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Research paper

New model of ethylene glycol intercalate in smectites for XRD modelling

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ABSTRACT

Several models of ethylene glycol (EG) intercalates were implemented in computer programs which are used to simulate XRD patterns of oriented clay minerals. So far the models assumed distributions of atomic positions perpendicular to the c* direction with similar or significantly higher temperature coefficients B for the EG molecules (B = 1 Å^2 or 11 Å^2) than for atoms of crystal structure (approximately: B = 1 Å^2). The temperature coefficients for the interlayer H_2O molecules and Ca^{2+} cations (B = 1 Å^2 or 1.68 Å^2) were close to these of clay minerals' atoms. This assumption is in disagreement with the distributions described recently with molecular dynamics (MD) simulations. An adjustable model of one and two EG planes in the interlayer is provided in this study. This new model is based on the results of MD simulations.

A wide range of EG and H_2O contents were considered in the simulated structures. Theoretical structures corresponding to certain basal spacings were chosen as representative for one- and two-plane intercalates. The electronic density profiles of EG molecules, H_2O molecules, and Ca^{2+} ions were fitted with Gaussian functions. Their number was minimized to achieve the simplest but yet flexible model of the interlayer structures.

The obtained new models show significant differences with regard to the former ones; especially in the atoms' positions. Based on the MD results, it was also possible to determine the relationships between positions of the atoms/molecules and basal spacing. For some atoms was also a relationship between basal spacing and intensity ratio of Gaussian distributions found. Temperature factors for interlayer species were larger than in the former models and Ca^{2+} ions can exist both as inner-sphere and/or outer sphere complexes, while its ratio can be optimized. All the relationships were implemented in the BGMN Rietveld refinement program.

Using the new model it is possible to receive slightly better or similar matching between experimental and theoretical X-ray diffractograms, comparing to the former models. The new model shows limitations due to the fact that electronic distributions of water and EG molecules in the interlayer space are quite similar. Therefore, EG and water molecules in the interlayer space were not treated fully separately during the minimalization procedure.

1. Introduction

Since the pioneering work of MacEwan (1946), the intercalation of ethylene glycol (EG) into layered silicates has been used to distinguish expandable clay minerals (smectites, vermiculites, and their interstratified varieties with non-expandable phyllosilicates) from other clay minerals. These minerals change their basal spacing upon glycolation and host two planes of EG molecules (2EG; ~17 Å) in the case of smectites or a one-plane structure (1EG; ~14 Å) in the case of vermiculites. The recording of X-ray diffraction (XRD) patterns of EG-clay intercalates is relatively simple due to the high stability of the EG complex against water vapor and quite constant basal spacings. Therefore EG solvated conditions are most often used to simulate XRD patterns of clay samples. The simulation, however, requires assumptions of the structure of the EG-interlayer complex. Models of the intercalate are based on two, over 50-year old papers of Bradley et al. (1963) and Reynolds (1965), and a more recent one of Ufer et al. (2012). In spite of their broad and successful application, these models are in disagreement with recent molecular dynamics (MD) models describing atomic density profiles of H_2O and EG molecules in the interlayer space of smectites (Szczerba et al., 2014; Szczerba and Kalinichev, 2016). The standard deviation of the atom's calculated position is represented by the temperature coefficient B and can be modelled with a Gaussian fit. In the case of atoms of the EG-interlayer complex this B value should not be interpreted in terms of thermal motions but describes distribution of atoms along the direction perpendicular to the smectite layer (Ferrage et al., 2005; Dazas et al., 2014).

The 2EG structure model proposed by Reynolds (1965) was

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obtained for low charge smectite (Clay Spur Bentonite; A. P. I. std. No. 26). The basal spacing of the complex was equal to 16.9–17.0 Å. The temperature coefficient of the atoms building the 2:1 layer structure was equal to 1.68 Å^2. In order to receive an agreement between experimental and calculated structural factors (F-factors), it was necessary to assume higher temperature coefficients (B = 11 Å^2) for atoms of the EG molecules. Surprisingly, Reynolds (1965) left the temperature coefficients for H_2O and Ca^{2+} atoms at the same value as these of the 2:1 layer structure. This model has been broadly and successfully used for decades to simulate XRD patterns of oriented specimens of expandable clay mineral samples, despite the counter-intuitively low B values for H_2O and Ca^{2+} in respect to EG,

The distribution of EG molecules in 1EG structure was calculated by Bradley et al. (1963) for a Na^+-saturated vermiculite with a basal spacing equal to 12.9 Å. They did not report the temperature factors of the EG molecules and the interlayer ions neither considered minor H_2O content.

More recently, Ufer et al. (2012) proposed a model of 2EG intercalate for Rietveld refinements. Two planes for EG molecules and for H_2O and Ca^{2+} were placed symmetrically on each side of the mid-plane. The structure of the EG molecule was based on quantum chemical calculations of Oie et al. (1994) and was kept fixed during the Rietveld refinements, as well as the Debye-Waller factors of all atoms, which were set to 1 Å^2. Only the distance of all atoms to the mid-plane and their occupancy was declared as refineable parameter.

One of the most successful approaches in XRD simulation was proposed by Sakharov et al. (1999) who applied the clay mineral models provided by Moore and Reynolds (1989) and the crystallite thickness distribution of Drits et al. (1997b) on Ca-saturated clay fractions. The approach was later implemented in the Sybilla program (proprietary software owned by the Chevron Corporation). The optimized parameters are the contents of 1EG and 2EG layers occurring as discrete structures in a mixed-layered phase, the basal spacing, the amount of interlayer Ca^{2+} cations, EG content, and a minor H_2O content in EG-saturated interlayers.

