Experimental Studies of the Exchange of Water Between the Atmosphere and Surface of Mars

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Laser Remote Sensing (LIDAR) Measurements of Clouds and Precipitation from the Surface of Mars

The LIDAR instrument on the Phoenix mission observed water ice clouds in the atmosphere of Mars that were similar to cirrus clouds on Earth. Fall streaks in the cloud structure traced the precipitation of ice crystals toward the ground. Measurements of atmospheric dust indicated that the planetary boundary layer (PBL) on Mars was well mixed up to heights of around 4 km by the summer daytime turbulence and convection. The water ice clouds were detected at the top of the PBL and near the ground each night in late summer after the air temperature started decreasing. The interpretation is that water vapour mixed upward by daytime turbulence and convection forms ice crystal clouds at night that precipitate back toward the surface.

LIDAR Instrument on the NASA Phoenix Mars Mission

The NASA Phoenix mission *(Smith et al., 2009)* obtained measurements from the surface in the Arctic region of Mars (68.22° N, 234.25° E). The spacecraft landed prior to summer solstice on Mars and operated over the next five months. This period encompassed the midsummer peak and decline in the abundance of atmospheric water vapour, so it was possible to observe the local processes that contribute to the water cycle. A unique instrument on the Phoenix mission was a LIDAR *(Whiteway et al. 2008)* that emitted pulses of laser light upward into the atmosphere and detected the backscatter from dust and clouds.

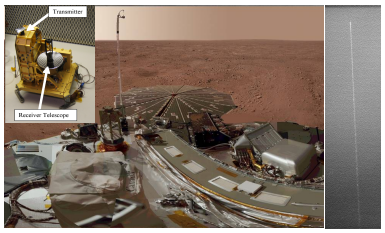

Figure 1. Images from the surface stereo imager instrument on the Phoenix spacecraft . Views pointing toward the horizon over the lander deck and also upward with the LIDAR laser beam. Top left is a a photo of the LIDAR instrument with it's cover removed during testing.

LIDAR Measurements of Clouds and Precipitation

The outline and internal structure of the clouds that drifted above the Phoenix landing site were seen in the contour of the backscatter coefficient *(Whiteway et al. 2009)*. On mission sol 99 (Fig. 2) the most striking features were the tilted vertical streaks after 05:00. This pattern is consistent with ice crystals precipitating from the cloud, and eventually sublimating in the dry air below the cloud. Such fall streaks are a well known feature in observations of cirrus clouds on earth. For each sol during the second half of the mission (L_s = 113° to 150°) clouds remained through the early morning hours and then dissipated when the atmosphere warmed sufficiently during daytime.

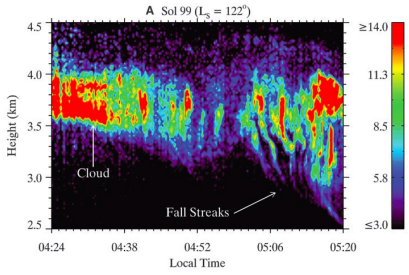

Figure 2. Contour plot of backscatter coefficient ($\times 10^{-6}$ m^{-1}sr^{-1}) derived from the lidar backscatter signal at wavelength 532 nm on mission sol 99 (L_s = 122°). Fall streaks indicate precipitation of ice crystals.

Snow Falls to the Surface of Mars

In the early morning hours on mission sol 109, the lidar observed clouds and precipitation that extended all the way to the ground (Fig. 3). In the period between 03:10 and 03:50 there were water ice clouds at the top of the boundary layer (heights 3 to 5 km) and at ground level. In the next lidar run, from 05:16 to 05:45, the base of the observed cloud had dropped to a height of about 1.5 km, and there were precipitation fall streaks starting at 05:30 that extended down through the ground level cloud. The essential point here is that precipitation moves water toward the surface from heights of up to 5 km.

