**The Role of Regolith in the D/H Variation on Mars from the Poles to the Equator.** R. Hu<sup>1,2</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, renyu.hu@jpl.nasa.gov, <sup>2</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125.

Summary: The regolith on Mars exchanges water with the atmosphere on a diurnal basis and this process causes significant variation in the abundance of water vapor at the surface. While previous studies of regolith-atmosphere exchange focus on the abundance [1,2,3], recent in-situ experiments and remote sensing observations measure the isotopic composition of the atmospheric water [4,5,6]. We are therefore motivated to investigate isotopic water exchange between the atmosphere and the regolith and determine its effect on the deuterium to hydrogen ratio (D/H) of the atmosphere. We model transport of water in the regolith and regolith-atmosphere exchange by solving a transport equation including regolith adsorption, condensation, and diffusion. The model calculates equilibrium fractionation between HDO and H2O in each of these processes. The fractionation in adsorption is caused by the difference in the latent heat of adsorption, and that of condensation is caused by the difference in the vapor pressure. Together with a simple, bulk-aerodynamic boundary layer model, we simulate the diurnal variation of the D/H near the planetary surface. We find that the D/H can vary by 300 - 1400‰ diurnally in the equatorial and polar locations, and the magnitude is greater at a colder location or season. The variability is mainly driven by adsorption and desorption of regolith particles, and its diurnal trend features a drop in the early morning, a rise to the peak value during the daytime, and a second drop in the late afternoon and evening, tracing the water vapor flow into and out of the regolith. The predicted D/H variation can be tested with in-situ measurements. As such, our calculations suggest that stable isotope analysis is a powerful tool in pinpointing regolith-atmosphere exchange of water on Mars.

**Model:** We construct a one-dimensional model to simulate transport of isotopic water in the Martian regolith and boundary layer. It has a thermal diffusion module, a water transport module, and a boundary layer module. The model includes the isotope fractionation effects of adsorption, condensation, and molecular diffusion. The water transport module includes water vapor, adsorbed water, and condensed water in the regolith. Adsorption and condensation are assumed to be in equilibrium [2]. The diffusion equation for water includes the effects of soil porosity, tortuosity, and both molecular and Knudsen diffusion regimes [7]. For the eddy diffusion coefficient and the rate of mass transfer between the atmosphere and the soil, we use the bulk aerodynamic method [8], with the surface temperature, the near-surface atmospheric temperature, and the wind speed as input parameters. These parameters are either measured in situ, or calculated by global circulation models. We use typical values for the thermal inertia, the particle size, the specific surface area, the adsorption isotherm, and the surface roughness length in the model, and explore sensitivity of the results to these parameters.

Regolith adsorption fractionates water because the latent heat of adsorption of HDO is higher than that of H<sub>2</sub>O. Ref. [9] conducted experiments of water transport in JSC Mars-1, a commonly used Martian regolith analog, and measured the effective diffusivities of H<sub>2</sub>O and HDO under temperatures, pressures, and the background atmosphere corresponding to Mars. Because the ratio between the effective diffusivity is the inversed ratio between the adsorption coefficient, we fit the effective diffusivity data of Ref. [9] to an Arrhenius form for use in the model. We also include the fractionation factor between vapor and ice caused by the vapor pressure isotope effect [10].

*Model Testing.* We test the water transport model and compare model results with the relative humidity measurements made in situ by Curiosity's REMS instrument [11]. In particular, we obtain the REMS recalibrated data of relative humidity, air temperature, surface temperature, and wind speed from the Planetary Data System (PDS) for two 10-day periods. We pick an initial amount of water so that the resulting water column in the atmosphere matches the value measured by Curiosity's ChemCam instrument in each season [12].

We confirm that the model results are consistent with the measured relative humidity and absolute humidity. Most of the variation in the relative humidity is caused by the variation of the temperature; however, the measured absolute humidity features a rise by a factor of 2 - 3 after sunrise. This feature is well captured by the model. We consider this exercise a bona fide test because for a fixed water column, should there be major errors in the model, the nighttime humidity would depart substantially from the data. The modeled variation of the surface water abundance is also consistent with the existing 1D and mesoscale 3D models [13,14], and follows the typical patterns of diurnal water exchange on Mars [2].

Result: The modeled D/H diurnal variation in a polar location (i.e., the Phoenix landing site) is shown in Fig. 1. We use the Mars General Circulation Model (MGCM) outputs [15] for the surface temperatures and the wind speed, and choose the starting atmospheric D/H so that the resulting  $\delta D$  matched with telescopic measurements [5]. The D/H variation is mainly driven by the regolith-atmosphere exchange coupled with the fractionation in regolith adsorption. Surface condensation causes an additional variation. Since the fractionation factor is larger at a lower temperature, the magnitude of the variation is larger for a colder season. The D/H variation is ~1400‰ at the surface during the season of aphelion. The magnitude of the D/H variation is sensitive to the fractionation factor of adsorption. The uncertainty in the fractionation factor causes to the D/H variation's magnitude to change by  $\sim 50\%$ .

To study more generally the diurnal variation of D/H at various latitudes and seasons, we model equatorial and mid-latitude locations, and the results are shown in Fig. 2. The diurnal variation follows a similar trend as the driving forces for the variation are regolith adsorption and desorption, and their coupling with the boundary layer. The adsorbed water is enriched in HDO compared to the water vapor. As a result, when there is a flux from the regolith to the atmosphere, we see an increase of the near-surface D/H (i.e., the midday rise), and when there is a flux from the atmosphere to the regolith, we see a decrease of the near-surface D/H (i.e., the morning and evening drop). In the evening when regolith-atmosphere exchange is weak, the near-surface D/H gradually returns to the diurnal average due to mixing in the atmosphere.

In all, the results indicate that the D/H variation traces the exchange flux. Measuring the diurnal variation of D/H in water on Mars's surface with sufficient precision will thus provide a new indicator for the regolith-atmosphere exchange of water.

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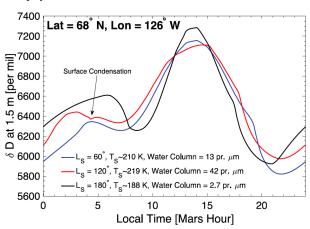


Fig. 1. Modeled diurnal variations of D/H in the province of the Phoenix landing site. The variation at the surface is up to  $\sim$ 1400‰ at the season of aphelion. The L<sub>S</sub>=120° model has surface condensation that causes a small dip in the D/H curve.

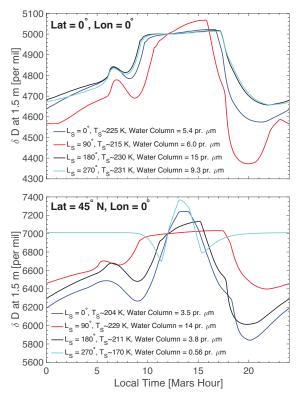


Fig. 2. Modeled diurnal D/H variations at the equatorial and mid-latitude locations of Mars. Labels show the mean surface temperature and the atmospheric water column, which we make to match with orbital remote sensing [16] by adjusting the initial water loading. The magnitude of the D/H variation is greater for a lower surface temperature, except when condensation occurs.