EXPERIMENTAL STUDY OF WATER TRANSPORT ACROSS AN ADSORBING REGOLITH. Pierre

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Introduction: The presence of subsurface water ice on Mars has now been recognized by several instruments, including *in situ* observation by the Phoenix Lander in high-latitude region [1]. This ice could represent a significant water reservoir and might participate actively in the global Mars water cycle [2]. Subsurface water ice is supposed to be buried below an ice-free regolith layer, produced by the propagation of diurnal, seasonal and secular surface temperature fluctuations. The exchange of water molecules between the subsurface and the atmosphere then occurs by diffusion through a dry regolith, which will control the coupling between the atmosphere and the subsurface.

Here, we report on water adsorption isotherm measurements of Martian soil analogs which we use to infer the transfer properties of the Martian subsurface. In addition, we have measured kinetics of water adsorption for the same materials, which sheds light on the possible timescale for subsurface/atmosphere exchange of water.

Methods: A simulation chamber in relation with an adsorption setup was designed and built as a complement to the LPG reflectance spectrometer. Extensive description of the chamber can be found in [3].

The source of water vapor is a volume of ultra pure, demineralized and carefully outgassed liquid water maintained at a temperature of +20°C. Prior to any injection of water, continuous reflectivity measurement at one wavelength inside a hydration band is started (at 1.93 or 3.10 µm).

Both thermodynamics and spectroscopy are used to determine the amount of water in the sample at each step of the hydration / dehydration process. For each adsorption step, the quantity of water adsorbed by the sample can simply be calculated from the difference of pressure in the chamber before and after sorption of water vapor on the sample. This calculation requires a good knowledge of the different volumes (which were previously measured).

In order to quantify the water content of the sample surface, reflectance was monitored inside one of the strong hydration band (at 1.93 or 3.10 µm). Because these wavelengths correspond to very strong absorption levels, only a few grains are involved in the reflection process. We then obtained the "intrinsic" adsorption kinetics on the grains, i.e. a kinetic that is not biased by chemical diffusion though the sample porosity. The conversion of reflectance at a single wavelength into water content is made by using an empirical relationship between the strength of absorp-tion bands and the water content from our previous study [3].

Samples: Six different types of materials were studied. They are: a basaltic volcanic tuff from the Massif Central, a synthetic ferrihydrite sample, the SWy-2 Na-Montmorillonite, the JSC-Mars 1 palagonitic soil, a Mg-sulfate/basaltic tuff mixture, and a dunite powder. All of these materials are either suspected to be major mineral components of the Martian regolith or are seen as good analogs of Martian surface materials. For each sample, the thickness in the holder is 1 mm and sample mass ranges between 0.4 and 1.0 mg.

Results: The isotherms obtained have been described elsewhere [3] and will not be discussed in details. For each material, these isotherms were fitted successfully according to the Langmuir theory [4].

$$\rho_a = C[\alpha P/(1+\alpha P)] \qquad \text{(eq. 3)}$$

Surface kinetic:
Timescales for the adsorption to reach equilibrium range between a few tens of seconds and a few minutes for the samples studied. In order to characterize and compare the kinetics of the process, we modelled each of the adsorption step by a second-order kinetic law. This choice was made because it was found to show the best fit among typical kinetical laws.

$$\rho_f = \rho_i + \frac{t}{t + \tau_{surf}} \left(\rho_f - \rho_i \right) \qquad \text{(eq. 4)}$$

ρ_f denotes the final concentration after the adsorption step while ρ_i is the amount of adsorbed water when equilibrium is reached. τ_{surf} is the time constant which is obtained through the numerical fit.

The values we obtained for τ_{surf} range from 0.1 minute for the ferrihydrite at $1.4 \ 10^{-3}$ mbar to 7 minutes in the case of the smectite sample at $2.5 \ 10^{-1}$ mbar.

Bulk kinetics:
The timescales to characterize bulk sample equilibrium is defined as the time to reach 95% of the equilibrium value. The obtained values are reported in Figure 1. The τ_{bulk} values typically increase when pressure decreases, and can be up to a few hours. This delay is due to a combination of diffusion and adsorption/desorption intrinsic kinetics.

