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Supplementary Information:

QM/MM simulations of organic phosphorus adsorption at the diaspore-water interface

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1. Force fields used in the current simulations

The MM level interaction between the diaspore (α -AlOOH) surface and water is defined based on the CLAYFF force fields [S1]. It is to be noted that the CLAYFF force fields are compatible with SPC water model. The total energy of the MM system using CLAYFF is given by:

$$E_{\rm sys} = E_{\rm bond} + E_{\rm angle} + E_{\rm vdW} + E_{\rm coulomb}$$

where, E_{bond} and E_{angle} are energies due to bond stretching and angle bending. E_{vdW} and $E_{coulomb}$ denote energies due to van der Waals (vdW) and electrostatic interactions. The total energy is sum of bonded interactions (bond/angle) and nonbonded interactions (vdW and electrostatic). The bond stretching energy is defined as:

$$E_{bond} = k_b (r_{ij} - r_0)^2$$

where, k_b denotes force constant, r_{ij} denotes distance between i, j atoms, and r_0 denotes equilibrium bond length. Similarly the energy of the angle bend is given by:

$$E_{angle} = k_{\theta} (\theta_{ijk} - \theta_0)^2$$

where, k_{θ} denotes a force constant, θ_{ijk} is bond angle between i, j and k atoms and θ_0 is equilibrium bond angle.

bond stretch				
species i	species j	-	$k_{\rm b}~(\rm kcal/mol {\rm \AA}^2)$	$r_0(\rm{\AA})$
water hydrogen	water oxygen		554.1349	1.0
hydroxyl hydrogen	hydroxyl oxygen		554.1349	1.0
	angle bend			
species i	species j	species k	$k_{\theta} \; (kcal/mol rad^2)$	$\theta_0 \ (deg)$
water hydrogen	water oxygen	water hydrogen	45.7696	109.47
aluminium	hydroxyl oxygen	hydroxyl hydrogen	30.0	109.47

Table S1: Bond and angle parameters for diaspore and water

The short range vdW interaction energy is represented as:

$$E_{vdW} = \sum_{vdW}^{i < j} D_{o,ij} \left[\left(\frac{R_{o,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{o,ij}}{r_{ij}} \right)^{6} \right]$$

where, $D_{\mathrm{o},ij}$ and $R_{\mathrm{o},ij}$ are empirical parameters. For unlike atoms, the parameters can be calculated using:

$$\begin{split} R_{o,ij} &= \frac{1}{2}(R_{o,i}+R_{o,j})\\ D_{o,ij} &= \sqrt{D_{o,i}D_{o,j}} \end{split}$$

The long range coulomb interaction energy is given by:

$$E_{\rm coulomb} = \sum_{\rm coulomb}^{i < j} e^2 \frac{q_i q_j}{4\pi \epsilon_0 r_{ij}}$$

species	charge (e)	$D_0(kcalmol^{-1})$	$R_0(\text{\AA})$
water hydrogen	0.41		
water oxygen	-0.82	0.1554	3.5532
bridging oxygen	-1.05	0.1554	3.5532
aluminium	1.575	1.3298e-6	4.7943
hydroxyl hydrogen	0.425		
hydroxyl oxygen	-0.95	0.1554	3.5532

Table S2: Nonbonded parameters for diaspore and water

where, q_i, q_j denote partial charges, e denotes electron charge and ϵ_0 is the dielectric permittivity of vacuum.

The MM level interaction between IHP/GP and water is defined with the CHARMM force field parameters obtained from SwissParm, a force field generation tool [S2]. Here also, the water is defined based on the SPC water model.

species	charge (e)	$D_0(kcalmol^{-1})$	$R_0(Å)$
CR	0.2800	0.0550	3.8754
O2CM	-0.7000	0.1200	3.0290
ORC2P	-0.5512	0.1520	3.1537
ORPOH	-0.7712	0.1520	3.1537
ORCOH	-0.6800	0.1520	3.1537
PO4	1.5136	0.5850	3.8308
HCMM	0.0000	0.0220	2.3519
HOCO	0.5000	0.0460	0.4000
HORCOH	0.4000	0.0460	0.4000

Table S3: Nonbonded parameters for IHP, GP



Figure S1: IHP and GP color-coded to denote atoms listed in Table S3.

