

THE H₂O SORPTION PROPERTIES OF A MARTIAN DUST ANALOG. J. Jänchen¹, R.V. Morris², D.L. Bish³, U. Hellwig¹, ¹TFH Wildau, c/o ZeoSolar e.V., Volmerstr. 13, D-12489 Berlin-Adlershof, Germany, e-mail address: j.e.jaenchen@t-online.de, ²NASA Jonson Space Center, 2101 NASA Park Way, Houston, TX 7705, USA, e-mail address: richard.v.morris@nasa.gov, ³Indiana University, 1001 E 10th St, Bloomington, Indiana IN 47405, USA, e-mail address: bish@indiana.edu.

Introduction: Palagonitic tephra (basaltic tephra containing hydrated and hydroxylated volcanic glass of basaltic composition) has received widespread attention in the planetary literature because many are basaltic spectral and magnetic analogs of bright Martian surface materials [1, 2]. Here we present the H₂O adsorption properties of two samples of palagonitic tephra (HWMK919, PA6-7) from the Island of Hawaii and compare their behaviour with that of two smectites (nontronite, NG-1, and montmorillonite, STx-1) similar to those that have been spectroscopically identified on Mars by the Mars Express/OMEGA Team [3]. One tephra sample (HWMK919) is the <5 µm size fraction of a phyllosilicate-poor palagonitic tephra and is thus a size analog for bright Martian dust [4]. The results are important for understanding the speciation of adsorbed H₂O, hydrated and hydroxylated phase on the near-equatorial Martian surface as detected by the presence of the 3 µm hydration feature across the entire planet (Mars Express/OMEGA) [5].

The work here builds on previous published work on the interaction of Martian atmospheric H₂O with Mars analog samples under simulated Martian environmental conditions [e. g. 6-9].

Experimental: The sorption properties of H₂O in HWMK919<5µm, Pahala Ash PA5-6, montmorillonite (STx-1), nontronite (NG-1) were investigated by means of isotherm measurements, thermogravimetry (TG) and differential scanning calorimetry (DSC). Sorption isotherms were measured gravimetrically from 255-313 K with a McBain quartz spring balance equipped with two MKS Baratron pressure sensors covering a range of 10⁻⁵-10 mbar. TG/DSC measurements were performed on a SETARAM TG-DSC 111 apparatus with a heating rate of 3 K/min to 673 K. Prior to the experiments the samples were loaded at a relative H₂O pressure of 0.3.

Scanning electron microscopy (SEM, JOEL JSM640), X-ray powder diffraction (XRD, Bruker D8, Cu Kα radiation) and N₂ adsorption (Quantachrome Autosorb-1) were applied to characterize the solids.

Before each adsorption experiment, about 150 mg of sample was degassed at 383 K and p<10⁻⁵ mbar for several hours. At these conditions, however, not all strongly adsorbed H₂O was removed (especially for HWMK919, which retained about one third of the total

H₂O compared with the total mass loss). We did not heat the samples to higher temperatures because low degassing temperatures are crucial to prevent possible modifications to the solids.

Results and Discussion: Table 1 and Figure 1 show the results of a general characterization of the samples to get information about surface area, pore diameter and particle size. As can be seen, significant differences in the N₂ BET surface area of the palagonites and the smectites were found because N₂, as opposed to H₂O, is unable to penetrate into the inter-layer spaces of the smectites. A formal application of the BET equation on the water adsorption isotherms (Table 1) supports this behavior.

XRD analysis of HWMK919 characterized it as phyllosilicate-poor in contrast to PA6-7. Furthermore, HWMK919 contains a considerable amount of allophane which is generally microporous and hydrophilic.

Table 1. BET surface areas, pore diameters, and particle sizes for all samples (partially after [9]).

Material	BET in m ² /g		Pore Ø in nm	Particle size, µm
	N ₂	H ₂ O		
HWMK919	203	265	4	<5
PA6-7	183	-	3.8	≥50
NG-1	66	239	3.8	9
STx-1	74	217	4	5

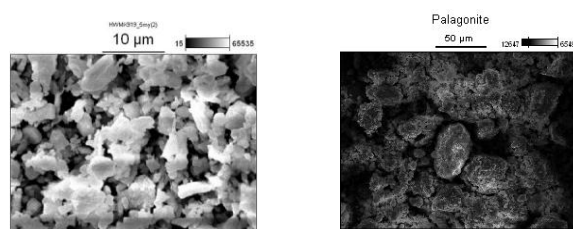


Figure 1. SEM images of HWMK919 (left, after [9]) and PA6-7 (right); note difference in magnification.

Figure 2 and Table 2 summarize the TG and DSC data for the palagonites and smectites. The desorbed amounts of H₂O range between 0.325 for HWMK919 and ~0.2 g/g for the other samples indicating a significant difference between the Martian dust analog and the other three samples. Similar results were obtained for the integral heats of desorption (last column in Table 2) indicating a stronger interaction of H₂O in

Table 2. Results of the TG/DSC measurements: sorption capacities (a) and integral molar heats of desorption (dehydration) (Q_{int}) of H_2O at ($p/p_s=0.3$).

