Earth’s water is conventionally believed to be delivered by comets or wet asteroids after the Earth formed. However, their elemental and isotopic properties are inconsistent with those of the Earth. It was thus proposed that water was introduced by adsorption onto grains in the accretion disc prior to planetary growth, with bonding energies so high as to be stable under high-temperature conditions. Here, we show both by laboratory experiments and numerical simulations that water adsorbs dissociatively on the olivine \( \{100\} \) surface at the temperature (approx. 500–1500 K) and water pressure (approx. \( 10^{-8} \) bar) expected for the accretion disc, leaving an OH adlayer that is stable at least up to 900 K. This may result in the formation of many Earth oceans, provided that a viable mechanism to produce water from hydroxyl exists. This adsorption process must occur in all disc environments around young stars. The inevitable conclusion is that water should be prevalent on terrestrial planets in the habitable zone around other stars.

1. Introduction

The presence of water on the Earth is an enigma. It is generally agreed that it was too hot at 1 astronomical unit (AU) for hydrous minerals to be stable in the accretion disc. Thus, the Earth’s water is conventionally believed to have been delivered by comets or wet...
asteroids after the Earth formed. However, wet asteroids and comets have elemental and isotopic properties that are inconsistent with those of the Earth [1], limiting the amount of water derived from comets and wet asteroids. It was thus proposed that water was introduced during planet growth in the accretion disc in a form stable under high-temperature conditions. This hypothesis is supported by the presence of water in the discs around young stars [2] and by numerical simulations [3,4] of water adsorption on silicate grains under conditions corresponding to those in the accretion disc [5,6]. Such studies showed that molecular chemisorption of water on forsterite (Mg-rich end member of olivine, one of the main constituents of dust grains) might account for the formation of several Earth oceans [4].

Until the work of Drake and co-workers [1,3,4], adsorption had not been considered a viable delivery source of water owing to the misconception that it only physisorbed (weakly bonded) to mineral surfaces and, consequently, was not stable at the high temperatures characteristic of the accretion disc at 1 AU. This view was shown to be incorrect by computational investigations of water interaction with olivine surfaces [3,4,7] that indicate the occurrence of chemisorption with binding energies strong enough to ensure the stability of molecular water even at a temperature \( T > 700 \text{ K} \) [4]. This information was then used in conjunction with kinetic Monte Carlo simulations [8] to predict the kinetics of water adsorption and to demonstrate that many Earth oceans could be delivered via molecular chemisorption alone [4]. These studies neglected, however, the possible occurrence of water dissociation. In this paper, we show that such process dominates the water–olivine interaction in laboratory experiments performed under controlled ultra high vacuum (UHV) conditions, in agreement with atomistic-based numerical simulations.

2. Experiments

The experimental apparatus is shown schematically in figure 1. It consists of a main UHV chamber with a base pressure of \( 10^{-10} \text{ mbar} \) combined with a supersonic molecular beam (SMB) of water. A quadrupole mass spectrometer (QMS) not aligned with the water beam measures the partial pressure of the gases in the main UHV chamber. The local water pressure on the olivine surface when the beam is on is of the order of \( 10^{-8} \text{ mbar} \). The sample is mounted in a cage that may be cooled by liquid nitrogen flux and heated either radiatively or by electron bombardment. While recording thermal desorption, spectra annealing was performed at constant power without electron bombardment. The temperature of the cage is measured by a chromel–alumel type thermocouple. To avoid possible contamination, the sample was not glued to the cage, although this implies a non-ideal thermal contact with the cage itself. Temperature readings during the annealing cycles were thus calibrated with respect to the water multilayer desorption that typically occurs at 165 K for ice [9,10]. This procedure implies a non-constant heating rate but allows a direct comparison among different measurements, once the same power is applied to the heater. The average heating rate is 0.55 K s\(^{-1}\) in the range from 138 to 165 K.

The sample is an approximately 1 mm thick slab of natural Pakistani olivine (Fo\(_{90}\)) cut from a single crystal parallel to \( \{100\} \) and polished on one side only to 1 \( \mu \text{m} \) smoothness (see image in figure 1). Adsorption of water was investigated both for the polished and for the unpolished \( \{100\} \) faces over a range of temperatures from 140 to 560 K.

The surface was cleaned by sputtering with Ne\(^+\) ions followed by annealing to 900 K. Annealing to temperatures higher than 900 K was not attempted even while cleaning the sample to avoid possible modifications in its surface composition (e.g. by oxidation of Fe\(^{2+}\) to Fe\(^{3+}\)).

