

Atomistic simulations of adsorption of water onto forsterite and fayalite planar surfaces: Implication for the origin of water in the inner solar system. Marilena Stimpfl¹, Krishna Muralidharan², Nora H. de Leeuw³, Keith Runge², Pierre A. Deymier², and Michael J. Drake¹; krishna@u.arizona.edu, ¹Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, 85721, USA, ²Material Science and Engineering, University of Arizona, Tucson, AZ, 85721, USA, ³Department of Chemistry, University College, London, 20 Gordon Street, London WC1H 0AJ, UK

Introduction: The origin of water in the inner solar system is not well understood. While comets, hydrous asteroids, and phyllosilicates migrating from the asteroid belt have all been proposed as possible sources of inner solar system water, there remains unresolved issues with these sources [1]. In a break with existing theories Drake [1] proposed that direct adsorption of water molecules in the accretion disk, during the early stages of planet formation could be a possible source of planetary water. The viability of this mechanism requires that the energy of interaction must be high enough to ensure retention of water onto planetesimal building blocks at conditions corresponding to the accretion disk.

Towards this end, rigorous computational methods have been employed in this research group to verify this possibility. Specifically, by using atomistic computational methods and first-principles density functional theory (DFT) in conjunction with kinetic Monte Carlo (kMC) methods, the energetics and kinetics of adsorption of water onto olivine grain surfaces was determined as a function of composition and planar orientation. Results obtained from these calculations, clearly indicate that **adsorption must be a significant source of terrestrial planetary water.**

In this work, we examine adsorption mechanisms of water on to olivine grains. In particular, the adsorption and dissociation mechanisms of molecular water on to the different surfaces ($\{100\}$, $\{010\}$, $\{110\}$) of forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) - the end members of olivine will be discussed. It should be noted that there has been no atomistic level computational investigations of water adsorption on to fayalite.

Models and Methods: Water molecules can adsorb on to a solid surface either by physisorption (Van der Waals interactions) or chemisorption that can include dissociation where the covalent bonds within the water molecule are broken and are substituted by covalent bonding between the $-\text{OH}$ and $-\text{H}$ water radical and the substrate. In this work, we study both 'associative' and 'dissociative' chemisorption of water.

Adsorption energy calculations: Using a combination of the SiO_2 potential of Sanders et al. [2], and MgO and FeO potentials of Lewis and Catlow [3] in combination with the potential model of de Leeuw and Parker for water [4], the various energy-minimized surfaces of forsterite (Fo) and fayalite (Fa) were obtained. Next, the associative adsorption energy (E_{ads})

landscapes of the different surfaces were quantified (Eq.1) by examining the geometry-optimized energetics of a water molecule interacting with the respective surfaces as a function of position. See [5] for more details.

Fo- and Fa- surfaces are characterized by underbonded oxygen anions and metal cations, leading to surfaces being very reactive and consequently making *dissociation* of a water molecule into H^+ and OH^- energetically favorable. In the case of dissociative adsorption, a water molecule was dissociated on the relaxed surfaces such that an underbonded surface oxygen was protonated, while the OH^- group was bonded to a surface Mg atom. Then, the hydroxylated surface was relaxed using the BFGS energy-minimizer and the adsorption energy was calculated according to Eq. 1.

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

where, E_{ads} corresponds to the associative/dissociative adsorption energy, E_{s+w} is the total potential energy of the energy-minimized hydrated system, E_s is the energy of the surface, and E_{H_2O} represents the self-energy of the water molecule.

Next, the energy minimized surfaces that were obtained using interatomic potentials were examined using DFT to see if any discrepancy existed between the classical approach of using interatomic potentials and the more accurate DFT calculations. It should be noted that while DFT is a robust electronic-structure method capable of predicting the ground-state properties (especially energetics) of many-electron systems, it is computationally much more expensive (as compared to using potentials) to use DFT for modeling extended systems, since electronic effects are included explicitly in DFT. Hence, to reduce computational costs, we used the classical energy-minimized structures as starting configurations for the DFT energy-minimizations.

Results and Discussion: Fig. 1 illustrates the relaxed structures for the different anhydrous surfaces (a detailed description is available in [5]). It should be noted that the surface energies of the Fa-systems were lower than that of Fo-systems. Using these surfaces, the adsorption landscapes were obtained.

Associative Adsorption: For all the systems, the hydrated surfaces were more stable than the anhydrous ones. In the case of the $\{110\}$ Fo- surface, the average E_{ads} was $-132 (\pm 19)$ kJ/mol, while it equaled $-112 (\pm 15)$ kJ/mol and $-135 (\pm 12)$ kJ/mol for the $\{010\}$ and

{100} surfaces respectively. For Fa, the average E_{ads} was about 10 kJ/mol higher than that of Fo surfaces. **Thus one can conclude that the adsorption characteristics of both Fa and Fo are very similar for the different surfaces.**

The {100} surface was particularly interesting as it presented three active adsorption sites (S2-S4: see Fig. 1) as opposed to two for {110}- (S2 and between S4,S5,S6, and S7 respectively) and one for {010} with energies ranging from -290 to 124 kJ/mol, as shown in Fig.2.

