**PHYSISORPTION OF CO\textsubscript{2} ON NON-ICE MATERIALS OF RELEVANCE TO ICY SATELLITES.**  C. A. Hibbitts\textsuperscript{1} and J. Szanyi\textsuperscript{2}, \textsuperscript{1}Johns Hopkins University Applied Physics Laboratory, 11130 Johns Hopkins Rd., Laurel, Md. 20723, karl.hibbitts@jhuapl.edu, \textsuperscript{2}Pacific Northwest National Laboratory, EMSL, Richland, Wa. 99352

**Introduction:** CO\textsubscript{2} has been detected in the surfaces of several of the Galilean and Saturnian satellites [1-6]. However, it’s physical state is poorly understood. On the Galilean satellites the CO\textsubscript{2} that is detected is bound to, or trapped within, the non-ice materials preventing it from sublimating or otherwise escaping from the surface. The non-ice material on surface of Callisto and Ganymede can reach 140K-160K [7] and similarly dark material at low latitudes on the Saturnian satellites would reach ~ 110K. At these temperatures the vapor pressure of CO\textsubscript{2} ice range from < 0.01 mbar to over 30 mbar and would quickly sublimate if not otherwise held in the surface [8]. Direct evidence that the CO\textsubscript{2} is held by a host material comes from infrared spectra obtained by both the Galileo and Cassini spacecrafts showing an absorption feature due to CO\textsubscript{2} that is shifted from either a solid or a gas. The CO\textsubscript{2} on Ganymede and Callisto is a trace material, with only a few hundred molecules responsible for the deepest absorption features and an estimated molar abundance of ~ 0.1% [2; 9-11]. The abundance of CO\textsubscript{2} in the Saturnian satellites Phoebe and Iapetus is similar, but whether the host is the ice and/or the nonice material is uncertain. Regardless of the origin of the CO\textsubscript{2} in the surfaces of the Galilean and Saturnian satellites, it’s infrared signature implies a similar bonding in the materials in each of Galilean and Saturnian moons where discovered.

All non-ice material on Callisto and Ganymede contain some CO\textsubscript{2}, implying long-term stability for some nominal CO\textsubscript{2} abundance [11]. There is also evidence that some of the CO\textsubscript{2} on the surface of Callisto has limited stability. A \textasciitilde 10^{-12} torr exosphere of CO\textsubscript{2} exists above Callisto which appears to be rejuvenated from a source on the surface approximately once every four years [12]. The CO\textsubscript{2} may be leaking from Callisto’s interior such as through recent impact craters that are rich in CO\textsubscript{2} relative to surrounding terrain or through the sublimation of CO\textsubscript{2}-rich ice [13], in both cases implying a subsurface reservoir.

**Trapping CO\textsubscript{2}:** Other mechanisms in lieu of physisorption can bound CO\textsubscript{2} to host materials. The CO\textsubscript{2} could be trapped inside the host molecules, similar to inclusions [2]. On surfaces colder than these satellites, CO\textsubscript{2} could be trapped by the deposition of water-ice. Amorphous water-ice at temperatures below that of these satellite’s surfaces can hold gases as dissolved species and clathrates [e.g. 14,15]. However, upon warming the gases are ejected during the amorphous to crystalline phase transition \textasciitilde 135K. This type of trapping could be active in radiation environments in the outer Solar System where ice is sputtered and redeposited locally. For instance co-deposition with water-ice is also the likely mechanism of trapping the CO\textsubscript{2} and other gases in the dust of molecular clouds [e.g. 16-21].

A physical mechanism that may be able to explain the spectral characteristics of the CO\textsubscript{2} and an apparently limited stability in the non-ice material (on Callisto) is physisorption. Thus, in this initial exploratory research we have begun to investigate the spectral properties of CO\textsubscript{2} adsorbed onto non-ice materials at cryogenic temperatures to determine if they are consistent with the spectral characteristics of CO\textsubscript{2} on the icy satellites.

