Experimental evidence of adsorption as a source of planetary water: L. Vattuone[1], M. Rocca[1], Krishna Murali-dharan[2], Nora H. de Leeuw[3], Keith Runge[2], Pierre A. Deymier[2], and Michael J. Drake[4]; krishna@u.arizona.edu, [1]Universita di Genoa, 16146, Genoa, Italy, [2]Material Science and Engineering, University of Arizona, Tucson, AZ, 85721, USA,[3] Department of Chemistry, University College, London, 20 Gordon Street, London WC1H 0AJ, UK, [4]Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, 85721, USA,

Introduction: Many theories have been proposed to explain the presence of water in the Earth and other inner-solar system planets. These include exogenous sources such as comets, hydrous asteroids, phyllosilicates migrating from the asteroid belt, as well as the possibility of introduction of water during the early stages of planetary accretion via the direct adsorption of water molecules on to planetesimal grains in the accretion disk [1]. In particular, adsorption of water onto grains in the accretion disk prior to planetary formation has been shown to be viable, as shown by the computational work carried out in this research group [2,3]. Specifically, using atomistic computational methods and first-principles density functional theory (DFT) in conjunction with kinetic Monte Carlo (kMC) methods, we have shown that water molecules strongly chemisorbed on to olivine grain surfaces (which constitute the most abundant grains in the accretion disk) and that the resultant hydrated surface is stable at thermodynamic conditions pertaining to the accretion disk [3]. The amount of planetary water that could be delivered due to adsorption was determined to be at least 2 Earth-oceans. Prior to these investigations, adsorption was not actively considered as a delivery source due to the misconception that water physisorbed to the mineral surfaces and consequently was not stable at high temperatures.

These results [2,3] do not account for the possibility of dissociation of water molecules during adsorption. Hence, in this work, we report on computational investigations of dissociation energetics of water molecules on forsterite surfaces. We also report the first experimental investigations of adsorption of water on to the olivine {100} surface. This two-pronged approach is adopted as experimental investigations of adsorption of water onto olivine at conditions pertaining to the accretion disk (high temperatures, low partial pressure) can provide an extremely valuable check on the results of our numerical modeling, especially since prior to this work, no reliable direct experimental data are currently unavailable.

Computational Methods: Atomistic computational methods are well suited to examine dissociation of water on forsterite surfaces, particularly if the underlying force-fields (or interatomic potentials) are suitably parameterized. A relevant example of robust interatomic force-field models that have been successfully parameterized to model interactions between olivine

and water are the suite of potentials derived by (i) Lewis and Catlow for MgO, (ii) Sanders et al. for SiO_2, and (iii) Baram and Parker for dissociated water respectively (see [2]). We use the above potentials in our work to examine water dissociation on forsterite surfaces, similar to the approach of Stimpfl *et al*. [2].

Experimental Approach: The experimental apparatus consists of a main ultra high vacuum (UHV) chamber with a base pressure of 10^{-10} mbar, equipped with a supersonic molecular water-beam (SMB), a quadrupole mass spectrometer (QMS) not in line of sight with the water-beam, and all other typical vacuum facilities. The local water pressure on the olivine surface with the beam on is of the order 10^{-8} mbar. The sample is mounted in a coolable cage whose temperature is measured by a chromel-alumel type thermocouple. The adsorption of water is measured by the retarded reflector method of King and Wells (KW) [4]. The latter has been successfully employed to examine adsorption of molecular species on different metallic and oxide surfaces and, as our experimental results demonstrate, it can also be successfully used to study water adsorption on mineral surfaces.
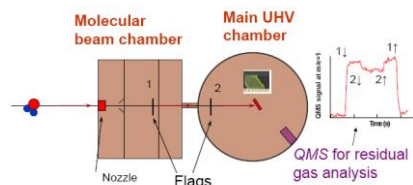

Figure 1. Schematic drawing of the Supersonic Molecular beam chamber coupled to the ultra high vacuum chamber