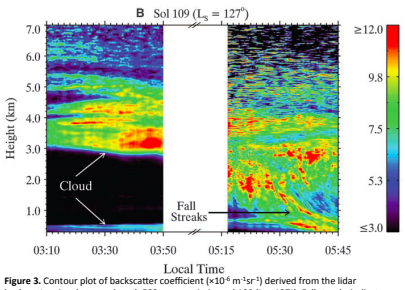

Figure 3. Contour plot of backscatter coefficient ($\times 10^{-6}$ m^{-1}sr^{-1}) derived from the lidar backscatter signal at wavelength 532 nm on mission sol 109 (L_s = 127°). Fall streaks indicate that precipitation was reaching the ground.

Laboratory Investigation of Perchlorate and Water at the Surface of Mars with Laser Raman Scattering

A major discovery during the NASA Phoenix Mars mission was the identification of perchlorate (ClO_4^-) in the surface regolith by the Wet Chemistry Laboratory instrument (Hecht et al., 2009). More recently, the Sample Analysis at Mars instrument on the NASA Curiosity Rover detected the presence of perchlorate in Gale Crater (Glavin et al., 2013), suggesting that it is globally distributed. Perchlorates are of great interest on Mars due to their high affinity for water vapor (deliquescence) as well as their ability to greatly depress the freezing point of water when in solution (Chevrier et al., 2009). This has intriguing biological implications as the resulting liquid brines could potentially provide a habitable environment for living organisms. Additionally, these salts may play a significant role in the hydrological cycle on Mars.

Raman Scattering LIDAR and Environmental Chamber

A stand-off Raman Lidar system developed at York University is based on the heritage of the LIDAR instrument on the NASA Phoenix Mars mission (Whiteway et al., 2008, 2009). It is capable of performing range-resolved atmospheric measurements as well as probing the near-range surface. The laser light was directed toward a sample located inside an environmental chamber which was providing the humidity and temperatures found at the surface of Mars.

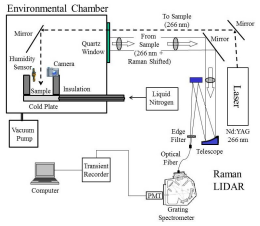

Figure 4. Raman Lidar optical arrangement and the environmental chamber.

Raman Scattering Spectra

When a beam of monochromatic light encounters a sample, a fraction of the scattered light is uniquely shifted in wavelength according the the properties of the molecules it interacts with. This is called Raman scattering and it allows for the discrimination of the molecular composition of the sample. Raman spectra consist of a plot of the measured signal amplitude of the Raman scattered light as a function of the shift in wavelength, or wavenumber (cm^{-1}).

Figure 5a shows the measured Raman spectrum of dry magnesium perchlorate hexahydrate. The unique series of peaks at wavenumbers less than 1500 cm^{-1} are attributed to the perchlorate ion Raman vibrational modes, while the peak near 3500 cm^{-1} is due to chemically bound water of hydration (*Patel et al.*, 1983).

Raman spectroscopy has proven to be a highly effective technique for discriminating between different states of water (*Durickovic et al.*, 2011) due to the O-H stretching band of water, located in the Raman shifted spectral region between 2800 cm^{-1} and 3800 cm^{-1}. This sensitivity of the O-H band is demonstrated in Fig. 5b, which shows measured Raman spectra of liquid water at 5°C, water ice at -15°C, and dry magnesium perchlorate hexahydrate. The vertical line indicates the location of the spectral feature at 3150 cm^{-1} used for the experiment (Fig. 6).

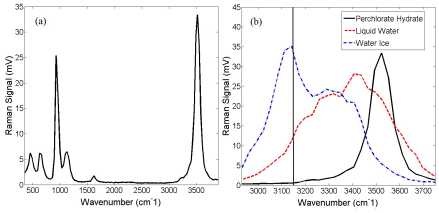

Figure 5. (a) Raman spectrum of dry magnesium perchlorate hexahydrate. The peaks at wavenumbers less than 1500 cm^{-1} are attributed to the perchlorate ion Raman modes while the peak near 3500 cm^{-1} is due to chemically bound water of hydration. **(b)** Raman spectra of liquid water, water ice, and magnesium perchlorate hexahydrate over the O-H stretch region. The vertical line indicates the location of the spectral feature used to generate the experimental results presented in Fig. 6.