The water beam is produced by carrying water vapour in a stream of inert gas. The adsorption of water is measured by the retarded reflector method of King & Wells (KW) [11], which has been widely used to examine adsorption of molecular species on different metallic [11] and oxide [12] surfaces. As our experimental results demonstrate, it can also be successfully used to study water adsorption on mineral surfaces. In this method, the partial pressure of the gas of interest (H\(_2\)O in this case) in the main UHV chamber is recorded by a QMS not in line of sight with the beam during the exposure. In a typical experiment, the beam trajectory is initially intercepted by two inert flags located, respectively, in the SMB chamber and in the main chamber just in front of
the sample. When the first flag is removed, the beam enters the main UHV chamber, resulting in an increase in the H$_2$O partial pressure to a value determined by the incoming flux and by the pumping speed (figure 1) but virtually no adsorption on the sample. Then, the second flag is removed and the beam strikes against the surface. Three collimators are present along the beam path. The diameter of the last one is chosen so that the beam spot at the sample position is smaller than the sample itself, thus ensuring a reliable measurement of the sticking probability at normal incidence. The position of impingement on the sample is checked optically by passing a laser beam through the same path travelled by the water molecules in the supersonic beam. As evident from figure 1, when the beam strikes on the clean unpolished olivine surface an abrupt decrease in partial pressure is observed, corresponding to water adsorption on the sample. The partial pressure may eventually tend to its initial value when the surface is saturated with the probe gas and either adsorption stops (case of stable adsorption systems) or the rate of adsorption equals that of desorption (metastable systems). The amount of adsorbed gas is calculated by integrating the missing QMS signal versus time and multiplying by the beam flux, which needs therefore to be determined independently and is often the main source of systematic error. In our set-up, the sticking probability, $S$, can be measured only if $S \geq 0.05$. For lower $S$ values, as is the case for the polished olivine surface, only thermal desorption spectroscopy (TDS) is suitable to quantify adsorption. $S$ can then be determined from the ratio between the amount of desorbed gas and exposure.

SMB expansion allows the attainment of water kinetic energies varying from $E = 0.06$ to $0.30$ eV, an interval spanning a large part of the velocity distribution at the temperatures of the accretion disc. Experiments were performed for both the polished and unpolished side of an olivine (100) sample prepared in situ by ion bombardment and annealing. TDS was used to probe water adsorption on the polished side, for which $S < 0.05$. For the more reactive non-polished surface, we could estimate $S$ both by TDS and by the more accurate KW method. The unpolished side better mimics real olivine surfaces in the accretion disc.

TDS spectra recorded after water exposure on the polished side of the olivine sample are shown in figure 2. The QMS trace at mass 18 (figure 2a) presents two desorption peaks. The one at higher $T$ corresponds to desorption from the water multilayer, because its intensity does not saturate with exposure. This assignment is reinforced by KW data recorded for the non-polished side, indicating that $S$ does not vanish even after prolonged exposure (up to 2400 s, not shown). Indeed, this desorption peak was used to calibrate the temperature scale, because water multilayer desorption is known to occur at 165 K [9,10].

The peak at lower $T$ is a minor contribution, saturates at high doses and is larger for the unpolished than for the polished side, indicating that it is due to nucleation of water at defect sites.
As evident from figure 2b, both water desorption peaks are associated with a corresponding signal at mass 2. Because such a peak is not present in the QMS cracking pattern of water, it is indicative of \( \text{H}_2 \) desorption resulting from water dissociation and consequent OH formation. No further \( \text{H}_2\text{O} \) or \( \text{H}_2 \) desorption (indicative of the presence of adsorbed H) was detected in the range from 165 to nominal 900 K. This result agrees with recent theoretical calculations [13] showing that forsterite is expected to be a good catalyst for \( \text{H}_2 \) formation and that the barrier for its desorption is approximately 0.1 eV. This value implies a \( \text{H}_2 \) desorption temperature lower than 138 K (the temperature of water uptake in this experiment). \( \text{H}_2 \) desorbs thus as soon \( \text{H} \) is formed, explaining the experimentally observed coincidence of \( \text{H}_2\text{O} \) and \( \text{H}_2 \) desorption peaks.

