Clays and Clay Minerals, Vol. 44, No. 4, 553–559, 1996.

MODEL FOR CRYSTALLINE SWELLING OF 2:1 PHYLLOSILICATES

DAVID A. LAIRD

USDA, Agricultural Research Service, National Soil Tilth Laboratory
2150 Pammel Drive, Ames, IA 50011

Abstract—A macroscopic energy balance model for crystalline swelling of 2:1 phyllosilicates is presented. Crystalline swelling for a static system is modeled by a balance among the potential energies of attraction, repulsion and resistance. The potential energy of attraction is due to both the electrostatic interaction between the interlayer cations and the negative surface charge sites and to van der Waals attraction between layers. The potential energy of repulsion is due to the net hydration energy for the interlayer cations, the net hydration energy for the negative surface charge sites and Born repulsion. The potential energy of resistance represents irreversible work needed to overcome the mechanical resistance of the clay water system to both expansion and collapse. The potential energy of resistance is responsible for both hysteresis and the stepwise nature of crystalline swelling.

A numerical solution of the crystalline swelling model is presented and shown to yield reasonable estimates of basal spacings for octahedrally charged clays. Measured and predicted basal spacings are directly compared and are in general agreement (r^2 = 0.39). Most of the scatter for the measured vs. predicted basal spacing relationship is attributed to inaccuracies of the assumptions used for the numerical solution. The crystalline swelling model readily accounts for the effects of layer charge and nature of the interlayer cations upon crystalline swelling, but does not account for the effect of charge site location upon crystalline swelling.

Key Words—Crystalline Swelling, 2:1 Phyllosilicates.

INTRODUCTION

The initial hydration of 2:1 phyllosilicates occurs during a series of steps corresponding to the intercalation of 0, 1, 2, 3 and 4 discrete layers of water molecules (Barshad 1949; Norrish 1954; Norrish 1973; Slade et al. 1991; Laird et al. 1995). Norrish (1954) termed this initial stage of hydration "crystalline swelling." Since 1954 there has been general agreement that crystalline swelling is controlled by a balance between forces of attraction due to both coulombic and van der Waals interactions between clay layers and forces of repulsion arising from hydration of the interlayer cations and negative surface charge sites (Norrish 1954; van Olphen 1965; Kittrick 1969a, 1969b; Parker 1986).

Modeling of crystalline swelling requires either a microscopic or a macroscopic approach. For the microscopic approach, the modeler attempts energy minimization calculations considering all possible interactions for a system consisting of two 2:1 phyllosilicate half-layers, 2 or 3 interlayer cations, and perhaps 30 or 40 water molecules. The microscopic approach has considerable potential for elucidating fundamental mechanisms, but utility of this approach is limited by the complexity of the mathematics. Furthermore, experimental verification of microscopic models is difficult because most analytical techniques, for example XRD, TGA and chemical analysis, measure macroscopic properties. The macroscopic approach requires spatial averaging of properties and draws governing equations from thermodynamics, mechanics and empirical relationships. Although the macroscopic approach is fundamentally less rigorous, the mathematics of the macroscopic approach are generally more accessible and the macroscopic approach provides for a greater level of conceptual understanding. Macroscopic models are also amenable to direct experimental verification.

Other authors (Norrish 1954; van Olphen 1965; Kittrick 1969a, 1969b; Parker 1986) have attempted to develop macroscopic models for crystalline swelling. However, none of these models predict crystalline swelling phenomena. Norrish (1954) proposed two different equations for estimating the electrostatic attraction energy between interlayer cations and the negatively charged surfaces of 2:1 phyllosilicates. The first equation describes the energy of attraction between a point charge and a thick-plane conductor. The second equation describes the energy of attraction between two plates of a capacitor. Norrish (1954) noted that neither equation is fully adequate for describing the electrostatic energy of attraction between two 2:1 phyllosilicate layers. Norrish offered no means for quantifying the energy of repulsion due to cation hydration. The crystalline swelling models proposed by van Olphen (1965) and Kittrick (1969a, 1969b) lack general applicability, because they require estimates of thermodynamic properties for specific minerals. Parker (1986) was the first to propose a complete, generalized macroscopic model for crystalline swelling. Parker

