

NEW ESTIMATES OF THE ADSORPTION OF H₂O ON MARTIAN SURFACE MATERIALS Aaron P. Zent., SETI Institute and NASA Ames Research Center, Moffett Field, CA, 94035

Adsorption of H₂O onto the martian regolith creates a potential reservoir of exchangeable volatiles. Water adsorbed onto the regolith exchanges within the atmosphere-cap-regolith system. Adsorption slows the diffusion of H₂O through the regolith. In effect the diffusion coefficient must be scaled by the slope of the adsorption isotherm in order to account for the fact that a given molecule spends considerably more time adsorbed onto the walls of the pores than in actual diffusion. Finally, H₂O adsorption retards formation of ice by segregating H₂O molecules into another phase. In climate models run without adsorption, H₂O sublimated from the north polar cap quickly condenses across much of the martian surface, forming extensive surface ice deposits.

The model of H₂O adsorption on basalt that has been used in the literature for years is based on a set of measurements made by Fanale and Cannon (1971; 1974). Measurement conditions were T = 250-300 K and P = 2 - 2000 Pa; they found on the order of 10⁻³ kg of H₂O kg⁻¹ were adsorbed. The data had to be numerically modeled to apply to Mars, since the conditions under which the measurements were made were different from Mars (T = 180-280 K, P = 10⁻³ to 0.1 Pa)

Several empirical representations of this data were later developed, and used extensively to estimate the total abundance of H₂O adsorbed in the regolith, the diffusion scale of H₂O over a variety of depths, the behavior of H₂O in the diurnal boundary layer, and the extent and distribution of ground ice.

Zent and Quinn (1995) reported on the measurement of simultaneous H₂O and CO₂ adsorption, as well as H₂O alone, onto Mauna Kea palagonite. Subsequently, we compared the measured H₂O adsorbate density on the palagonite to the predicted adsorbate density on basalt, using an interpolation of the measured adsorption data on palagonite.

$$\rho_a = A_s \delta P^\gamma T^\beta \quad (1)$$

The variables δ , γ , and β are fit via a least-squares technique to the data. We calculated that the density of H₂O adsorbate at partial pressures of 4x10⁻² Pa, and T = 200 K was 4.88x10⁻⁹ kg m⁻². When the Fanale and Cannon (1974) basalt isotherm was calculated for the same conditions, the predicted density of adsorbate is 1.87x10⁻⁷ kg m⁻². The difference is a factor of 38, which was considered to be unacceptable. Interestingly, when the same calculation was done for partial pressures of 50 Pa, and T = 260 K, the densities differed by only a factor of four, which is well within the range anticipated for mineralogical differences. At the high P and T conditions, both basalt and palagonite isotherms are being used to interpolate between data points. At Mars-like conditions, the basalt isotherm is being used to extrapolate (by 1 to 2 orders of magnitude in pressure), while the palagonite isotherm is still in an interpolation domain.

Our hypothesis was that extrapolation of an unrealistic adsorption isotherm accounts for much of the apparent discrepancy between the number densities measured for

New H₂O Adsorption Data: Zent, A. P.

the palagonite and those predicted for basalt. As a check on this, and to examine the possible importance of mineralogical variations, we collected a sample of Page Mill basalt, a Miocene basalt from the Franciscan complex of the San Francisco Peninsula, and similar to the Vacaville basalt on which Fanale and Cannon acquired their adsorption data. We ground the sample, sieved it to less than 34 μm , and measured H₂O adsorption at $P = 0.34$ Pa, and $T = 209$ K. The results indicate that 2.9×10^{-4} kg/kg adsorbed onto the basalt; we measured its specific surface area as 1.801×10^4 m² kg⁻¹, and the resulting adsorbate density was 1.6×10^{-8} kg m⁻². At very similar conditions, ($P = 0.47$ Pa, $T = 210$) the average of seven separate measurements of H₂O adsorption on palagonite is 1.052×10^{-8} kg m⁻², a difference of approximately 50% (c.f. the factor of 38 difference with which we started).

Geologic materials are composed of a variety of minerals, and poorly-crystalline solids. The surface of a solid of complex chemical composition contains many exposed atoms and functional groups, which interact in various ways with adsorbent molecules. Surface imperfections of molecular dimensions such as dislocations, vacancies, flaws, cracks, and chemical contaminants also may be a major source of heterogeneity (e.g. Jaronic and Madey, 1988). All realistic models of the adsorptive behavior of the martian regolith must take this heterogeneity into account.

The empirical adsorption isotherm heretofore used to estimate H₂O adsorption on basalt at Mars-like conditions implicitly assumes adsorbents are homogeneous. This can be demonstrated by using Equation (1) to generate an adsorption isotherm, and then using the Clausius-Clapeyron equation to calculate the partial molar enthalpy of adsorption for a variety of coverages. The adsorption energies is found to be independent of coverage. Alternative forms of this equation also implicitly assume homogeneous adsorbents.

We have used a revised version of the basalt isotherm, which incorporates our low P and T basalt adsorption data, to assess the effective diffusion coefficient of H₂O through the martian regolith.

Hour	New Isotherm		Old Isotherm	
	D_f (m ² s ⁻¹)	δ (m)	D_f (m ² s ⁻¹)	δ (m)
1200 h	1.4×10^{-9}	1.5×10^{-2}	3.8×10^{-9}	2.6×10^{-2}
2400 h	6×10^{-11}	3.3×10^{-3}	9×10^{-13}	4×10^{-4}

Where we have calculated the adsorption at appropriate temperatures, and where the effective length scale for diffusion is $\delta = (2tD_f)^{1/2}$ and $t = 8.874 \times 10^4$ s, Mars' rotation period. When the Ames Boundary Layer model is amended to take into account the reduced adsorption at low temperatures, ice is predicted to stabilize in the uppermost few mm of the regolith at night, a consequence of the fact that the greatest difference between the old and current basalt isotherms are at low temperature.