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Introduction: Diurnal variations in atmospheric water content on Mars have been debated for ~30 years [1-5]. It has been suggested that the adsorption of water in the regolith may explain the observed behavior [4,6,7]. Clay and basalt have been shown to be abundant over much of the martian surface [8,9]. In previous work we determined diffusion and adsorption coefficients for water vapor diffusing through clay and basalt layers [10,11]. We observed that while both materials could adsorb water in amounts sufficient to explain the diurnal cycle, the rate of adsorption for basalt was rapid enough but the clay this was not necessarily so. Our previously determined kinetic coefficients of adsorption for the clay are over a small range of thermodynamic conditions, and the coefficients are temperature and pressure dependent [8]. The previous basalt results reached steady state rapidly, and therefore the kinetic coefficients could not be determined with that experimental setup. Therefore, because of the critical role played by adsorption for the diurnal cycle, we are performing high precision measurements of the kinetics coefficients of adsorption for both clay and basalt under simulated Mars conditions at various temperatures and pressures.

Experimental: Montmorillonite from Panther Creek, CO and basalt from Somerset Co., NJ were ground and sieved to < 63μm, baked for one day at 102 to 104ºC and 35 mbar, sealed in a desiccator, and cooled to -20ºC. A beaker of water was placed in the planetary environmental chamber [10-14] to simulate humidity. The chamber was then evacuated to less than 1.9 mbar, filled with dry $CO_{2(g)}$ to atmospheric pressure, and cooled to predetermined temperatures between -10 and 3ºC. Once stable conditions has been obtained, the chamber was opened and a ~10 g sample in a 13.5 cm Petri dish on a top loading analytical balance was placed inside the chamber, which was then evacuated to 7 mbar. $CO_{2(g)}$ was continually bleed into the chamber to keep the relative humidity at the required value between 5 and 80%, and the chamber was continuously pumped to maintain the pressure between 6.5 and 7.5 torr. Experiments were run for 4 to 8 hours to allow the sample to reach steady state during which mass, pressure, temperature and humidity were recorded every minute.

Results: Figure 1 shows a representative example of our data where the average humidity and temperature were 20.3 ± 0.6% and -5 ± 1ºC, respectively. The
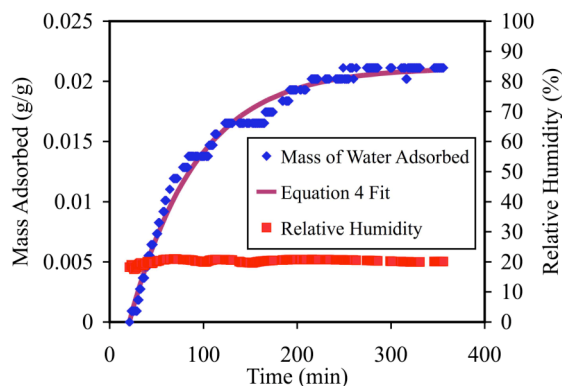

Figure 1 – *Representative data for an experiment to determine water adsorption by montmorillonite under simulated Mars conditions at -5ºC and 20% humidity. Equilibrium is reached in ~5 hours.*

mass of water adsorbed ranged from 1.7×10^{-2} to 6.0×10^{-2} g/g of montmorillonite, depending on the humidity and temperature. To date, we have only performed preliminary measurements for basalt, but we find values in the order of ~2.0×10^{-2} g/g, similar to the values for montmorillonite, confirming our previous observation [10]. However, the basalt reached steady state much more rapidly than montmorillonite, ~4 hours compared with ~5 hours.

Discussion: Adsorption of gases onto surfaces is usually described by the Langmuir isotherm:

$$\frac{1}{\theta} = 1 + \frac{1}{\alpha P} \qquad (1)$$

where P is the partial pressure of water. α is the Langmuir adsorption constant, and θ is the percentage of the area covered by water molecules:

$$\theta = \frac{m_a}{\rho_{H_2O} A_s l} \qquad (2)$$

where m_a is the mass of the adsorbed water (g/g), A_s is the effective grain size area, l is the monolayer thickness, and ρ_{H2O} is the density of water. This is only true for low pressures, because at higher pressures multiple molecular layers of water are adsorbed.

Our data range in pressure, so we used the BET isotherm which is the Langmuir expression adjusted for multiple water molecule layers [15]:

$$\frac{p'}{v(1 - p')} = \frac{1}{v_m c} + \frac{p'(c - 1)}{v_m c} \qquad (3)$$

where p' is the measured pressure divided by the saturation pressure of the adsorbate, v is the volume of the adsorbed gas, v_m is the monolayer adsorbed gas volume, and c is the BET constant. The volume of the
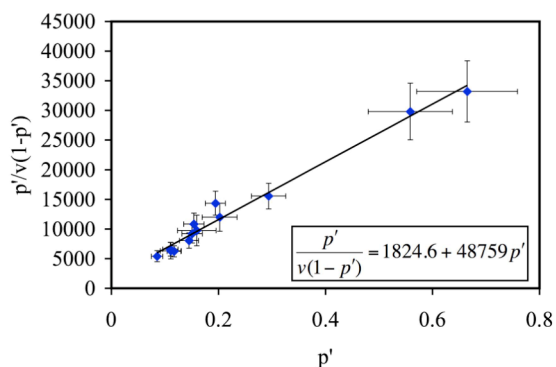
Figure 2 – *The adsorption data for montmorillonite plotted using the BET isotherm, an extension of the Langmuir isotherm, with multiple adsorbed molecular layers. From this we were able to determine the surface area based on the data at all pressures.*

