H₂O Adsorption on Smectites: Application to the Diurnal Variation of H₂O 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

Submitted to: J. Geophys. Res.
September 13, 2000

23 pages
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 H₂O adsorption kinetics on SWy-1, a Na-rich montmorillonite from Wyoming. The highest-temperature (273 K) data equilibrates rapidly. Data gathered at realistic H₂O 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$_2$O 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$_2$O 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$_2$O 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 H₂O per unit mass than other silicate compounds.

One important assumption must be made however, in order to force PBL models to predict observable diurnal H₂O 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 H₂O 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$_2$O is adsorbed by these clays as a function of the temperature and partial 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$_2$O 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$_2$O 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$_2$O 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$_2$O 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 Ls 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$_2$O 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$_2$O vapor, but not to H$_2$O 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$_2$O 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 H₂O 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 H₂O abundance throughout the observational period. Davies then compared the derived H₂O variation against changes in airmass and phase angle with a variety of numerical models of predicted H₂O 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 H₂O was uniformly mixed in atmosphere with the same scale height as the aerosol dust. This conclusion removed the necessity of substantial daily H₂O exchange between the atmosphere and surface in order to explain the observations. Reported variations in the diurnal H₂O 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 Flasar and Goody model, which had required that H₂O 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 H2O 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 H2O abundances based on the Viking observations. They assume that H2O was a passive atmospheric tracer, and employed soil adsorption isotherms using the data reported by Fanale et al (1978) for H2O adsorption of basalt.

They found that there was a very limited exchange of H2O between the atmosphere and subsurface, primarily because the nighttime atmosphere stabilizes when the surface cools, and effectively strands most atmospheric H2O at altitude. Importantly, their model does not account for the radiative effects of H2O 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 H2O ice opacity in the visible wavelengths than would be expected without nighttime condensation, strengthening the case for including the
radiative effects of H$_2$O 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$_2$O exchange on a diurnal timescale.

This apparent stability of the atmospheric H$_2$O 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$_2$O 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$_2$O 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$_2$O in Mars, over the period 1991-1995. The data were acquired in the 0.87 $\mu$m 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$_2$O 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$_2$O 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$_2$O. 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$_2$O vapor. An increase in H$_2$O 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$_2$O 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$_2$O, and,
release a plume of H$_2$O 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$_2$O, 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$_2$O 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$_2$O. After several sols, the H$_2$O 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$_2$O 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$_2$O and N$_2$ adsorbates via the BET method. Because H$_2$O 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$_2$O (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 H₂O 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 H₂O 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 H₂O 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 H₂O 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 than 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 H₂O reservoir have achieved their target temperature, recorded with Pt thermocouples threaded into the glassware, the evacuated manifold is opened, to the H₂O source. We typically allow an hour for the H₂O source to fill the manifold, and satisfy adsorptive equilibrium there. At very low H₂O abundances, and short exposure times, we are careful not to measure the kinetic variations due to the fact that the H₂O 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 LN₂ trap, and opened to the trap. The sample is again heated to 120 °C, and the degassed H₂O trapped under LN₂ for an hour. This serves to remove the adsorbate, to the LN₂ 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$_2$O. 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

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

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

$$R_d = K_2Y$$

And the net change in adsorbate population is then given by

$$\frac{dY}{dt} = R_n - R_d = K_1(1 - Y) - K_2Y$$
And hence

\[ Y = \frac{t}{(m_1 + t)} \]

where \( m_1 = \frac{1}{K_1 + K_2} \).

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 its 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 % H₂O.

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 interlamellar 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 ~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 K, P=0.26 data set, the sample equilibrates at about 0.018 g H₂O g⁻¹ clay. If one assumes 14 Å² molecule H₂O on smectite clays, (Trillo et al., 1990), then the area covered by the adsorbed water is only about 84 m². 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 H₂O g⁻¹ clay. Performing the same calculation suggests an occupied area of about 37 m². 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$_2$O 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$_2$O 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$_2$O column abundance of the martian atmosphere.

In summary, there are both kinetic and equilibrium reasons that H$_2$O adsorption on smectite clays is not a suitable explanation for the observations of H$_2$O 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

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$^{-1}$. 

Water Vapor Flux
Montmorillonite, 1000 m$^2$ g$^{-1}$
Toth isotherm

Integrating Area is 3500 pr μm
Exchanged H$_2$O
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$_2$O 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-RH space followed by the martian surface at the VL1 site on a summer day (Zent et al., 1993). The dashed line is the H$_2$O adsorbate population of SWy-1 in this T-RH 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.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>P (Pa)</th>
<th>$R_H$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>R</th>
<th>$t_{50}$ (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>122</td>
<td>0.2</td>
<td>0.81304</td>
<td>0.032256</td>
<td>0.0689</td>
<td>0.8</td>
</tr>
<tr>
<td>273</td>
<td>62.5</td>
<td>0.1</td>
<td>0.88625</td>
<td>0.024909</td>
<td>0.0911</td>
<td>0.9</td>
</tr>
<tr>
<td>273</td>
<td>0.26</td>
<td>0.04</td>
<td>0.37816</td>
<td>0.008094</td>
<td>0.0731</td>
<td>0.4</td>
</tr>
<tr>
<td>211</td>
<td>0.26</td>
<td>0.32</td>
<td>65.827</td>
<td>0.01833</td>
<td>0.0901</td>
<td>65.0</td>
</tr>
</tbody>
</table>