Where on Earth has our water come from?

Nora H. de Leeuw,*[a] C. Richard A. Catlow,[a] Helen E. King,[b] Andrew Putnis,[b]
Krishna Muralidharan,[c] Pierre Deymier,[c] Marilena Stimpfl[d] and Michael J. Drake[d]

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.[3–6] 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, combined or individually, these sources could not have delivered the bulk of the Earth's water. For example, comet contribution to the Earth's water budget is limited to no more than 15% by Ar/H_2O ratios[7] and the three long-period comets measured to date have a D/H ratio, which is about twice that of terrestrial seawater.[2] Similar isotopic arguments can be used to show that the input of water from asteroids is also restricted, despite the observation that they would be a dynamically plausible water source.[5] Therefore, we must assume either that these sources had a unique chemical composition or that they are not responsible for the bulk of the water on Earth.

Astronomical observations show that dust clouds around Young Solar Objects (YSOs) consist of Mg-rich olivine (Mg_2SiO_4, forsterite), pyroxenes and other refractory minerals with radii < 1 μm. Several authors suggest that these refractory minerals could coalesce by means of low-velocity impacts that would create low-density, irregularly shaped fractal structures.[8–10] In conjunction with recent astronomical observations by Eisner[11] that showed the presence of water vapour and atomic hydrogen in the dust and gas around the young stellar object MWC80 at 1 AU, we can postulate a scenario whereby water is incorporated into the Earth's building material by means of

[a] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK. E-mail: n.h.deleeuw@ucl.ac.uk; Fax: +44 (0)207 6797463; Tel: +44 (0)207 6791015
[b] Institut fuer Mineralogie, University of Muenster, Corrrenstrasse 24, 48149, Muenster, Germany
[c] Department of Materials Sciences and Engineering, University of Arizona, Tucson AZ 85721, USA
[d] Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721, USA
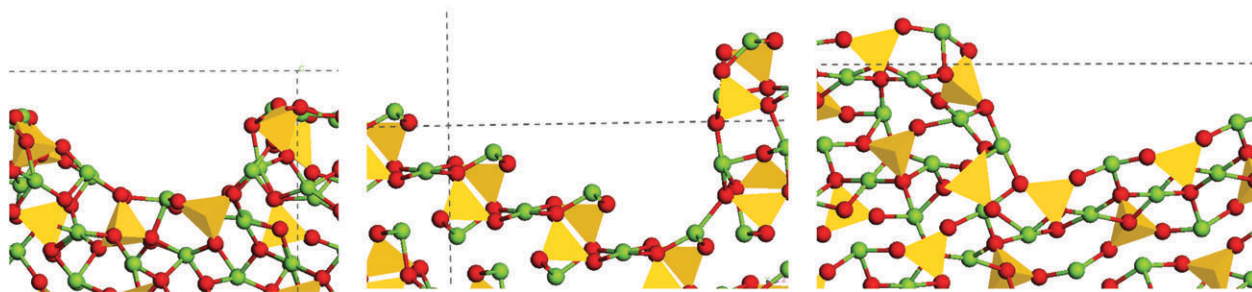
gas–solid interactions. Although theoretical estimates of the lifetime of gas in the accretion disk vary greatly from 0.1 My to 100 My,[12] even the lowest estimate should allow sufficient time for adsorption. If strong bonds could be developed during adsorption, the products would be resistant to desorption even at high temperatures.

Preliminary studies by Stimpfl et al.[13] and Muralidharan et al.[14] have shown that physisorption of water on defect-free terraces of forsterite surfaces at temperatures prevalent in the accretion disk could occur—a necessary preliminary to dissociation and chemisorption of the adsorbed water. However, these studies have not taken into account the real nature of the surfaces of such grains, which are highly fractal with a high proportion of low-coordinated surface sites. Here we show that dissociative chemisorption of water at such sites on the forsterite surfaces is highly exothermic, enabling water retention under the conditions of planetary accretion.

