H_2O Adsorption on Smectites: Application to the Diurnal Variation of H_2O in the Martian Atmosphere

Aaron P. Zent,

NASA Ames Research Center, Moffett Field, CA, 94035,
azent@mail.arc.nasa.gov

J. Howard, R. C. Quinn

SETI Institute/NASA Ames Research Center,

Moffett Field, CA, 94035

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5 Figures

1 Table

Abstract

Observations of the Martian planetary boundary layer lead to interpretations that are baffling and contradictory. In this paper, we specifically address the question of whether or not water vapor finds a substantial diurnal reservoir in the Martian regolith. To address this issue, we have measured H_2O adsorption kinetics on SWy-1, a Na-rich montmorillonite from Wyoming. The highest-temperature (273 K) data equilibrates rapidly. Data gathered at realistic H_2O partial pressures and temperatures appropriate to early morning show two phenomena that preclude a significant role for smectites in diurnally exchanging a large column abundance. First, the equilibration timescale is longer than a sol. Second, the equilibrium abundances are a small fraction of that predicted by earlier adsorption isotherms. The explanation for this phenomenon is that smectite clay actually increases its surface area as a function of adsorptive coverage. At Mars-like conditions, we show that the interlayer sites of smectites are likely to be unavailable.

1. Introduction

A. The Martian Boundary Layer Is Puzzling

Observations of the Martian planetary boundary layer, although incomplete and difficult to reduce, lead to interpretations that are baffling and contradictory. In this paper, we specifically address the question of whether or not water vapor finds a substantial diurnally-exchangeable reservoir in the Martian regolith. The planetary boundary layer (PBL) is the lowest section of the atmosphere, which is diurnally affected by substantial momentum transfer from the heated planetary surface. Observations disagree on whether or not the total atmospheric column abundance of H_2O varies significantly at a specific location as a function of hour angle. Some observations, chiefly from ground-based telescopes, and from the ISM instrument on Phobos, indicate a tremendous variation over the course of the day. Other observations, specifically those from Pathfinder and the Viking Orbiters, are most conveniently interpreted to indicate no measurable diurnal variations in the H_2O column abundance. Numerical models of the PBL, coupled with an adsorbing material on the Martian regolith, have been developed, and exercised in a variety of configurations. They are uniformly are unable to predict observable diurnal variations in atmospheric H_2O abundance, when constrained with independent variables that are most compatible with observations.

That said, there are clearly ways in which models can be forced to predict substantial diurnal exchange, although this comes at the cost of violating observational constraints. The simplest technique for forcing substantial exchange is to posit that the Martian surface is locally covered with a highly adsorbing smectite clay. These clays have a much larger adsorptive capacity than ordinary particulates comprising regolith material, because they have interlayer sites that are available for adsorption. These swelling clays can therefore adsorb and exchange a much larger inventory of H_2O per unit mass than other silicate compounds.

One important assumption must be made however, in order to force PBL models to predict observable diurnal H_2O exchange with smectite clays: the clays must equilibrate with the surrounding pore gases on a timescale short compared to a Martian sol. If that condition is not assumed, then the clays are unable to exchange H_2O in response to the extraordinary thermal variations they experience over the course of the Martian diurnal cycle.

There are uncertainties about how rapidly smectites will equilibrate their adsorptive load at conditions that are representative of the Martian near-surface environment. Although the sticking coefficients that ordinarily control adsorptive uptake are quite high under these conditions, smectites require an additional process in order to take advantage of their extraordinary adsorptive capacity: surface diffusion. The primary constraint on adsorptive uptake in smectites is that adsorbates cannot diffuse to the interlayer sites from the vapor phase. Instead, they must form mobile precursor complexes on the outer surfaces of the clay particles, and be transported across grain surfaces to access the interlayer sites. This process is temperature dependent, and raises the complex issue of whether the interlayer sites are accessible on a timescale that permits clays to play a role in exchanging a substantial fraction of the atmospheric column

B. Laboratory Investigation of Clay Adsorption Kinetics

To address this issue, we have measured adsorption kinetics in SWy-1, a Na-rich montmorillonite from Wyoming. The specific issue we address is the rate and magnitude at which H_2O is adsorbed by these clays as a function of the temperature and parital pressure of water.

In brief, we precondition the clay to remove as much water as possible, and cool it to Mars-like temperatures. We expose the clay to appropriate levels of H_2O vapor, and measure the adsorptive load on the clay as function of time. These so-called uptake curves are analyzed in the context of the martian diurnal boundary layer. The equilibration timescales are clearly a function of the temperature and relative humidity of the surrounding pore gases. Soil temperatures are well understood, and a variety of partial pressures of H_2O can be modeled. We find that the timescale for equilibration of smectites under appropriate Martian boundary layer conditions is long compared to the timescales required for any species playing a significant role in the Martian boundary layer. We further find that more realistic isotherms for smectites do not suggest substantial adsorptive capacity at Mars-like conditions.

