Supplementary Material

1 ADDITIONAL QM/MM TECHNICAL DETAILS

The electrostatic embedding QM/MM method is implemented here using the CP2K package (CP2K, 5.1, 2017) where QM is simulated by the quickstep method (VandeVondele et al., 2005) and MM by FIST (Mundy et al., 2017). For the QM part, density functional theory (DFT) is adopted in which Goedecker-Teter-Hutter (GTH) pseudopotentials (Krack, 2005) and the Perdew-Burke-Ernzerhof (PBE) (Perdew et al., 1996) exchange correlation functional are used together with the D3 empirical dispersion correction (Grimme et al., 2010). The double-ζ valence polarised (DZVP-MOLOPT-SR-GTH), MOLOPT (VandeVondele and Hutter, 2007) basis set has been selected for all QM atoms except water for which single-ζ valance basis was selected to reduce computational costs.The HBs between diaspore-water and between water molecules could be well defined using these basis sets (Kubicki, 2016). The SCF convergence threshold of 10^{-5} hartree was chosen. The counterpoise scheme (Boys and Bernardi, 1970) is used to correct the basis set superposition error (BSSE) for interaction energies.

For the MM part of the modeled system, the bottom three layers of diaspore surface (480 atoms) has been modeled with CLAYFF force fields (Cygan et al., 2004), water with SPC based water model (Berendsen et al., 1987) and IHP/GP using the CHARMM force fields obtained via SwissParam force field generation tool (Zoete et al., 2011). The SPC based water model is compatible with both CLAYFF and CHARMM force fields. More details about force fields used here are given in (Ganta et al., 2019). The QM/MM coupling driver is part of the CP2K package, namely we used the gaussian expansion of the electrostatic potential method (GEEP) (Laino et al., 2006). The QM/MM simulations here are performed within a canonical (NVT) ensemble that means simulation of molecular systems at constant number of atoms (N), volume (V), and temperature (T).

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2 FIGURES

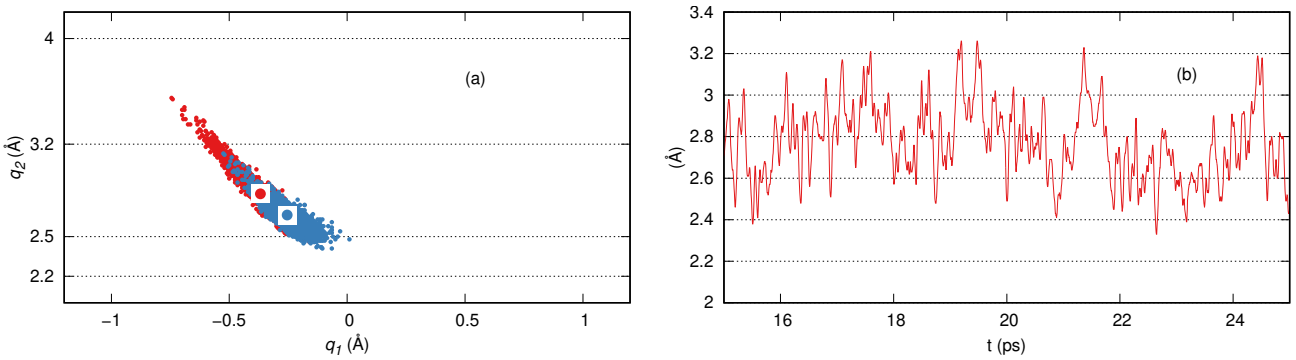

Figure S1: Correlation plot of hydrogen bond (HB) length (q_2) and deviation of the H atom from the HB center (q_1) of two HBs formed between the diaspore surface and water for the diaspore–GP–water **M** motif (a) Al1-O11 bond length for the diaspore–IHP–water **M(2)** motif (b).