The interlayer structural models implemented in Sybilla use the model of Reynolds (1965) for 2EG structure, whereas a modified model of Bradley et al. (1963) is used for the 1EG structure. The same values of temperature coefficients of the EG interlayer species were assumed for 1EG and 2EG structures. Instead of the Na^+ positions taken from Bradley et al. (1963) for the 1EG structure, Ca^{2+} ions are located in the mid-plane in Sybilla. The same models were assumed also in other computer programs used for simulations of XRD data of oriented clay minerals: NEWMOD (Reynolds Jr., 1985; 1EG of Bradley et al., 1963) and PyXRD (Dumon and Van Ranst, 2016; 1EG of Sybilla).

MD simulations for water intercalates in smectites show that water molecules and interlayer ions have relatively broad distributions and should be modelled with larger temperature coefficients than these of the 2:1 layer structures (Ferrage, 2016). Szczerba et al. (2014) also showed significantly broader distributions of H_2O and ions than that postulated by Reynolds (1965). These findings suggest that, in spite of the successful applications of the models of Reynolds (1965) and Bradley et al. (1963) in XRD simulations, the distributions of interlayer EG, H_2O, and cations in these models should be revised.

Atomic distributions obtained from MD simulations can be significantly more accurate than structures received from fitting of XRD patterns or of F-factors received for oriented clay specimens. This is due to the fact that in the case of XRD patterns simulation, only the electronic distribution is modelled without assessing the actual atoms contributing to the diffracted intensity. Using MD it is possible to receive an equilibrium distribution of all interlayer species. Accuracy of this methodology relies on the atomic interaction parameters and on their ability to provide a realistic description of the experimental sample structure. Several examples showed that MD simulations can be very useful to describe the interlayer structure of H_2O and ions for the transfer these structures to XRD pattern calculations (Ferrage, 2016 and references therein).

The aim of this study was to employ the same approach for EG intercalates: use MD simulations to provide a new, adjustable model of 1EG and 2EG structures that will take into account more accurate distributions of the interlayer species than in to-date used models. The relationships between parameters currently fitted independently during the XRD pattern simulation may also be calculated with MD. If such a relationship is found, it would limit the number of independent parameters to make the fitting more robust and realistic.

2. Methodology

2.1. MD simulations

Szczerba and Kalinichev (2016) found that using the combination of *ClayFFmod – CVFF* or *ClayffFFmod – OPLS-aa* force fields (Jorgensen et al., 1996; Dauber-Osguthorpe et al., 1988; Ferrage et al., 2011) provides the best agreement between calculated and experimental XRD patterns for the EG-H_2O intercalate structure in Ca^{2+}-smectites. The first set was used to obtain an average interlayer structure corresponding to 1EG and 2EG intercalates, because the best fit was obtained for low charge smectites for the first combination of force fields (the structure of Reynolds, 1965 also was determined for a low-charge smectite). Models of three smectite structures with different layer charge and charge location were used in MD study: low charge montmorillonite (LCM), high charge montmorillonite (HCM), and high charge beidellite (HCB) (Table 1). Localization and value of the charges corresponds to SWy-1, SAz-1 and SbCa-1 smectites, respectively. The range of the EG content used in the MD simulations was set in between 0.6 and 2.0 with an increment of 0.2 per half unit cell (phuc), while the range for H_2O content was in between 0.0 and 1.2, every 0.3 phuc.

The MD models of smectites were built based on the pyrophyllite crystal structure (Lee and Guggenheim, 1981). Isomorphic substitutions were introduced at particular atomic sites for the adaption of smectite. Relevant numbers of octahedral Al atoms were substituted with Mg or tetrahedral Si with Al. The Al for Si substitutions in the tetrahedral sheet were randomly distributed following the Löwenstein rule, whereas the Mg/Al ordering in the octahedral sheets was set according to the work of Ortega-Castro et al. (2010). The simulation cell was built as 8 × 4 × 2 unit cells in the *a*, *b*, and *c* crystallographic directions, respectively, resulting in the simulated system size of ca. 41.6 Å × 36.1 Å × *X*Å. The double value of basal spacing, *X* was one of the modelling results. It depended on the amount of EG and H_2O in the interlayer space, and to some extent, also on the layer charge and charge location in smectites.

In all simulations, the energy minimization was followed by a *NPT*-ensemble MD simulations with three temperature and pressure steps. In order to place the smectite layers close to each other, the pressure was set to 100 bar and $T = 298$ K during the first 20 ps step. In the second 500 ps step, the temperature was increased to 398 K and pressure dropped to 1 bar. This allowed the EG and water molecules to move freely in the interlayer space in order to reach optimal positions. In the last 1 ns step the temperature decreased to 298 K at pressure of 1 bar. The atomic positions were recorded for further analysis during the last 500 ps period.

The time step was set to 1 fs and the positions of all atoms were recorded every 1 ps. The Ewald summation was applied to calculate the

Table 1
Smectites used in the study.

Smectite	Tetrahedral charge phuc	Octahedral charge phuc
LCM	0.0	0.28
HCM	0.0	0.56
HCB	0.50	0.0