2. Importance of Smectite Adsorption Kinetics

The origins of our interest in the adsorption kinetics of smectites under Mars-like conditions stems from a variety of observations of the behavior of water vapor in the Martian atmosphere. These observations disagree in the most profound way about the behavior of the water, and call out for some explanation. In this section, we will review the literature describing H_2O in the Martian boundary layer, and then explore the reasons that smectite clays have been invoked as means of ameliorating the observational conflicts.

A. H_2O in the Mars Boundary Layer

The initial descriptions of diurnal variations in the martian atmosphere came from telescopic observations of Mars published by Baker (1976). He observed Mars during the 1972-1974 oppositions, and published observations covering the period L_s 118 through 268 (northern summer and autumn). The observations were taken along EW orientations over two periods, separated by 5 months. Accordingly, the first set of observations covered the evening terminator and morning limb. By the time of the second set of observations, the slit crossed the morning terminator and evening limb.

The results in each set of observations, and in the combined data set, indicated that there was a factor of 2-3 exchange diurnally in the total amount of H_2O in the martian atmosphere. The data reduction procedure corrected for the geometric airmass traversed by the solar photons, but did not account for scattering in the atmosphere. Barker's analysis of this observation was that there was a remarkably strong diurnal variation in the atmospheric T profile, causing condensation. His observations were sensitive to H_2O vapor, but not to H_2O in condensates. He predicted that wide-spread and optically thick ground fogs would be observed in consequence of the strong T profile changes.

Working with these results before they were even published, and getting their analysis into the literature before the data on which it was based, Flaser and Goody (1975), tried to fit the behavior reported by Baker (1976) with a boundary layer model. Their model incorporated all of the relevant physics, and was based upon terrestrial boundary layer models that had been validated in a number of field studies. They found that it was necessary to cap the atmospheric H_2O within 2 km of the ground in order to prevent continuous atmospheric saturation. The model as constructed predicted persistent and optically thick ground fogs which were not observed, and lead the investigators to suggest waiting for additional data from the then-imminent Viking missions.

Working with the Viking data, Davies (1979), analyzed the Mars Atmospheric Water Detector (MAWD) results for evidence of diurnal H_2O variations. A special observational campaign was conducted for the specific purpose of addressing the photometric effects of atmospheric observations from the Viking Orbiters. On rev 42, the MAWD instrument observed the VL1 landing site continuously from the time it came over the horizon until it disappeared in the spacecraft's wake. The assumption was that the data reflected an invariant H_2O abundance throughout the observational period. Davies then compared the derived H_2O variation against changes in airmass and phase angle with a variety of numerical models of predicted H_2O abundance based on dust distribution in the atmosphere.

The results of the analysis indicated that the best fit to the data was derived by assuming that H_2O was uniformly mixed in atmosphere with the same scale height as the aerosol dust. This conclusion removed the necessity of substantial daily H_2O exchange between the atmosphere and surface in order to explain the observations. Reported variations in the diurnal H_2O abundance were then explained by increases in airmass. As the airmass increases, and hence the scattering by airborne dust at the same altitudes, the apparent column abundance decreased because more photons were scattered back to the detector before penetrating and sampling the entire atmospheric column. This conclusion was inconsistent with the Flaser and Goody model, which had required that H_2O remain sequestered at a low altitude (unlike the atmospheric dust) and predicted ground fogs that were not observed.

Study of the martian boundary layer then was dormant for some while, until Haberle et al (1993) produced another 1-dimensional model of the martian boundary layer. The model, akin to Flaser and Goody's, was based on terrestrial atmosphere models. They used VL1 and VL2 early northern summer data to validate their model. Temperature profiles at the height of 1.6m (the height of the atmospheric temperature sensor on the boom) agreed well with model predictions. Results from predictions of wind fields were more problematic. They found that they were able to match the surface wind data, or atmospheric T profiles, but not both simultaneously. In a qualitative way, they reproduced measured hodographs at the Viking sites with the model, when it was sufficiently tuned to match the data.

Using this model, Zent et al (1993) incorporated a planetary surface that adsorbed and exchanged H_2O between the atmosphere and the subsurface. They incorporated much of the same physics as Flaser and Goody (1975), but had the advantage of using more accurate atmospheric H_2O abundances based on the Viking observations. They assume that H_2O was a passive atmospheric tracer, and employed soil adsorption isotherms using the data reported by Fanale et al (1978) for H_2O adsorption of basalt.

They found that there was a very limited exchange of H_2O between the atmosphere and subsurface, primarily because the nighttime atmosphere stabilizes when the surface cools, and effectively strands most atmospheric H_2O at altitude. Importantly, their model does not account for the radiative effects of H_2O ice, and hence tends to allow more nighttime cooling than would be expected. In this context, Timpani and Richardson (2000), have reported that there is more H_2O ice opacity in the visible wavelengths than would be expected without nighttime condensation, strengthening the case for including the radiative effects of H_2O clouds in boundary layer models. However, the results of Zent et al. (1993) were quite robust, in that no reasonable parametric variations allowed substantial H_2O exchange on a diurnal timescale.

