

Adsorption as a Water Delivery Source in the Inner Solar System: A Kinetic Monte Carlo Study. Krishna Muralidharan¹, Pierre A. Deymier¹, Marilena Stimpfl² and Michael J. Drake²; drake@lpl.arizona.edu, ¹Material Science and Engineering, University of Arizona, Tucson, AZ, 85721, USA, ² Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, 85721, USA.

Abstract: *Many Earth oceans of water can be adsorbed on to grains in the accretion disk in the region of the terrestrial planets.*

Introduction: Suggested sources of water in the inner solar system include comets, hydrous asteroids, phyllosilicates migrating from the asteroid belt, and hydrous minerals forming in the inner solar system and accreting directly to the terrestrial planets. However there are problems with these sources [1]. Here we explore the possibility of direct adsorption of water on to forsterite grains- the major silicate phase in protoplanetary disks, as being a possible source of water. Adsorption has only recently been considered a potential mechanism to bring water to the inner solar system [1]. This neglect is probably due to the misconception that adsorption energies are not high enough to capture and maintain gaseous water on mineral surfaces at high T. However, de Leeuw [2] and subsequently Stimpfl et al. [3] carried out theoretical calculations using energy minimization techniques and showed that water molecules could strongly chemisorb (via chemical bonds) on to forsterite surfaces. The energy minimization calculations of Stimpfl et al. were carried out at 0° K. Using these calculations in conjunction with kinetic Monte Carlo (KMC) simulations, both of which are described below, we estimate the amount of water that could have been delivered via adsorption.

Models and Methods:

Adsorption energy calculations: Using interatomic potential parameters derived for bulk Mg₂SiO₄, in combination with the potential model of de Leeuw and Parker for water (see Ref. [3] more details), the chemisorption energy (E_{ads}) landscapes of the {010} and {100} surfaces of forsterite were quantified. Specifically, each surface was divided into a grid, with the grid spacing equaling 0.25 Å in each direction. Next, the water molecule was positioned at each grid point, and the total potential energy of the system (E_{s+w}) was systematically obtained (using the BFGS energy-minimizer), as a function of water molecule location. The in-plane coordinates of the water molecule were held fixed, while the orientation as well as the height of the water molecule was allowed to vary. From the knowledge of E_{s+w} the surface adsorption energy map (E_{ads}) was given by Eq. 1, where E_s is the energy of the slab, and E_{H_2O} represents the self-energy of the water molecule. Note that the calculated adsorption energies do not include the energetics of the dissociation of the water molecule.

$$E_{ads} = [E_{s+w} - (E_s + E_{H_2O})] \quad (1)$$

Kinetic Monte Carlo Calculations: The KMC method uses the probabilistic Monte Carlo procedure to numerically model any dynamically evolving chemical system, by cataloging the reaction rates of all possible chemical events that could occur in the system under study. At every KMC step, the ‘reaction-times (δt)’ of all possible events are calculated from Eq.2, where is R_n the reaction-rate of the n^{th} event and r_n is a positive random number less than unity. Next, the event corresponding to the smallest reaction time is chosen to occur, and the system is propagated for a time equaling the size of the smallest time step. The above steps are repeated and the system is propagated in time until it attains equilibrium.

$$\delta t_n = -\log(1 - r_n) / R_n \quad (2)$$

Simulation Procedure: In order to model the adsorption of water molecules on to forsterite surfaces, (i) adsorption, (ii) desorption of water molecules (on to or from the mineral surface), and (iii) diffusion of water molecules in space were cataloged at every time KMC time step. The adsorption (R_{ads}) and desorption (R_{des}) rates were expressed via a Boltzmann distribution (Eq. 3), where the pre-exponents v_a and v_d are a measure of the probability of adsorption and desorption respectively. v_d is a measure of the probability of the molecule to ‘escape’ from the adsorption site and is related to product of the frequency of vibration of the water molecule on forsterite surfaces (η_v) and the fraction of occupied sites θ_a , while v_a is a function of the fraction of unoccupied surface adsorption sites, the partial pressure of water and the flux of water molecules on to the substrate. E_{des} and E_{ads} are the energies of desorption and adsorption, respectively, and E_{des} is chosen to equal the negative of E_{ads} .

$$R_{ads} = v_a \exp(-E_{ads}/RT) \quad (3)$$

$$R_{des} = v_d \exp(-E_{des}/RT)$$

The temperature and pressure of the simulated system were chosen to represent the conditions corresponding to the accretion disk, when dust and gas were still present. In particular, the thermodynamic conditions during the initial stages were characterized by partial pressures (p_{H_2O}) of around 10^{-8} bars [4] and high temperatures (700-1400 K). Given the vacuum-like conditions, ideal-gas conditions were considered and a random-walk procedure was adopted to represent diffu-

sion of water molecules in space, with a characteristic mean-free path (~ 34 mm) and diffusion-time ($= 1.08 \times 10^{-3}$ s). At the start of each simulation, the surface-slabs were initially water-free and the positions of the water molecules in space were assigned randomly. Periodic boundary conditions were imposed in the plane of the surface, to ensure number conservation. Further, if any molecule was adsorbed on to the substrate, a new molecule was introduced at Z_{max} , corresponding to the spatial extent of the simulated system in the direction perpendicular to the surface. If a molecule was desorbed, the molecule further away from the substrate was ejected from the simulation system. Any water molecule could adsorb if the given site and neighboring sites that were within a cutoff radius equaling the typical hydrogen bond length (~ 1.8 Å) were unoccupied.