Our simulations are based on energy minimization, where we have employed atomistic simulation techniques based on the Born model of solids to model the dissociative adsorption of water at a range of fractal surfaces of forsterite. The interatomic potential functions used to model the surface-water systems have been successfully applied previously to both associative and dissociative adsorption of water at mineral surfaces, and these have shown that the calculated adsorption energies and structures for smaller surface systems are in excellent agreement with both electronic structure calculations and experiment. For example, associative adsorption of water at the planar (010) surface of forsterite was calculated to release 119 kJ mol^{-1} using Density Functional Theory simulations[15] and 124 kJ mol^{-1} with the interatomic potential model.[16] Temperature programmed desorption (TPD) studies of water desorption from a range of mineral surfaces have measured binding energies for water chemisorption of 145–170 kJ mol^{-1} for CaO and approximately 200 kJ mol^{-1} for the SiO_2 quartz surface,[17] compared to calculated energies of 160–180 kJ mol^{-1} and 214 kJ mol^{-1}, respectively, for the same systems,[18,19] 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

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

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):

$$\text{Surface} + \text{H}_2\text{O}_{(g)} \xrightleftharpoons{K} \text{Surface} \cdot (\text{H}_2\text{O}) \qquad (1)$$
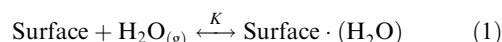
where K is the equilibrium constant for the above reaction, Surface is the mineral surface before water adsorption and Surface$^\bullet$(H$_2$O) is the system after adsorption. The equilibrium constant K is then calculated as shown in eqn (2), from the

Gibbs free energy G of adsorption, where $a_{(s)}$ and $a_{(g)}$ 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, $P_{\text{H}_2\text{O}_{(g)}}$ 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.

$$k = \frac{a_{(s)}}{a_{(g)}a_{(\text{surface})}} = \frac{x}{(1 - xP_{\text{H}_2\text{O}_{(g)}})} = e^{-\Delta G^0/RT} \qquad (2)$$

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 ΔH is the enthalpy of the adsorption process per water molecule, T is the temperature of interest and ΔS is the change in entropy.

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

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
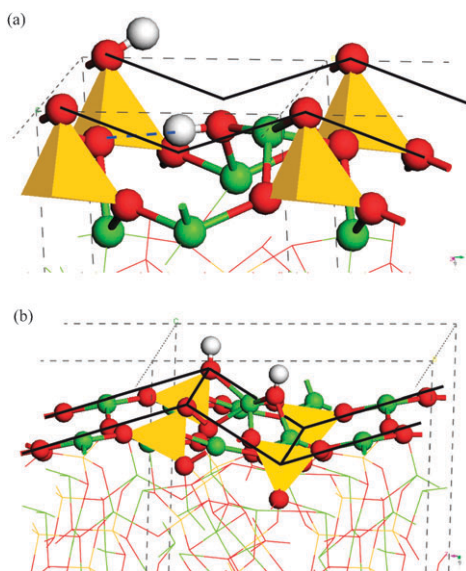

Fig. 2 Dissociated water adsorbed at (a) the reconstructed dipolar (010) surface, and (b) the stepped (110) surface of forsterite (Mg = green, O = red, H = white, SiO$_4$ tetrahedra = yellow).

Table 1 Adsorption energies calculated for each of the surfaces studied and the coverage generated by the adsorption of a single dissociated water molecule

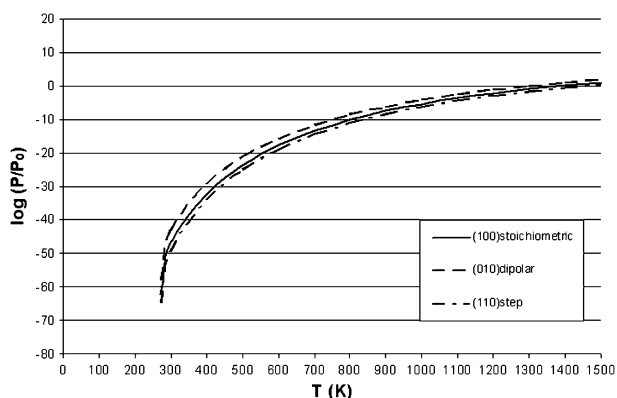| Surface structure/ orientation	Fraction of hydration sites	Adsorption energy/ kJ mol^{-1}
(100)	1/8	−320.2
Reconstructed dipolar (010)	1/6	−299.7
Stepped (110)	1/10	−334.2

Fig. 3 Partial pressures required to retain chemisorbed water at the modelled surface features for temperatures expected in the accretion disk.

that in calculating the temperature dependence of the free energies of the adsorption processes we need only take into account the temperature dependence of the entropy of the gas phase water. Taking into account these two approximations, which previous work has shown to be acceptable,[21,22] we can calculate the Gibbs free energies for the adsorption processes, according to eqn (3) and using these calculated Gibbs free energies at each temperature, we can calculate from eqn (2) the partial pressures of water at which this adsorption would occur.