This apparent stability of the atmospheric H_2O column was almost immediately challenged by Titov et al (1995), who based their contention on results from ISM observations of Mars during the Phobos 2 mission. It may be significant that the channel to channel calibration of the ISM data was not established to be better than 10%. Moreover, the data reduction method employed by Titov et al, like the analysis by Baker (1976) ignores variations in aerosol scattering. Titov et al found a factor of 3 variation in the diurnal H_2O abundance, but this was preferentially limited to the areas over the large martian volcanoes. They also reported that the atmosphere over brighter, and hence colder regions had more atmospheric H_2O than observed over the warmer regions.

Titov et al explained the apparent variations in the atmospheric column by invoking the presence of high adsorption capacity materials, such as smectite clays on the flanks of the martian volcanoes. It was not clear in the analysis why the clay coverage would be preferentially restricted to the high flanks of the large martian volcanoes, nor was it clear how the substantial anomalies were maintained against atmospheric transport to lower altitude regions.

The following year, Sprague et al., (1996) published their report of telescopic observations of H_2O in Mars, over the period 1991-1995. The data were acquired in the 0.87 μm line with a spectral resolution of 0.05 Å, at the échelle spectrograph. They reported, among other results that there were strong diurnal variations, showing the lowest water column abundance near the evening terminator. They interpreted this result as a real variation in the total amount of water vapor in the atmospheric column, although they did not require that the vapor exchange with a regolith source.

Finally, Titov et al. (1999) returned in situ observations, using the H_2O channel in the Pathfinder IMP data set to do a series of solar observations as a function of hour angle. In this case, they reported that there were no evident variations in H_2O column with hour angle, a finding which need not necessarily conflict to their previous reports of a diurnal column variation, because in the earlier case, the variation had been substantially restricted to the flanks of the martian volcanoes.

B. Motivation for Experiment

The summary of observational results brings us to the motivation for the present set of experiments, which was designed to test a specific hypothesis put forward by Titov et al (1995). They hypothesized that the presence of substantial reservoirs of smectite clays, such as montomorillonite, areally restricted to the flanks of the martian volcanoes. The structure of smectites is at first blush, ideally suited to the requirement for a substantial surface reservoir of H_2O. The specific surface area of smectites can be considerable, because of the presence of exchangeable cations in the interlayer sites. These cations are typically solvated in the presence of H_2O vapor. An increase in H_2O vapor pressure leads to additional complexation in the cation solvation shells, and consequently, a swelling of the clay. This swelling is then responsible for an increase in the specific surface area of the clay as measured by BET isotherms (Brunauer et al., 1938), which permits smectites to hold an order of magnitude or more H_2O than non-layer silicates. In principal, based on numerical models of exchange presented in the literature (e.g. Zent and Quinn, 1997), it would be possible for smectite clays to hold a considerable inventory of H_2O, and, release a plume of H_2O which might stand out against the background of the atmospheric column. As a simple illustration of this possibility, Figure 1 shows the integrated flux through a model regolith consisting of SWy-1, according to the adsorption isotherm published by Zent and Quinn (1997). The integrated flux from the subsurface to the atmosphere totals 3500 pr μm of water. It is also worth noting that smectites have been identified in SNC meteorites, and hence presumably exist at some level on the martian surface (Thomas-Kerpta et al., 2000). Finally, note that there is considerable exchange in the early morning hours, and that this calculation assumes, and indeed requires, that uptake be essentially instantaneous at low temperatures.

There are at least two compelling problems with the strong-exchange interpretation however, The first is that the exchange models of Zent et al (1993) and Titov et al (1995) are inherently one-dimensional. Therefore they do not predict the full dynamics of transport through the martian atmosphere. In particular, a concentrated plume of H_2O, if present above a hypothetical clay-enrichment, would not be sustainable. During the day, advection would sweep the plume downwind, and replace the atmospheric column with background gas, which would not have the H_2O enhancement. At the end of the martian afternoon, when the surface cooled, and the surface began to adsorb, the atmosphere above the clay would be depleted in H_2O, After several sols, the H_2O anomaly above the clay would be erased, because the adsorptive load of the clay would be reduced to the point where it could no longer support an anomaly. This possibility was discussed by Zent et al., (1995).

Another problem with the hypothesis as stated is that it requires very rapid equilibration between the interlayer sites and the surrounding pore gases. It is this particular question that we focus on in this experiment. Could smectite clays, held at Mars-like conditions, equilibrate rapidly on a diurnal timescale, and hence respond to the changing environmental drivers of the martian diurnal boundary layer?

3. Experiment

In order to answer this question, we have designed a very standard uptake experiment that is commonly done to assess the rate at which adsorptive equilibration is achieved in a given adsorbent-adsorbate system. The objectives of this experiment are to determine how quickly, and at what abundance, H_2O equilibrates on smectite clays under Mars-like conditions. We selected the experimental conditions and timescales in order to allow comparison of our data to the exchange processes that are required over the course of a diurnal cycle.