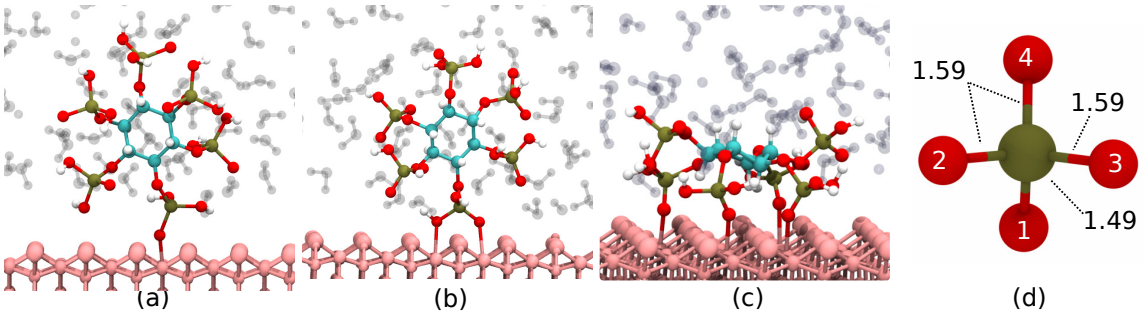

Figure S2: Diaspore–IHP–water initial binding motifs, **M(1)** case intial motif: **M** (a), **M(2)** case intial motif: **B** (b), **2M** case intial motif: **4M** (c), free tetrahedral PO_4^{3-} (d).

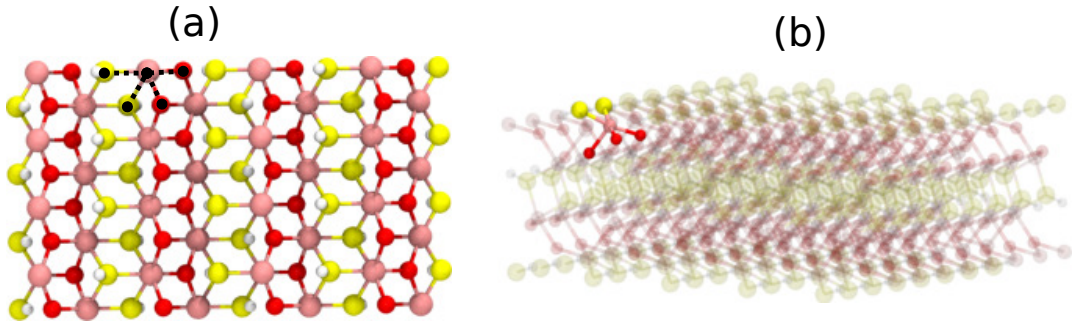

Figure S3: Side view of the neutral and pure 010 and 100 diaspore surface planes. Surface Al atoms of the diaspore 010 surface plane are coordinated by four oxygen atoms (a) and 100 diaspore surface plane are coordinated by five oxygen atoms (b). Pink, red, yellow and white colors correspond to Al, bridging oxygen, hydroxyl oxygen and hydrogen respectively.

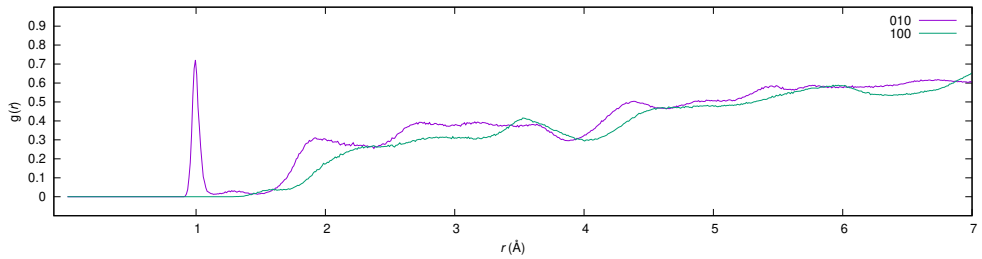

Figure S4: Comparison of radial distribution functions calculated for the 010 and 100 diaspore surface oxygen atoms and water hydrogen atoms.