Figure 3 shows TDS traces recorded after subsequent water exposures on the polished (figure 3a, \( \text{H}_2\text{O} \) doses of 600 s with \( E = 0.30 \text{ eV} \)) and unpolished (figure 3b, \( \text{H}_2\text{O} \) doses of 300 s with \( E = 0.30 \text{ eV} \)) face of the olivine crystal at 138 K. The sample was prepared for the subsequent doses by annealing it to temperatures just above the end of the main desorption peak (300 K reading on the sample holder). Subsequent doses yield decreasing desorption signals, in accord with the saturation of sites where dissociation has occurred in the previous cycle. For the polished side, four doses are sufficient to readily passivate the surface, and no further desorption occurs even when the sample is prepared by prolonged heating to 900 K. Only sputtering with \( \text{Ne}^+ \) ions and annealing to 850 K for several minutes to recover surface order could restore the initial reactivity.

The behaviour of the non-polished side is similar, except for the previously discussed, additional low \( T \) peak. Even if the absolute intensities of the desorption traces are not directly comparable, longer exposures are needed to passivate the polished side, indicating its lower reactivity. Indeed, the estimated sticking coefficient for \( \text{H}_2\text{O} \)/olivine is approximately 0.2 and
below the experimental sensitivity (i.e. less than 0.05) for the non-polished and polished sides, respectively. The reactivity is thus at least four times higher for the rough surface. Moreover, a compatible conclusion was reached comparing the position of the maximum of the TDS peak.

Experiments performed dosing water beams with $E = 0.06 \text{ eV}$ yielded similar results. The reported phenomena do not depend therefore significantly on the kinetic energy of the reactant.

The TDS traces overlap in the low temperature side. This, together with the shift to higher temperatures of the peak maximum, indicates the independence of the desorption rate on coverage, i.e. that the dominant process is of zeroth order. The non-ideal zeroth-order shape on the high-temperature side indicates that a minor contribution with a different desorption order is present. A similar shape of TDS traces was reported in the literature for H$_2$O/Cu(111) [14]. Dose 4 in both figure 3a and figure 3b clearly corresponds to submonolayer coverage, because the onset of the multilayer is signalled by the superposing TDS traces on the low $T$ side.

Given the strong dependence of $S$ on the surface conditions, the water SMB was used to check for its chemical state. This information is difficult to obtain for insulating samples, because...
electron-based spectroscopies are useless and optical spectroscopies explore also the subsurface region which, in the case of olivine, contains OH groups and prevents thus the observation of adsorbates at low coverage.

In figure 4, we compare the effect of doses performed at low crystal temperature on a clean surface and on a surface pre-exposed with water well above room temperature. TDS spectra are reported for the polished side (figure 4a), whereas a direct measurement of $S$ by KW is shown for the unpolished one (figure 4b). Figure 4a compares three TDS traces recorded after exposing the polished side of the olivine crystal at $T = 136$ K to 1800 s water SMB. The sample has been pre-treated in different ways: (i) exposed to 1800 s of H$_2$O at 136 K and then annealed until complete desorption of the water multilayer (blue trace); (ii) exposed to 1800 s of H$_2$O at 560 K (red trace); and (iii) annealed to 560 K for 1800 s without H$_2$O exposure (green trace). Note that in case (ii) no desorption features appear in the spectrum, indicating a complete passivation of the surface after water pre-treatment at high $T$. On the contrary, desorption of the multilayer (and partial dissociation) occurs for preparations (i) and (iii) indicating that passivation is caused by water exposure at 560 K and not just by annealing to such temperature.
Similar experiments performed on the unpolished side (for which H\textsubscript{2}O exposures of only 20 s were used to compensate for the higher reactivity; figure 4b) show a decrease in $S$ from 0.2 to below experimental sensitivity upon high $T$ water exposure, thus confirming our conclusion.

The absence of the low temperature peak in preparation (iii) indicates that clustering of water at defects occurs more effectively if the nucleation centre is represented by an undissociated water molecule rather than by OH, which is most probably produced at defects upon annealing.

The surface coverage ($\Theta$) is given by $\Theta = \langle S \rangle \Phi \Delta t$, where $\langle S \rangle$ is the average sticking probability, $\Phi$ the water flux and $\Delta t$ the duration of the uptake. Because $\Phi \sim 0.02$ ML s$^{-1}$ for the H\textsubscript{2}O/He beam, we estimate that for high-temperature exposures $\langle S \rangle$ must be larger than $5 \times 10^{-4}$ for the polished surface and close to approximately 0.015 for the unpolished side (i.e. still lower than KW sensitivity [11]). The unpolished surface best mimics a real surface of fractal, micrometre-sized olivine in the accretion disc. Its higher reactivity is not unexpected because surface corrugation may enhance the accommodation into the physisorption well [15] and under-coordinated sites can lead to an easier breaking of intra-molecular bonds and to the formation of stronger molecule–surface bonds. This has been experimentally proved for several substrates [16] and demonstrated by simulations for defected forsterite [17].