The sample material that we employ is SWy-1, a Na-rich montomorillonite from Cook County Wyoming. The clay is a well-characterized, often-used standard from the US Clay Repository, The specific surface area of the clay has been measured both for H_2O and N_2 adsorbates via the BET method. Because H_2O is a polar molecule, and has access to the interlayer sites, the BET surface area of SWy-1 is 663 m^2/g^{-1} for molecules for H_2O (van Olphen and Fripat, 1979).. Conversely, for N_2, a non-polar molecule which has virtually no interaction with the exchangeable interlayer cations, the specific surface area is only 37 m^{-2} g^{-1}. The exchangeable cation abundance is characterized by the cation exchange capacity, which in total is 81 meq/l for SWy-1. The breakdown by species is: 48 meq $Na,^+$; 1.1 K^+; 12 Mg^{2+}; 21 $Ca.^{2+}$ (Hall and Astill, 1989).

Sample pre-conditioning is a critical variable to describe in any experiments such as these. We performed no cation exchange on the sample, using them as received for the purposes of this experiment. This is critical to note, because as already mentioned, it is the solvation of the exchangeable interlayer cations that is responsible for the swelling, and hence the considerable adsorptive capacity of these clays; the adsorptive capacity of a smectite is a function of the exchangeable ion load.

We do not know the exchangeable ion load of martian smectite clays, nor even whether they exist in quantities adequate to dominate the adsorptive capacity of the regolith even locally. Since the adsorptive capacity of these clays can be 2 to 3 orders of magnitude greater than that of other silicates, a few percent smectite could in principal dominate the local adsorptive exchange between the atmosphere and subsurface. That abundance is still allowed by available observational constraints, (e.g. Christensen et al., 2000).

The samples are pre-conditioned before use to remove as much water as possible, without extracting the exchangeable cations, and hence wholly collapsing the interlayer sites. Clays were baked at 110 °C for 1 hour, under vacuum. Differential scanning calorimetry data (Figure 1) show that essentially all H_2O is removed by this process. The additional endothermic transitions evident in Figure 1 is due to dehydroxylation of the clay, and a fundamental change in crystal structure, which we intended to avoid. Further heating of the clays at high temperature leads to less than 10^{-5} g H_2O g^{-1} clay, which is well below our experimental range.

The clay is preconditioned on the experimental manifold, of solid glass construction, and provided with greaseless stopcocks to minimize sorption in the system. The double distilled H_2O source for our experiments is held in clean glassware attached to the system with greaseless stopcocks. The source is cooled to a pre-determined temperature in an immersion cooler, and the headspace above the resulting ice is pumped down for 15 minutes to remove additional headspace gases.

The soil is likewise cooled in a separate immersion cooler to a predetermined temperature that is always warmer than the temperature of the ice, to prevent the relative humidity over the soil sample from reaching unity. This assures that H_2O in the soil sample is not in the form of ice, but is entirely adsorbate. The temperature stability of the immersion coolers at low Mars-like temperatures is not better that about ±1 °C, meaning that the relative humidity of the sample generally cannot be higher than about 40%, without risking saturation of the soil sample.

Once the soil sample and H_2O reservoir have achieved their target temperature, recorded with Pt thermocouples threaded into the glassware, the evacuated manifold is opened, to the H_2O source. We typically allow an hour for the H_2O source to fill the manifold, and satisfy adsorptive equilibrium there. At very low H_2O abundances, and short exposure times, we are careful not to measure the kinetic variations due to the fact that the H_2O source must satisfy adsorption sites throughout the manifold before pressures in the soil sample reach the expected source pressure. Finally, we open the manifold to the soil sample, and begin equilibration.

Equilibration is allowed to proceed for a specified period of time, from 20 minutes to 72 hours. At the end of the prescribed period, the soil sample is isolated from the manifold, and disconnected. It is carried to a separate evacuated LN_2 trap, and opened to the trap. The sample is again heated to 120 °C, and the degassed H_2O trapped under LN_2 for an hour. This serves to remove the adsorbate, to the LN_2 trap. The trap is connected to the evacuated injection port of a gas chromatograph, and all surfaces heated to 140 °C in order to vaporize the H_2O. Once the temperature throughout the plumbing has stabilized at the desired temperature, the injection is made. All GC plumbing is heated to greater than 140 °C in order to prevent trapping in the column.

The GC is calibrated with the same traps and injection hardware, and temperature controlled saturated Cl^- solutions of Li^+, Ca^{2+}, Na^+ and Mg^{2+}.

In Figure 3, we show the results of the uptake experiments The pressures of the upper two curves are 62 and 122 Pa, which are orders of magnitude higher than the martian soil ever actually sees.