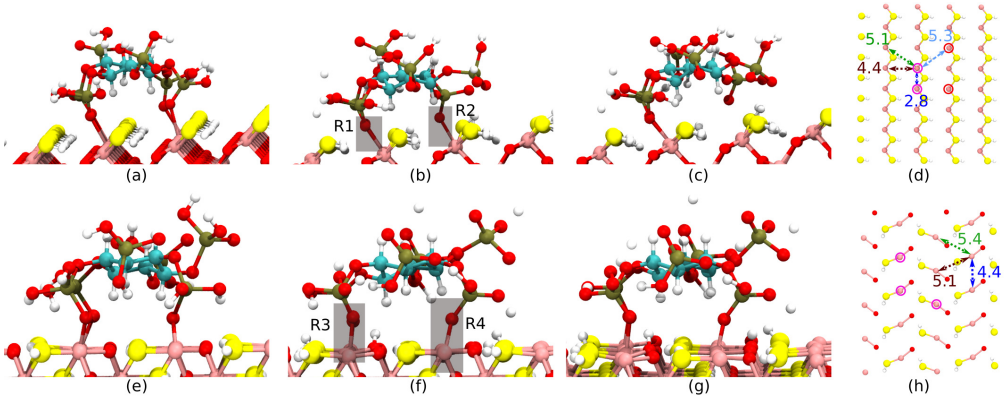

Figure S5: Snapshots along the MD trajectory for the 100 diaspore–IHP–water **2M** motif (a-c) and the top view of surface atoms showing interatomic Al-Al distances (d). Similarly, the snapshots of **3M** motif (e-g) and top view of surface atoms showing interactomic Al-Al distances (h). The circle around Al atom denote the site of Al-O_P bonds in **2M** and **3M** motif, respectively wherein the red circle denotes the site where Al-O_P bond dissociated. Note that water is ignored in this image for better view.

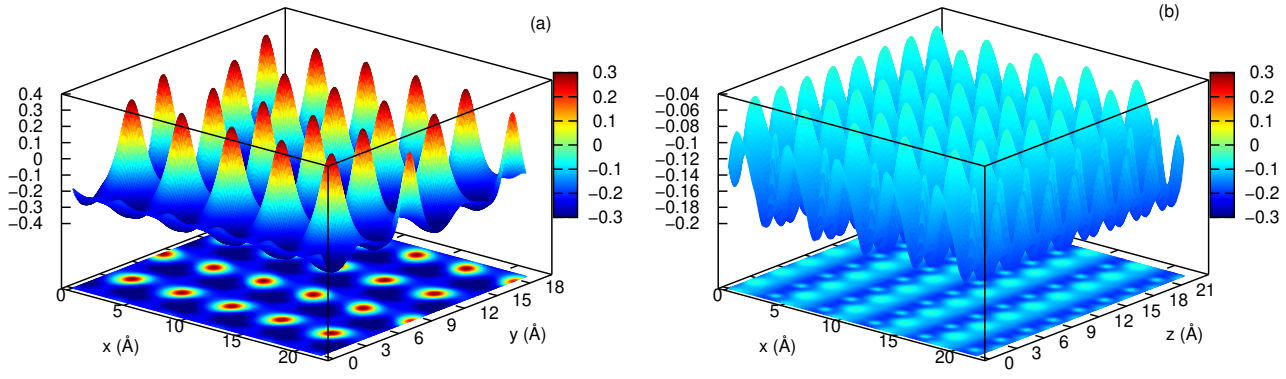

Figure S6: Electrostatic potential (a.u.) at 1 Å (perpendicular to surface) for the bare 010 diaspore surface plane (a) as well as for the bare 100 diaspore surface plane (b). These have been calculated for bare surfaces without involving phosphates and water.