2. Description and validation of the present QM/MM approach

For the current applied electrostatic embedding QMMM approach, the MM parameters are used for calculating

- interaction between the MM subsystems
- coupling interaction between the QM and MM subsystems

The whole MM subsystem consists of two subsystems, 1- bottom six layers of diaspore surface (480 atoms) and 2about 175 water molecules in the simulation box. Here, the CLAYFF parameters for the diaspore surface and the SPC model parameters for water molecules (which are completely compatible with the CLAYFF parameters) are sufficient to simulate the diaspore-water interactions.

Regarding QM and MM coupling the following approach is implemented:

- QM(water+diaspore+IHP/GP) interaction with MM(diaspore): Here, water_{QM} diaspore_{MM} and diaspore_{QM} diaspore_{MM} interactions are defined with respect to two compatible force fields CLAYFF and SPC based water model. Regarding IHP/GP_{QM} diaspore_{MM} interactions, the long range interactions are ignored, since the corresponding parameters are not available.
- QM(water+diaspore+IHP/GP) interaction with MM(water): Here, MM water is defined based on SPC water model which is compatible with both CLAYFF (diaspore) and CHARMM (IHP/GP) force fields.

To validate our approach, pure QM(DFT) NVT-MD simulation using IHP 2M(1) model is performed for 5 ps. The trajectory analysis showed similar pair correlation functions between the corresponding QM and QMMM trajectories, please refer Fig. S2. In addition, the trajectories obtained using pure QM and QMMM have similar Al-O-P bond formations, please ref Fig. S3.

3. Modeling of diaspore surface with unsaturated active sites

- Diaspore has a point of zero charge (PZC) around 6 [S3, S4]. This means that below pH 6 the surrounding water molecules will dissociate and donate more protons than hydroxyl groups to the diaspore surface leading to a positively charged surface. This explains that the diaspore surface at pH below 6 will be partially unsaturated and has the ability to attract/adsorb anions such as phosphate and/or hydroxyl groups at its surface. Hence, this adsorption process (or binding reaction) could happen mainly by direct reaction to the unsaturated surface centers (active sites) without need for a ligand-exchange mechanism. Conversely, above pH 6 the surface will be negatively charged and more saturated by hydroxyl groups from water. Here the surface saturation will increase upon increasing the solution pH and the surface will have the ability to attract cations and repel anions. Under these conditions, the chemisorption process of anions at surfaces (i.e. inner-sphere complexes) should take place via a ligand-exchange mechanism. Considering the fact that most soils and especially forest soils are acidic [S5, S6], gives the motivation to model the diaspore surface as a partially unsaturated one.
- In addition to the poor knowledge of the molecular reaction mechanisms of the phosphate binding at the diaspore surface, diaspore has been modeled in the current contribution for two main reasons. The first one is that diaspore

is isomorphous with goethite (α -FeOOH) which is most abundant and common mineral containing iron atom in the form of ferric (Fe⁺³). Hence, by investigating the adsorption process at both diaspore and goethite surfaces with same degree of unsaturation the effect of central metal ion (Fe/Al) on adsorption process could be understood in more detail. The second reason is arising from the fact that Fe/Al hydroxide mixtures are highly abundant in soils thus affecting P fixation and release. It is to be noted that goethite has PZC around 9 [S3]. Therefore, goethite surface will be unsaturated below pH 9 and thus can adsorb phosphate and form inner-sphere complexes via a direct interaction mechanism and not a ligand-exchange one. Keeping in mind the PZC of diaspore and goethite one may expect the amorphous Fe/Al hydroxide mixtures should have PZC values in the range of pH 6-9. So according to reported PZC values, which are in that range, a more realistic model for both diaspore and goethite should be partially unsaturated and not saturated completely. This holds true unless one is studying a high pH range which, however, is not in the focus of the present investigation.