4. Discussion and Summary

We have chosen to fit curves to the data in Figure 3 as follows. We assume, because it is conceptually simple, and reasonably accurate, that ordinary Langmuir-style monolayer adsorption occurs. The adsorption rate is then taken to be

$$R_a = K_1(1 - Y)$$

Where K_1 is a constant describing the adsorption rate, and Y is the equilibrium coverage. The desorption rate is

$$R_d = K_2 Y$$

And the net change in adsorbate population is then given by

$$\frac{dY}{dt} = R_a - R_d = K_1(1 - Y) - K_2 Y$$

And hence

$$Y = \frac{t}{(m_1 + t)}$$

where $m_1 = 1/(K_1+K_2)$.

This equation describes the approach to equilibration, but does not describe the equilibrium amount. Accordingly, we add another variable, to describe the equilibrium amount and

$$Y = m_2\left(\frac{t}{(m_1 + t)}\right)$$

Note that $m_2 = K_1 m_1$, and is equal to the equilibrium load for the uptake curve.

Table 1 gives the fit and R values for the four uptake curves plotted in Figure 3. This fit allows us to estimate the time constant involved in adsorptive loading, which is also shown in Table 1, for the 50% loading point.

Note that for high temperatures, regardless of pressure, the adsorptive uptake is quite rapid, reaching half of it's equilibrium value in under an hour. However, at low temperatures, the kinetics of uptake are much slower. The time required to load to half of the equilibrium value is greater than two sols. Prima facia, this precludes adsorptive responses that track the insolation.

There is another interesting aspect of the low temperature uptake curve in Figure 3; the equilibrium adsorbate load is only about 1/6th of the amount predicted by the isotherms published by Zent and Quinn (1997). The explanation for this differential is based on surface area. The predictions made by Zent and Quinn (1997), as well as the calculations of the adsorption isotherm, were predicated on the assumption that the specific surface area of the adsorbate was independent of the adsorptive coverage. In fact, this turns out not to be the case.

In a series of experiments carried out on a variety of montomorillonites, it has become clear that the uptake of water occurs in discrete stages as the montmorillonite structure expands (e.g. Del Pennino et al., 1981; Medout-Marère et al., 1998). Consequently, the specific surface area of the mineral is a complicated function of the temperature, pressure, and history of the sample (Kraehenbuehl et al., 1987). Although generalizations can be dangerous, the break points in the expansion of montomorillonites tend to occur at roughly at 1%, 7% and 15%. wt % H_2O.

Cases et al., (1992) reported that for $R_H < 0.16$, water absorbs only on the external surfaces of the tactoids. Between 0.16 and 0.5 R_H, a first-layer hydrate is formed on about 40% of interlammelar space. For R_H from 0.5 to 0.93, two and 3 layer hydrates are formed after the bilayer capacities set up on the exterior surfaces. A wholly dry state is reached at $R_H \sim 0.05$. Other workers have reported similar, though not identical results, always from isothermal experiments, and usually on homoionic montmorillonites.

With reference to Figure 3, we see that for the T=211 P=0.26 data set, the sample equilibrates at about 0.018 g H_2O g^{-1} clay. If one assumes 14 $Å^2$ molecule H_2O on smectite clays, (Trillo et al., 1990), then the area covered by the adsorbed water is only about 84 m^2. This represents more area than is available on the external surface of the clay particles, and requires substantial interlayer access. Conversely, the T=273 K, P = 0.26 Pa the system equilibrates at about 0.008 g H_2O g^{-1} clay. Performing the same calculation suggests an occupied area of about 37 m^2. This is very near the available external surface area. It is likely therefore that the extraordinary difference in equilibration time is due to the need for H_2O molecules to undergo surface diffusion to the interlayer sites at the lower temperature.

We can further address the question of how effective smectite clays actually are as high-capacity H_2O reservoirs by plotting (in Figure 4) the mass of adsorbed water on SWy-1, alongside the temperature, R_H path followed by the martian surface/atmosphere interface. The adsorption contour uses results from Figure 3, as well as previous equilibrium results on the same clay (Zent and Quinn, 1997). As can clearly be seen in this plot, smectites on Mars do not reach a T/R_H domain in which interlayer sites are commonly accessible. Therefore, smectite adsorption is not a plausible mechanism by which to account for strong diurnal variations in the H_2O column abundance of the martian atmosphere.

In summary, there are both kinetic and equilibrium reasons that H_2O adsorption on smectite clays is not a suitable explanation for the observations of H_2O variation over the course of a diurnal cycle on mars. The relative humidity at Mars-like conditions is sufficiently low that interlayer adsorption sites are not accessed. Also, the timescale of adsorptive equilibrium seems to be many sols at morning temperatures, in direct contract to the assumptions made by Zent et al (1993), and incorporated in Figure 1.

References

Baker, E. S., Martian atmospheric water vapor observations: 1972-1974, *Icarus*, **28**, 247-268, (1976).

