LABORATORY STUDIES OF DELIQUESCENCE AND ADSORPTION AT THE SURFACE OF MARS WITH RAMAN SCATTERING

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Introduction: Sensors on board the NASA Mars Phoenix lander and the NASA Curiosity rover have provided high frequency measurements of relative humidity and temperature directly from the surface of Mars for the first time [1][2]. One of the more striking features common to both data sets is the observation that the atmospheric water vapour content near the surface appears to decrease slowly in the evening, in many cases prior to 100% relative humidity being reached, and then increase again during the daytime. This indicates that a significant exchange of water is likely occurring between the atmosphere and surface of Mars on a diurnal time scale. Current knowledge of Martian surface mineralogy suggests that the processes most likely responsible for this exchange are deliquescence of salts such as perchlorate and/or the adsorption of water onto mineral grains such as zeolites. The aim of this work is two-fold; first to determine whether laser Raman spectroscopy is capable of detecting and discriminating between different processes and minerals associated with the Martian hydrological cycle, and secondly to conduct water exchange process studies by simulating the conditions found at the Phoenix landing site.

Raman lidar and environmental chamber: A stand-off Raman lidar system has been developed at York University in order to study these processes. It was built on the heritage of the Lidar instrument on the NASA Phoenix Mars mission [3][4] and is capable of performing range-resolved atmospheric measurements as well as probing the near-range surface. The 266 nm laser light is directed toward a sample located inside an environmental chamber which is capable of simulating the thermodynamic conditions found at the surface of Mars. A schematic diagram of the experimental setup is shown in Figure 1.

Perchlorate deliquescence experiments: A major accomplishment of the NASA Phoenix Mars mission was the identification of perchlorate (ClO_4^-) in the surface regolith by the Wet Chemistry Laboratory instrument [5]. More recently, the Sample Analysis at Mars instrument on the NASA Curiosity Rover detected the presence of perchlorate in Gale Crater [6], suggesting that it is globally distributed. Perchlorates are of great interest on Mars due to their high affinity for water vapour (deliquescence) as well as their ability to greatly depress the freezing point of water when in solution [7]. This has intriguing biological implications as resulting brines could potentially provide a habitable environment for living organisms. Additionally, it has been speculated that these salts may play a significant role in the hydrological cycle on Mars.

In this work a sample of magnesium perchlorate was subjected to the water vapour partial 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. As the temperature was lowered, water uptake continued as saturation was reached and 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. These results are displayed in Figure 2 [8].

Zeolite adsorption experiments: Water adsorption is an easily reversible process in which water vapour molecules become attached to regolith grains as a result of van der Waals forces between the dipolar water molecules and the negatively charged mineral grains [9]. This results in a thin film of liquid-like water forming on the surface of the grains. Modelling results have suggested that adsorption is likely to be an ongoing process on Mars [10], however prior experimental work demonstrated that the kinetics of water adsorption may be too slow for it to be occurring on present day Mars [11].

Here we have used Raman spectroscopy to study the adsorption properties of zeolites, a naturally occurring mineral detected in the dust of Mars [12], under conditions found at the Mars Phoenix site. Preliminary experimental results indicate that zeolites on the sur-

face of Mars are capable of adsorbing water from the atmosphere on diurnal time scales and that Raman spectroscopy provides a promising method for detecting this process during a landed mission. Additionally, when the water vapour pressure is sufficiently low, the zeolites are able to also adsorb carbon dioxide, resulting in the presence of co-adsorbed water and carbon dioxide on the surface mineral grains.

References: [1] Zent A.P. et al. (2010) JGR 115, E00E14. [2] Harri A.M. et al. (2014) JGR 119, 2132–2147. [3] Whiteway J.A. et al. (2008) JGR 113, E00A08. [4] Whiteway J.A. et al. (2009) Science 325, 68-70. [5] Hecht M.H. et al. (2009) Science 325, 64-67. [6] Glavin D.P. et al. (2013) JGR 118, 1955–1973. [7] Chevrier V.F. et al. (2009) GRL 36, L10202. [8] Nikolakakos G. & Whiteway J.A. (2015) GRL 42, 7899–7906. [9] Mohlmann D. (2005) Astrobiology 5(6):770-777. [10] Savijarvi H.I. et al. (2016) Icarus 265, 63-69. [11] Zent, A.P. et al. (2001) JGR 106(E7), 14667–14674. [12] Ruff S.W. et al. (2004) Icarus 168, 131-143.