• It is well-known from sorption experiments that the phosphate adsorption decreases with increasing the soil solution pH [S7, S8]. This means that in the presence of OH⁻ at high pH, OH⁻ groups can replace the adsorbed phosphate indicating a stronger adsorption for OH⁻ than for phosphate at mineral surfaces. This behaviour has been observed and explained in more details at a molecular level by our group [S9, S10]. The modelling results indicated that phosphate can replace the competing water molecules at the goethite surface, but phosphate could be replaced by OH⁻ groups. This shows that the reverse reaction, i.e. replacement of OH⁻ groups by phosphate, is mainly a non-spontaneous reaction and unlikely to take place. This indicates that formation of inner-sphere complexes of phosphate with goethite/diaspore surfaces could happen mainly due to direct reaction of phosphate with the surface unsaturated centers and not with a ligand-exchange mechanism. Consequently, this points to the necessity of the presence of some unsaturated centers at the mineral surface to form inner-sphere complexes with phosphates.

4. Model conditions (soil pH and pKa for phosphates)

As mentioned in the previous section and according to the diaspore's PZC value, we are simulating common and normal acidic soil conditions, i.e. at pH in the range of 3-6. Consequently, the diaspore surface was modeled with active unsaturated centers. According to the best of our knowledge, there are some differences and conflicts between the available pKa values for IHP and GP. For example, the estimated pKa values by the "ChemAxon" software are 0.14 for IHP and 1.5 for GP. Experimentally, it was mentioned that IHP is a relatively reactive phosphate compound having 12 dissociable protons with pKa values in the range of about 1.5 to 10 [S11]. In view of these conflicts, we have started our simulation with the neutral forms for both IHP and GP. However, we have observed deprotonation of the phosphates (IHP and GP) in the first few pico-seconds (ps) of the simulation trajectories (see Figs. S7 and S8), according to the acidic character of these phosphates which is thus properly taking into account by our modelling approach.

5. Proton transfer in the bulk and at the interface

The proton transfer events have been triggered by the surface. But in general, these processes could take place either in the presence or absence of the surface (i.e. for simulations carried out in the bulk). To investigate such goal practically, two additional MD simulations have been performed with the same applied approach. One simulation was carried out with GP in the presence of the diaspore surface with a separation distance of about 5 Å between them. The second simulation involved GP in a pure water without diaspore. Both simulations showed proton transfer processes during the simulation trajectory (see Figs. S7 and S8).

6. Description of the interaction energy calculations

In general, the effect of water on the calculated diaspore-phosphate interaction has been considered during the MD trajectory due to the diaspore-phosphate-water interactions based on the electronic and Van der Waals interactions. Here phosphate refers to GP and IHP. However, this effect has not been considered explicitly for computing the interaction energy in Eq. 1. In practice, each diaspore-phosphate-water model could be considered as three sub-systems (fragments). These fragments are diaspore (fragment1), IHP/GP (fragment2) and water (fragment3). Within CP2K it is possible to calculate the pair interaction energy between two fragments. According to Eq. 1 of the main paper

$$E_{int} = E_{diaspore-phosphate-complex} - (E_{diaspore} + E_{phosphate}),$$

we have defined diaspore as the first fragment and phosphate as the second fragment. Water enters only insofar as it determines the actual geometry of the interacting fragments. The interaction energy is calculated within the BSSE counterpoise correction philosophy, i.e. by performing five energy calculations as follows: diaspore including only the diaspore basis functions ($E_{diaspore}^{diaspore}$), total electronic energy of phosphate including only the phosphate basis functions ($E_{phosphate}^{phosphate}$), diaspore including the basis functions of phosphate and diaspore ($E_{diaspore}^{diaspore+phosphate}$) and finally diaspore-phosphate complex including the basis functions of diaspore and phosphate ($E_{diaspore+phosphate}^{diaspore+phosphate}$) and finally diaspore-phosphate complex including the basis functions of diaspore and phosphate as $E_{int} = E_{diaspore+phosphate}^{diaspore+phosphate}$. From these numbers one gets the interaction energy between diaspore and phosphate as $E_{int} = E_{diaspore-phosphate-complex}^{diaspore+phosphate} - (E_{diaspore}^{diaspore+phosphate})$. Similarly, the interaction energies between phosphate and water ($E_{int} = E_{phosphate-complex}^{phosphate+water} - (E_{phosphate}^{diaspore+water} + E_{phosphate}^{phosphate+water})$) and between diaspore and water ($E_{int} = E_{diaspore-phosphate-complex}^{diaspore+water} - (E_{diaspore+phosphate}^{diaspore+water})$) could be calculated.

