WATER SORPTION ON MARTIAN REGOLITH ANALOGS: NEAR-INFRARED REFLECTANCE SPECTROSCOPY AND THERMODYNAMICS. Antoine Pommerol[1], Bernard Schmitt[1], Pierre Beck[1], and Olivier Brissaud[1]. [1]Laboratoire de Planétologie de Grenoble, BP 53, 38041 Grenoble cedex 9, France. (E-mail: antoine.pommerol@obs.ujf-grenoble.fr)

Introduction: Due to large variations of both surface temperature and amount of water vapor in the atmosphere, relative humidity at the Martian surface is subject to variations of several orders of magnitude. As a result, minerals of the regolith that are in direct contact with the atmosphere are susceptible to adsorb and desorb water over diurnal and seasonal cycles [1,2,3].

Near-infrared reflectance spectroscopy (1-5 µm) probes the first layers of grains of the regolith and is particularly sensitive to even tiny amounts of hydration. For these reasons, it is an ideal tool to study the interactions between atmospheric water vapor and the very surface of the regolith. The OMEGA (Mars Express) and CRISM (MRO) imaging spectrometers have already acquired extensive datasets allowing the study of temporal changes in surface hydration [4,5,6].

The aim of the present work is to provide both experimental constraints for thermodynamical models of regolith / atmosphere interactions and an appropriate spectral database for the interpretation of the OMEGA and CRISM datasets.

Methods: We have designed and built a simulation chamber [7] as a complement to the LPG bidirectional reflectance spectrometer [8]. This chamber is optimized for measurements at low temperature and permits the exposure of a mineral sample to low (~10^{-5}) to high (~1) values of water vapor relative pressure.

After an initial step of sample dehydration at high temperature (170°C) under secondary vacuum (<10^{-6} mbar), small quantities of water vapor are successively introduced in the simulation chamber. Adsorption isotherm is obtained by calculation of the amount of water adsorbed in the sample and by measurement of water vapor pressure after each introduction of water in the system. In the same time, a complete near-infrared spectrum (1 – 4.8 µm) is measured.

Only measurements at thermodynamical equilibrium are discussed in this abstract. However, both thermodynamical calculation and reflectance spectroscopy are also used to study the kinetics of water exchange. Results and discussion concerning kinetics are presented in a separated abstract [9].

Results and discussion: Figure 1 shows the adsorption and desorption isotherms measured at 243 K for a suite of six samples chosen as potential analogs of the regolith minerals: palagonite JSC Mars-1 [10],

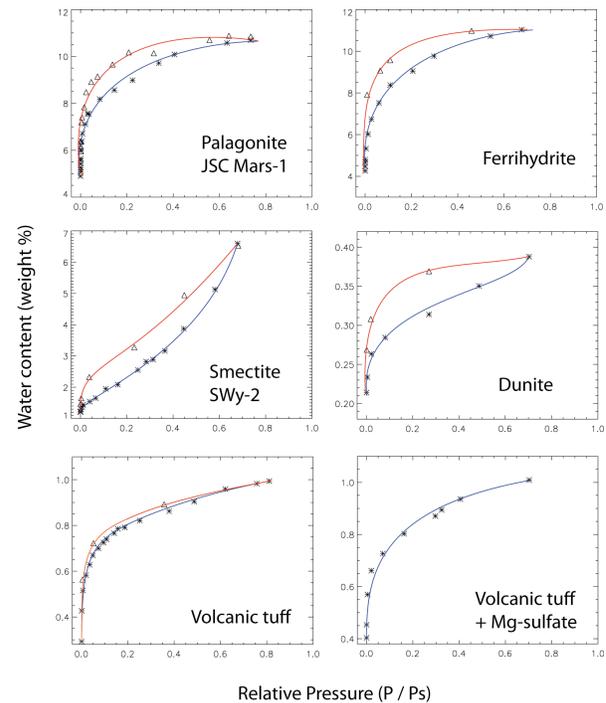ferrihydrite, sodic smectite, dunite and volcanic tuff, pure or mixed with 25 % of Mg-sulfate.

Figure 1: Adsorption and desorption isotherms of six potential analogs of the Martian regolith measured at 243 K.