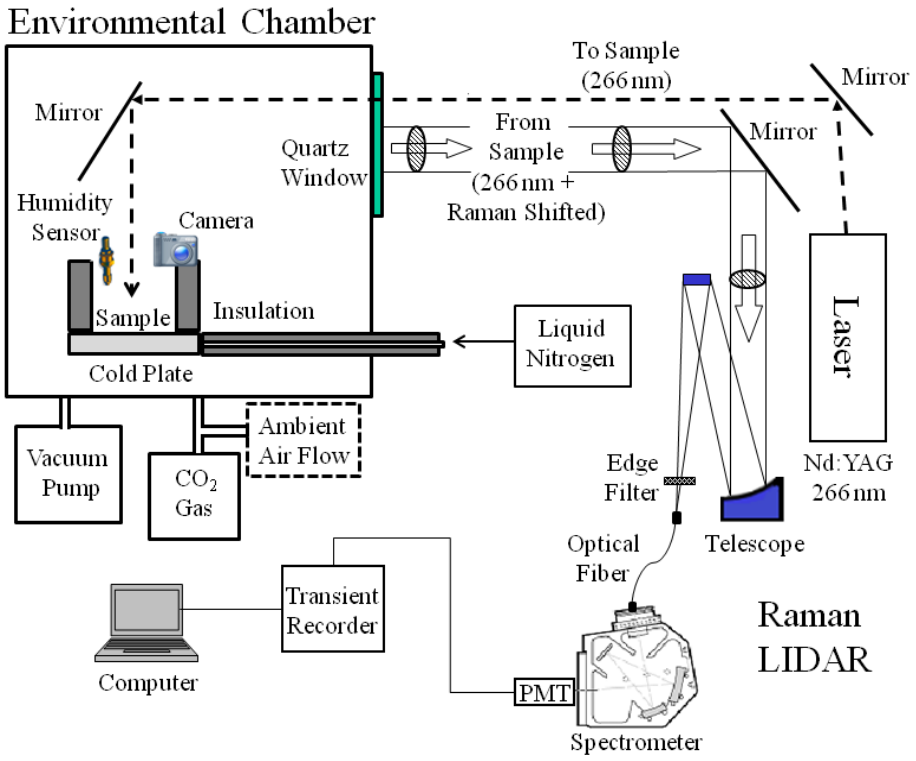

Figure 1. Schematic diagram of the Raman lidar optical arrangement and the environmental chamber.

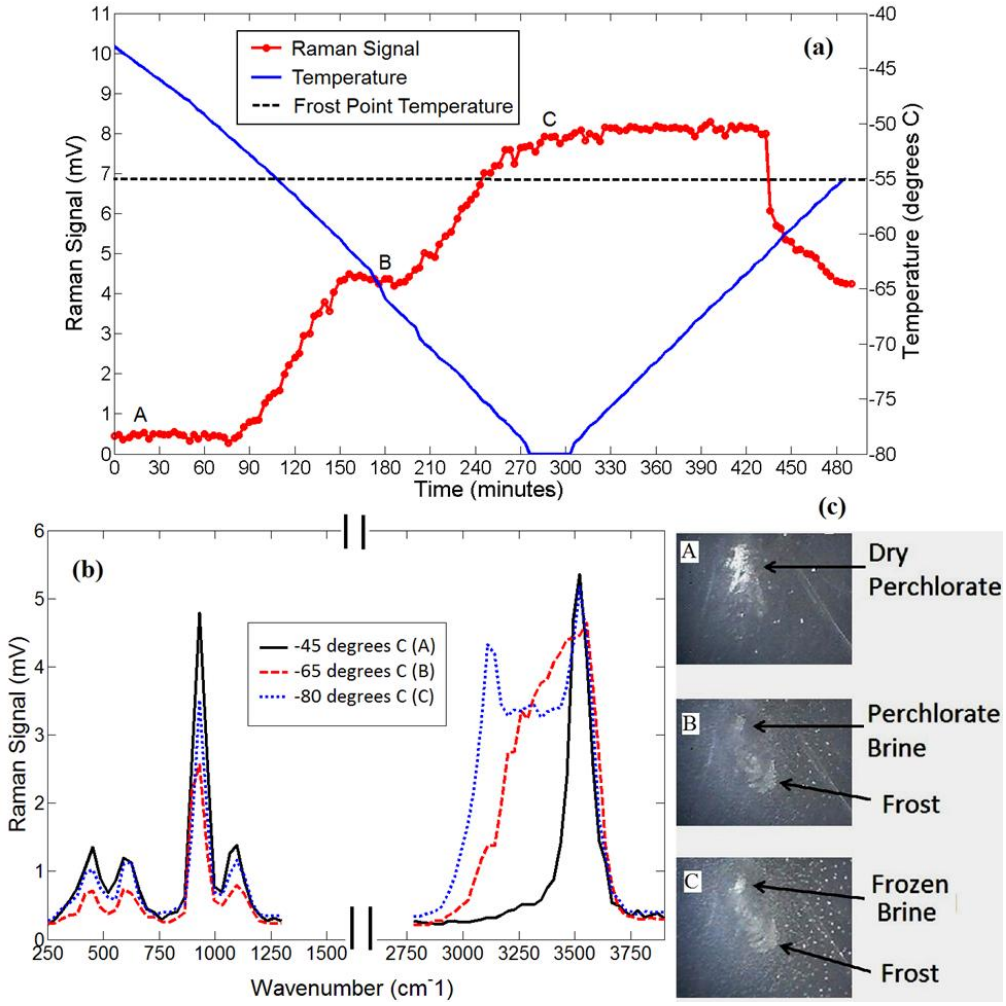

Figure 2. (a) Measured Raman signal at a wavenumber shift of 3150 cm^{-1} as the temperature was lowered from -42^{0}C to -80^{0}C and then increased. Water uptake began at the 80 minute mark as the temperature reached -51^{0}C (60% RHi) and ceased after 150 minutes. Freezing began at the 200 minute mark as the temperature was decreased below the eutectic temperature of -67^{0}C. Melting occurred when the temperature was increased above -62^{0}C at the 440 minute mark. **(b)** Spectra of magnesium perchlorate hexahydrate at various temperatures corresponding to points A, B, and C indicated in Fig. 4a. 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. **(c)** Visual images of magnesium perchlorate hexahydrate and the surrounding surface at points A, B and C. 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.