**Laboratory Measurements:** We have measured the mid-IR absorption feature of CO\textsubscript{2} physisorbed onto pellets of Ca-montmorillonite, Na-montmorillonite, (Mg,Li)-montmorillonite, palagonite, Mg-serpentine, goethite, and kaolin at room temperature and, in some cases, at 125K using transmission spectroscopy. Only physisorbed CO\textsubscript{2} has been detected. Each montmorillonite mineral and kaolin was found to absorb CO\textsubscript{2}, though kaolin only did so at cryogenic temperatures. The Mg-serpentine, palagonite, and goethite did not absorb CO\textsubscript{2} even when cooled. Montmorillonite absorbs more CO\textsubscript{2} than kaolin, with the position of the ~4.26 \textmu m CO\textsubscript{2} absorption band dependent on the cation charge density (Figure 1) in a similar manner observed for the adsorption of CO\textsubscript{2} onto zeolites [22]. The IR absorption band of CO\textsubscript{2} in montmorillonite tends to shift toward longer wavelengths as the density of the electric field associated with the principle cation decreases, with the exception that the IR absorption band of the Na-rich endmember occurs at a shorter wavelength than for the Li-rich endmember. Also, CO\textsubscript{2} physisorbed onto montmorillonite at cryogenic temperatures has a different shape than for CO\textsubscript{2} physisorbed at room temperature (Figure 2). The apparently larger adsorbance at room temperature compared with cold temperatures (even for greater manifold pressures) is an artifact due to low pressures in the chamber because of cold-trapping CO\textsubscript{2} onto the exposed portion of the cryostat in lieu of adsorption onto the sample. This phenomenon prevents temperature-
programmed desorption experiments to quantify the stability of the adsorbed CO$_2$.

**Conclusions:** The physisorption of CO$_2$ onto non-ice materials can explain some of the characteristics of CO$_2$ discovered in the surfaces of the Galilean and Saturnian satellites. Clay minerals montmorillonite and kaolinite physisorb CO$_2$ under vacuum at temperatures relevant to the icy satellites, but other materials studied: goethite, palagonite, serpentine do not. It is likely the presence of charge-compensating ions, and the resulting negative charge of the remaining structure, enable CO$_2$ to physisorb by inducing a dipole in the CO$_2$ molecule. The distorted mid-IR spectral absorption feature of CO$_2$ in the surfaces of the icy satellites is similar to the spectral characteristics of CO$_2$ physisorbed on Ca-montmorillonite at 125K. The wavelength position of the maximum IR absorbance is related to the bulk composition and to the charge density of the major cation in the clay structure. Cations of large charge density tend to shift the wavelength to smaller numbers than for lower charge density cations. There is also a temperature dependence on the spectral characteristics of adsorbed CO$_2$. The wavelength of the maximum absorption for CO$_2$ in Ca-Montmorillonite at 125 K is ~ 30 nm longer than for CO$_2$ at room temperature and its shape is similar to the spectrum of CO$_2$ on the icy satellites. However, physisorption of CO$_2$ in unirradiated laboratory samples is too weak to account for the long-term stability of CO$_2$ in the satellites’ surfaces. It remains to be determined if radiation damage of non-ice materials could alter them so physisorbed CO$_2$ would be stable over geologic time.


![Figure 1. Room-temperature spectra of CO$_2$ physisorbed onto various montmorillonite minerals. Black: Mg,Li. Gray: Na (scaled x8), Dotted: Ca.](image1.png)

**Figure 1.** Room-temperature spectra of CO$_2$ physisorbed onto various montmorillonite minerals. Black: Mg,Li. Gray: Na (scaled x8), Dotted: Ca.

![Figure 2. The effect of temperature on the shape and position of the IR absorption band for a Ca-rich montmorillonite. The room temperature results are from a separate run than presented in Figure 1, but is consistent with those results in both band shape and position of maximum absorbance.](image2.png)

**Figure 2.** The effect of temperature on the shape and position of the IR absorption band for a Ca-rich montmorillonite. The room temperature results are from a separate run than presented in Figure 1, but is consistent with those results in both band shape and position of maximum absorbance.