

SPECTRAL NATURE OF CO₂ ADSORPTION ON METEORITES G. Berlanga¹, C. A. Hibbitts¹, D. Takir², M. D. Dyar³; JHU-APL, Laurel, Md. 20723¹, University of Tennessee, Department of Earth & Planetary Sciences, Knoxville, TN 37996², Department of Astronomy, Mount Holyoke College, South Hadley, MA 01075³; gesis.berlanga@gmail.com

Introduction: Outer main belt asteroids provide insight to the early solar nebula chemistry and composition. Volatiles such as carbon dioxide serve as markers for materials that primarily condensed in the outer portions of the solar system. Large quantities likely travelled into the inner solar system via comets and asteroids [3], probably as ices, but possibly in different physical states. CO₂ has also been detected in surfaces too warm for CO₂ to exist and may be held by structural trapping, physisorption, and chemisorption [2]. Here we investigate the adsorption of CO₂ onto outer main belt carbonaceous chondrite meteorite matrix material; material thought to reflect regions of the primordial solar nebula that did not undergo significant heating (>200 C) [6] and thus have potentially aided in the delivery of CO₂ into the inner solar system. Additionally, understanding the presence of CO₂ on meteorites may provide insight for potential adsorption processes in non-ice materials on icy satellites orbiting Jupiter and Saturn, as well as for comparison with asteroid spectra from space and ground-based telescopes [2][4].

Procedures: We collected biconical reflectance spectra ($i=15^\circ$, $e=45^\circ$) from ~ 1.7 to $5.5 \mu\text{m}$, for one CI and three CM meteorites in powder form, using a nitrogen purged Bruker Vertex 70 FTIR spectrometer at a 8 cm^{-1} resolution. We investigated the spectral nature of CO₂ adsorbed onto meteorites under space like conditions: high vacuum ($\sim 10^{-8}$ – 10^{-7} torr) and at temperatures of $\sim 123 \text{ C}$ (150 K) to room temperature. The vacuum and initial baking to $\sim 201 \text{ C}$ (475 K) removed adsorbed terrestrial water [4]. Fine-grained meteorites provide a large surface area for CO₂ adsorption thus bidirectional spectroscopy serves as an effective tool for detection of low concentrations of adsorbate [1].

The powdered sample is held vertically in a copper holder and retained in place via a 1 mm thick MgF₂ window. Spectra were measured with reference to a powdered MgF₂ standard, also mounted vertically just below the sample holder and retained with a MgF₂ window. A 1/8" stainless steel gas line was connected directly to the sample holder to directly dose the material with CO₂ in-situ, while under vacuum and cryogenic conditions. The copper holder was mounted on the end of a cryostat which could be heated to $\sim 402 \text{ C}$ (675 K), and cooled with liquid nitrogen to $\sim -123 \text{ C}$ (150 K). Background reference and sample reflectance measurements were acquired by raising and lowering the cryostat within the chamber [3][11].

Spectra were taken under ambient conditions and after being under vacuum at room temperature (23 C / 297 K) overnight (16 hours). Chamber pressures reached 10^{-8} torr by morning. The sample was then heated to $\sim 201 \text{ C}$ to fully desiccate the meteorite of terrestrial adsorbed water and then conductively cooled to $\sim 123 \text{ C}$. Spectra were obtained throughout this process, before heating, during heating and cooling, and during and after CO₂ dosing. Upon reaching $\sim 123 \text{ C}$, the meteorite was dosed with CO₂. Effort was made to infuse enough CO₂ to create an obvious CO₂ spectral signature. (Figure 1) This often only required a small amount of dosing, raising the chamber pressure to $\sim 10^{-4}$ torr.

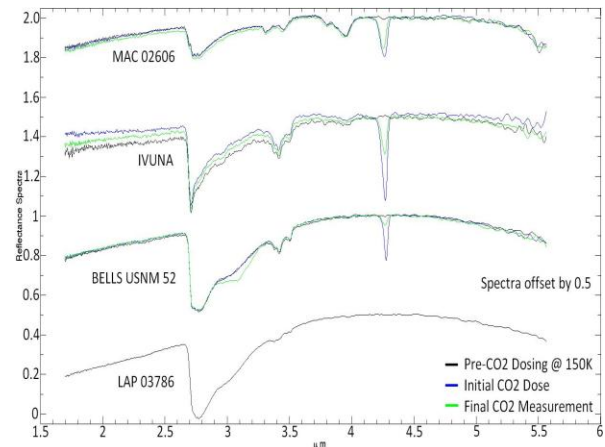


Figure 1: Reflectance spectra for CM and CI meteorites after desiccation at 150 K before CO₂ dosing, at initial dosing, and ~ 3 hours later. CO₂ did not bind to LAP 03786. Ivuna adsorbed CO₂ and retained it without loss the entire time.

Results: LAP 03786, MAC 02606, Bells USNM 5293, and Ivuna were analyzed. Bells USNM 5293 and MAC 02606 received detailed CO₂ desorption analyses at the $4.27 \mu\text{m}$ asymmetric stretching fundamental (ν_3) [5]. (Figure 2) All are CM meteorites except for Ivuna which is from the CI group [4]. CO₂ did not bind to LAP 03786. CO₂ bound very strongly to Ivuna and resulted in the deepest, as well as the most stable band of all four meteorites. The rate of desorption was extremely slow despite high vacuum pressures. These results are qualitatively similar to previous CO₂ physisorption experiments on clays and other materials [1][2][5][7]. The band position of adsorbed CO₂ is shifted from that of CO₂ ice. However, Bells and MAC 02606 exhibit different initial absorption sites than those produced by clay [2]: a predominant $4.27 \mu\text{m}$

band at -123 C (150 K) instead of at the 4.22 μm band for the calcium-rich clays [3].