Material	a in g/g	Q_{int} in kJ/mol
HWMK919	0.325	88
PA6-7	0.21	65
Nontro. NG-1	0.19	63
Montmo. STx-1	0.17	64

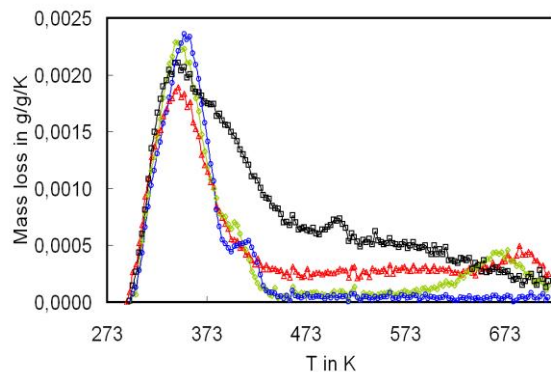


Figure 2. Differential thermogravimetric profiles of (from top to bottom): HWMK919 (squares), PA6-7 (triangles), nontronite (diamonds) and montmorillonite (circles).

HWMK919, most probably due to differences in the mineralogical composition (allophane). Consequently, HWMK919 retains much more H_2O at 383 K (degassing temperature, see above) than the smectites or PA6-7. These materials had already lost most of their H_2O at 383 K.

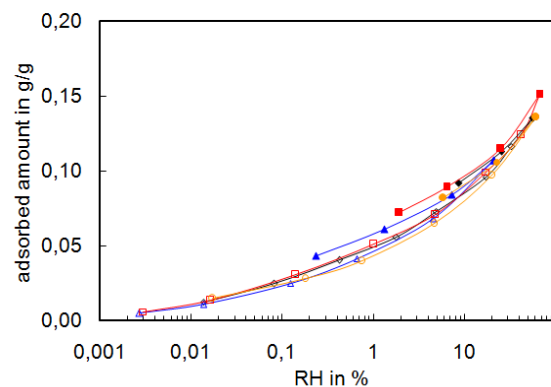


Figure 3. H_2O adsorption isotherms for HWMK919 at 255 (diamond), 273 (squares), 293 (circles) and 313 K (triangles); filled symbols denote desorption; the abscissa is a logarithmic relative humidity scale (RH).

Figure 3 gives the H_2O adsorption isotherms for HWMK919 measured after degassing at 383 K for

different temperatures down to very low values of relative humidity. Because of the remaining amount of water after the degassing procedure the isotherms in Figure 4 have been corrected by these amounts of H_2O . Figure 4 compares the isotherms of HWMK919 and NG-1 (nontronite). It can easily be seen that the Martian dust analog contains remarkable amounts of H_2O even at very low RH.

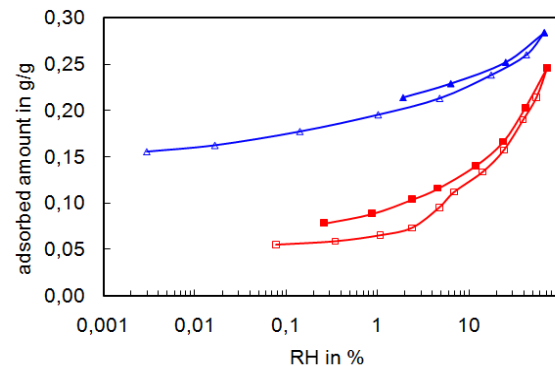


Figure 4. Corrected H_2O isotherms for HWMK919 (top) and nontronite based on the measured TG data from Table 2.

These results show that the fine-grained, phyllosilicate-poor palagonitic dust derived from palagonitic tephra HWMK919 can hold significantly more H_2O than smectites under $p(H_2O)$ and temperature conditions approaching those on the Martian surface. Palagonitic dust is a geologically reasonable hydrated and hydroxylated phase on the surface of Mars, and its presence as dust may account for the presence of the $3\mu m$ absorption band as seen by OMEGA and CRISM at the Martian surface for the entire planet.

References: [1] Morris R.V. et al. (2000) *JGR* 105, 1757-1817. [2] Morris R.V. et al. (2001) *JGR* 106, 5057-5083. [3] Poulet F. et al. (2005) *Nature* 438, 623-627. [4] Lemmon M.T. et al. (2004) *Science* 306, 1753-1756. [5] Jouglet et al. (2007) *JGR* 112, E08S06, doi: 10.1029/2006JE002846. [6]. Zent A.P. et al. (2001) *JGR*, 106, 14667-14674. [7] Bish D.L. et al. (2003) *Icarus*, 164 96-103. [8] Jänchen et al. (2006) *Icarus*, 180, 353-358. [9] Jänchen et al. (2009) *Icarus*, in press.

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