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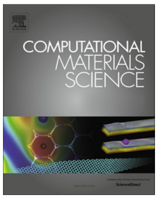

# Influence of interlayer cations on structural properties of montmorillonites: A dispersion-corrected density functional theory study

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ABSTRACT

Dispersion-corrected density functional theory calculations are performed to investigate the structural distortions and counterion positions of montmorillonites (MMTs) with different alkali ($Li^+$, $Na^+$, $K^+$) and alkaline-earth ($Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$) cations. The determined interlayer thickness varies in a quadratic function manner with the ionic radius of counterions. Moreover, as the size of counterion increases (from $Mg^{2+}$ to $K^+$), the tetrahedral sheet thickness increases and the octahedral sheet thickness decreases slightly. In addition, the counterions have notable effect on the tetrahedral sheet distortions and the intercalation of larger cations leads to smaller rotation and tilting of tetrahedral sheets. The counterion is in the region bounded by two opposite ditrigonal cavities but is not located symmetrically between them. The cation with larger radius deviates from the center of the ditrigonal cavity near it. The valence state also affects the location of counterion in the interlayer and the higher charge cation tends to lie closer to the middle of the interlayer space with respect to the cations with the similar size.

## 1. Introductions

Montmorillonite (MMT), which is widely distributed in soils and sedimentary rocks, is one kind of clay minerals [1]. Its characteristic physicochemical properties, such as swelling, adsorption, catalysis, and ion-exchange [2–4], enable it have extensive applications in water pollutant removal, radioactive waste storage, petroleum exploitation and cosmetics [5–14]. In addition, MMT can be used in organic–inorganic hybrid nano-composites to improve mechanical, thermal, optical and chemical properties [15–22]. On the other hand, the swelling of MMT with water adsorption may impact the stability of engineering structure seriously, which is undesirable in civil engineering and mining engineering [23–25]. A very important factor that affects the nature and behavior of MMT is the type of cations located in the interlayer space.

As a member of 2:1 dioctahedral phyllosilicates, MMT is composed of a stack of separated silicate layers in which one octahedral (O) alumina sheet sandwiched between two tetrahedral (T) silica sheets. The crystal layers of MMT are negatively charged for isomorphic substitution of ions in octahedral sheets ($Al^{3+}$ by $Mg^{2+}$) and tetrahedral sheets ($Si^{4+}$ by $Al^{3+}$), so cations should be absorbed in the interlayer to compensate the layer charge, known as the interlayer counterions. The interlayer counterions could be exchanged in hydrated state. During the hydration of interlayer cations, water molecules can enter the interlayer spacing and form a discrete number of water layers, the number of water layers can increase from zero to three [6]. Correspondingly, different hydration states are defined for MMT: dehydrated (0 W), monohydrated (1 W), bihydrated (2 W), and trihydrated (3 W) [26]. Moreover, the variation of the counterions would change the structure of MMT to some extent [27,28], and further influence its properties such as swelling and adsorption [29–34]. The impact of the counterions to the MMT structure is associated with their locations in the interlayer and the interactions between the counterions and the crystal layers. The investigation of the interactions in the interlayer space of MMTs with different counterions is useful to establish a firm theoretical understanding of their structures which is necessary for the application of their valuable properties.

Many first-principles calculations have been carried out to investigate the crystalline structures, interlayer interactions and various properties of clays including MMT [35–59]. Sainz-Díaz et al. [44,46,53,55] studied the distribution of octahedral substitutions in smectites and illites with different counterions. Their

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results indicated the lattice parameter *c* of samples with $K^+$ in the interlayer were smaller than those with $Na^+$ although the ionic radius of $K^+$ is larger than $Na^+$ [53]. Tunega et al. [56] found the interlayer $Na^+$ cation had a tendency to locate close to the substitution site in the dry smectites with octahedral or tetrahedral substitution. Using density functional theory(DFT), Chatterjee et al. [39] and Berghout et al. [35] investigated the relationship between the hydration of the cations and the structure expansion in clays with monovalent and divalent exchangeable cations. In addition, the adsorption and elastic properties of MMT were also studied by means of first-principles calculations [48,54,58,59].

However, it is known that standard DFT methods cannot describe long-range dispersion interactions accurately which play a very important role in binding the layers of clays together. So in recent years dispersion correction schemes such as DFT-D and vdW-TS have been combined with DFT methods to study the crystal structures and properties of clay minerals [60–67]. Tunega et al. [64] used different DFT methods to predict the structures of four clay minerals in which the layers are electrically neutral. Their results showed if the dispersion corrections were included in the DFT calculations the predicted structural parameters were more agree with the experimental data, especially the parameter *c* which is controlled by non-bonding interactions. Voora et al. [66] calculated the lattice constants and bulk moduli of MMTs with different counterions by DFT with and without dispersion corrections. Their calculations showed the relationship between the layer spacing and the ionic radius of the interlayer cations is linear approximately and the calculated values of the layer spacings decrease remarkably if dispersion interactions were considered. Shi et al. [68] concluded that the dispersion correction had a little influence on the crystal structures when they investigated the effect of tetrahedral substitutions on the adsorption of cations in the interlayer space of MMT. Although the influence of interlayer cations on the structure of MMT had been investigated in these studies, yet most interest was focused on the variation of the lattice parameters and little consideration was given to structural distortion of MMTs with different counterions. However, the structural distortion is an important crystal feature of phyllosilicates including MMT, and many physical and chemical properties of these minerals are closely related to the amount of structural distortion in them. Moreover, the theoretical research of Lahav and Bressler [27] showed the extent of the distortion in tetrahedral changed with variations of the interlayer cations in MMTs. So determining the relationship between the structural distortion and the counterions is very necessary for interpreting and predicting the experimental behavior of different MMTs.