Copyright © 1996, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1996.0440415 Published online by Cambridge University Press

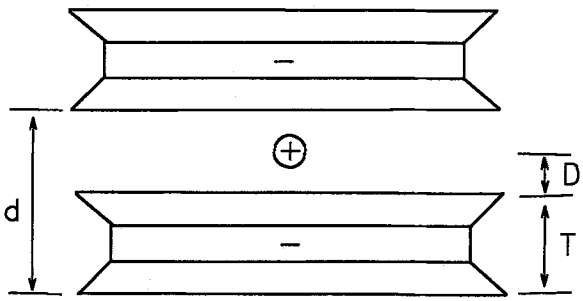


Figure 1. Schematic diagram of an expanding 2:1 phyllosilicate illustrating dimensional parameters used for the crystalline swelling model.

used the point-charge/thick-plane conductor equation to estimate the electrostatic energy of attraction. Parker quantified the energy of repulsion as the difference between the total hydration energy of the interlayer cations and the total hydration energy of the same cations if they were in the bulk solution. Parker's model does not yield quantitative estimates of crystalline swelling phenomena because the point-charge/thick-plane conductor equation does not adequately account for the effects of surface charge density on crystalline swelling. Furthermore, there is no means within Parker's model to account for hysteresis or the stepwise nature of crystalline swelling.

My objective is to propose a generalized macroscopic energy balance model for crystalline swelling of 2:1 phyllosilicates. The model draws heavily on the work of Norrish (1954) and Parker (1986), but includes several new key elements. A numerical solution of the proposed crystalline swelling model is presented along with a direct comparison of measured and predicted basal spacings for a variety of clay-cation-water systems.

MODEL

Crystalline swelling of 2:1 phyllosilicates must be modeled using an open system. During expansion mass (water) is transferred from the surroundings to the clay and the layers move farther apart displacing solvent in the surrounding media. During collapse, mass is transferred from the clay to the surroundings, the layers move closer together and solvent molecules must fill the void left by the retreating layers. Each of these steps requires that mass be transferred from one location to another and mass transfer requires work. Crystalline swelling is irreversible because work for mass transfer is required for both expansion and collapse. The energy that must be transferred into a clay-water system to effect irreversible work during crystalline swelling has been described previously as the "free energy of transition" (Laird et al. 1995) and accounts for both hysteresis and the step-wise nature of crystalline swelling.

A balance of potential energies is used in the present model to describe the extent of crystalline swelling for a clay that is in apparent equilibrium with its environment. Thus, "apparent equilibrium" means a system at thermal and mechanical equilibrium but not necessarily at material equilibrium. For a smectite at apparent equilibrium, the extent of crystalline swelling is determined by a balance between potential energies of repulsion (G_{rp}), attraction (G_{at}) and resistance (G_{rs}):

$$G_{rp} = G_{at} + G_{rs} \quad [1]$$

All of the potential energy terms in Equation [1] are most conveniently expressed relative to the surface area of the clay (J m^{-2}).

The potential energy of resistance for a static system (Equation [1]) is not equal to the free energy of transition as described previously (Laird et al. 1995) for a dynamic system. The free energy of transition is equal to one half the amount of energy that must be transferred into a clay-water system to effect a complete cycle of expansion and collapse. The potential energy of resistance is the contribution of mechanical stress upon the clay water system to the overall energy balance for a system at apparent equilibrium.

The potential energy of attraction is the sum of potential energies for the electrostatic interaction between the interlayer cations and the negative surface charge sites ($G_{c(i)}$) and for van der Waals interactions between adjacent layers (G_v).

