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**The H₂O and CO₂ adsorption properties of phyllosilicate-poor palagonitic
dust and smectites under martian environmental conditions**

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ABSTRACT

The recent detection of up to ~10 wt.% water-equivalent H heterogeneously distributed in the upper meter of the equatorial regions of the martian surface and the presence of the 3- μ m hydrations feature across the entire planet raises the question whether martian surficial dust can account for this water-equivalent H. We have investigated the H₂O and CO₂ adsorption properties of palagonitic dust (<5 μ m size fraction of phyllosilicate-poor palagonitic tephra HWMK919) as a martian dust analog and two smectites under simulated martian equatorial surface conditions. Our results show that the palagonitic dust, which contains hydrated and hydroxylated volcanic glass of basaltic composition, accommodates significantly more H₂O under comparable humidity and temperature conditions than do the smectites nontronite and montmorillonite.

Key Words: Mars, surface; mineralogy; geochemistry; palagonite; smectite; water, adsorption

1. Introduction

Palagonitic tephra (basaltic tephra containing hydrated and hydroxylated volcanic glass of basaltic composition) have received widespread attention in the planetary literature because many are basaltic spectral and magnetic analogs of bright martian surface materials (e.g., Morris et al. 2000, 2001). Here we report the H₂O and CO₂ adsorption properties for the <5 μm size fraction of phyllosilicate-poor palagonitic HWMK919 from the Island of Hawaii under simulated martian conditions. This size fraction was chosen because it is a size analog for martian dust, which has a mean diameter of $3.4 \pm 0.6 \mu\text{m}$ and $3.0 \pm 0.4 \mu\text{m}$ from measurements made by Mars Pathfinder and the Mars Exploration Rovers, respectively (Markiewicz et al., 1999; Lemmon et al., 2004). For comparison, we acquired equivalent data for two smectites (nontronite and montmorillonite) which have been spectroscopically identified on Mars by visible-near-infrared instruments on orbiting spacecraft (Bibring et al. 2005; Poulet et al. 2005; Mustard et al. 2008). Although these smectites are localized in Noachian bedrock terrains, and do not appear to be important components of the martian dust, their H₂O contents under martian surface conditions can be on the order of 2-8 wt% (Bish et al., 2003; Jänchen et al., 2006) and they have been suggested as possible hosts for H₂O on the martian surface.

Our results are important for and focus on understanding the speciation (e.g., H₂O ice, adsorbed H₂O, and hydrated and hydroxylated phases) of up to ~10 wt% H₂O-equivalent H in the upper meter of the near-equatorial martian surface as detected by the gamma-ray and neutron spectrometer instruments on Mars Odyssey (Feldman et al. 2004; Boynton et al. 2004). The presence of the 3- μm hydration feature across the entire planet as detected by OMEGA (Jouglet et al., 2007; Milliken et al., 2007) could also result from martian dust, if the dust contains a component that is able to accommodate sufficient H₂O and satisfy spectroscopic constraints under martian environmental conditions.

This paper builds on previous published work on the interaction of Martian atmospheric H₂O and CO₂ with Mars analog samples under simulated Martian environmental conditions (e.g., Fanale and Cannon, 1978; Yen et al., 1998; Bish et al., 2003; Zent et al., 1987, 1997, 2001).

2. Experimental

The samples selected for this comparative adsorption study were a palagonitic tephra and two smectites. The palagonitic dust sample is the <5 µm size fraction of palagonitic tephra HWMK919 from Mauna Kea Volcano, Hawaii is phyllosilicate-poor (Morris et al., 2001) and served as a size analog for martian dust. The sample does contain plagioclase, pyroxene, magnetite, and allophane (an H₂O/OH bearing phase) according to powder X-ray diffraction. The primary Fe-bearing phase is nanophase ferric oxide (potentially an H₂O/OH-bearing phase by analogy with ferrihydrite) according to Mössbauer measurements. Although Morris et al. (2001) show that HWMK919 contains less than 3% smectite (the detection limit), we refer to this sample as phyllosilicate poor rather than phyllosilicate free, for clarity. The smectite samples are Ca-montmorillonite (Clay Minerals Society Source Clay STx-1, Gonzales County, Texas, USA) and nontronite (NG-1, Hoher Hagen, Darnsfeld, Göttingen, Germany). Scanning electron microscopy (SEM, JEOL JSM640), and X-ray powder diffraction (Bruker D8, Cu Kα radiation) were applied to characterize the solids.