We observe an important diversity of behaviors among our sample suite in terms of absolute amount of water adsorbed, shape of the isotherm and hysteresis between adsorption and desorption branches (figure 1). Application of the BET model [11] to measured isotherms allows us to retrieve values of specific surface area (SSA) and adsorption constant (C). These values show large variations between the most adsorbent (ferrihydrite: SSA = 1.4 10^5 m^2/kg) and the less adsorbent sample (dunite: SSA = 2.8 10^3 m^2/kg). The shape of the isotherm for the smectite SWy-2 is very different from the one for all other samples, due to the swelling behavior of this type of phyllosilicates.

Figure 2 provides an example of the reflectance spectra of the sodic smectite SWy-2 measured for each of the points from the adsorption isotherm plotted in figure 1. Those series of spectra reveal the evolutions of water absorption bands at 1.4, 1.9 and around 3 µm

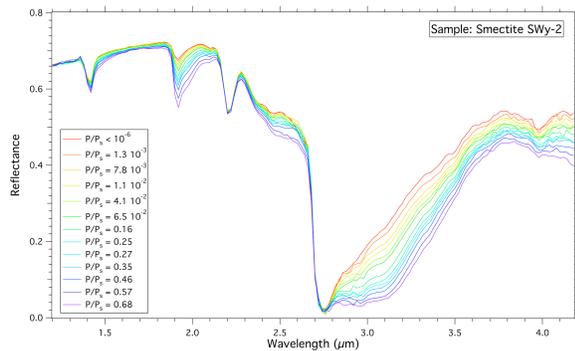while continuum and absorption bands due to hydroxyl ions remain unchanged.

Figure 2: Reflectance spectra of a sodic smectite (SWy-2 from Source Clay repository) measured at 243 K under varying water vapor relative pressure.

One can calculate a ratio between the most hydrated and the driest state for each sample to isolate the absorption due to water from other mineral absorptions. The ratios, normalized at two wavelengths, one in the continuum and the other at the maximum of the absorption band, are presented in figure 3.

Several differences from one sample to another are clearly seen in figure 3. Bands shapes and position of the absorptions maxima are variable among samples. However, adsorbed water is always responsible for absorption features very similar to liquid water contrary to structural water in some nominally hydrated minerals (sulfates for example) that presents absorptions very similar to crystalline ice (not shown here).
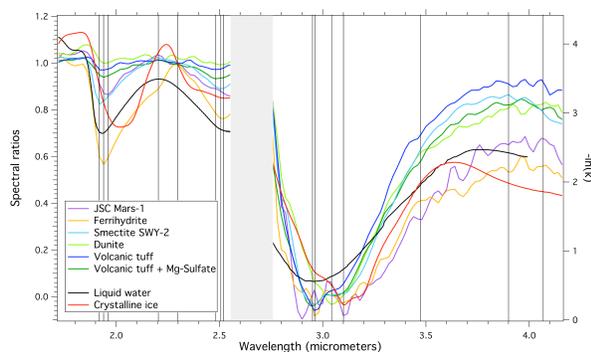

Figure 3: Normalized spectral ratios calculated between the most hydrated and the driest state for each sample. Absorption coefficients of liquid water and crystalline ice [12] are over plotted in logarithmic units, -ln(k), for comparison.

Conclusion and perspectives: Both the thermodynamic and spectroscopic part of this study have implications for the study of the interactions between Martian surface and atmospheric water.

Adsorption and desorption isotherms are crucial parameters for any model of interaction. Values of specific surface area determine the absolute amount of water that can be trapped in the regolith. The strong variability of the measured values of specific surface area among a suite of plausible Martian minerals analogs makes difficult the choice of one constant value in models of interactions between surface and atmosphere. Comparison between the shapes of isotherms reveal the particular case of the smectite, due to its unique swelling behavior. The use of the smectite "type III" shape instead of the classical "type II" isotherm (BDDT classification, [13]) will influence the impact of the regolith on the global water cycle. Finally, hysteresis between adsorption and desorption, variable among the sample suite, is also susceptible to introduce differences in the models results.

Near-infrared spectra of the six analog samples, measured under variable conditions representative of the Martian surface in terms of relative humidity constitute a first step toward a database of minerals reflectance spectra particularly adapted to the interpretation of the Martian surface spectra [14]. Furthermore, spectral ratios calculated between different hydration states reveal the detailed shape of water spectral features and their variability between samples. These results can be used to asses which variabilities in mineral hydration are detectable on the Martian surface from the OMEGA and CRISM datasets.

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