

DECIPHERING THE HYDRATION STATE OF THE MARTIAN SURFACE FROM NEAR-INFRARED SPECTROSCOPY. A. Pommerol¹, P. Beck², B. Schmitt², G. Montes-Hernandez³, and E. Quirico², ¹University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland (antoine.pommerol@space.unibe.ch), ²UJF-Grenoble 1 /CNRS-INSU, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) UMR 5274, Grenoble, F-38041, France, ³Laboratoire de Géodynamique des Chaînes Alpines, Maison des Géosciences, BP 53, 38041 Grenoble Cedex 9, France.

Introduction: The Martian surface displays clear spectral signatures of mineral hydration in the near-infrared (1-4 μm) range. While the 1.9- μm H_2O feature is only detected over localized areas and associated to various types of hydrated minerals [1,2], the wide 3- μm OH/ H_2O feature is present over the entire surface of Mars but has not been assigned to a particular mineralogy [3,4]. This absorption band is frequently interpreted as a result of water adsorption onto mineral grains. We have experimentally studied how mineral analogs of the Martian surface interact with water in low-temperature/low humidity environment from a spectroscopic and a thermodynamic point of view [5]. Comparison between experimental results, spectra of the Martian surface and temperature/humidity of the lower atmosphere allow us to discuss in more details the state of hydration of the Martian surface.

Hydrated and hydroxylated minerals: The term “hydrated mineral” is rather vague and regroups different types of interactions between water and minerals that span a wide range of bounding energy, from weak Van der Waals forces involved in physisorption to ionic and covalent bounds. The distinction between hydration (involving molecular water: H_2O) and hydroxylation (involving the hydroxyl group: OH) is also frequently omitted and both types of minerals are confused. Yet, these different types of hydration and hydroxylation are related to very different physical and geological processes, from surface/atmosphere interactions at the timescale of diurnal and seasonal cycles to alteration of primary mafic minerals billions years ago. Thus, it is crucial to be able to distinguish between these different types of interactions.

The spectral signatures of H_2O and OH in minerals: The spectral range of the near-infrared, 1-4 μm is the most appropriate to characterize mineral hydration from remote-sensing because of the strong spectral signature of the H_2O and OH groups at 1.9- and 3- μm . The 1.9- μm band is attributed to a combination of stretching and bending modes of the water molecule H_2O and is thus absent in the case of hydroxylated minerals. The 3- μm region is dominated by the fundamental O-H stretching and combination with bending modes and absorption can be either due to OH or H_2O .

Figure 1 shows the evolution of the reflectance spectra of the mineral ferrihydrite as relative humidity increases and water adsorbs onto the sample (see [5]

for details about the experimental procedure). About 7 wt. % water was adsorbed at the end of the run. As water adsorbs onto the mineral grains, changes in spectra are visible at 1.9-, 2.5-, and 3- μm . However, there is a significant difference between the behavior of the 1.9- and 3- μm bands: while the 1.9- μm band is almost absent in the driest state (Fig. 1, red curve), the 3- μm band is still extremely strong and close to saturation at 2.8 – 2.9 μm . The absorption at 1.9 μm actually corresponds to adsorbed water while the absorption at 3- μm is dominated by structural OH groups.

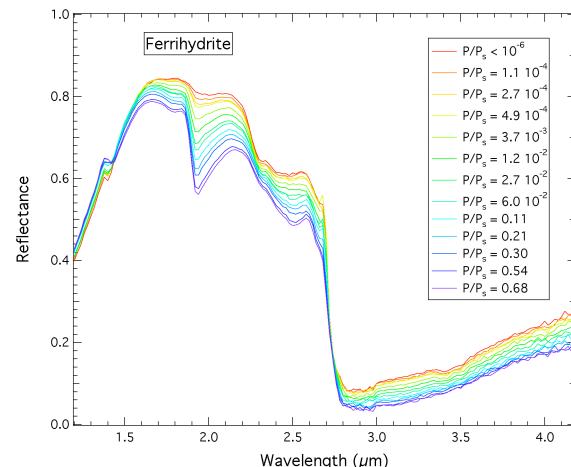


Figure 1: Near-infrared reflectance spectra of ferrihydrite recorded during the course of an adsorption experiment [5]. Temperature of the sample was fixed at -30°C. Relative humidity is indicated as P/P_s where P_s is the saturation pressure of water vapor at -30°C.

