EXPERIMENTAL STUDY OF THE WATER VAPOR INTERACTION WITH CLAY REGOLITH DURING ICE SUBLIMATION ON MARS.

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Introduction: The presence of liquid water on the surface of Mars has generated interest and research in the fields of chemistry, biology, and geosciences. Our research group has conducted previous work on the evaporation rate of pure liquid water [1], water and ice [2], brines [3] and through JSC Mars-1 palagonitic soil stimulant [4]. Amongst the various phases possibly present in the Martian regolith, clays are important for the behavior of water. Indeed, these minerals can adsorb important quantities of water that can be released when conditions vary [5].

The OMEGA imaging spectrometer onboard Mars Express has identified large outcrops of smectite-type clays [6]. Therefore a part of these outcrops could be present in the regolith and act as a reservoir of water on the surface. In addition, clays could also act as protective barrier against ice sublimation, and explain the presence of subsurface metastable ice in the equatorial regions [7]. However, the lack of direct correlation between subsurface ice and clay deposits suggest a complex behavior. Therefore, the aim of our study is double: investigating the sublimation of ice below clay regolith layers, and the adsorption of water vapor during the diffusion process. We aim also in developing quantification methods to estimate water content in the regolith from reflectance measurements. Here we show the preliminary results conducted on both aspects of the water vapor – clay interaction.

Experimental setup: The dry <63 μm montmorillonite samples are prepared by baking the clay in a vacuum oven at 105°C and 0.3 atm for one day. The sample is placed in a dessicator in a -20°C freezer for one day. Pure water is frozen in a beaker with a thermocouple on the surface. The dry, cold montmorillonite is then placed onto the ice, with thickness varying from 0.5 to 2.0 cm. The experiments are run in a 0.6 m^3 planetary environmental chamber [1-3] that is evacuated to less than 0.09 mbar and filled with dry gaseous CO$_2$ to atmospheric pressure. Then the chamber is cooled to below 0ºC using methanol/dry ice slurry. The sample is placed into the chamber on a top loading analytical balance. The platform supporting the balance and sample is lowered into the chamber. The chamber is then evacuated to 7 mbar. Experimental runs last 2 to 3 hours with mass, pressure, temperature, and humidity recorded every 2 minutes. After each run the montmorillonite is analyzed on a Thermo Nicolet FT-IR 6700 reflectance spectrometer using an ever-glo IR source, a KBr beam splitter and a DTGS detector. The spectral range is 2.5-8 μm. Finally, the wet montmorillonite is dried in a vacuum oven at 105°C and 0.3 atm and the mass difference corresponding to adsorbed water is measured.

Sublimation results: The figure 1 shows a typical sublimation run. Sublimation rate increases from 8.8 10^{-2} to 0.25 mm h^{-1} (converted from g min^{-1}) between the 30 first minutes and the 50 last minutes, i.e. a factor about 3. Linearity in the 1 cm experiment is reached after about 80 min and indicates that steady-state in the diffusion of water vapor through the regolith layer is reached. In our former studies, we always observed that steady-state is reached very fast, i.e. in a few tens of seconds to a few minutes [4] (see also Bryson *et al.* abstract in this issue). Such increase of the sublimation rate suggests that a phenomenon slows down the diffusion process by modifying the diffusion rate with time. This was verified since the initial clay was deprived of adsorbed water by our oven treatment, while the samples contained between 3 and 5 wt% H$_2$O at the end of the experimental runs.

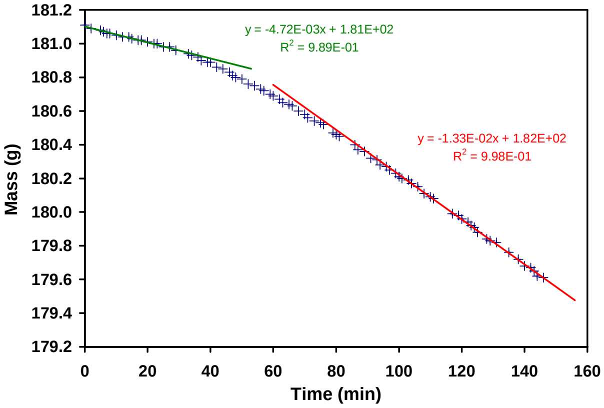

Figure 1: Mass loss versus time curve of water ice sublimating below a 1 cm-thick layer of montmorillonite. The green line represents the regression on the 30 first minutes data, while the red one is on the 50 last minutes. There is a clear increase in the sublimation rate (slope of the lines) with time.

Effect of adsorption: Since there is no significant physical difference (grain size, porosity) between this regolith and the previous ones we used, we suggest that the important adsorption by the smectite are responsible for this behavior by blocking the molecules of water until adsorption equilibrium is reached.