Discussion: In the case of a non-adsorbing sample, the water transfer will be controlled by the gradient of water partial pressure, water molecules diffusivity, porosity and tortuosity of the regolith. An apparent diffusion coefficient D can be written as:

$$D = D_{H_2O} \frac{\phi}{T} \qquad \text{(eq. 1)}$$

where D_{H2O} is the diffusion coefficient in the pure gas environment, Φ is the porosity and T is the tortuosity. Using typical values of D_{H2O} (10^{-4} m^2/s)[5], $\Phi=0.5$, and T=1 we calculates that diffusion timescale across our 1 mm sample is less than 1 s. However in our experiments we observed that the bulk equilibration timescale can be as long as a few hours.

In the case of an adsorbing sample, the water diffusion will be slowed down as the molecule will exchange many times between the adsorbed and the gaseous state during diffusion through the porous sample. The apparent diffusion coefficient is then smaller [6-7] than in the non-adsorbing case and might be written as:

$$D_A = D_{H_2O} \frac{\phi}{\tau} \frac{1}{1 + \frac{RT}{18} \frac{\partial \rho_a}{\partial P}} \qquad \text{(eq. 2)}$$

Where $\partial \rho_a / \partial P$ is the pressure derivative of the amount of water adsorbed per mass unit (kg/kg). Equation 2 thus implies that in the case of an adsorbing regolith, $\partial \rho_a / \partial P$, i.e. the slope of the isotherm curve ($\rho_a = f(P)$), will control the transfer.

From our modelled isotherms, we calculated the expected slowing factor (i.e. D_A/D) from eq. 2. Results show that for samples that have a very steep slope in their isotherms (ferrihydrite and JSC-Mars-1) the apparent diffusion coefficient can vary by almost three order of magnitude for relative pressure ranging from 10^{-4} to 1. As one can see on Fig. 1, for the same sample the bulk equilibration time varies by almost three orders of magnitude within this range of relative pressure. The pressure dependence is quite similar between the model and the measurements for the ferrihydrite and JSC Mars-1 samples. However, there are strong differences in the case of the other samples. These differences are chiefly due to the fact that the model presented in eq. 2 hypothesizes that the intrinsic adsorption/desorption kinetics are instantaneous. As we measured for our six samples, this is far from being the case since the surface equilibration timescales were found to range between a few seconds up to seven minutes.

Conclusions: We have developed an experimental setup that enables to measure adsorption kinetics and to discriminate between adsorption/desorption kinetics and diffusion. Our measurements show that, as expected, diffusion can be slowed down by many orders of magnitude when it occurs across an adsorbing sample. Futher work will be performed to take into account the intrinsic diffusion kinetics in a physical model of the Martian sub-surface.

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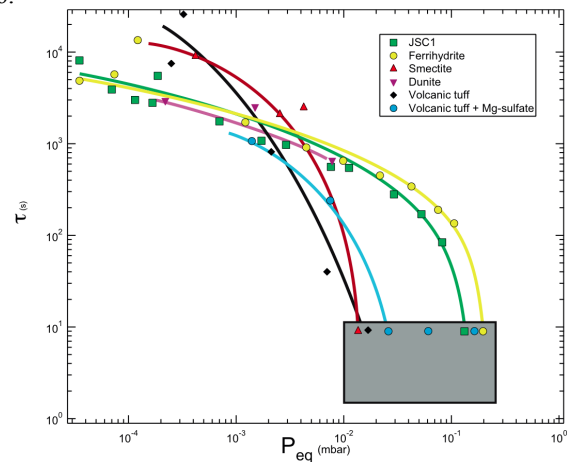

Figure 1: Equilibrium time for the bulk sample obtained from pressure measurements in the chamber. Curves are guides to reading.
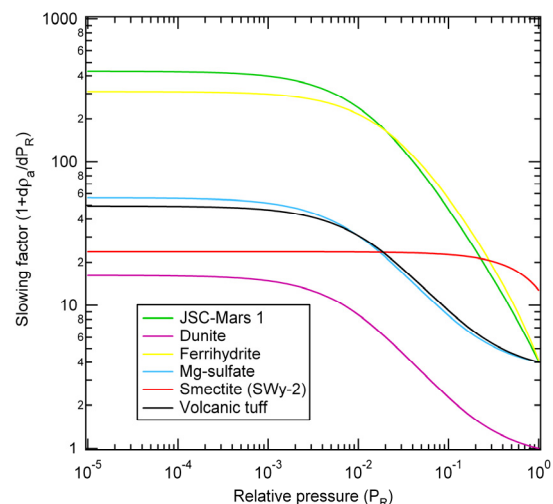

Figure 2: Slowing factor in adsorption/diffusion regime calculated from our isotherms fit.