H₂O adsorption and desorption isotherms were measured gravimetrically from 255 to 313 K at 10⁻⁴ to 10 mbar with a McBain quartz spring balance (sensitivity 4 mg/mm, resolution 10⁻² mm) equipped with MKS Baratron pressure heads of high sensitivity in the range 10⁻⁵ to 10³ mbar. The error of the isotherm measurements corresponds to 2.5-4% related to the adsorbed amount, *a*, in g/g adsorbent. CO₂ adsorption and desorption isotherms were determined volumetrically from 196 to 293 K and from 0.1 to 1000 mbar using a Quantachrome Autosorb-1 instrument. This instrument was also used for the standard N₂ BET surface area

and isotherm measurements at 77 K. The micropore analysis (micropore volume) of the samples was carried out by applying the t-method (De Boer et al., 1965) using the N₂ isotherms. This technique involves the same N₂ isotherm measurements as that employed in the BET method, but extended to some what higher pressure values. The t-plot is a plot of the volume of gas adsorbed versus t, the statistical thickness of the adsorbed film. The t values are a function of the relative pressure and can be calculated by equations of De Boer. Differences in slope of the t-plot between the micropore- and mesopore adsorption region of the material allow to distinguish between the corresponding surface area and pore volume values of that porous material.

Before each H₂O-, CO₂- and N₂-adsorption experiment, about 150 mg of sample was degassed at 383 K and $p < 10^{-5}$ mbar for several hours. Under these conditions, however, not all strongly adsorbed or structural H₂O was removed (especially for HWMK919, which retained about one third of the total H₂O compared with the total mass loss). For these measurements we did not heat the samples to higher temperatures because low degassing temperatures are crucial to prevent possible modifications to the solids. To evaluate the impact of heating on the properties of HWMK919 we also measured the N₂ BET surface area and the CO₂ adsorption isotherms after heating at 623 K.

Hg intrusion measurements were carried out with the Pascal 140 and 440 instrument in a pressure range of 0-400 MPa to obtain information on the particle size distribution (Mayer and Stowe method was used). The samples were evacuated for 15 minutes before the measurements.

Thermogravimetry (TG) was performed on a SETARAM TG-DSC 111 apparatus with a heating rate of 3 K/min from ambient to 723 K. Samples of about 12-14 mg were equilibrated at room temperature in a desiccator for about two weeks at p/p_0 (H₂O) of 0.3 prior to the TG experiments. The TG and N₂ isotherm measurements were repeated twice and the CO₂ isotherms were repeated once showing high reproducibility of the measurements.

3. Results and Discussion

The gas adsorption behavior of porous materials is determined by the energetic properties of adsorption sites, by specific surface area, by pore size distribution, and pore volume. The values of specific surface area, pore diameter, and micropore volume (average of triplicate measurements), average particle diameter, and mass loss after equilibration at H_2O $p/p_0 = 0.3$ are given in Table 1 for the palagonitic dust and smectites.