Results and Discussions: Simulations were carried out for the two surfaces for a temperature range of 700–1200 K in steps of 100 K. The surface areas of the {100} and {010} slabs equaled 245.36 and 114.52 Å² with the number of corresponding surface adsorption sites equaling 3924 and 1836 respectively. In all simulations the number of water molecules (N) equaled 10, and the simulations were carried out until equilibrium was attained. Fig. 1 illustrates the variation in equilibrium surface-coverage of {100} as a function of temperature. An exponential-like temperature dependence dictates the amount of surface-coverage. The significant amount of coverage even at high temperatures, suggests that there is retention of water even at these temperatures, implying that adsorption of gaseous water on to dust grains could start from the early stages of accretion. The much smaller molecular coverage at the higher temperatures can be attributed to the larger kinetic energies of the adsorbed water molecules at higher temperatures, which increases the ability of molecules to desorb from the surface. Coverage for {010} was much smaller than {100} at all temperatures; even at 700 K, the surface coverage was only ~ 1 H₂O/nm². The enormous difference in surface coverage is a direct consequence of the fact that the {100} surface is much more energetically favorable for water adsorption [3].

Next, the amount of adsorbed on to Earth was estimated using the surface coverage data in conjunction with the knowledge of Earth's mass ($\sim 6 \times 10^{24}$ Kg), and the mass of oceans (~ 0.05 % of Earth's mass). Keeping in mind that the dust particles are essentially crystalline, with no preferred facets, the data in Fig. 1 was expressed in terms of Earth oceans by assuming that a percentage of the dust particle's total surface area consisted of {100} surface grains (Fig. 2). As evident, depending on {100} surface percentage, different

amounts of water adsorption is predicted. Nevertheless, it is clear that adsorption is an important player in bringing water to the inner solar system, and is responsible, at least in part for the Earth's water budget.

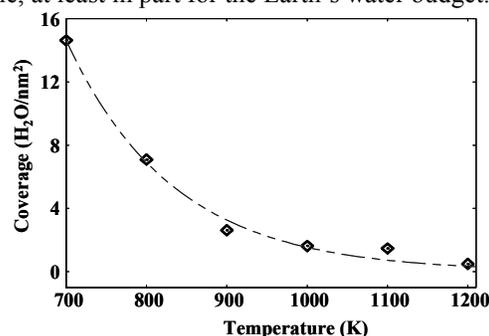


Figure 1: Variation in water-coverage of the {100} surface as a function of temperature.

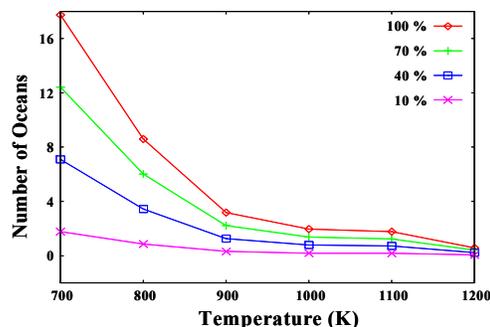


Figure 2: Variation in the amount of adsorbed water (expressed as Earth-oceans) as a function of {100} surface percentage at different temperatures.

Conclusions: Using atomistic computation techniques, the amount of water that could possibly adsorb onto forsterite grains, a primary constituent of silicates in the accretion disk was quantified. The results show that adsorption can bring many Earth oceans of water to planets growing in the inner solar system. A minimum of two Earth oceans should be adsorbed. Further, the most conservative assumptions have been made in this work. Specifically, the simulations were restricted by assuming that only a monolayer of water could be adsorbed on high energy sites. Bulk diffusion of water into the grains was ignored. The far more energetically favorable dissociative adsorption process was not considered. Perhaps most importantly, the fractal nature of cosmic dust grains was not taken into account. Fractal surfaces vastly increase the number of energetically available sites for adsorption. Thus the estimations provide an absolute lower limit for the amount of adsorbed water on to grains prior to accretion.

References: [1] Drake M.J. (2005) *Meteoritics & Planet. Sci.*, 40, 519. [2] de Leeuw N. H. et al. (2000) *Phys. Chem. Minerals*, 27 332. [3] Stimpfl et al. (2006) *J. Cryst. Growth*, 294, 83. [4] Lodders K. (2003) *Astrophys. J.* 591 1220.