Where on Earth has our water come from?


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The presence of water in the Earth has long been an enigma. However, computer modelling techniques have shown that the adsorption of water onto the fractal surfaces of interplanetary dust particles, which are present in the planetary accretion disk, is sufficiently strong to provide a viable origin of terrestrial water.

The origin of the abundant water throughout the solar system has long been debated. In particular, the mechanism whereby water becomes incorporated into terrestrial planets such as the Earth has been a perplexing question. The three central theories for this mechanism differ both in the nature of the water-bearing material and the process whereby the water was incorporated during or after accretion. However, exogenous water sources such as comets and asteroids that originate farther than 2.5 astronomical units (AU) from the growing planet, display geochemical and isotopic fingerprints that differ from those observed on Earth, indicating that, whereas only associative adsorption of water at the planar (010) surface of forsterite was calculated to release 119 kJ mol$^{-1}$, compared to calculated energies of 145–170 kJ mol$^{-1}$ for CaO and approximately 200 kJ mol$^{-1}$ for the SiO$_2$ quartz surface, compared to calculated energies of 160–180 kJ mol$^{-1}$ and 214 kJ mol$^{-1}$, respectively, for the same systems, using the same potential parameters employed in this work. This quantitative agreement indicates that the interatomic potentials are sufficiently accurate to calculate the adsorption behaviour at the fractal surfaces, where we need to explore very large surface areas and a wide range of highly complex topologies, which makes electronic structure calculations of these surface systems unfeasible.

We have created models for a number of highly complex forsterite surfaces, including low-coordinated step edges and corner sites, with variously sized terraces in between. Examples of the complex surface topologies considered in this work are shown in Fig. 1 for the (010) surface, which dominates the forsterite morphology. Whereas only associative adsorption of...
water occurs at the perfectly planar (010) surface, releasing approximately 120 kJ mol\(^{-1}\), dissociative adsorption of water at the low-coordinated and highly reactive sites was calculated to release large energies, from 300 kJ mol\(^{-1}\) on the reconstructed dipolar (010) surface to 335 kJ mol\(^{-1}\) on the highly defective, stepped (110) surface, shown in Fig. 2, illustrating the crucial role played by reactive surface sites and surface defects in promoting strong dissociative adsorption.

The picture that emerges from the results discussed above is that the energies associated with the process of water adsorption are of such magnitude that it becomes plausible to speculate whether water could be adsorbed and retained on grains of forsterite in the accretion disk. In order to calculate the partial pressures of gaseous water required for appreciable adsorption of water at any particular temperature, one needs to consider the process of adsorption of a water molecule at the mineral surface, according to the following eqn (1):

\[
\text{Surface} + \text{H}_2\text{O}_\text{(g)} \rightleftharpoons \text{Surface} \cdot (\text{H}_2\text{O})
\]

where \(K\) is the equilibrium constant for the above reaction. Surface is the mineral surface before water adsorption and Surface*\((\text{H}_2\text{O})\) is the system after adsorption. The equilibrium constant \(K\) is then calculated as shown in eqn (2), from the Gibbs free energy \(G\) of adsorption, where \(a_{(g)}\) and \(a_{(s)}\) are the activities of the water molecule adsorbed at the solid surface or in its gaseous state respectively. Following the simple Langmuir model, we can then write the activities of the partially hydrated surfaces as \(x/(1-x)\), where \(x\) is the fraction of surface sites occupied by water, \(P_{\text{H}_2\text{O}}\) is the partial pressure of gaseous water, which is the quantity we seek to calculate, \(R\) is the gas constant and \(T\) is the temperature of interest.

\[
k = \frac{a_{(s)}}{a_{(g)}a_{\text{(surface)}}} = \frac{x}{(1-xP_{\text{H}_2\text{O}})} = e^{-\Delta G^0/RT}
\]

Due to the low partial pressure of water (\(p \approx 10^{-8}\) bars) in the accretion disk, adsorption of a complete monolayer is unrealistic and we have therefore used the hydration energies for the isolated water molecules at the energetically preferred adsorption sites, where we can calculate the fractional occupancy \(x\) from our knowledge of the maximum number of water molecules in a full monolayer, which is determined by the number of accessible surface sites in each simulation cell.

The change in the standard Gibbs free energies for adsorption of water at the various forsterite surfaces according to eqn (1) was calculated from the enthalpies and entropies at the required temperatures (eqn (3)), where \(\Delta H\) is the enthalpy of the adsorption process per water molecule, \(T\) is the temperature of interest and \(\Delta S\) is the change in entropy.

\[
\Delta G = \Delta H - T\Delta S
\]

The enthalpies for the hydration of forsterite surfaces are obtained directly from our simulations (Table 1). The entropies of the gaseous water molecule have been taken from experimental entropies for temperatures between 400–1500 K\(^{20}\)

In order to calculate the Gibbs free energies of the adsorption processes, we now make two assumptions. Firstly, if we assume that the entropies of forsterite remain largely unaffected by the presence of the water molecule, then we need only take into account the change in entropy due to the loss of the free water molecule from the gaseous state. Secondly, we assume

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** Representative structures of the fractal (010) surface of forsterite (Mg = green, O = red, SiO\(_4\) tetrahedra = yellow).

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** Dissociated water adsorbed at (a) the reconstructed dipolar (010) surface, and (b) the stepped (110) surface of forsterite (Mg = green, O = red, H = white, SiO\(_4\) tetrahedra = yellow).

<table>
<thead>
<tr>
<th>Surface structure/orientation</th>
<th>Fraction of hydration sites</th>
<th>Adsorption energy/ (\text{kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>1/8</td>
<td>−320.2</td>
</tr>
<tr>
<td>Reconstructed dipolar (010)</td>
<td>1/6</td>
<td>−299.7</td>
</tr>
<tr>
<td>Stepped (110)</td>
<td>1/10</td>
<td>−334.2</td>
</tr>
</tbody>
</table>
In conclusion, using this simple Langmuir adsorption model, we have shown that retention of water at fractal surfaces of forsterite grains is thermodynamically possible at temperatures prevalent in the accretion disk, even at low partial pressures of gaseous water. Our calculations clearly strengthen the argument that adsorption to dust grains in the accretion disk could be a viable source of water for rocky planets. Indeed, our results strongly support models where water retention on mineral surfaces is responsible for the water content of the Earth.

Notes and references

20 D. R. Lide, CRC Handbook of Chemistry and Physics, Boca Raton, USA, 81st edn, 2000.