A modified version of the capacitor model is used for estimating $G_{c(i)}$. The original capacitor model (Norrish 1954) was derived by assuming that both interlayer cation charge and negative layer charge are uniformly distributed upon the outer surfaces of parallel plates made of a conducting material, thus, the capacitor plates. However, phyllosilicates are nonconductors and the excess negative charge is not uniformly distributed across the surface, but rather is localized in the framework oxygens adjacent to sites of isomorphous substitution. Excess positive charge in phyllosilicates is localized in discrete cations within the clay interlayers. Furthermore, the original capacitor model does not consider valence of the interlayer cations.

In an attempt to compensate for these deficiencies, new terms for the effective anionic radius (r_s) of the negative charge sites and a dimensionless proportionality constant (f_i) related to the valence of the interlayer cations have been introduced into the original capacitor model to estimate $G_{c(i)}$. The revised capacitor model is:

$$G_{c(i)} = \frac{f_i \pi \sigma^2 (D + r_s)}{\beta_I} \quad [2]$$

where σ is the surface charge density, D is one half of the layer separation (Figure 1) and β_I is the interlayer diabattivity.

https://doi.org/10.1346/CCMN.1996.0440415 Published online by Cambridge University Press

Table 1. Parameters values used for the numerical solution of the crystalline swelling model.

Parameter	Value, range, or source
G_{rs}	Assumed to equal 0
e	1.602×10^{-19} C
ϵ_o	8.854×10^{-12} C^2 N^{-1} m^{-2}
ϵ_B	78.15
ϵ_C	6
ϵ_I	Equation 9
β_B	8.695×10^{-9} C^2 N^{-1} m^{-2}
β_I	Equation 8
H	2.2×10^{-20} J
T	9.4×10^{-10} m
D	Between 6.0×10^{-11} and 1.3×10^{-9} m
f_i	0.5 for monovalent cations and 1 for divalent cations
r_s	4.7×10^{-10} m
r_i	Pauling radii plus 8.5×10^{-11} m
σ	Between 0.103 and 0.344 C m^{-2}
z_i	Interlayer cation valence
L	1.4627×10^{-124} J m^{10}
C1	1.46×10^{-9} m
C2	9.0×10^{-10} m

The energy of attraction due to Van der Waals interactions between two parallel plates of thickness T and separation 2D is given by:

$$G_v = \frac{H}{12\pi}\left(\frac{1}{(2D)^2} + \frac{1}{(2D + 2T)^2} - \frac{2}{(2D + T)^2}\right) \quad [3]$$

where H is the Hamaker constant (Quirk and Murray 1991).

The potential energy of repulsion between 2:1 phyllosilicate layers is the sum of the net hydration energy for the interlayer cations ($G_{h(i)}$), the net hydration energy for the negative surface charge sites ($G_{h(s)}$) and Born repulsion energy (G_b). Net hydration energies may be estimated using the Born equation (Basu and Sharma 1994) as the change in electrostatic free energy of an ion on reversibly and isothermally moving the ion from a solution of one dielectric to another. By using this approach, the net hydration energy for interlayer cations in 2:1 phyllosilicates becomes:

$$G_{h(i)} = \frac{\sigma z_i e}{2r_i}\left(\frac{1}{\beta_I} - \frac{1}{\beta_B}\right) \quad [4]$$

where e is the unit charge on a proton, r_i is the effective radius of the cation, β_I is the diabattivity of the interlayer and β_B is the diabattivity of the bulk solution. Similarly, the net hydration energy for the negative surface charge sites may be estimated as:

$$G_{h(s)} = \frac{\sigma e}{2r_s}\left(\frac{1}{\beta_I} - \frac{1}{\beta_B}\right) \quad [5]$$

where r_s is the effective radius of the negative surface charge sites.

Born repulsion prevents the electron clouds of two atoms from occupying the same space (Güven 1992). The potential energy due to Born repulsion between two 2:1 phyllosilicate layers may be estimated by:

$$G_b = \frac{L}{(2D)^{12}} \quad [6]$$

where L is a constant. For the crystalline swelling model, Born repulsion prevents the clay layers from collapsing below 10 Å, but has little influence on the energy balance for basal spacings larger than 10.5 Å.