[Table 1, Figure 1]

The HWMK919 palagonitic dust has a significantly higher surface area than the smectites and has pores <2 nm in diameter (micropores) in addition to some mesopores (~ 4 nm diameter). The smectites have small N_2 BET surface areas and only mesopores because N_2 , as opposed to H_2O , is unable to penetrate into the interlayer spaces of the smectites. All data in Table 1, column 2-4 were derived from the N_2 adsorption isotherms (Figure 1). The shape and position of the isotherms in the diagram illustrate the difference in the two types of samples. Low N_2 uptake at low relative pressures for the smectites indicates the absence of micropores for N_2 , and the pronounced adsorption hysteresis for $p/p_0 > 0.4$ is very characteristic of capillary condensation in mesopores. Much higher uptake at low p/p_0 and the less pronounced hysteresis loop for the phyllosilicate-poor palagonitic dust in Figure 1 indicate the presence of significantly smaller pores compared to the smectites. Because the particle diameter for the three samples is comparable (Table 1), the particle diameter cannot control the difference in adsorption properties between the palagonitic dust and the two smectites. Figure 2 shows an SEM image for the palagonitic dust that confirms the particle size distribution of <5 μm reported by Morris et al. (2001). Column 6 of Table 1 summarizes the total mass loss of the samples (means of three different measurements) determined by TG between 293 and 673 K after equilibration at a water vapour pressure of $p/p_0 = 0.3$. HWMK919 shows by far the largest mass loss.

[Figure 2]

The results of the TG measurements are illustrated in more detail in Figures 3 and 4. The HWMK919 palagonitic dust accommodated significantly more H₂O than the two other samples if the total mass loss of 0.325 g/g is assigned to H₂O. Desorption of a considerable amount of this H₂O (i.e., insignificant dehydroxylation) is consistent with the high BET surface area of this sample which is in fact >203 m²/g if the dry mass would be corrected by subtracting the residual H₂O remaining in the sample after degassing at 383 K. Samples NG-1 and STx-1 lost most of their H₂O below 383 K upon heating (Figures 3 and 4), whereas HWMK919 lost only half of the H₂O from its pore system up to 383 K. The derivative TG (DTG) pattern of HWMK919 in Figure 4 confirms the differences from the two other samples and illustrates the more strongly bonded H₂O associated with this sample. Based on these data, we expect that HWMK919 palagonitic dust has the potential to hold more H₂O under martian environmental conditions than do smectites, a somewhat unexpected result.

[Figure 3, Figure 4]

Figure 5 shows the H₂O adsorption isotherms for HWMK919 palagonitic dust at temperatures between 255 and 313 K. The isotherms become steep approaching the corresponding condensation pressure of H₂O (e.g., 1.1 mbar at 255 K, 6.1 mbar at 273 K, and 23 mbar at 293 K). This behavior indicates unlimited multilayer adsorption between aggregates of small particles or in large pores at high relative pressures as seen also with nitrogen adsorption (Figure 1). The H₂O uptake measured at 0.001 mbar (martian surface pressure of water vapor; dashed line in Figure 5) amounts to 2.5 wt.% (0.025 g/g) at 255 K and is significantly higher than the amounts observed by Zent and Quinn (1997). It should be mentioned that the adsorption and desorption of H₂O in HWMK919 is a slow process and therefore an equilibration time of 12 h between data points (dosing) in the isotherms was used. The slow adsorption/desorption kinetics will be important in determining whether or not

phyllosilicate-poor palagonite can be considered to be important in affecting the diurnal martian atmospheric H₂O cycle, and the slow kinetics suggest that it will not.

[Figure 5, Figure 6]

Figure 6 compares the H₂O adsorption isotherms for HWMK919 with those for NG-1 at 293 K. The maximum uptake of H₂O up to 10 mbar appears to be the same for both materials, although HWMK919 adsorbed more H₂O at significantly lower $p(\text{H}_2\text{O})$ compared with NG-1 (and also STx-1; cf. Jänchen et al., 2006). Moreover, HWMK919 retained about 0.1 g/g “extra” H₂O after the degassing procedure prior to the isotherm measurements and NG-1 retained much less (cf., results of the TG measurements).

