The mechanism of Clay swelling

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INTRODUCTION

With the increased use of dredged materials for building, it has become more important to understand clay mineral behaviour and its impact on sediment strength and stability [1]. Clays, such as montmorillonite (MMT), have been observed to expand in a step-wise fashion when in contact with water in a process called clay swelling [2]. The mechanism underlying such abrupt change of clay thickness and how it affects the stability of sediment are not clear. The aim of this study is to use molecular dynamics to investigate how water adsorption occurs in clay swelling and how clay minerology affects this process.

METHODOLOGY

All the molecular dynamics simulation are performed with LAMMPS [3] package. A MMT particle consisting of two nano-layers was placed in a water box of 2.1*10*10 nm^3 (*Fig. 1*). Each layer contains 8 $Si_8(Al_{3.25}Mg_{0.25})O_{20}(OH)_4$ units, leading to a charge of -0.75 e/unit. Sodium (Na), potassium (K) and calcium (Ca) were placed in the interlayer region to balance the charge, with 12, 12 and 6 ions, respectively. The interactions between atoms were described with the swell-CLAYFF forcefield [4], which includes both pair-wise Lennard-Jones interaction (accounts for Pauli repulsion and Van der waals attraction) and coulombic (electric) interaction. The simulation was equilibrated under isothermal-isobaric ensemble with 300 K temperature and 1 atm pressure. Throughout the simulation, the bottom layer was kept fixed. The top layer was fixed for the 1 ns simulation, and was allowed to move vertically afterwards. A timestep of 1fs was applied for the first 1ns simulation, and a timestep of 0.5 fs was applied for the following simulation.

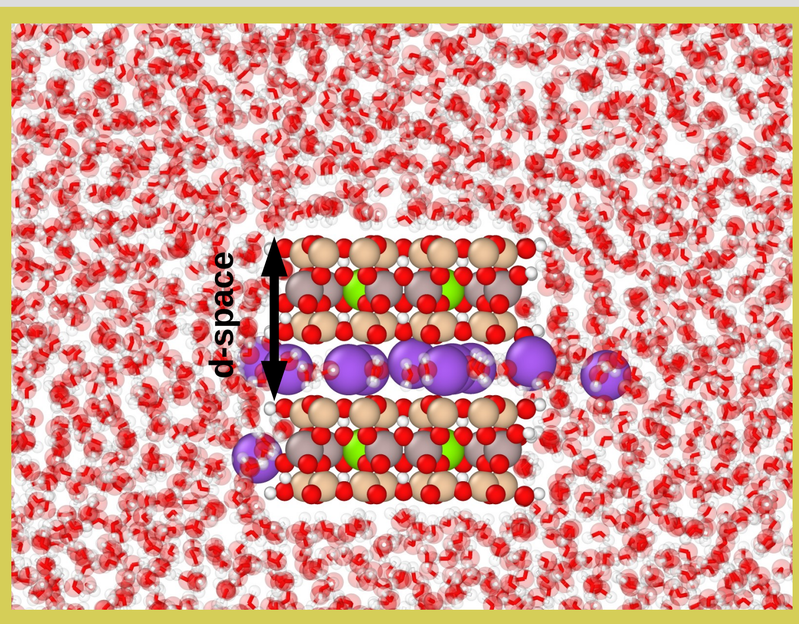

Fig. 1 Geometry, atoms presented are Na (purple), Si (silicon, brown), Al (grey), Mg (green), H (clay hydrogen, white), H_w (water hydrogen, white stick), O_w (water oxygen, red stick) and O_b (clay oxygen, red). D-space is the sum of layer thickness and interlayer distance.

RESULT

- The simulation identifies slow swell from one water layer (1W) to two water layer hydration state (2W) for case Na12 (*Fig. 2 (a)*), stable 1W state for K12 (*Fig. 2 (b)*) and a quick swell from 1W to 2W for case Ca6 (*Fig. 2 (c)*). Step-wise transition is observed for the cases Na12 and Ca6.

- 1W-2W transition is linked to the Na detaching from clay oxygen (O_b) and hydration with water (i.e., bond with O_w), see *Fig. 3 (a)*, *(b)*. As a result, the Ow profile shifts from one peak around Na at 1W state (*Fig. 3 (c), (d)*) to two peaks around Na at 2W state (*Fig. 3 (e)*). The relatively lower peaks at higher *z* position in *Fig. 3 (d), (e)* are due to the flocculation of the top clay layer.

- Analysis shows a decreasing clay-cation interaction, decreasing hydration capacity and increasing cation migration speed, for Ca, Na and K (*Fig. 4*). The radial distribution function of cation and O_w supports such descending tendency in hydration capacity.

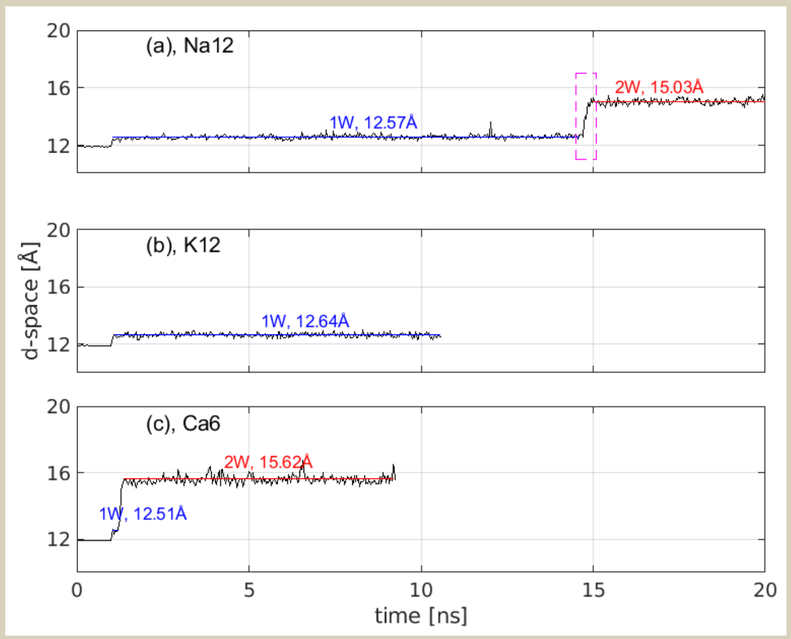

Fig. 2 Top left, swell of MMT, of (a), case Na12, with 12 Na in interlayer; (b), case K12, with 12 K; and (c), case Ca6, with 6 Ca.