Brunauer S. P. H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, *J. Amer. Chem. Soc.* **60**, 309-319, 1938

Cases, J. M., I. Brerend, G. Besson, M. Francois, J. P. Uriot, F. Thomas, J. E. Poirier, Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite. 1. The sodium-exchanged form, *Langmuir*, **8**, 2730 – 2739, 1992

Christensen, P. R., J. L. Bandfield, M. D. Smith, V. E. Hamilton, R. N. Clark, Identification of a basaltic component on the martian surface from Thermal Emission Spectrometer data, *J. Geophys. Res.*, **105**, 9609-9621, 2000

Davies, D. W., The vertical distribution of Mars water vapor, *J. Geophys. Res.*, **84**, 2875-2879, 1979.

Del Pennino, U., E. Mazzega, S. Valeri, A. Alietti, M. F. Brigatti, L. Poppi, Interlayer water and swelling properties of monoionic montmorillonites, *J. Col. Interface Sci.*, **84**, 301-309, 1981.

Fanale, F. P., W. A. Cannon,. Exchange of adsorbed H2O and CO2 between the regolith and atmosphere of Mars caused by changes in surface insolation, *J. Geophys. Res.*, **83**, 2321-2325, 1978.

Flaser, F. M., R. M. Goody, Diurnal behavior of water on Mars, *Planet. Space* **24**, 161-181, 1976.

Haberle, R. M., H. C. Houben, R. Hertenstein, T. Herdtl, A boundary-layer model for Mars: Comparison with Viking lander and entry data, *J. Atmosph. Sci.*, **50**, 1544-1559, 1993.

Hall, P. L, D. M Astill, Adsorption of water by homoionic exchange forms of Wyoming montmorillonite (SWy-1), *Clays and Clay Min*, **37**, 355-363, 1989

Kraehenbuehl, F., H. F. Stoeckli, F. Brunner, G. Kahr, M. Mueller-Vonmoos, Study of the water-bentonite system by vapour adsorption, immersion calorimetry and x-ray techniques: I. Micropore volumes and internaal surface areas, following Dubinin's theory, *Clay Mineral.*, 22, 1-9, 1987.

Medout-Marère, V. H. Belarbi, P. Thomas, F. Morato, J. C. Giuntini,. J. M. Douillard, Thermodynamic analysis of the immersion of a swelling clay, *J. Colloid Interface Sci.* **202**, 139 – 148, 1998

Sprague, A. L., D. M. Hunten, R. E. Hill, B. Rizk, W. K. Wells, Martian water vapor, 1988-1995, *J. Geophys. Res.*, **101**, 23229-23241, 1996.

Thomas-Keprta, K. L.,S. J. Wentworth, D. S. McKayE. K. Gibson, Field emission gun scanning electron and transmission electron microscopy of phyllosilicates in martian meteorites ALH84001, Nakhla, and Shergotty; *Proc. LPSC XXI*, 2000.

Titov, D. V., J. Rosenqvist, V. I. Moroz, A. V. Grigoriev, G. Arnold, Evidences of the regolith-atmosphere water exchange on Mars from the ISM (Phobos-2) Infrared spectomometer observations, *Adv. Space Res.*, **16**, 623-633, 1995.

Titov, D. V., W. J. Markiewicz, N. Thomas, H. U. Keller, R. M. Sablotny, M. G. Tomask, M. T. Lemmon, P. H. Smith. Measurements of the atmospheric water vapor on Mars by the Imager for Mars Pathfinder, *J. Geophys. Res.*, **104**, 9019-9026, 1999.

Trillo, J. M., J. Poyato, M. Tobias, M. A. Castro, Sorption of water vapour by M-montmorillonite (M=Na,Li,La). *Clay Miner.* **25**, 485-498, 1990

van Olphen, H. and J. J. Fripat, *Data Handbook for Clay Minerals and Other Non-metallic Materials*, Pergamon Press, 346 pp. 1979

Zent, A. P., R. M. Haberle, H. C. Houben, B. M. Jakosky, A coupled subsurface-boundary layer model of water on Mars,*J Geophys. Res,*, **98**, 3319 - 3344, 1993.

Zent A. P., R. M. Haberle, J. R. Murphy, Anomalous H_2O Concentrations Over Tharsis: Analysis Of equilibrium Models, LPSC XXIX, 1555-1556, 1995.