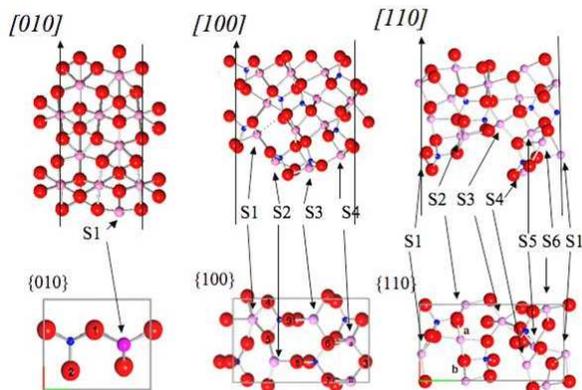


Figure 1: Location of adsorption sites on forsterite surfaces; Mg, O, and Si atoms are represented by pink, red and blue respectively.

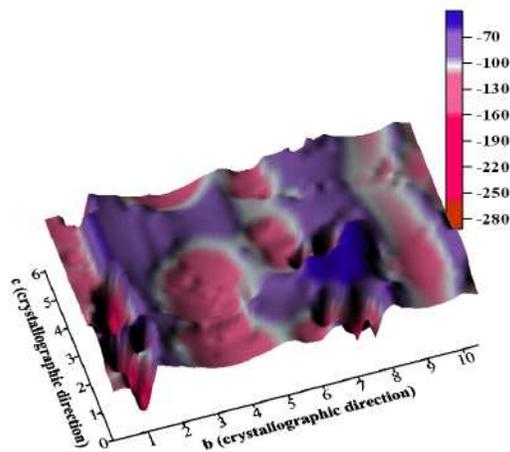


Figure 2: Associative adsorption landscape of the {100} landscape.

Using the associative adsorption energies obtained for the different surfaces in conjunction with kMC simulations, it was shown that water could be retained even at conditions corresponding to the accretion disk [6]. Further, using the equilibrium coverage obtained from the kMC calculations for the different surfaces, in conjunction with the knowledge of the Earth's mass ($\sim 6 \times 10^{24}$ Kg), the mass of oceans, and an average grain size of 0.1 μm , the amount of adsorbed water onto Earth was estimated as shown in Fig.3

Dissociative Adsorption: The dissociation of water molecules is particularly favored on the {100} and {110} surfaces, and a comparison with the corresponding associative adsorption energies shows that dissociation was favored by about 40 kJ/mol, implying that the dissociative process is much more energetically favorable, thus lending further credence to the possibility of adsorption as being a source of planetary water.

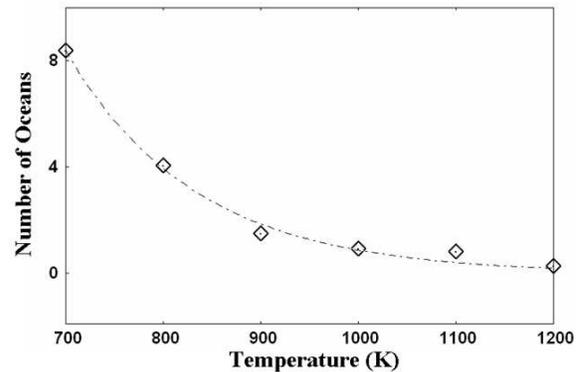


Figure 3: Variation in the amount of adsorbed water expressed in terms of Earth-Oceans at different temperatures

DFT calculations were carried out using a 6-31G** basis and a B3-LYP hybrid functional. The dissociative adsorption results were very consistent with those obtained using interatomic potentials, while there was a notable discrepancy in the associative adsorption energetics of the {100} surface (over-estimation by the classical interatomic potentials). Nevertheless, the above calculations clearly demonstrate that **adsorption would inevitably lead to the delivery of water to the terrestrial planets.**

Conclusions: Using rigorous atomistic computation techniques, we have examined the adsorption of water at the surface of dust grains. The results obtained, clearly show that adsorption can bring many Earth oceans of water to planets growing in the inner solar system.

References: [1] Drake M.J. (2005) *Meteoritics & Planet. Sci.*, **40**, 519. [2] Sanders, M. J et al. (1984) *J. Chem. Soc. Chem. Comm.* 1271. [3] Lewis, G. V. and Catlow, C. R. A., (1985) *J. Phys: Condens. Matter* **6** 393. [4] de Leeuw, N. H. and Parker, S. C., (1998) *Phys. Rev. B* **58**, 13901. [5] Stimpfl *et al.*, (2006) *J. Cryst. Growth* **294**, 83. [6] Muralidharan K. *et al.*, (2008) *Icarus* **198**, 400.

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