When Equations [1] through [6] are combined:

$$G_{rs} = -\frac{f_i 2\pi\sigma^2(D + r_s)}{\beta_I} - \frac{H}{12\pi}\left(\frac{1}{(2D)^2} + \frac{1}{(2D + 2T)^2} - \frac{2}{(2D + T)^2}\right) + \left(\frac{\sigma z_i e}{2r_i} + \frac{\sigma e}{2r_s}\right)\left(\frac{1}{\beta_I} - \frac{1}{\beta_B}\right) + \frac{L}{(2D)^{12}} \quad [7]$$

a generalized model for crystalline swelling of 2:1 phyllosilicates is obtained.

NUMERICAL SOLUTION OF THE MODEL

Numerical solution of the crystalline swelling model requires quantitative estimates for all of the parameters in Equation [7] (Table 1). Some of the parameters are constants (π, e, H, T, L) and others are variables (z_i, D, σ, f_i, r_i, r_s, β_B, β_I, G_{rs}) that depend upon properties of the interlayer cations, properties of the bulk solution or nature of the clay being modeled. Four of these variables (z_i, D, σ, β_B) are readily determined. The other five require careful consideration.

The standard form of the Born equation yields nearly quantitative estimates of total hydration energies for ions if the radius of the ion being evaluated is set equal to the Pauling radius plus 0.85 Å for cations and plus 0.10 Å for anions (Parker 1986). Adjustment of Pauling radii is necessary because the Born equation treats water as a dielectric continuum rather than as a medium composed of discrete water molecules. The same adjustment factor is needed for estimating effective radii of interlayer cations (r_i) for the crystalline swelling model. The effective radius for a negative surface charge site (r_s) is related to the location of the charge site within a 2:1 phyllosilicate layer. With octahedrally charged clays r_s is estimated to be about 4.7 Å. Estimation of r_s for tetrahedrally charged clays is less certain because of asymmetry and increased localization of the surface charge. As a first approximation, f_i is set equal to the valence of the interlayer cations divided by 2.

Diabattivity of the interlayer is related to the dielectric constant of the interlayer (ϵ_I) through

https://doi.org/10.1346/CCMN.1996.0440415 Published online by Cambridge University Press

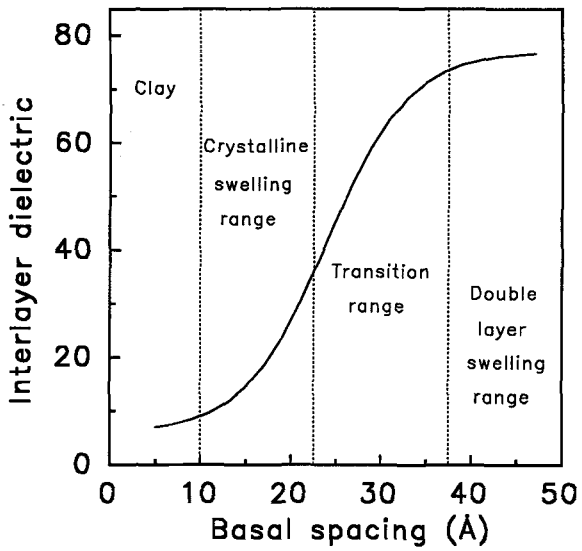


Figure 2. Relationship between basal spacing and interlayer dielectric constant as predicted by Equation [9].

$$\beta_I = 4\pi\epsilon_0\epsilon_I \quad [8]$$

where ϵ_0 is the permittivity of a vacuum. Thus accurate estimation of ϵ_I is critical to the success of the crystalline swelling model.