The present experiments clearly indicate that

(i) significant water uptake takes place when dosing at 138 K, leading to multilayer adsorption;
(ii) when annealing, part of the water layer desorbs and part of it must dissociate forming OH and H, because the surface gradually passivates as demonstrated by the smaller coverage attained with subsequent doses. Dissociation is possible only for molecules in contact with the olivine surface; and
(iii) dosing water at high $T$ causes the formation of a passivating layer of hydroxyls. The so-produced surface is passive with respect to low $T$ water adsorption and stable up to at least 900 K, because annealing to this temperature does not restore the reactivity.

While (i) and (ii) are expected and prove the reactivity of olivine with respect to water, result (iii) is more surprising and implies that the heat of adsorption of water at the hydroxylated surface is lower than the heat of condensation of the multilayer.

The absence of detectable recombinative desorption, usually occurring around 500 K, indicates that either this process takes place at temperatures higher than the one reached in the experiments or that it is inhibited, because no adsorbed hydrogen is available at the temperature at which the OH–surface bonds break. Indeed, in the absence of adsorbed H, recombinative desorption can occur only involving two OH and a vacancy which is saturated by the exceeding O atom.

This issue is clearly relevant from the geochemical point of view because if H\textsubscript{2} is released at quite low temperature, then the hydrogen atoms needed for water synthesis from adsorbed OH must be provided by some external source.

One might object that we are just observing the passivation of oxygen vacancies with hydroxyls. However, this explanation would imply an unrealistically high density of vacancies to account for the high measured water uptake. Moreover, if adsorption were not occurring at regular olivine sites, we would not observe multilayer formation, contrary to experimental evidence. If ice nucleation would start from a few defected sites on an otherwise unreactive surface, then the sticking probability should finally increase with coverage, again contrary to experimental evidence. Moreover, the passivation of a few sites during high-temperature exposure to water would not affect so strongly the overall chemical behaviour of the surface.

Finally, the absence of a desorption peak owing to the first layer of chemisorbed water, as observed for many systems at temperatures higher than the one of the multilayer, indicates that the molecular heat of adsorption is comparable to the heat of condensation, thus accounting for desorption around 165 K, independently of surface coverage.
Figure 5. Illustration of the (100) surface with the dissociated water molecule ('w' represents oxygen from water). Red, yellow, blue and white spheres represent oxygen, magnesium, silicon and hydrogen atoms, respectively. (a) A schematic representation of a part of the olivine slab viewed perpendicular to the surface. (b) The view parallel to the surface unit cell. ‘S’ identifies the possible adsorption sites.

3. Theoretical calculations

To complement the experimental observations, we have undertaken density functional theory (DFT)-based calculations of adsorption of water on the (100) forsterite (the Mg-end member of olivine) surface. DFT methods are robust electronic structure techniques that have been widely adopted due to their ability to accurately model the ground-state properties (especially energetics) of many-electron systems. In this work, we use the Vienna \textit{ab initio} simulation package (VASP), v. 4.6 [18,19], within the framework of DFT and the generalized gradient approximation functional PBE [20]. We have used the projected augmented wave [19,21] as provided with the VASP package [22]. A cut-off energy of 400 eV was chosen for the plane-wave basis. We refer the reader to [23] for more detail on the simulation procedure as well as adsorption energetics on other forsterite surfaces.

Bulk forsterite was appropriately cleaved to yield the (100) surface, such that all SiO$_4$ groups were left intact [24]. The surface was subsequently relaxed, yielding a surface characterized by one under-coordinated surface oxygen and two under-coordinated surface magnesium atoms per unit cell. To study dissociation energetics, it was assumed that the constituents of a water molecule, namely hydrogen (−H) and the hydroxyl (−OH), coordinate with under-coordinated surface oxygen and magnesium atoms, respectively (figure 5). The resultant hydration energy
(\(E_{\text{diss}}\)) for the dissociation of a single water molecule was evaluated according to

\[
E_{\text{diss}} = E_{\text{hyd}} - (E_{\text{uhyd}} + E_{W}),
\]

(3.1)

where \(E_{\text{hyd}}\), \(E_{\text{uhyd}}\) and \(E_{W}\) are the hydrated surface energy, energy of the unhydrated surface and cohesive energy of a single water molecule, respectively. For the (100) surface, the dissociation energy was found to be \(-270 \text{ kJ mol}^{-1}\); such a large value for the dissociation energy is consistent with experimental observations corresponding to the high-temperature stability of the hydroxylated (i.e. passivated) olivine surface. Note that the dissociative adsorption energy of a single water molecule on the (100) surface was energetically much more favourable than the corresponding associative adsorption process as discussed in [23].