Zent A. P., and R. C. Quinn, Measurement of H_2O adsorption under Mars-like conditions: Effects of adsorbent heterogeneity, *.J. Geophys. Res.*, **102**, 9085-9095, 1997

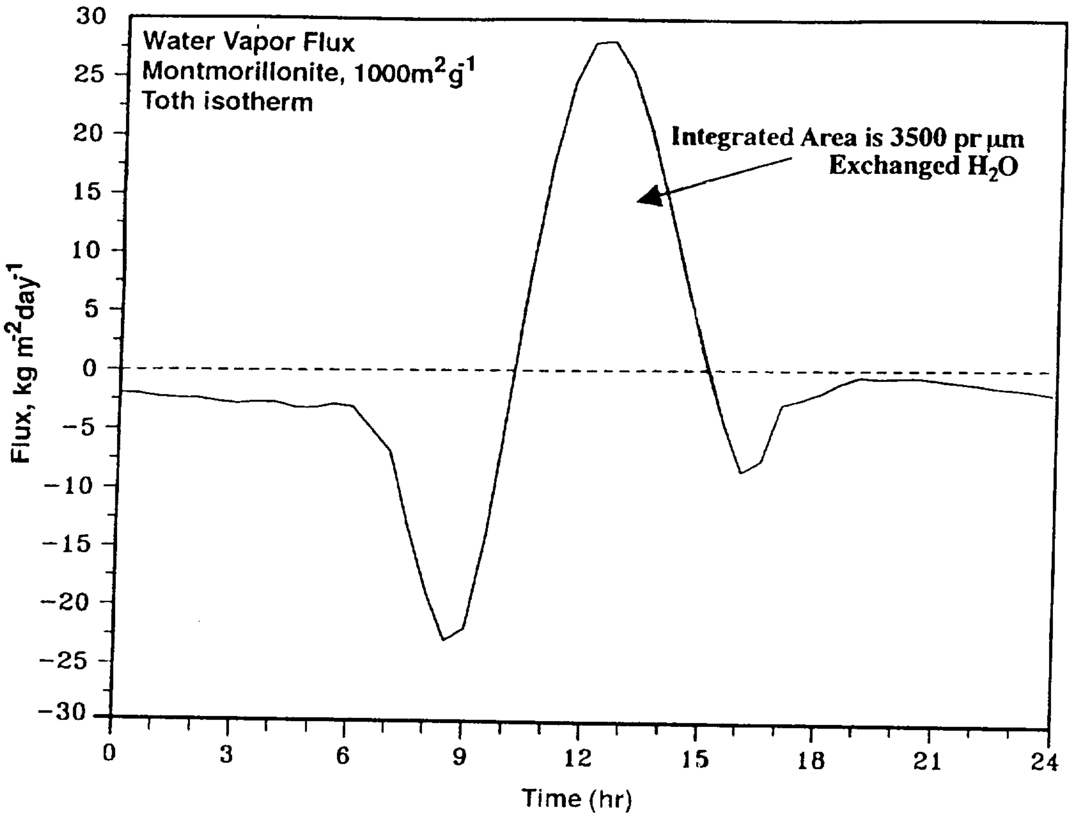

Fig. 1. The flux through the regolith as a function of hour angle, using the Haberle et al (1993) boundary layer model, and the Zent and Quinn (1997) SWy-1 adsorption isotherm. The integrated flux through this hypothetical surface is 3500 pr µm day^{-1}

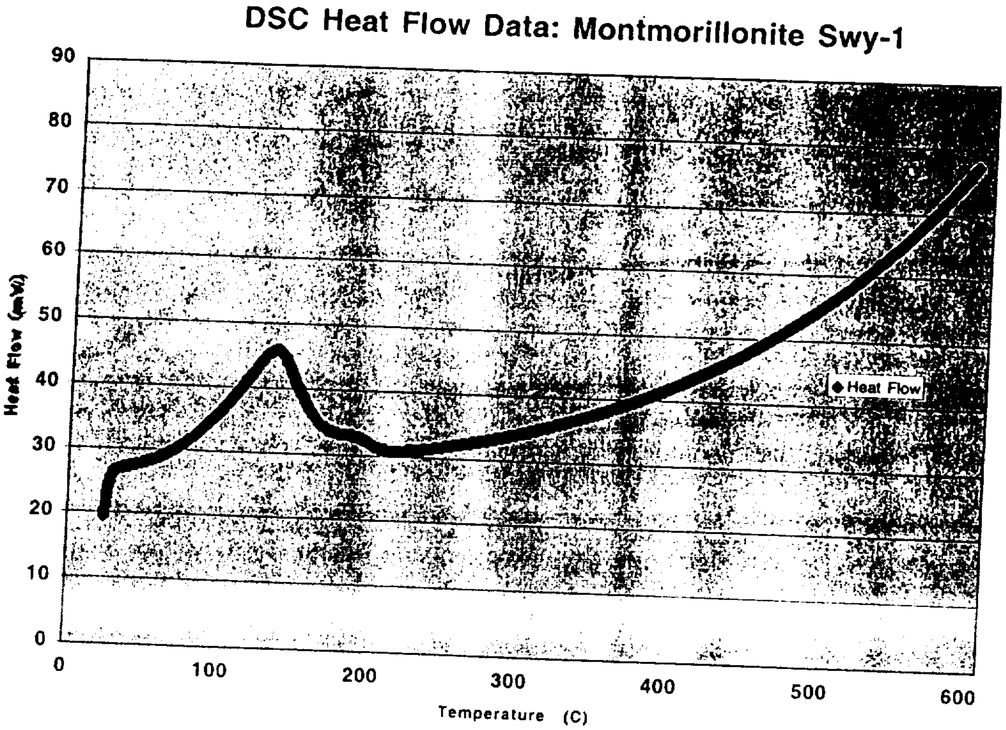

Fig. 2. - Differential Scanning Calorimeter data of SWy-1. The peak just above 100 C corresponds to a majority of the dehydration; no further discrete transitions corresponding to collapse of interlayers structures are observed.

