Influence of layer charge and charge location on the swelling pressure of dioctahedral smectites

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ABSTRACT

Swelling pressure of dioctahedral smectites in the montmorillonite – beidellite series was investigated by molecular dynamics simulations. The pressure was found to correlate inversely with the magnitude of the layer charge in the range of −0.5 to −1.0 per unit cell. The beidellite type smectites were found to have lower swelling pressure than the montmorillonite type smectites. A clear effect of the type of interlayer cations on the swelling pressure was found. The sodium smectites sustained significant pressure even at longer interlayer distances, while in calcium smectites the pressure decreased soon after the initial swelling. The simulation results are in good agreement with experimental observations and provide a tool for predicting macroscopic swelling behavior in smectites.

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1. Introduction

Smectites are lamellar phyllosilicate minerals with a wide variety of physiochemical properties, such as swelling [1,2], adsorption [3], ion exchange [4,5], etc. In particular, swelling of smectites is a process that plays a key role in many industrial processes such as catalysis [6], drilling for hydrocarbons [2], and nuclear waste disposal [7,8]. Smectite is a key component of the engineered barrier system considered in the geological disposal of spent nuclear fuel.

The swelling properties of smectites are complex and closely related to the structure of smectites [9–13]. Smectites are organized as a cluster of particles. The particles are sets of 2:1 phyllosilicates oriented in parallel layers [14]. Each particle consists of between two and thousands of individual layers stacked together, whereas the individual layer consists of an octahedral sheet sandwiched between two tetrahedral sheets. Isomorphous replacements with lower-valency metal ions, Mg^{2+} and Fe^{2+} substituting Al^{3+} in the octahedral sheet and, to lesser degree, Al^{3+} substituting Si^{4+} in the tetrahedral sheets, give the structure a net negative charge. The negative charge is balanced by the interlayer cations stoichiometrically; Na^+, Ca^{2+}, and Mg^{2+} are the most common counterion species in natural smectites [15].

Smectites swell by uptake of water between smectite particles, and between the individual layers within particles [16]. Research has focused on the swelling behavior and the dynamics of clay–water systems [5,9,11,16–25]. The studies have shown that the swelling process is regulated by multiple factors, such as the composition of the minerals [22], the interlayer cation species [23], and the amount and location of the layer charge resulting from isomorphic substitutions in the tetrahedral and octahedral sheets [16,20,21]. Slade et al. reported that the high charge smectites do not exhibit extensive swelling in dilute solutions when saturated with sodium, whereas low charge end of the smectite minerals swell continuously to very high *d*-spacings [9]. This finding is consistent with that of Christidis et al. who reported that swelling displays a clear negative relationship with layer charge ranging from −0.85 to −0.98e per unit cell [21]. However, there are also studies suggesting that swelling increases with an increasing layer charge due to the greater number of interlayer cations and greater ion hydration enthalpies at high layer charge [26–28]. Regarding to the influence of charge location, Sato et al. and Teich-McGoldrick et al. reported that *d*-spacings are larger when the charge is located in the octahedral sheet than when it is in the tetrahedral sheets [20,29]. In these papers, it was generally found that the swelling of clays is due to the combined effects of the charge amount and location. Nevertheless, the influence of layer charge and charge location on the swelling pressure of smectites has not been systematically and quantitatively examined.

Based on the layer charge, octahedral structure and charge location, Emmerich et al. [30] proposed 96 structural variations for montmorillonite – beidellite smectite series. The understanding

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of the influence of the structural variations of clay minerals on their industrial applications has become increasingly important. On the other hand, the properties of smectites can be altered by the environmental induced conditions such as the thermal pulse resulting from the nuclear waste package when bentonite clay that is of high montmorillonite content serves as a buffer material in the spent nuclear fuel disposal [31,32]. Many studies suggest that smectite could transform to illite. The transformation could involve the change from low-charge montmorillonite with dominant octahedral charge to beidellite-like smectite with additional charge in tetrahedral sheets [33–35], a transition that may change its designated function [31]. To fully understand the swelling of smectites, it is necessary to know and predict how the layer charge and charge location influence on the swelling potential of smectites.
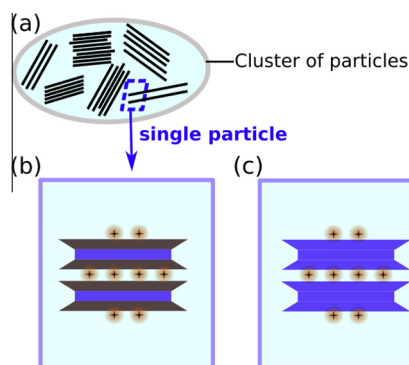
Swelling pressure is known as the maximum stress applied to expansive soil in contact with external solutions so that a constant volume is maintained [36]. It has become an important quantitative indication for swelling potential of smectites [37,38]. The development of swelling pressure has hence become a key criteria for screening smectite minerals for various industrial applications. With respect to the structural variables of smectites, it is not yet clear how and to what extent the layer charge and charge location will influence on the swelling pressure of smectites. In our previous work, we have successfully modeled the swelling pressure of montmorillonites by molecular dynamics method [5]. The model simulates a swelling pressure experiment. A pressure sensor is used to monitor the delamination of the smectite layers in a solution environment. The predicted pressures reproduce the experimental results for montmorillonites in water and salt solutions.