Implications for the surface of Mars: On Mars, the 1.9- μm band is observed at many places but only locally, associated to the presence of different types of nominally hydrated minerals as sulfates, phyllosilicates... On the other hand, the wide 3- μm band is observed everywhere and does not appear to be associated to a particular type of mineralogy, consistent with a possible attribution to adsorbed atmospheric water. However, comparison with our experimental results (Fig. 2) shows that the strength of the 3- μm band and the absence of a 1.9- μm band are in disagreement with an attribution of the 3- μm band to H_2O only. In addition, complementary thermodynamic measurements conducted simultaneously with our spectroscopic stud-

ies demonstrate that the amount of adsorbed water at daytime in equatorial and tropical regions of Mars should be extremely minor (<0.5 wt %) and could hardly explain the strength of the 3- μm band. Our preferred interpretation of the spatial occurrence of the 1.9- and 3- μm spectral features on Mars' surface is that hydroxilated minerals in the surface dust are the main contributors to the NIR absorption at 3- μm . Adsorption does only play a role at high latitudes but its effect on the spectra is rather limited. Iron (oxy)hydroxides, like ferrihydrite or goethite, are the most likely candidates for the hydroxilated phase because they are suspected to be an important component of the "nanoparticle oxides" (np-Ox) that give to the Martian surface dust its red color [8].

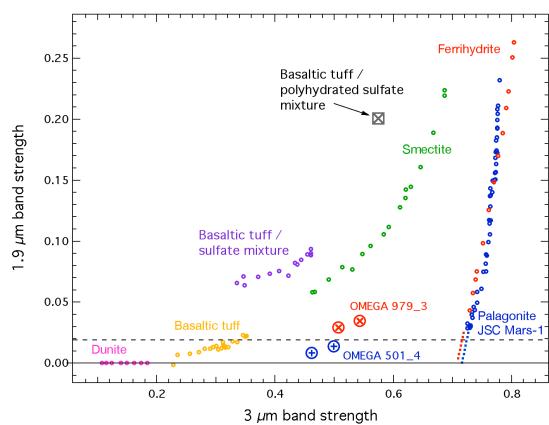


Figure 2: Strength of the 1.9- μm band plotted as a function of the strength of the 3- μm band. Both spectral criteria are calculated from series of laboratory reflectance spectra measured by [5] (see Fig. 1 for an example). For all minerals, adsorption of water results in a simultaneous increase of the 1.9- and 3- μm bands. In the case of the ferrihydrite and palagonite JSC Mars-1 samples, the 3- μm band is already very close to saturation in the driest state because of the high amount of hydroxyl groups in these two samples. We compare band strength values calculated from laboratory spectra with values calculated from OMEGA spectra of Mars' surface: observations 501_4 (Olympus Mons) and 979_3 (Vastitas Borealis Area). The horizontal dashed line at 0.02 represents the detection threshold of OMEGA for this spectral signature [6]. In the case of observation #979_3, a small gradient of hydration as a function of latitude [7] is responsible for variations of both spectral signatures (the two red circles with crosses correspond to extreme latitudes in the observation). Except this minor variability at high latitude, the 3- μm band always stays strong while the 1.9- μm band is usually absent, similar to the behavior of the dried ferrihydrite and palagonite JSC Mars-1 samples.

Conclusions: The comparison between laboratory simulations of mineral/water interactions, knowledge of Mars' surface conditions and remote-sensing near-infrared observations suggests that the red dust that

covers most of the Martian surface is not only oxidized but also hydroxilated. The identification of the mineral phase responsible for this hydroxylation will require additional work on laboratory analogs to reproduce to exact shape of the 3- μm feature. The formation mechanism for this hydroxylated phase remains unknown but is likely water-related. If most Martian dust is hydroxylated, it provides a significant hydrogen and thus water-equivalent reservoir.

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