On approaching a solid-liquid interface, water molecules become increasingly oriented by short-range forces emanating from the surface and lose their ability to orient within an electric field. Such orientation reduces the dielectric constant of water near the surface relative to that of water within the bulk solution. For the first layer of water molecules adjacent to a surface, the dielectric constant is believed to be less than 10. However the dielectric constant is also believed to increase rapidly with distance from the surface (Conway 1981; Sposito 1984; Newman 1987). Recent experimental evidence obtained using time domain reflectometry (Dirksen and Dasberg 1993) indicates that the dielectric constant for Wyoming bentonite increases from 7 to about 24 as the volumetric water content increases from 0.1 to 0.35 ($cm^3\ cm^{-3}$). This range of volumetric water content corresponds to a range of approximately 1 to 3 layers of interlayer water molecules. Thus, for the numerical solution of the crystalline swelling model, the dielectric constant of the interlayer is treated as a variable with respect to basal spacing.

To estimate ϵ_I we assume that: 1) ϵ_I for an infinitely expanded 2:1 phyllosilicate (basal spacing >100 Å) is equal to that of the bulk solution (ϵ_B = 78); 2) ϵ_I for a fully collapsed clay (basal spacing = 10 Å) approaches the dielectric constant of a typical aluminosilicate mineral (ϵ_C = 6); and 3) the relationship between ϵ_I and basal spacing is described by a hyperbolic tangent function:

$$\epsilon_I = \left(1 + \tanh\left(\frac{2D - C1}{C2}\right)\right)\left(\frac{\epsilon_B - \epsilon_C}{2}\right) + \epsilon_C \quad [9]$$

where C1 and C2 are empirical constants.

The relationship between the interlayer dielectric and basal spacing described by Equation 9 is illustrated in Figure 2. Values for the constants (C1 and C2) were determined by numerical optimization of the crystalline swelling model. For the numerical optimization a K-saturated smectite with a layer charge of 0.30 per formula unit was assumed to have a basal spacing of 20.4 Å, and a K-saturated vermiculite with a layer charge of 0.65 per formula unit was assumed to have a basal spacing of 10.0 Å. The relationship between ϵ_I and basal spacing illustrated in Figure 2 is consistent with the experimental results of Dirksen and Dasberg (1993).

The potential energy of resistance from crystalline swelling is due to the mechanical resistance of the clay water system to both expansion and collapse (Laird et al. 1995). Obtaining an independent estimate of G_{rs} is perhaps the most daunting challenge to a numerical solution of the crystalline swelling model. However, by definition G_{rs} must equal zero for the specific conditions that cause a phase transition. For example, assume that the relative humidity of an equilibrating atmosphere is gradually increased until a Ca-smectite with a layer charge of 0.45 (per formula unit) spontaneously expands from 15.5 to 19.0 Å. For the conditions at the moment of expansion (basal spacing = 19.0 Å, interlayer cation = Ca, σ = 0.45, β_B = f(relative humidity at expansion), β_I = f(ϵ_I @ 19.0 Å), etc.) the crystalline swelling model can be solved. However, for conditions not causing a change in basal spacing G_{rs} is not equal to zero and the model can not be solved.

RESULTS AND DISCUSSION

One application of the crystalline swelling model is the prediction of basal spacings. For this prediction, quantitative estimates are made for all parameters in Equation [7] except D and then the model is solved for D using an iterative approach. Presented in Table 2 are basal spacings predicted by the crystalline swelling model for 2:1 phyllosilicates saturated with various alkaline and alkaline earth cations and having values of layer charge ranging from 0.30 to 0.70 per formula unit. The results in Table 2 illustrate three consistently observed phenomena in crystalline swelling: 1) decreased swelling with increasing layer charge; 2) increased swelling with increasing hydration energy of the interlayer cation; and 3) fixation of weakly hydrated cations by highly charged clays.

A direct comparison between measured and predicted basal spacings for five clays saturated with various cations are shown in Figure 3 (measured data are the "in water" results presented by MacEwan and

https://doi.org/10.1346/CCMN.1996.0440415 Published online by Cambridge University Press

Table 2. Basal spacings predicted by the crystalline swelling model.

