. However, because volatiles would only condense in the outer portions of the solar system, a transport mechanism such as comets, asteroids, etc. are needed to enable transport of large quantities to the inner solar system. However, recent discoveries demonstrate that significant amounts of volatiles can be stabile against thermal sublimation by bonding with refractory regolith materials: examples include CO2 on the icy satellites of Jupiter and Saturn [1-6], and water/hydroxyl on the illuminated portions of the Moon [7-9]. Here we explore the spectral nature of cryoadsorbed CO_2 on one analog to the surface material on icy satellites, clays. It is possible that significant volatiles can be adsorbed on the surfaces of fine grain particles [10]. Here, in an attempt to better understand this, we are characterizing the spectral nature of this adsorbed carbon dioxide and providing qualitative information on its thermal stability.

On Callisto and Ganymede, the CO_2 that is detected is bound to, or trapped within, the non-ice materials that prevent it from sublimating or otherwise escaping from the surface [e.g. 2]. It appears to be similarly bound in nonice materials on Iapetus and Phoebe [11]. On Europa, it resides within both the ice and nonice materials [12,13]. While greater abundances of CO_2 may exist in the interiors of these moons, or small amounts may be continually created through particle bombardment of the surface, the observed CO_2 is only a trace material, with a few hundred molecules responsible for the deepest absorption features and an estimated molar abundance of 0.1% [2; 14-16]. Yet its presence may provide essential clues to processes that shape the surfaces of the moon [17] and potentially key to understanding the composition of potential oceans in the subsurfaces. We continue measurements [18] of the infrared properties associated with CO_2 adsorbed onto nonice materials under pressures and at temperatures relevant to these icy satellites to understand its physical state, trapping processes, and nature of the non-ice adsorbent.

Procedures: Using biconical reflectance spectroscopy from ~ 1.5 to 5.5 μm, we are measuring the spectral nature of CO_2 adsorbed onto clays under high vacuum (~ 10^{-8} – 10^{-7} torr) at temperatures relevant to the Galilean satellites (~ 135K and warmer). Bidirectional spectroscopy enables detection of low concentrations of adsorbate on fine-grained materials such as clays due to the large surface area to volume ratios of small particles and thus a large surface area for coverage by adsorbate [14].

An environmental system has been constructed for these experiments. The clay sample is placed in a copper sample holder that has a 1/8" Swagelok gas line for dosing the sample directly and a $MgFl_2$ window for retaining the sample while collecting spectra. The holder is mounted on the end of a cryostat that vertically penetrates the environmental chamber (Figure 2), and which can be cooled with liquid nitrogen to ~ 135K, heated to ~ 700K, raised and lowered for acquiring reference reflectance measurements off various standards.

Before dosing with gas, the sample is first desiccated of loosely bound water by heating to ~ 120C overnight. The sample is then cooled via conduction by the liquid-nitrogen filled dewar on the cryostat, with spectra obtained during cooling, when cooling is complete but before dosing, during dosing, and after dosing is completed to obtain a thorough understanding of the spectral nature of adsorbed clay and insight into its thermal stability. During dosing, the pressure in the chamber reaches ~ 10^{-4} torr and is presumed higher in the sample holder due to the presence of a confining, but unsealed, window over the sample. After dosing, the chamber quickly returns to ~10^{-7} torr.

Results: CO_2 adsorbs onto montmorillonite clays, with the adsorption onto a calcium-rich montmorillonite being investigated in detail, with the position of its ν_3 fundament absorption band dependent on the cation composition, adsorbent temperature, and possibly partial pressure of adsorbate. The adsorption of CO_2 onto clay only affects the 4.25-μm region containing the fundamental absorption. There is not evidence for weaker absorption bands elsewhere, such as near 2 μm, which are present in CO_2 ice (Figure 1).

Current results confirm previous experiments reliant on infrared transmission measurements [18] that at temperatures of 150K and higher, adsorbed CO_2 has a band minimum near 4.22 μm and at temperatures near 130K and below, a band near 4.256 μm dominates [4]. These new measurements shows the relationship between temperature and band position to be more complex (Figure 1). Dosing at 135K results in two large bands forming at ~ 4.22 and 4.26 μm (Figure 2), with the 4.26 μm band growing while the sample is held at

135K (blue lines). After dosing, while under vacuum as the temperature increases to ~ 140K, CO_2 is lost from the adsorption sites responsible for the 4.26-mm band and the 4.22-μm band dominates (gray lines). CO_2 is lost (the band depth decreases) at this temperature on the order of hours (green lines). There are also several bands near 4.35 μm which show a temperature dependent and abundance effect. There is no evidence for the formation of ice, which has a sharp singlet at 4.27 μm.

Conclusions: The spectral nature of CO_2 adsorbed on clay is dependent on composition, dosing temperature, and abundance (partial pressure). At 'high' pressure physisorption dominates, inducing several bands not present under high vacuum. This may be relevant to bodies with atmospheres such as Mars. The transition temperature between two strong spectral bands of CO_2 adsorbed onto calcium montmorillonite under

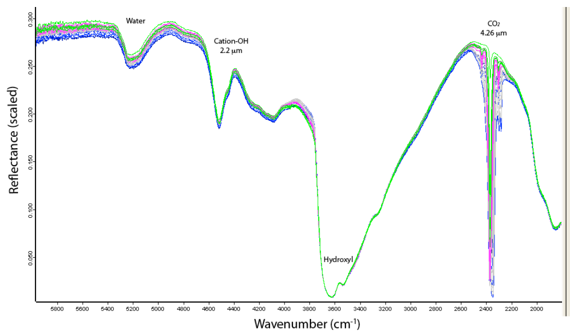

Figure 1. Reflectance spectra obtained of montmorillonite clay under high vacuum ~ 10^{-7} torr after baking out under vacuum for about a day and then cooled to ~ 135K.

high vacuum occurs consistently between 135K and 140K. CO_2 is stable at one type of adsorption site near 4.22 μm under high vacuum, and when pressure increases to medium vacuum, the CO_2 begins to accumulate onto a second type of adsorption with a characteristic absorption at 4.26 μm. Previous experiment showed that at 130K and lower, CO_2 is stable at those sites. This position is very similar to the CO_2 detected on the icy Galilean satellites, but as it is unstable at Galilean satellite daytime temperatures, it is probably not analogous. Other materials may have CO_2 adsorption sites that are stable at 150K and spectral consistent with the CO_2 detected on the Galilean satellites.

Future work includes measuring the nature of the CO_2 absorption band for CO_2 adsorbed onto a variety of clays at several different dosing temperatures.

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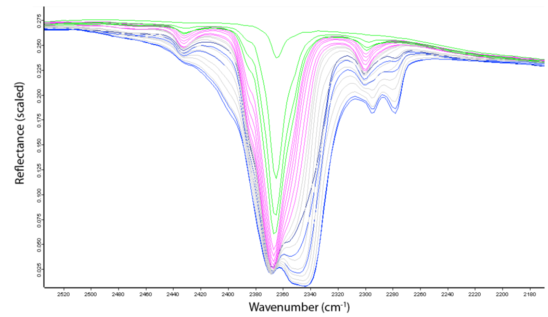

Figure 2: CO_2 adsorbed onto calcium montmorillonite exhibits spectral characteristics unlike gas or ice, and possesses several band centers. Band strength and position is temperature dependent.

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