adsorbed gas was determined from the values of m_a. Thus a plot of *p'* vs. *p'/(v(1-p'))* is a straight line with a slope of *(c-1)/(v$_m$c)* and the intercept of *1/(v$_m$c),* from which *v$_m$* and *c* were determined (Fig. 2).

For montmorillonite, values for *c* and *v$_m$* were 2.77 ± 0.95 and 1.98 ± 0.68 x 10^{-5} m^3g^{-1}, respectively. By dividing *v$_m$* by *l*, the value for A_s was determined to be 6.6 ± 0.98 x 10^4 m^2kg^{-1}. This is very close to the value we determined in the previous study [11]. We have yet to obtain a value for A_s for the basalt, so we used the value 2.6 ± 0.1 x 10^4 m^2kg^{-1} [12] for all further analysis.

Knowing the effective surface area of the samples it is possible to determine the amount of surface covered as a function of time and by obtaining a fit to the data in Fig. 1 and determine k_a and k_d, the kinetic constants of adsorption and desorption, from the expression [8]:

$$\theta = \frac{k_a}{k_a + k_d}\left[1 - e^{-(k_a + k_d)t}\right] \qquad (4)$$

substituting the value of θ applicable to multiple molecular layers (Table 1). From our preliminary basalt measurement, k_a and k_d were determined to be 2.67 ± 0.03 x 10^{-4} Pa s^{-1} and 5.21 ± 0.13 x 10^{-5} s^{-1}, respectively for 3 adsorbed molecular layers at -1 ± 1°C and 20.4 ± 0.6% relative humidity. Using Eq. 4 we calculated a

Table 1 - *Montmorillonite adsorption and desorption kinetic constants*

T (K)	R$_h$ (%)	N*	k_a (10^{-4} Pa s^{-1})	k_d (10^{-5} s^{-1})	1/e** (hours)
273	15.2	2	2.47±0.02	4.03±0.28	0.44
268	20.3	2	1.35±0.01	9.71±0.21	0.55
264	16	3	1.94±0.02	1.66±0.40	0.61
262	31.6	4	1.63±0.03	5.98±0.07	0.57

*N is number of layers
** 1/e loading time to reach equilibrium abundance

characteristic 1/*e* value of the loading time for each experiment to reach an equilibrium abundance $(k_a/(k_a+k_d))$. The 1/e loading time for montmorillonite are in Table 1 and for the preliminary basalt experiment it is 0.40 hours.

Both kinetic constants k_a and k_d are related to the adsorption constant α ($\alpha = k_a$ / (p*k_d)), which represents thermodynamics of the adsorption process (i.e. its efficiency). It has been suggested that large values of k_a and small values of k_d would allow for both high values for α and rapid times to reach steady state [11]. However, these results indicate that with a higher humidity more molecular layers of water are adsorbed, but the time to reach steady state is similar, with an increased value of k_d.

Conclusions: Our preliminary results for the montmorillonite indicate that at this range of temperature (262 to 273 K) the kinetics of adsorption may be rapid enough to account for diurnal variations in atmospheric water content, but mean surface temperature on Mars is ~230 K. If the relationship between temperature and the 1/*e* folding time is as linear as our initial results appear, at 230 K the montmorillonite 1/*e* lolding time will only be 3 times greater then at 273 K and may still be able to describe the diurnal variations. Our preliminary basalt result indicates that it has similar kinetics, but adsorbs more molecular layers of water. Therefore, basalt may be a better sink for the diurnal variations in atmospheric water.

References: [1] Farmer (1976) *Icarus* 28, 279. [3] Davies (1979) *JGR* 84, 2875. [4] Rosenqvist et al. (1992) *Icarus* 98, 2, 247. [5] Titov et al. (1995) *Adv. Space. Res.* 16, 6, 23. [6] Sprague (2006) *Icarus* 184, 372. [7] Zent et al. (1993) *JGR* 98, 3319. [8] Zent et al. (2001) *JGR* 106, 7, 14677. [9] Fergason et al. (2006) *JGR* 11, E02521. [10] Bryson et al. (2007) *Icarus*, submitted. [11] Chevrier et al. (2007) *Icarus*, submitted. [12] Sears & Moore. (2005) *GRL* 32 (16) L16202. [13] Moore & Sears (2006) *Astrobiology,* 6, 644. [14] Sears & Chittenden (2005) *GRL,* 32, L23203. [15] Brunauer et al. (1938) *J. Chem. Soc.,* 60, 309-319.