CO₂ adsorption measurements gave results similar to those for H₂O adsorption (Figures 7 and 8), although the hysteresis obvious in Figures 5 and 6 was not seen with CO₂ adsorption, and in contrast to the results of Zent (1986), was reversible for CO₂. The hysteresis observed for H₂O adsorption on HWMK919 appears to be a kinetic effect (Figure 6; filled triangles shift towards adsorption branch within 30 days). However, this was not the case for smectites (NG-1 in Figure 6), which exhibited marked hysteresis resulting from structural phase transitions involving interlayer H₂O that are obvious in controlled-humidity X-ray diffraction data (e.g., Chipera et al., 1997).

[Figure 7, Figure 8]

The CO₂ adsorption isotherms for HWMK919 palagonitic dust measured at 196-293 K (Figure 7) plotted in an a vs. $\log(p)$ diagram give the adsorbed amount, a , in g CO₂ /g adsorbent as function of the CO₂ pressure on a logarithmic scale. Figure 7 shows that a considerable amount (~ 0.04 g/g) of CO₂ can be adsorbed at 196 K and 6 mbar, the CO₂ surface pressure on Mars. However, this amount of adsorption occurs only in the absence of H₂O vapor. It has been demonstrated (Jänchen et. al, 2007) that for energetic reasons H₂O is preferred over CO₂, even at a surplus of CO₂ as is the case for the atmosphere on the martian surface. Figure 8 compares the CO₂ isotherms for HWMK919 with those for NG-1,

illustrating that HWMK919 has a higher affinity for polar molecules (including CO₂) than do the smectites (again because CO₂ might not be able to penetrate into the smectite interlayer regions).

The reason for the high affinity of HWMK919 for H₂O may have to do not only with the pore structure (very small pores) but also with the chemical composition and the surface functional groups on the solids in this material. The <5 µm fraction of HWMK919 contains a large amount of allophane which may contribute to the high level of H₂O adsorption at low partial pressures, possibly because of the presence of surface hydroxyl species (Hamayoon et al., 2006) such as Al(OH)Al, Si(OH), Al(OH)₂, Si(OH)₂ and Al(OH)Si, all of which are known as strong specific adsorption sites for H₂O.

The strongly bonded H₂O on specific sites (and possibly some structural water) account for the weight losses that occurred for HWMK919 at high temperatures in TG experiments (Figures 3 and 4). This H₂O loss is not completely reversible because it changes the structure of the sample. Our experiments with HWMK919 degassed at 623 K instead of 383 K show a significant decrease in the specific surface area (from >203 to 185 m²/g), and the CO₂ adsorption isotherms indicate a diminished uptake by about 35%, demonstrating the occurrence of irreversible structural changes in HWMK919 at elevated temperatures.

Equilibrium (isotherm) measurements with H₂O on samples degassed exclusively at 383 K show the existence of reversibly adsorbed H₂O, with the highest amount adsorbed for the palagonite HWMK919 (Figure 6). In addition to the (remaining) strongly bonded H₂O of about 10 wt.%, the “total” H₂O in HWMK919 amounts to 12.5 wt.% at 255 K and 0.001 mbar (Figure 5). This is significantly more water compared with only 1-3 wt.% for nontronite or montmorillonite found previously under the same conditions (Jänchen et al., 2006).

4. Conclusions

These results show that fine-grained, phyllosilicate-poor palagonitic dust derived from

palagonitic tephra HWMK919 can hold significantly more H_2O than smectites under $p(\text{H}_2\text{O})$ 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, at least in part, for the observations of heterogeneously distributed elevated concentrations of water-equivalent H near the martian surface as detected by Mars Odyssey and the 3- μm absorption band as seen by OMEGA and CRISM at the martian surface for the entire planet.

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Tables

Table 1

Characterization data for palagonitic dust and smectite samples.