Interlayer cation	Layer charge [per $O_{10}(OH)_2$]				
	0.3	0.4	0.5	0.6	0.7
Li	22.8	20.6	18.6	16.8	15.1
Na	21.5	19.1	17.0	15.0	13.2
K	20.4	17.8	15.5	13.3	9.95
Rb	20.0	17.3	14.9	12.5	9.95
Cs	19.5	16.7	14.2	9.95	9.95
Mg	21.7	19.3	17.1	15.2	13.5
Ca	20.3	17.6	15.2	13.2	9.96
Sr	19.5	16.6	14.2	11.9	9.95
Ba	19.5	16.7	14.2	9.95	9.95

Wilson 1980). Excluded are measured data (MacEwan and Wilson 1980) for the Unterrupsroth beidellite, St Cyrus saponite and the Loch Scye vermiculite due to uncertainty about the effects of tetrahedral charge, interstratification and about the appropriate values of layer charge for these clays. Although there is considerable data scatter, there is at least general agreement between the measured and predicted basal spacings (r^2 = 0.39).

Much of the data scatter presented in Figure 3 is attributed to the fallacy of the assumption that G_{rs} is equal to zero. This assumption was necessary for the numerical solution of the model, but it is clearly wrong for most clay-cation-water systems. The assumption that G_{rs} is equal to zero is equivalent to assuming that crystalline swelling is both continuous and non-hysteretic, whereas experimental evidence clearly indicates that crystalline swelling is both hysteretic and occurs as discrete steps (Laird et al. 1995). The measured data in Figure 3, for example, are clustered about basal spacings of 10 Å, 12.5 Å, 15 Å and 19 Å corresponding to 0, 1, 2 and 3 discrete layers of water molecules, respectively.

Another application of the crystalline swelling model is quantification of the relationship between the net interaction energy and basal spacing. The net interaction energy for a clay at apparent equilibrium with its environment equals G_{rs}. Figure 4 illustrates the net interaction energy-basal spacing relationship for a Mg-saturated smectite with a layer charge of 0.40 per formula unit. The model predicts excess attraction energy for basal spacings larger than 19.4 Å and excess repulsion energy for basal spacings between 10.2 Å and 19.4 Å. Thus, the model predicts an equilibrium basal spacing of 19.4 Å, which is consistent with measured basal spacings of Mg-saturated smectites within water (MacEwan and Wilson 1980). However, the model also predicts negative G_{rs} values for basal spacings between 10.0 Å and 10.2 Å. This indicates that if the Mg-smectite were dehydrated it would remain collapsed upon exposure to water. This is inconsistent with experimental data for Mg-smectites. One possible explanation for this discrepancy is that Equation [3]

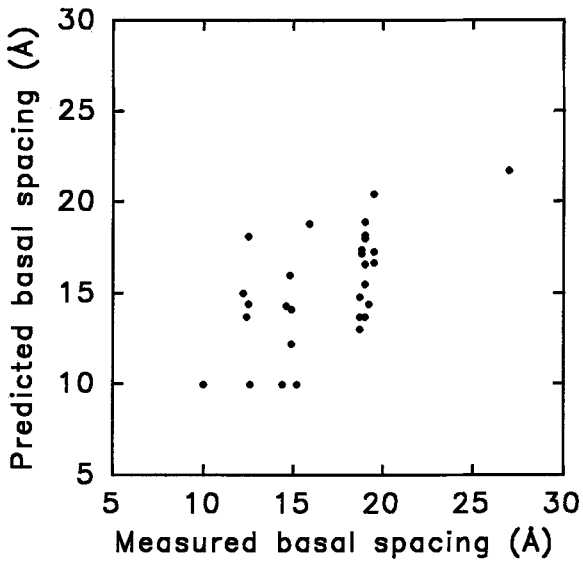


Figure 3. Relationship between measured and predicted basal spacings for various clay-cation-water systems. The measured values are the "in water" data given by MacEwan and Wilson (1980).

overestimates the contribution of van der Waals attraction energy for smectites with small basal spacings. Quirk (1994) reported that Equation [3] is valid for layer separations between 2 Å and 70 Å.