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FIGURES



Figure S2: Comparison of pair correlation functions calculated using QM and QMMM methods. Al of diaspore and oxygens of water (a), oxygens of diaspore and hydrogens of water (b), hydrogens of IHP and oxygens of water (c), oxygens of IHP and hydrogens of water (d). The red and black lines denote correlation function obtained using QM method and QMMM method respectively.



Figure S3: Snapshots along the trajectory of IHP 2M(1) model simulated using QM (DFT) only. Initial M(O + Al) motif (a), proton transfer from O13 and O62 to surface (b), proton sharing between P1 and P6 phosphate groups (c), and formation of Al2-O61 covalent bond (d). Similar events are observed in IHP 2M(1) model trajectory simulated using QM/MM.



Figure S4: GP \mathbf{M} motif potential energy (top), temperature (middle), root mean square deviation (RMSD, bottom) along MD trajectory. This figure suggests that the GP \mathbf{M} motif diaspore-GP-water complex is equilibrated within the first 10 ps of the whole trajectory.







Figure S5: Interatomic distances between phosphorus and corresponding oxygens of orthophosphate (a), GP **M** motif (b), GP **B** motif (c), IHP **2M(1)** motif (d), IHP **2M(2)** motif (e), IHP **3M** motif (f). Note that P-O-Al angle is also provided for relevant cases, where O and Al are covalently bonded. Only Al bonded phosphate groups and Al are shown in all motifs for better visualisation.



Figure S6: Interatomic distances between Al-nonbonded oxygens in phosphate group and Al. GP M motif (a), GP B motif (b), IHP **2M(1)** motif (c), IHP **2M(2)** motif (d), IHP **3M** motif (e).



Figure S7: Snapshots along 10 ps trajectory of diaspore-GP-water model with GP above 5 Å from diaspore surface. Initial configuration (a), proton transfer from O3 to water (b), proton transfer from O2 to water (c) and (d).



Figure S8: Snapshots along 10 ps trajectory of GP-water model. Initial configuration (a), proton transfer from O3 to water (b), proton transfer from O5 to water (c) and proton transfer from O2 to water (d).



Figure S9: HB correlation q_2 vs. q_1 of a few diaspore oxygens and water molecules in GP **M** motif (a), (b) and HBs strength between O1, O2 and protons transferred to diaspore in GP **B** motif (c). Here, the symbols $*, \bullet$ and \checkmark denote strong to moderately strong HB, moderately strong HB and moderately strong to weak HB respectively.



Figure S10: Al-O bond lengths in GP \mathbf{B} motif with \mathbf{B} motif along MD trajectory. Observe that a stable \mathbf{B} motif is maintained until the end of the trajectory.



Figure S11: HB correlation q_2 vs. q_1 of selected HBs observed in IHP/GP with water. Observe that IHP and GP often formed moderately strong HBs with water.



Figure S12: In IHP 2M(1) motif, distance between surface Al1 contributed to M motif and all phosphorus atoms in IHP (a), distance between surface Al1 contributed to M motif and bonded phosphate oxygens (b), distance between a few different surface Al and water oxygens (c), distance between a few different diaspore oxygens and water hydrogens (d).



Figure S13: Al-O bond lengths in IHP **2M(2)** motif along MD trajectory. Observe disassociation of Al1-O11 and formation of Al2-O62 resulting in **2M** motif until the end of the trajectory.