LABORATORY MEASUREMENTS OF THE SPECTRAL FEATURES OF WATER AND CARBON DIOXIDE ICE LAYERS AND MIXTURES. W. M. Calvin¹, J. A. Isem², and I. B., Smith², Department of Geological Sciences, University of Nevada, Reno, NV (wcalvin@unr.edu), ²Department of Earth and Space Science, York University, Toronto.

Introduction: Both water and carbon dioxide ices are dominant components of the seasonal and perennial polar caps of Mars. In the north, water ice develops a collar around the retreating edge of the seasonal CO₂ ice and becomes the primary spectral signature of the upper surface in the last stages of retreat [1-3]. In the seasonal south cap, the spectral signature of water is noted early in the retreat, switching to CO₂ only at ~ Ls 225 [4,5]. Water is inferred to be the dominant component of the large topographic dome at each pole based on transparency in radar signals [6,7]. In the north, the perennial high albedo deposit has the spectral signature of water ice that evolves in grain size over the summer [8,9], whereas in the south, water ice has been identified in exposures surrounding the perennial CO₂ ice [10-12].

Recently, Cartwright et al. [13,14] analyzed both targeted and mapping CRISM data of the perennial south polar ices to identify surfaces that range in the spectral dominance of water and CO₂ ice features. Surprisingly, CO₂ signatures were identified well beyond the boundary of the canonical high albedo bright CO₂ ice and the exposures of water ice at the margins of the CO₂ appear to vary over longer timescales. This suggests longer-term cycles of deposition and erosion and a complex interplay between the annual CO₂ cycle and the upper CO₂ surface of this perennial ice deposit.

Although the spectral features of each ice alone are well known and measurements have been made of thin film mixtures relevant for outer satellites, comets, and interstellar grains [e.g. 15, 16], spectral measurements of mixtures of these two ices at densities relevant to Martian polar caps are less explored. In this work we examined layered water and CO₂ ice surfaces a few mm thick, as well as co-deposited ices to explore whether such surfaces mimic the spectral features observed in both seasonal and perennial deposits on Mars.

Experimental Set Up and Measurements: MARVIN Chamber. Our experiments were conducted in the specially developed MARs Volatile and Ice evolutionN (MARVIN) chamber at York University [17]. MARVIN is unique in that CO₂ ice can be grown under cold sky conditions. The setup consists of a meter-long and 70 cm diameter cylindrical stainless steel vacuum chamber. Ice is deposited on an LN₂ cooled plate that is surrounded by an LN₂ cooled shroud, simulating the cold sky environment and direct deposition from gas that occurs on Mars. The ice growth (sample) plate is 10 cm x 10 cm. To date the group at York has focused on the properties of CO₂ ice alone [17,18].

Ice Deposition. The majority of our experiments were not conducted under a cold shroud, but rather only cooling the sample plate under Mars pressure conditions (6 to 10 mbar of CO₂ gas). While the setup can include a heater, we controlled the temperature of the plate through the duty cycle of LN₂ circulation. We performed multiple experiments to layer and co-deposit water and CO₂. Small amounts of water vapor were added through a side port. We measured:

- “Frosty” or relatively small path length CO₂ ice with a layer of fine water frost over it.
- Semi-transparent or large path length CO₂ ice with a layer of fine water frost over it.
- A small block of water ice with CO₂ deposited over it.
- Co-deposition of water and CO₂.

Measurements. We collected images from small cameras within the chamber looking at the sample plate from various angles. Images were acquired every second allowing us to put the sequence together into time-lapse movies that show ice evolution. We collected moderately high-resolution images using a 20x magnification microscope during several experiments. These microscope images were similarly turned into time lapse movies. Spectra were collected from 1000 to 2500 nm relative to Spectalon or aluminum plate references. The spectrometer records data every nm with a resolution of 6 nm. Spectra were also acquired every second to observe transitions and portions from stable periods were averaged.

Results: Figure 1 compares our measurements of CO₂ ice to spectra previously measured [19] or calculated [using 20]. In order to get an accurate match, we needed to add a small, 27 nm, wavelength offset to the MARVIN measurements. These spectra are also quite low in albedo, which may be due to the observation geometry (source and sensor fiber optics in a single cable) or the use of aluminum as the reference. Figure 1 presents the MARVIN measurement using continuum removal in order to better see the ice absorption features on this scale. The signal-to-noise of the spectrometer is low for this set up, as signal is lost in coupling the fiber optics into the chamber, and it is particularly poor at the ends of the wavelength range so that measurements are acceptable from ~ 1.2 to 2.3 μm.
We are able to clearly identify all the strong CO$_2$ features in the 2.0 µm region as well as the feature at 1.43 µm. Two weaker features at 1.58 and 1.61 µm are also observed. We are less confident in weak features in at 2.12, 2.16, and 1.21 µm, as these are only present in some measurements. Analysis shows subtle variations in absorption feature strength and the breadth of the 2-µm envelop, depending on the nature of the CO$_2$ ice. Layered water and CO$_2$ combinations show features of both ices and we are still analyzing the data for comparison to the endmembers determined by CRISM.

**Morphological Evolution.** In all cases where we deposit water over CO$_2$ and then let the sample warm naturally over time, we see CO$_2$ gas accumulation under the water ice layer. This then deforms the water ices, forming bubbles that eventually burst as seen in Figures 2 and 3. In several experiment runs, as the surface continued to deflate, pores were re-sealed, and a second round of bubble formation and popping was observed. In some experimental runs pore space did not heal and CO$_2$ gas was continuously released from under the water ice layer with small surface deformations as the CO$_2$ ice sublimed. We are still trying to understand if these pressure and temperature conditions are resulting in a CO$_2$ gas hydrate as CO$_2$ features will be only slightly shifted from those of CO$_2$ ice [21].

We will present these results and additional analysis at the meeting.

**Acknowledgments:** This work was supported by a grant from Fulbright Canada to WMC as a Research Chair at York for fall semester 2023. Support for materials and consumables was provided by NSERC funding to IBS.