The purpose of the present work is to examine how the interactions between interlayer cations and the crystal layers affect the structural distortion of MMTs and the locations of counterions by employing dispersion-corrected density functional theory methods. Various alkali and alkaline-earth ions are involved to reveal the relationship between the internal features of MMT structure and the type of counterions. For this purpose, only dehydrated MMT structures are studied in this work, and the influence of hydrated counterions on the structure and properties of MMT will be taken into account in our future research.

## 2. Computation details

There are very little available structural data (especially accurate atomic positions) of MMT in X-ray crystallographic databases because of the structural disorder and compositional heterogeneity. So the MMT model was often built from the structure of closely related clay minerals in past simulation studies [57,58,61,69–73]. Pyrophyllite has the same aluminosilicate layers as MMT except no isomorphic substitutions in both tetrahedral and octahedral sheets. A $1 \times 1 \times 1$ unit cell of pyrophyllite was constructed from the structural data determined by X-ray powder diffraction analysis [74], and then the pyrophyllite model was optimized as outlined below. From the optimized structure of pyrophyllite, a $2 \times 1 \times 1$ supercell of MMT was obtained, in which one of the octahedral $Al^{3+}$ was replaced by $Mg^{2+}$ per unit cell. In order to examine the effect of counterions on the structure, different unhydrated cations (two for $Li^+$, $Na^+$, $K^+$ and one for $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$) were added in the cell to keep the crystal structure electrically neutral (Fig. 1). Previous studies have shown that counterions are underneath (above) the ditrigonal cavities of the tetrahedral layer of MMT [35,51,57,66,68]. So, for every kind of counterions, several configurations with the ions located in different ditrigonal cavities were relaxed to obtain the equilibrium states of these configurations, then the configuration with the minimum total energy among them was selected to be investigated in the present work.

All the DFT total-energy calculations were performed using CASTEP code [75] which is based on the plane-wave pseudopotential approach under periodic boundary conditions. Interactions of electrons with ion cores were represented by the Vanderbilt-type ultrasoft pseudopotential [76]. The Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) was employed for the electronic exchange-correlation functional [77], and a dispersion potential of DFT-D2 based on Grimme [78] was introduced to describe long-range dispersion interactions. The plane-wave basis set cutoff was set as 700 eV to reduce the Pulay stress [79] during the lattice optimization. The *k*-point grid to sample the Brillouin zone was determined by the Monkhorst–Pack [80]. The $3 \times 2 \times 2$ mash was used for pyrophyllite and $2 \times 2 \times 2$ for MMT models. This is established by performing a convergence test, in which a very small energy difference of about 0.5 meV per atom is obtained. The forces on the atoms were obtained by the Hellmann–Feynmann theorem [81] and the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [82] was used for the structure relaxation. In the process of geometry optimization, the full relaxation of atomic locations and cell parameters was performed without symmetry restrictions. The convergence thresholds were set as $5 \times 10^{-6}$ eV/atom for the total energy, $1 \times 10^{-2}$ eV/Å for the maximum atomic force, $5 \times 10^{-4}$ Å for the maximum atomic displacement and $2 \times 10^{-2}$ GPa for the maximum stress.

## 3. Results and discussion

The optimized lattice parameters, $d_{001}$ spacing and equilibrium volumes of MMTs with six kinds of counterions are shown in Table 1, in which previous experimental values [83,84] and the calculated results of Voora et al. [66] by DFT-D2 and vdW-TS methods are also included for comparison. The lattice vector *a*, *b* and the lattice angle $\gamma$ are in good agreement with the data from the experiment and calculation in Table 1, the lattice vector *c* and $d_{001}$ spacing is very close to the values Voora et al. [66] obtained, but about 0.5 Å smaller than earlier measured results [83,84] except K-MMT. For Sr-MMT, our calculated value of the lattice vector *c* is appreciably smaller than the result obtained by Berghout et al. [35], which used PW92 functional and did not consider the dispersion correction in their DFT calculation.

The lattice angles $\alpha$ and $\beta$ characterize the relative shift of neighboring layers which is helpful to reduce the electrostatic repulsions between them. Pyrophyllite, in which there are no interlayer cations, has a stable configuration when the angle $\alpha$ is close to 90° and the angle $\beta$ is about 100° according to the experimental research [74,85]. In our work the results of K-MMT display a remarkable change in comparison with pyrophyllite, and the intercalations of other counterions have certain impact on them.