Experiment: Detection of Magnesium Perchlorate Deliquescence, Brine Freezing and Thawing in Mars Environmental Conditions

A sample of magnesium perchlorate was subjected to the water vapour pressure and temperatures found at the landing site of the Phoenix Mars mission. Laser Raman scattering was applied to detect the onset of deliquescence and provide a relative estimate of the quantity of water taken up and subsequently released by the sample. As the temperature of the sample decreased at the same rate as measured on Mars during the evening, significant uptake of water from the atmosphere was observed to occur prior to the frost point temperature being reached. It was found that water uptake began to take place several degrees above the -55°C frost point temperature, with initial deliquescence occurring at -51°C (60% relative humidity over ice). As the temperature was lowered, water uptake continued. When saturation was reached at -55°C (100% relative humidity over ice), frost formed on the surface surrounding the perchlorate sample. Freezing of the brine film was observed at the eutectic temperature of -67°C and thawing occurred at a temperature of -62°C. (Nikolakakos and Whiteway, 2015)

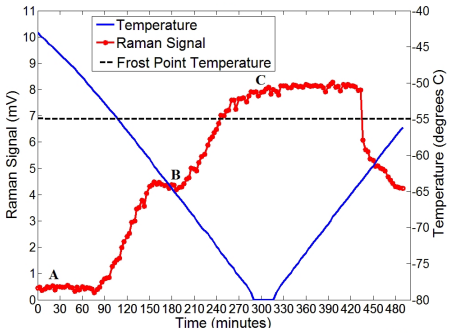

Figure 6. Measured Raman signal at a wavenumber shift of 3150 cm^{-1} as the temperature was lowered from -42°C to -80°C and then increased. Water uptake began at the 80 minute mark as the temperature reached -51°C (60% RHi) and ceased after 150 minutes. Freezing began at the 200 minute mark as the temperature was decreased below the eutectic temperature of -67°C. Melting occurred when the temperature was increased above -62°C at the 440 minute mark.

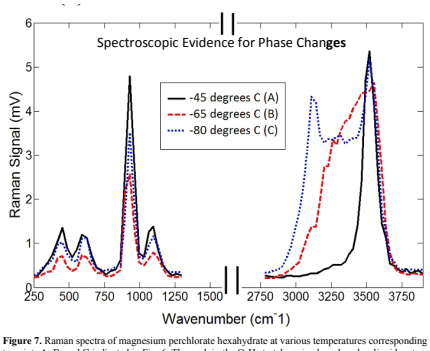

Figure 7. Raman spectra of magnesium perchlorate hexahydrate at various temperatures corresponding to points A, B, and C indicated in Fig. 6. The peak in the O-H stretch region broadened as liquid water was taken up. As the solution froze, the characteristic water ice peak near a wavenumber shift of 3100 cm^{-1} became apparent.

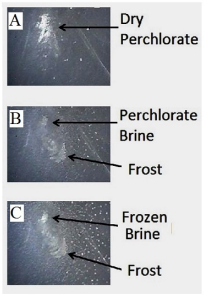

Figure 8. Visual images of magnesium perchlorate hexahydrate and the surrounding surface at points A, B and C indicated in Figs. 6 and 7. The perchlorate sample began to fade as water was taken up and aqueous solution formed (point B). As the brine froze at point C, the sample region appeared to increase in brightness. Frost was visible on the sample plate in panels B and C.

Conclusions

Observations from the surface of Mars with the Phoenix LIDAR instrument have shown that water ice clouds form within the planetary boundary layer that are similar to cirrus clouds on Earth. Ice crystal precipitation from the clouds transported water from heights of 5 km to the surface

Laboratory experiments demonstrated that perchlorates in the surface material on Mars can contribute to the hydrological cycle by absorbing water vapour directly from the atmosphere (deliquescence). When exposed to the water vapour pressure and temperatures found at the Phoenix landing site, bulk magnesium perchlorate hexahydrate samples of the size found on Mars began to undergo deliquescence 4°C above the frost point temperature. The resulting liquid brine remained as liquid until the eutectic temperature was reached and then freezing occurred.

Raman spectroscopy can provide an effective method for directly detecting the processes associated with surface-atmosphere water exchange on Mars. These measurements could be acquired with a Raman Lidar instrument from a stand-off distance.

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