The absolute contributions of all 5 energy terms to the net interaction energy for the Mg-saturated smectite (layer charge = 0.40 per formula unit) are shown in Figure 5. The van der Waals attraction energy and Born repulsion energy dominate the energy balance for basal spacings approaching 10.0 Å, whereas electrostatic and hydration energies dominate the energy balance for basal spacings larger than 12.0 Å.

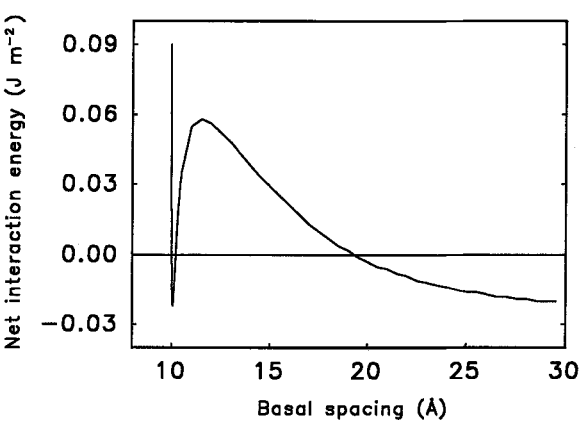


Figure 4. Relationship between basal spacing and net energy of interaction for a Mg-smectite with a layer charge of 0.40 per formula unit. The net interaction energy is equal to G_{rs} for a stable clay-cation water system.

https://doi.org/10.1346/CCMN.1996.0440415 Published online by Cambridge University Press

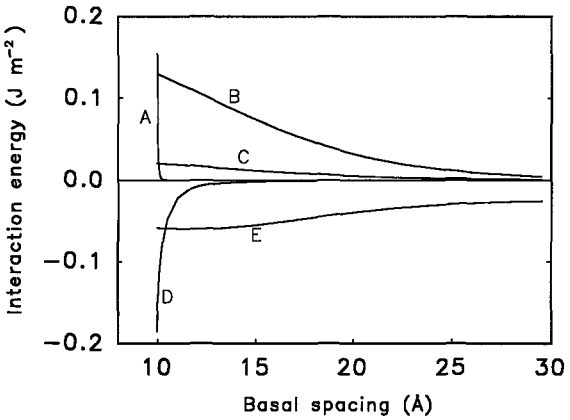


Figure 5. Relationship between basal spacing and interaction energies for: A) Born repulsion; B) interlayer cation hydration; C) negative charge site hydration; D) van der Waals attraction; and E) cation-charge site electrostatic attraction. The data are for a Mg-smectite with a layer charge of 0.40 per formula unit.

A third application of the crystalline swelling model is quantification of the dielectric constant of the interlayer. To do so, all parameters except β_I are estimated and Equation [7] is solved for β_I, which is related to ϵ_I through Equation [8]. Such an analysis has been performed for a series of hypothetical clay-cation-water systems and the results yield a distribution similar to that shown in Figure 2. This is not surprising because the constants in Equation [9] were estimated by the reverse calculation for K-clay-water system. However, no attempt has been made to use experimental data to estimate ϵ_I using this technique, because G_{rs} is unknown for most real clay-cation-water systems.

A major limitation of the crystalline swelling model is the lack of an obvious means of accounting for the effect of charge site location upon swelling. The numerical solution yields reasonable results for octahedrally charged clays only. Intuitively, one might expect an increase in percentage of the tetrahedral charge to be modeled as a decrease in r_s. However, if r_s is decreased, Equation [7] predicts increased swelling, which is inconsistent with experimental evidence. The most likely explanation for the failure of the crystalline swelling model to account for charge site location lies within the inadequacy of the capacitor model for quantifying $G_{c(i)}$.

SUMMARY

A macroscopic energy balance model for crystalline swelling of 2:1 phyllosilicates has been presented. The model readily accounts for the effects of layer charge and nature of the interlayer cations on crystalline swelling. It does not account for the influence of charge site location on swelling. Uncertainty exists when estimating values for several of the parameters needed for a numerical solution of the model. However, with a combination of "best guesses" and empirical parameter fitting, these parameters can be adjusted such that the model yields reasonable estimates of basal spacings for octahedrally charged 2:1 phyllosilicates.