The partial pressure *versus* temperature plots for the dissociative adsorption of water at the different surface sites, listed in Table 1, are shown in Fig. 3. If adsorption is a potential delivery source of water, then it is likely that it began at the initial stages of planet accretion, when dust and gas were still present in the accretion disk, with the thermodynamic conditions during the initial stages characterized by partial pressures (P_{H_2O}) of around 10^{-8} bars[23] and high temperatures of 500–1500 K.[1] Fig. 3 shows that on the three surfaces discussed above, adsorption of water could occur up to approximately 900 K at the low partial pressures of water prevalent in the early accretion disk, *i.e.* well within the required temperature range.

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[4] where water retention on mineral surfaces is responsible for the water content of the Earth.

Notes and references

1 A. P. Boss, *Annu. Rev. Earth Planet. Sci.*, 1998, **26**, 53.
2 M. J. Drake and K. Righter, *Nature*, 2002, **416**, 39.
3 F. Ciesla and D. Lauretta, *Earth Planet. Sci. Lett.*, 2005, **231**, 1.
4 M. J. Drake, *Meteorit. Planet. Sci.*, 2005, **40**, 519.
5 J. I. Lunine, J. Chambers, A. Morbidelli and L. A. Leshin, *Icarus*, 2003, **165**, 1.
6 A. Morbidelli, J. Chambers, J. I. Lunine, J. M. Petit, F. Robert, G. B. Valsecchi and K. E. Cyr, *Meteorit. Planet. Sci.*, 2000, **35**, 1309.
7 M. J. Drake and H. Campins, *Asteroids, Comets, Meteors, Proc. IAU*, 2005, **229**, 381.
8 J. Blum and G. Wurm, *Icarus*, 2000, **143**, 138.
9 M. E. Fogel and C. M. Leung, *Astrophys. J.*, 1998, **501**, 175.
10 S. J. Weidenschilling and J. N. Cuzzi, *Protostar and planets vol. III*, University of Arizona Press, Tucson, 1999.
11 J. A. Eisner, *Nature*, 2007, **447**, 562.
12 B. Fegley Jr., *Space Sci. Rev.*, 2000, **92**, 177.
13 M. Stimpfl, A. M. Walker, M. J. Drake, N. H. de Leeuw and P. Deymier, *J. Cryst. Growth*, 2006, **294**, 83.
14 K. Muralidharan, M. Stimpfl, N. H. de Leeuw and M. J. Drake, *Icarus*, 2008, **198**, 400.
15 N. H. de Leeuw, *J. Phys. Chem. B*, 2001, **105**, 9747.
16 N. H. de Leeuw, S. C. Parker, C. R. A. Catlow and G. D. Price, *Phys. Chem. Miner.*, 2000, **27**, 332.
17 B. Fubini, V. Bolis, M. Bailes and F. S. Stone, *Solid State Ionics*, 1989, **32/33**, 258.
18 N. H. de Leeuw, G. W. Watson and S. C. Parker, *J. Phys. Chem.*, 1995, **99**, 17219.
19 Z. Du and N. H. de Leeuw, *Surf. Sci.*, 2004, **554**, 193.
20 D. R. Lide, *CRC Handbook of Chemistry and Physics*, Boca Raton, USA, 81st edn, 2000.
21 Z. Du and N. H. de Leeuw, *Dalton Trans.*, 2006, 2623.
22 N. H. de Leeuw and T. G. Cooper, *Geochim. Cosmochim. Acta*, 2007, **71**, 1655.
23 K. Lodders, *Astrophys. J.*, 2003, **591**, 1220.