In fact, the adsorption effect is very complex, since it affects the pressure in the pores of the regolith. According to [8], the differential equation accounting for both diffusion and adsorption processes is:

$$\frac{\partial C_g}{\partial t} = D\frac{\partial^2 C_g}{\partial z^2} - \frac{\partial C_a}{\partial t} \qquad (1)$$

C_g is the water vapor concentration in the regolith, and C_a the concentration of adsorbed molecules on the surface of the particles. This equation is equivalent to:

$$\frac{\partial p}{\partial t} = \frac{D}{\left[1+\Psi\frac{\partial\theta}{\partial p}\right]}\frac{\partial^2 p}{\partial z^2} \qquad (2)$$

P is the pressure, D is the absolute diffusion coefficient, θ is the surface coverage and Ψ is a thermodynamic term equal to:

$$\Psi = \frac{RT_S\rho_{H_2O}\rho_{reg}A_S l}{M_{H_2O}} \qquad (3)$$

T_S is the surface temperature, ρ_{H2O} the density of liquid water, ρ_{reg} the density of the regolith, A_S the specific surface area of the regolith, l the thickness of the monolayer and M_{H2O} the molar mass of water. Thus, adsorption process affects the diffusion of water, by apparently modifying the diffusion coefficient.

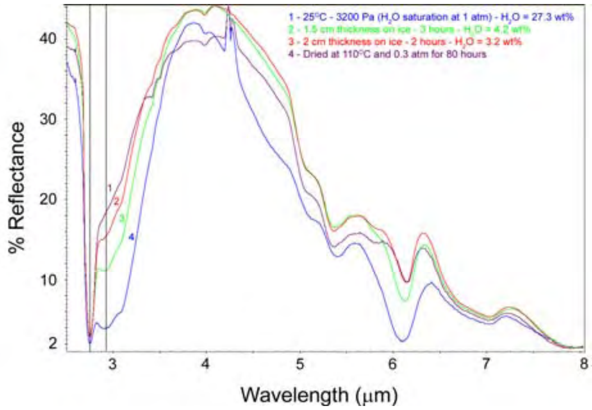

Figure 2: reflectance spectra of 4 samples of clay containing various amounts of water, from dry to water vapor saturation at 1 atm. The 3 µm band attributed to water evolves with the water content. The two small positive bands at 4.4 µm result from a small contamination by the atmosphere.

Quantification of the adsorption: These results suggest that adsorption properties of the clays must be determined to fully understand diffusion through clay layers. Therefore, for each experiment we measured the water content as well as the reflectance properties (Fig. 2). These are efficient methods to remotely measure water content on the Earth and Mars. The complex 3 µm band is usually referred as the water band and includes structural as well as adsorbed water and could be used to quantify the amount of water on the surface of Mars [9]. In the case of the montmorillonite we can distinguish 2 different components in this band: the first band is constant with adsorbed water, and is located at 2.75 µm. The second band strongly varies in intensity with the water content of the clay but is located at ~2.9 µm. The 2.9 bands of the samples evolved in the environmental chamber are systematically located between the band of a very dry sample and the band of a sample exposed to a saturated atmosphere with water (Fig. 2). The 2.9 µm band normalized to the 2.75, to avoid absolute reflectance effects, shows a linear dependance with the water content (Fig. 3). This suggests that such parameter could be used to quantify surface water content from reflectance observations.

Conclusions: sublimation below a clay regolith under martian conditions is more complicated than for other materials, since adsorption process affects the diffusion of water vapor. Our preliminary results indicate however that both can be modelled. In addition, use of the reflectance properties could help determining the water content of the regolith, and eventually state the equilibrium or not of the regolith with the atmosphere.

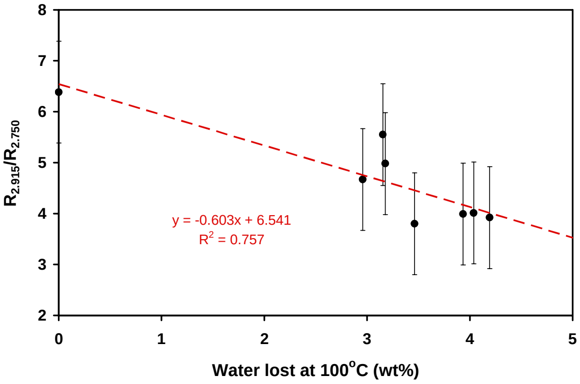

Figure 3: correlation between the depth of the 2.9 µm band normalized to the 2.75 µm band with the water content of the sample, measured by dehydration at 110ºC.

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References: [1] Sears D. W. G., S. R. Moore (2005) *Geophys. Res. Lett.* 32. [2] Moore S. R., D. W. G. Sears (2006) *Astrobiology* 6, 644-650. [3] Sears D. W. G., J. D. Chittenden (2005) *Geophys. Res. Lett.* 32. [4] Chevrier V. et al. (2006) *Geophys. Res. Lett.* in press. [5] Zent A. P. et al. (2001) *J. Geophys. Res.* 106, 14667-14674. [6] Poulet F. et al. (2005) *Nature* 481, 623-627. [7] Jakosky B. M. et al. (2005) *Icarus* 175, 58-67. [8] Jakosky B. M. (1985) *Space Science Reviews* 41, 131-200. [9] Chevrier V. et al. (2006) *Planet. Space Sci.* 54, 1034-1045.