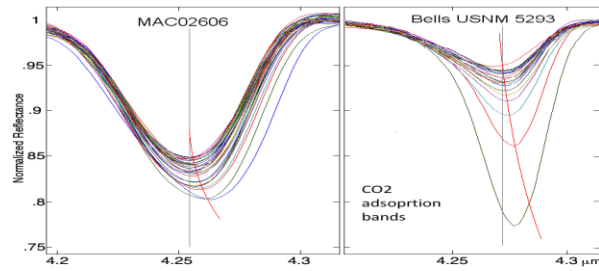


Figure 2: CO_2 band positions range between 4.25-4.27 μm . MAC 02606 has higher CO_2 absorption than Bells.

Bells' desorption was analyzed over the span of ~ 3 hours. As CO_2 desorbs, the band depth (relative to the band continuum) decreases linearly resulting in a band area proportionally linear to the band depth. An asymmetry factor ($a = \text{band minimum wavelength} - \text{CO}_2 \text{ band centroid}$) was calculated to profile the band shape and we found that it decreases linearly with the band minimum but the band shape never reaches symmetry, remaining 0.017-0.009 μm shorter in wavelength than the centroid.

The desorption of CO_2 from MAC 02606 was monitored over the span of 3.5 hours. The meteorite exhibits similar trends to Bells except for its asymmetry factor which began 0.009 μm shortward of the centroid, reached symmetry at 4.259 μm , and continued 0.007 μm past the centroid into the higher wavelengths. This suggests that given enough desorption time, Bells may also have reached symmetry. (Figure 3)

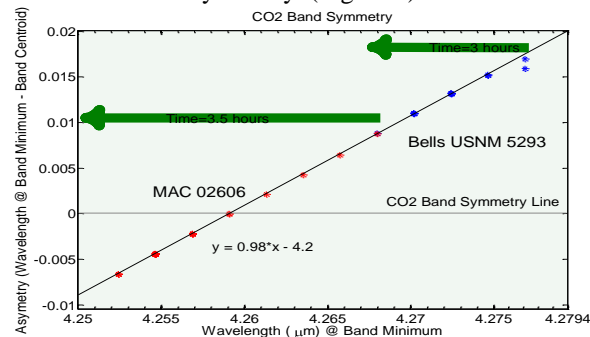


Figure 3: Bells' CO_2 band position linearly shifts at a slower rate than MAC 02606.

Additional meteorite spectral characteristics include a weak CO_2 band at 4.27 μm that is present in MAC 02606 before, during, and after desiccation and after baking. This may be atmospheric CO_2 structurally trapped. There is also a band near 4 μm indicative of CO_3 , possibly due to strongly chemisorbed CO_2 that has complexed with the meteorite material to form carbonate [8]. Adsorbed CO_2 would not be retained under vacuum at room temperature. No CO_2 ice formation is evident in any of these spectra. All meteorites exhibit an OH band at 3 μm and organics at $\sim 3.5 \mu\text{m}$. The

abundance of organics may be related to terrestrial alteration and contamination [9]. MAC 02606 and Ivuna show spectral evidence of carbonates at $\sim 4 \mu\text{m}$.

Conclusions: Measurements of IR reflectance properties associated with CO_2 adsorbed onto carbonaceous meteorites under vacuum at -123 C shows an infrared band whose position and width are abundance-dependent [5] and show compositional dependencies, varying between meteorites and from clays [1]. For both MAC 02606 and Bells the CO_2 band shifts towards shorter wavelengths from that of CO_2 ice, characteristic of shorter, higher-energy bonds. Also, there is no evidence of a doublet that would be expected from CO_2 gas [5]. (Figure 4)

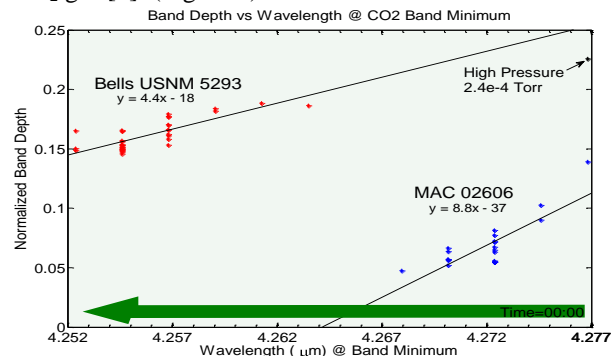


Figure 4: CO_2 binds at lower energy sites in Bells where the rate of desorption is slower.

Future work will involve investigating CO_2 behavior for longer time spans, at cooler/warmer temperatures, and a potential determination of temperature, abundance, or pressure-dependent binding site preferences or transitions. Further research into the relation between the ν_3 fundamental absorption band position and cation composition, mineralogy, temperature, and adsorbate abundance is necessary to address differences between meteorite and clay spectra. A greater sampling of meteorite types and classes is needed in order to delineate correlations between mineralogy and pressure-temperature relationships.

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References: [1] Hibbitts et al., (2000) *J. Geophys. Res.*; [2] Hibbitts & Szanyi, (2007) *Icarus*; [3] Hibbitts et al., (2012) *43rd LPSC Abstract #2400*; [4] Takir et al., (2012) *MAPS* (in review); [5] Sandford & Allamandola., (1989) *ApJ*; [6] Norton, (2002). *Cambridge Encyclo. of Met.*, Cambridge Uni. Press. p121–124.; [7] Clark et al., (2005) *Nature*; [8] Palmer, (2009) *U. Arizona.*, Ph D. diss.; [9] Pearson et al., (2002) *33rd LPSC Abstract #1311*; [10] Nave and Jackson, (2007) *J. Chem. Phys.*; [11] Greenspon et al., (2012) *43rd LPSC Abstract #2490*