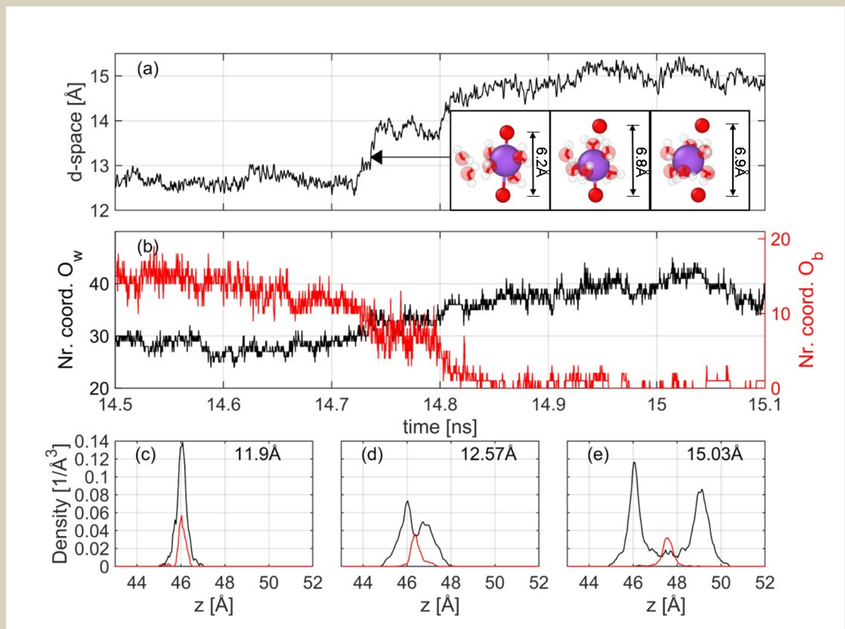

Fig. 3 Top right, detailed 1W-2W swell process of case Na12 (zoom in plot of magenta rectangle in Fig. 2 (a)), showing (a), the change of d-space, (b) change in the number of coordinated Ow and O_b, where coordinated oxygen is defined as within 3 Å radius of cation. The illustration plot in (a) describes a detachment of Na from O_b and a form of bond with O_w. The density profile of O_w (black) and Na (red) at interlayer space is present in (c) at d-space of 11.9 Å; (d), 12.57 Å (1W) and (e) 15.03 Å (2W).

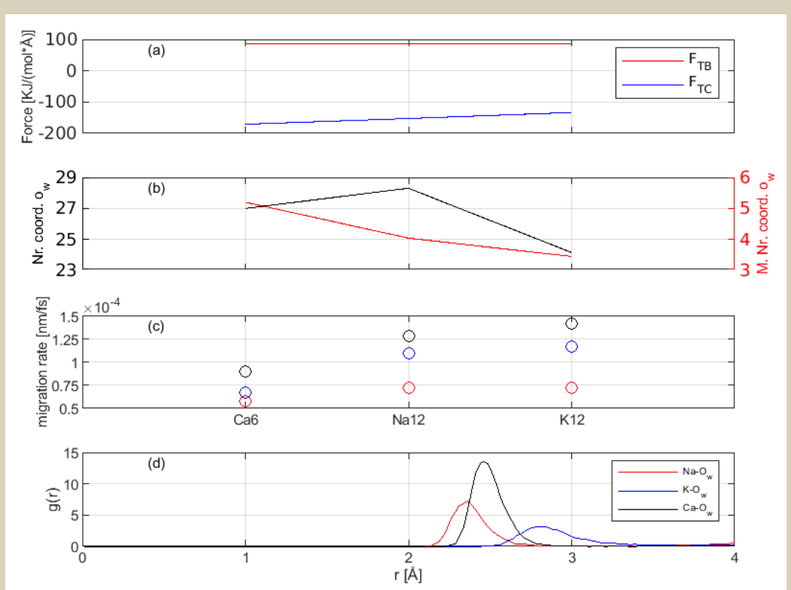

Fig. 4 Bottom, analysis of (a), force imposed on top layer, from bottom layer (F_{TB}), cation (F_{TC}); (b) number of coordinated Ow and mean Ow for each interlayer cation; (c), migration rate of cation in interlayer region (red circle), 1nm away from clay (blue circle) and bulk water (black); (d) radial distribution of cation and O_w.

DISCUSSION & CONCLUSION

- This study reproduced the free swell of MMT layers in clay hydration, in particular, the step-wise 1W-2W transition was captured.
- The mechanism underlying 1W-2W MMT swell is found to be the detachment of cations from the clay surface along with the their full hydration.
- The various hydration behavior of Ca-, Na- and K-MMT depends on the hydration capacity of the cations as well as the cation migration speed.
- Although the hydration of cation is responsible for the 1W-2W transition, cation provides the dominant attractive force in stabilizing the 1W and 2W hydration states.
- Future work should look into the effect of water chemistry on the swelling behavior of clay, as this can be an important point for the safety use of dredged materials.

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