

Some – Perhaps Most - Water in the Earth must result from Adsorption on to Grains in the Accretion Disk

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Abstract: Muralidharan *et al.* [1] have shown that up to 8 Earth oceans of water could be associatively adsorbed on to grains in the accretion disk at 1 AU. Here we expand on that work using atomistic and electronic-level calculations to investigate dissociative adsorption, and use density functional theory to investigate the difference in D/H ratios between water on Earth and in the accretion disk. We find that dissociative adsorption leads to even stronger bonding than associative adsorption, demonstrating that adsorption must be a significant source of terrestrial planetary water. Using density functional theory we show that HDO may be preferentially retained relative to H₂O in adsorption/desorption kinetics.

Introduction: Comets, hydrous asteroids, phyllosilicates migrating from the asteroid belt, and hydrous minerals forming in the inner solar system have all been proposed as possible sources of inner solar system water, but there remain unresolved issues with these sources [2]. Recently, Drake [2] proposed that microscopic-level processes such as molecular adsorption of water in the accretion disk could in fact lead to the delivery of water to the inner solar system planets. Previously, adsorption on to grains had been dismissed due to the misconception that adsorption energies were too low to capture and retain gaseous water at high temperatures. We have shown [1,3] that the direct adsorption of water on to forsterite grains, the major silicate phase in protoplanetary disks, could be a significant source of terrestrial planetary water.

Specifically, we [3,4] have carried out atomistic and electronic-structure calculations to map out the adsorption energy landscapes of water on forsterite surfaces and showed that water molecules could strongly chemisorb (via chemical bonds) on to forsterite (especially the {100} surfaces in a *non-dissociative* fashion. Next, we [1] used kinetic Monte Carlo (KMC) simulations in conjunction with the results of [3] to show that water could be retained even at conditions corresponding to the accretion disk (Fig. 1). We concluded that adsorption of gaseous water on to dust grains would start from the early stages of accretion. Many conservative assumptions were made in the above work. For example, only *associative adsorption* was considered. But forsterite surfaces are characterized by underbonded O and Mg atoms [4], leading to the surfaces being very reactive and consequently making *dissociation* of a water molecule into H⁺ and OH energetically favored.

Here we calculate the *dissociative adsorption* energy landscapes of water on different forsterite surfaces and compare these results with associative adsorption [3]. If the resultant *dissociative adsorption* energy landscapes are similar to, or much lower than, the previous results, then *adsorption is an even more significant source of terrestrial planetary water*.

This work also addresses why the D/H ratio of water on Earth is higher than in the accretion disk. Currently there is no quantitative theory. Using first-principles density functional theory (DFT), we calculate the activation barriers for adsorption/desorption of H₂O and HDO molecules in order to see if differences could lead to preferential retention of HDO. If HDO is preferentially retained, as adsorption on to grains in the accretion disk would be a plausible alternative to the hypothesis that Earth's water came from exogenous sources such as comets or wet asteroids.

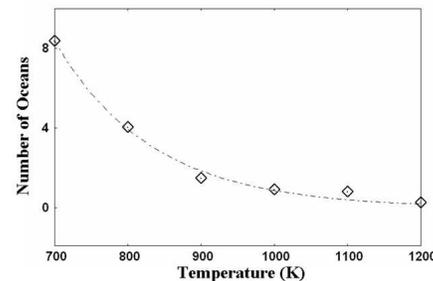


Figure 1: Variation in the amount of adsorbed water expressed in terms of Earth-Oceans at different temperatures

Models and Methods:

Dissociative adsorption energy calculations: Using interatomic potential parameters derived for bulk Mg₂SiO₄ [4], the different surfaces ({100}, {010}, and {110}) were relaxed using the L-BFGS method [5] (which accurately locates the lowest surface energy configuration). Each surface is characterized by the presence of underbonded O and Mg atoms, with the number of underbonded atoms being a function of the surface geometry. Next, in order to calculate the adsorption energy, using an appropriate potential for water [4], 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 L-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 dissociative adsorption energy, E_{s+w} is the total potential energy of the energy-

minimized hydroxylated system, E_s is the energy of the surface, and E_{H_2O} represents the self-energy of the water molecule.

Density Functional Theory (DFT) calculations: DFT [6] is a robust electronic-structure method capable of predicting the ground-state properties (especially energetics) of many-electron systems. Since, electronic effects are included explicitly in DFT, it is computationally much more expensive (as compared to using parameterized potentials) to use DFT for modeling extended systems. Thus, as a first step, we used DFT to calculate the adsorption and desorption energies of a H_2O and a HDO molecule onto a silica nanostructure (as a surrogate for forsterite), in order to see if adsorption/desorption could be responsible for the D/H ratio in the Earth's water compared to the accretion disk.