Sample	Specific surface area (m ² /g)	Mesopore diameter (nm)	Micropore volume ^a (cm ³ /g)	Particle diameter (μm)	Mass loss ^d (g/g)
HWMK919 <5 μm	203 ± 1	4	0.05	<5 ^b	0.325±0.01
Nontronite, NG-1	66 ± 2	3.8	0	9 ^c	0.19±0.01
Montmorillonite, STx-1	74 ± 2	4	0	5 ^c	0.17±0.01

^a Micropore volume for N₂ adsorption according to t-method, see text^b From Morris et al. (2001).^c From Hg intrusion.^d TG mass loss after equilibration at H₂O p/p₀=0.3.

Figure captions

Figure 1. Nitrogen adsorption (open symbols) and desorption (filled symbols) isotherms at 77 K for <5 μ m HWMK919 (diamond), STx-1 (squares), and NG-1 (triangles); adsorbed amount, a , in cm³ nitrogen gas, stp.

Figure 2. Scanning electron micrograph of <5 μ m HWMK919.

Figure 3. TG profiles for STx-1, NG-1, and HWMK919 (from top to bottom on the right).

Figure 4. Mass losses in g/g/K (DTG) of <5 μ m HWMK919 (squares), NG-1 (triangles), and STx-1 (circles).

Figure 5. H₂O adsorption (open symbols) and desorption (closed symbols) isotherms for HWMK919 <5 μ m at 255 (circles), 273 (triangles), 293 (diamonds), and 313 K (inverted triangles), adsorbed amount, a , in g H₂O/g HWMK919, the dashed line indicates the H₂O vapor pressure on the martian surface.

Figure 6. H₂O adsorption/desorption isotherms for <5 μ m HWMK919 (triangles) and NG-1 (circles) at 293 K after degassing at 383 K in high vacuum, filled symbols denote desorption, adsorbed amount, a , in g H₂O/g mineral.

Figure 7. CO₂ adsorption (open symbols) and desorption (closed symbols) isotherms for HWMK919 <5 μ m, at 196, 273, and 293 K (from top to bottom), adsorbed amount, a , in g CO₂/g HWMK919.

Figure 8. CO₂ isotherms for <5µm HWMK919 (filled symbols) and NG-1 (open symbols) at 196 (triangles), 273 (squares), and 293 K (circles), adsorbed amount, a , in cm³ liquid CO₂/g mineral.

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Figure 1. Nitrogen adsorption (open symbols) and desorption (filled symbols) isotherms at 77 K of HWMK919 <5 μ m (diamond), STx (squares), and NG-1 (triangles); adsorbed amount, a , in cm³ nitrogen gas, stp.

Figure 2. Scanning electron micrograph of <5 μ m palagonitic dust HWMK919.

Figure 3. TG profiles for STx, NG-1, and HWMK919 $<5\mu\text{m}$, (from top to bottom on the right)

Figure 4. Mass losses in g/g/K (DTG) of HWMK919 $<5\mu\text{m}$ (squares), NG-1 (triangles) and STx (circles).

Figure 5. H₂O adsorption (open symbols) and desorption (closed symbols) isotherms for HWMK919 <5 μ m at 255 (circles), 273 (triangles), 293 (diamonds), and 313 K (inverted triangles), adsorbed amount, a , in g H₂O/g HWMK919, the dashed line indicates the H₂O vapor pressure on the martian surface.

Figure 6. H₂O adsorption/desorption isotherms for <5 μ m HWMK919 (triangles) and NG-1 (circles) at 293 K after degassing at 383 K in high vacuum, filled symbols denote desorption, adsorbed amount, a , in g H₂O/g mineral

Figure 7. CO₂ adsorption (open symbols) and desorption (closed symbols) isotherms for HWMK919 <5μm, at 196, 273, and 293 K (from top to bottom), adsorbed amount, a , in g CO₂/g HWMK919.

Figure 8. CO₂ isotherms for <5μm HWMK919 (filled symbols) and NG-1 (open symbols) at 196 (triangles), 273 (squares), and 293 K (circles), adsorbed amount, a , in cm³ liquid CO₂/g mineral.