In addition, we have also examined the energetics of molecular adsorption of a water molecule on a hydroxylated surface; here, the water molecule associatively adsorbs onto the passivated surface, with an adsorption energy of \(-33.7 \text{ kJ mol}^{-1}\). Such molecular adsorption energy is smaller than that of multilayer condensation (40 kJ mol\(^{-1}\)) and is in accord with the experimental finding that no multilayer adsorption occurs at \(T = 140 \text{ K}\) for a surface which has been previously hydroxylated at high \(T\) (see red trace in figure 4).

Thus, numerical results agree well with the experiments reported here, in which the dissociated state is found to be the most stable. Experiments show, moreover, that annealing a water layer deposited at 138 K as well as dosing at high surface temperature clearly promotes dissociation, implying that the activation energy barriers separating all such molecularly adsorbed states from the dissociated state(s) are lower than the barrier for molecular water desorption.

### 4. Conclusions

These experiments show that, under the conditions corresponding to the early stages of planetary accretion (5–6), the \(\{100\}\) surface of olivine undergoes hydroxylation. Because water adsorbs dissociatively at accretion disc temperatures (approx. 500–1500 K (5)), the difference between the water partial pressure in our SMB (approx. \(10^{-8}\) mbar) and that in the accretion disc (\(10^{-8}\) bar (6)) is irrelevant. Both experimental and computational investigations presented in this work confirm that dissociation of water on olivine surfaces is the dominant adsorption mechanism. Because the lower heat of adsorption of molecularly chemisorbed water could account for the formation of a number of the Earth’s oceans ranging from 1 to 17 [4], even more hydroxyl would be adsorbed because of the stronger adsorption energy of dissociative adsorption.

However, terrestrial planets today have (or had) \(\text{H}_2\text{O}\), not \(\text{OH}\). Thus, there must be a chemical pathway that leads from hydroxyl to water during their formation. Although we cannot conclusively establish the path, we can imagine at least three possibilities.

The first involves the presence of \(\text{H}_2\) in the accretion disc as an obvious source of hydrogen to recombine with hydroxyl. Adsorption of \(\text{H}_2\) onto olivine has only been studied at low temperatures [25] that are irrelevant with respect to our experiments. However, our work shows no desorption of \(\text{H}_2\) between 160 and 900 K, and independent calculations [24] indicate that atomic hydrogen produced by water dissociation on olivine is too weakly bonded (\(E_{\text{ads}} \sim 102 \text{ kJ mol}^{-1}\)) to remain on the surface at the temperatures of the accretion disc, thus ruling out recombinative desorption as a source of water.

A second hydrogen source is represented by the high energy protons from the solar wind, which could either react directly to form water or be implanted into olivine and recombine with hydroxyl to give water after the olivine has been accreted into planets and the planets start to melt owing to the release of gravitational potential energy. Direct reaction is energetically plausible, because it is well known that reaction of gas phase atomic hydrogen with adsorbed OH is strongly exothermic (by 511 kJ mol\(^{-1}\)) and barrierless [26]. Reaction in a magma ocean environment will occur late in the accretion of planets. Unfortunately, it is still unclear whether the amount of hydrogen impacted on or implanted into the olivine surface is adequate to account
for the water budget of the Earth, the only planet for which there is a reasonable estimate of water content [1] (though highly uncertain, 1.32–60 Earth oceans, with most workers estimating about 10 Earth oceans).

Third, recombination of OH with OH to form H2O and liberate oxygen in planetary magma oceans has not been studied. Because the process is exothermic by about 66 kJ mol\(^{-1}\) in the gas phase [27] and because the surface–O and surface–OH binding energies are similar, adsorption of OH on to grains in the accretion disc could account for both the water content of terrestrial planets such as the Earth, and the relatively oxidized state of their silicate mantles.

Elkins-Tanton [28] showed that once water is dissolved in a magma ocean it outgasses within 10 million years to produce either a liquid water ocean, or a steam atmosphere that collapses into a water ocean, depending on the water content of the magma ocean. Thus, if water in the accretion disc is adsorbed onto grains as hydroxyls, then it seems inevitable that oceans will exist on the Earth and other rocky planets in our Solar System within 10 million years of the end of accretion.

Finally, this adsorption process must occur in all disc environments around young stars. The inevitable conclusion is that water should be prevalent on terrestrial planets in the habitable zone around other stars.

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