Results and Discussion:

Dissociative Adsorption: Relaxation of the three different surfaces yielded very different surface geometries. Specifically, for the {010} surface, there was only one surface Mg cation and three surface oxygens that were available for hydroxylation (Fig. 2); the dissociation energies were weaker than those of the corresponding associative adsorption energies for the {010} surface, making the dissociation of water molecule unlikely on the {010} surface. In contrast, the relaxed {100} and {110} surfaces have many more active adsorption sites (see Fig. 2), thereby favoring the dissociation of water molecules on these surfaces. A comparison with the corresponding associative adsorption energies [3] shows that dissociative adsorption is favored by about 40 KJ/mol on the {110} and {100} surfaces. Given the previous results of Muralidharan *et al.*, [1], where it was shown that associative adsorption energies were large enough to ensure retention of water on forsterite surfaces even at high temperatures, one can conclude that the much stronger dissociation energies would inevitably lead to the delivery of water to the terrestrial planets due to adsorption of water.

DFT Simulations: DFT simulations of H_2O and HDO dissociation were carried out using a 6-31G** basis and a B3-LYP hybrid functional. The dissociative adsorption of H_2O and HDO were both exothermic. By locating the transition states of the forward (for adsorption) and the reverse (for desorption) reactions (Fig. 3), activation energy barriers were computed. The results showed that the reverse activation barrier (i.e., the activation barrier to desorption) for H_2O was 0.6 KJ/mol lower than that of HDO, which is about 8 % of the barrier height. This is solely attributed to the zero-point energy differences between the two molecules, even though chemically the dissociation-reactions are identical. Since the desorption rate is related to the activation energy barrier via a Boltzmann

equation, the probability of H_2O desorption is incrementally higher, implying that there could be preferential retention of HDO. The complete adsorption and desorption kinetics of both species onto forsterite surfaces needs to be thoroughly examined, in order to make quantitative predictions.

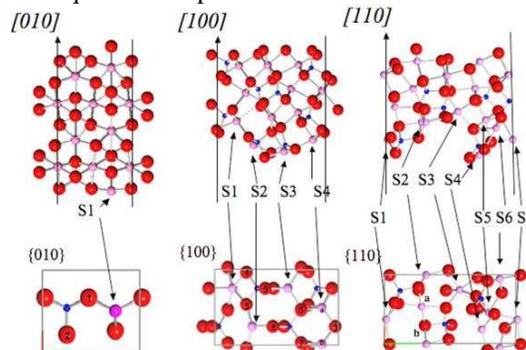


Figure 2: Location of adsorption sites on forsterite surfaces; Mg, O, and Si atoms are represented by pink, red and blue respectively.

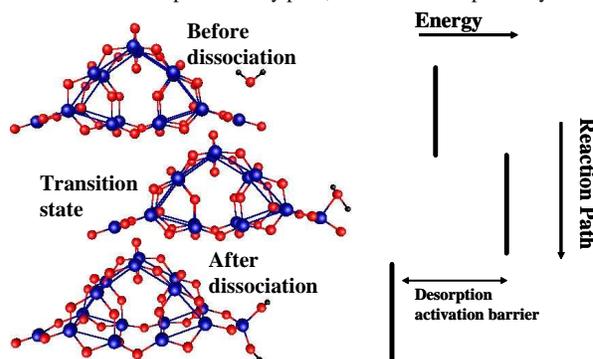


Figure 3: Illustration of the dissociation of a H_2O molecule onto a silica nanocluster; Mg, O, and Si atoms are represented by pink, red and blue respectively.

Conclusions: Using atomistic and electronic-structure calculations, we show that *dissociative adsorption* of water on to grains in the accretion disk leads to even stronger bonding than *associative adsorption*, demonstrating that adsorption must be a significant source of terrestrial planetary water. Using density functional theory we show that HDO will be preferentially retained relative to H_2O in adsorption/desorption kinetics. Significant work remains to quantify the magnitude of these processes, but they must play a role in the origin and isotopic composition of Earth's water.

References: [1] Muralidharan K. *et al.*, (2008) *Icarus* **198**, 400. [2] Drake M.J. (2005) *MAPS* **40**, 519. [3] Stimpfl *et al.*, (2006) *J. Cryst. Growth* **294**, 83 [4] . de Leeuw N. H. *et al.*, (2000) *Phys. Chem. Minerals*, **27** 332. [5] Broyden C. G., *Journal of the Institute of Mathematics and Its Applications* **1970**, 6, 76-90. [6] Martin R. M., Cambridge University Press, 1st Edition, October 27, 2008.