

ELECTRONIC STRUCTURE CALCULATIONS OF WATER ADSORPTION ON FORSTERITE GRAINS: IMPLICATIONS FOR PLANETARY WATER

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Introduction: Recent computational investigations have clearly indicated that adsorption occurring during the early stages of planetary accretion is a viable delivery source of planetary water [1,2]. In this study we use rigorous electronic structure and atomistic simulations to examine and accurately characterize the mechanisms of water adsorption on to forsterite grains—a primary planetary building block. Specifically, we focus on examining dissociative adsorption of water. Previous investigations had focused on associative molecular adsorption, which serves as a precursor to the ultimate dissociative adsorption of water.

Results and Discussion: Using density functional theory (DFT), the dissociation energy-landscapes of three surface orientations ($\{100\}$, $\{110\}$, $\{010\}$) of forsterite were studied. Of particular interest is the $\{100\}$ surface, as it contains multiple adsorption sites. The unhydrated $\{100\}$ surface, which is a primary cleavage plane of olivine, contains three possible dissociation sites (S2, S3, S4), each characterized by the presence of under-coordinated oxygen and magnesium atoms, thereby lending themselves well to the dissociation of a water molecule. The S2 site is coordinated to three oxygen atoms, while S3 is nested between two surface tetrahedra and is bonded to 4 oxygen atoms. S4 is also four-coordinated, with three oxygen atoms lying on the surface. In order to calculate the dissociative adsorption energies of the three sites, plane wave-DFT utilizing the Troullier Martin pseudopotential [3] to represent the electron-nuclear interaction, in conjunction with the local density approximation [4] (LDA) for exchange-correlation was used. Amongst the 3 sites, S2 yields the highest dissociation energy, corresponding to 420 KJ/mol, which can be attributed to the fact that it is the least coordinated cation as well as to the fact that it is located close to the surface and is extremely susceptible to hydroxylation. S3 and S4 also yield very high dissociation energy values of 288 KJ/mol and 180 KJ/mol, respectively. Note that molecular water can associatively bind to the $\{100\}$ surface very strongly, with energies ranging between 100-150 KJ/mol. Thus from a computational standpoint, one can assume that on $\{100\}$ both associative and dissociative adsorption can occur, though based on energetics dissociation is preferred.

Conclusion: Using electronic-structure calculations, we have shown that adsorption of water on to forsterite grains is energetically stable at thermodynamic conditions pertaining to the accretion disk. Further, we identify that water dissociation is the dominant adsorption mechanism and conclude that adsorption can be a significant source of terrestrial planetary water. The conclusions of Muralidharan et al. [2] that Earth could acquire many oceans of water by adsorption remain robust. Terrestrial planetary systems around other stars should also contain water.

References: [1] M.E. King et. al., 2010 *EPSL* **300**, 11. [2] K. Muralidharan et al., 2008 *Icarus* **198**, 400 [3].N. Troullier, J.L. Martin, 1991, *Phys. Rev. B* **43**, 1993. [4] D.M. Ceperley, B.J. Alder, 1980, *Phys. Rev. Lett.* **45**, 566.