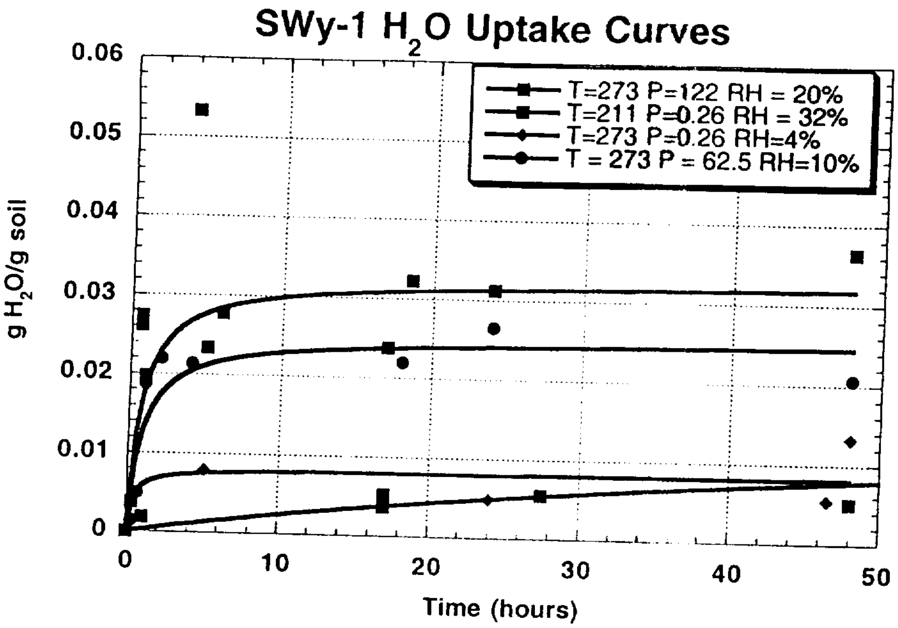

Figure 3. The uptake curve of H_2O on SWy-1. The adsorbate is substantially loaded in only a few hours at T = 273, but more slowly at low temperatures.

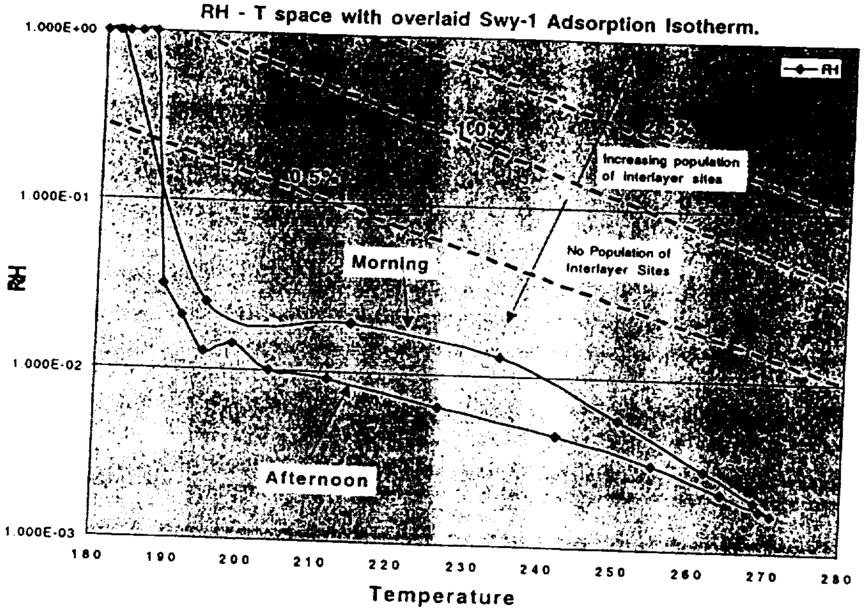

Figure 4. The solid line is the path through T-R_H space followed by the martian surface at the VL1 site on a summer day (Zent et al., 1993). The dashed line is the H_2O adsorbate population of SWy-1 in this T-R_H domain, using the adsorption data measured here. The likely adsorbate population is confined to the external surfaces of the clay.

Table 1. SWy-1 Uptake curves, fit parameters, and equilibration timescales.

T (K)	P (Pa)	R_H	m_1	m_2	R	t_{50} (hours)
273	122	0.2	0.81304	0.032256	.0689	0.8
273	62.5	0.1	0.88625	0.024909	.0911	0.9
273	0.26	0.04	0.37816	0.008094	.0731	0.4
211	0.26	0.32	65.827	0.01833	.0901	65.0