The aim of the present study is to determine by using molecular dynamics simulations for montmorillonite – beidellite dioctahedral smectites the dependence of the swelling pressure on the total layer charge and charge location in the clay sheets. The influence of the interlayer cations in the smectites will be also explored. The ultimate aim is to give a comprehensive understanding of the factors causing the swelling in the montmorillonite – beidellite series.

2. Models and methods

2.1. Simulation system

A smectite particle model was simulated in water as a simplification of a real smectite schematically visualized in Fig. 1(a). The model includes two negatively charged smectite layers, which both consists of 2×4 arrangement of $O_{20}(OH)_4$ unit cells, and charge compensating cations equally distributed on the basal surfaces. The smectite layers are continuous along the [1 0 0] direction through periodic boundary conditions, whereas the exchange of the interlayer cations and water molecules between the interlayer and solution phase is possible via OH and H_2O saturated [0 1 0] surfaces [5,29]. The dimensions of the simulation system, including the smectite model and surrounding water phase of about 6500 water molecules, are $2.06 \times 10 \times 10$ nm^3. A model with double sized smectite layers, each layer of 4×4 unit cells, was also tested. Exploratory simulations with a larger model reproduced the swelling pressure results of the smaller size model.

2.2. Smectite series

Layer charge of dioctahedral smectites induced by isomorphous substitutions ranges roughly from −0.4 to −1.2e per unit cell [39]. The layer charge can originate solely from the octahedral or the tetrahedral sheets or be spread in both octahedral and tetrahedral sheets as shown in Fig. 1(b)–(d). The first two scenarios correspond to montmorillonite and beidellite series, respectively. To sample the whole variable space, ten smectite models were designed. The corresponding smectites are specified in Table 1 together with the unsubstituted pyrophyllite reference. Each smectite is identified by an individual letter followed by the total charge per unit cell and charge percentage in tetrahedral sheets.

For each combination of layer charge and charge location, there are actually multiple ways to arrange the substitutions. The substitution arrangements in the smectite layers were designed with the following principles: (1) the substitutions appear with dispersed arrangements, (2) have similar arrangement patterns, (3) do not appear at the edge sites and (4) are related by mirror or inversion symmetry in the periodic lattice. The principle 1 is justified by previous studies that two substitutions should not appear in neighboring sites [40–42], while the principle 2 aims for similar charge distribution throughout the layer. The principle 3 is applied to avoid over-emphasizing the model edge surfaces. Finally, the electric polarization of the layers is avoided with the principle 4. Following these principles, ten smectite models obeying the specifications in Table 1 were constructed. The smectite structures are visualized in Fig. 2(b). The corresponding smectite series were simulated in the presence of both sodium and calcium counterions, noted as Na-smectites and Ca-smectites.

Fig. 1. (a) Smectite is a cluster of particles. Negative charge due to isomorphous substitutions within a single smectite layer, represented in dark blue, can locate (b) in octahedral sheets, (c) in both octahedral and tetrahedral sheets or (d) in tetrahedral sheets. Brown color represents unsubstituted sheets while light blue color represents the surrounding water phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Total layer charge and charge distribution within tetrahedral (T) and octahedral (O) sheets in the studied clay mineral models.

| Structure | Charge (e) | | | |
	Per unit cell	Per layer	Ratio in TOT sheets[a]	Percentage in T sheets
Pyrophyllite	0	0	0:0:0	0
A (−0.5/0%)	−0.5	−4	0:4:0	0
B (−0.5/50%)	−0.5	−4	1:2:1	50
C (−0.5/100%)	−0.5	−4	2:0:2	100
D (−0.75/0%)	−0.75	−6	0:6:0	0
E (−0.75/33%)	−0.75	−6	1:4:1	33
F (−0.75/66%)	−0.75	−6	2:2:2	67
G (−0.75/100%)	−0.75	−6	3:0:3	100
H (−1.0/0%)	−1.0	−8	0:8:0	0
I (−1.0/50%)	−1.0	−8	2:4:2	50
J (−1.0/100%)	−1.0	−8	4:0:4	100

[a] Number ratio of the isomorphous substitutions within one smectite layer, which composing of a top tetrahedral sheet, an octahedral sheet and a bottom tetrahedral sheet.