The present study suggests numerous areas for possible future work. Theoretical work is needed to refine the capacitor model or to develop an entirely new macroscopic model for estimating $G_{c(i)}$. Development of an independent means of estimating G_{rs} would greatly facilitate use of the crystalline swelling model and permit routine estimation of ϵ_I from basal spacing measurements. The crystalline swelling and DLVO models could be combined to predict the full range of swelling phenomena. The numerical solution of the model could be extended to predict swelling of clays at equilibrium with either an electrolyte solution or an atmosphere of known relative humidity by integrating the relationship between water activity and β_B into the crystalline swelling model.

REFERENCES

Barshad I. 1949. The nature of lattice expansion and its relation to hydration in montmorillonite and vermiculite. Am Miner 34:675–684.

Basu S, Sharma MM. 1994. Effect of dielectric saturation on disjoining pressure in thin films of aqueous electrolytes. J Coll Interface Sci 165:355–366.

Conway BE. 1981. Ionic hydration in chemistry and biophysics. Amsterdam: Elsevier Scientific Publishing Co. 741 p.

Dirksen C, Dasberg S. 1993. Improved calibration of time domain reflectometry soil water content measurements. Soil Sci Soc Am J 57:660–667.

Güven N. 1992. Molecular aspects of clay/water interactions. In: Güven N, Pollastro RM, editors. Clay-water interface and its rheological implications. Boulder, CO: The Clay Minerals Society. p 1–80.

Kittrick JA. 1969a. Interlayer forces in montmorillonite and vermiculite. Soil Sci Soc Am Proc 33:217–222.

Kittrick JA. 1969b. Quantitative evaluation of the strong-force model for expansion and contraction of vermiculite. Soil Sci Soc Am Proc 33:222–225.

Laird DA, Shang C, Thompson ML. 1995. Hysteresis in crystalline swelling of smectites. J Coll Interface Sci 171: 240–245.

MacEwan DMC, Wilson MJ. 1980. Interlayer and intercalation complexes of clay minerals. In: Brindley GW, Brown G, editors. Crystal structures of clay minerals and their x-ray identification. London, UK: Mineralogical Society. p 197–248.

Newman ADC. 1987. The interaction of water with clay mineral surfaces. In: Newman ADC, editor. Chemistry of clays and clay minerals. New York: John Wiley & Sons. p 237–274.

Norrish K. 1954. The swelling of montmorillonite. Discuss. Faraday Soc 18:120–134.

Norrish K. 1973. Forces between clay particles. In: Serratosa JM, et al, editors. Proc. Int. Clay Conf., Madrid, Spain, June 1972. Madrid, Spain: Div. de Ciencas, CSIA. p 375–383.

Parker JC. 1986. Hydrostatics of water in porous media. In: Sparks DL, editor. Soil physical chemistry. Boca Raton, FL: CRC Press. p 209–296.

https://doi.org/10.1346/CCMN.1996.0440415 Published online by Cambridge University Press

Quirk JP. 1994. Interparticle forces: A basis for the interpretation of soil physical behavior. Adv in Agron. 53:121–183.
Quirk JP, Murray RS, 1991. Towards a model for soil structural behaviour. Aust J Soil Res 29:829–867.
Slade PG, Quirk JP, Norrish K. 1991. Crystalline swelling of smectite samples in concentrated NaCl solutions in relation to layer charge. Clays & Clay Miner 39:234–238.
Sposito G. 1984. The surface chemistry of soils. New York: Oxford University Press. 234 p.
van Olphen H. 1965. Thermodynamics of interlayer adsorption of water in clays. J Coll Sci 20:822–837.

(Received 5 July 1995; accepted 3 December 1995; Ms. 2666)

https://doi.org/10.1346/CCMN.1996.0440415 Published online by Cambridge University Press