In this method (Fig. 1) the partial pressure of water in the UHV chamber is recorded by the QMS during exposure. During a typical experiment, the beam trajectory is first intercepted by an inert flag (1) located in the first chamber. When the beam is allowed to enter the Main UHV chamber but is intercepted by a second inert flag (2), the partial pressure increases to a value determined by the incoming flux and by the pumping speed. When the second flag is removed and the supersonic molecular beam strikes the sample, an abrupt decrease in partial pressure is observed corresponding to the adsorption of water on olivine. With repeated bombardment, the partial pressure returns to the initial value because the olivine becomes saturated. and either adsorption stops (stable systems) or the rate of adsorption equals the desorption rate. In the latter case, when

the beam is intercepted again by the inert flag, isothermal desorption is observed and the partial pressure shows a transient. The amount of adsorption is derived by integrating the missing signal versus time and multiplying by the beam flux. Sticking is only observable when the signal exceeds a critical value, and if the signal strength is less than the sensitivity of the KW system, Temperature Programmed Desorption (TPD) is used for characterizing adsorption.

Results and Discussion:

Computational Investigations: Forsterite 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. Three surface orientations ({010}, {100} {110}) were considered. In order to characterize dissociative adsorption, water molecules were dissociated on relaxed surfaces such that an underbonded surface oxygen was protonated, while the OH^- group bonded to a surface Mg atom. Then, the hydroxylated surface was relaxed using the BFGS energy-minimizer [5] and the adsorption energy was calculated according to Eq. 1.

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

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_{H2O} represents the self-energy of the water molecule.

The {100} and {110} surfaces were particularly interesting as they presented multiple active adsorption sites whose energies varied from -289 to 350 kJ/Mol for {100} and -120 to -200 kJ/Mol for {110} which are significantly larger than associative (molecular H_2O) adsorption. In the case of {010}, both dissociative adsorption as well as molecular adsorption energetics were very similar (~ -75 kJ/Mol). Thus, one can expect dissociation to be the dominant adsorption mechanism.

Experimental Investigations: Fig. 2 illustrates the outcome of experiments performed on a polished olivine {100} surface which was first exposed to a supersonic water beam for 600 s at 138 K. We observe a single water desorption peak which we assign to multilayer adsorption, since its intensity does not saturate with exposure. The crystal is then annealed to 900 K and cooled back to 138 K. Olivine is again bombarded with the same amount of water. It is apparent that subsequent doses yield decreasing desorption signals. After the fourth dose no further desorption occurs..
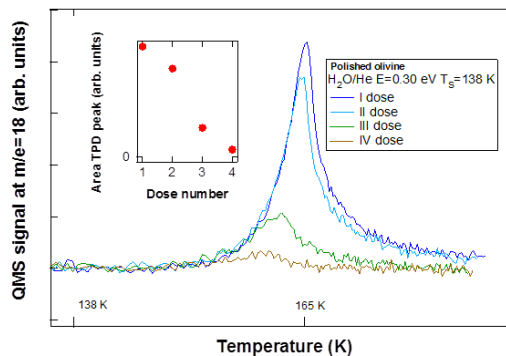

Fig. 2 TPD spectra for identical doses. The highest peak corresponds to desorption of molecularly adsorbed water in multilayers. Prior to performing a new dose the sample was heated well above the multilayer desorption temperature.

These experiments clearly indicate that a) significant water uptake takes place when dosing at 138 K, which can be correlated with multilayer adsorption; b) when annealing, some water desorbs while some must dissociate, since the concentration of free sites available for further water adsorption decreases with the doses; c) the resulting hydroxylated surface is stable up to at least 900 K since reactivity cannot be restored by annealing up to this temperature.

The experimental findings agree well with the simulations of the {100} surface, which show that dissociation is the dominant adsorption mechanism. Further, experiments show that the activation energy barriers separating all such molecularly adsorbed or physisorbed molecular states from the dissociated state(s) are lower than the barrier for molecular water desorption, and elevated temperatures help overcome the barrier to favor dissociation over desorption.

Conclusions: Experimental and computational investigations presented in this work clearly establish that adsorption is an important player in accounting for planetary water. Both confirm that dissociation of water on olivine surfaces is the dominant adsorption mechanism. Many Earth oceans of water could have been adsorbed on to grains in the accretion disk prior to the formation of the terrestrial planets.

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