Role of London Energy in Determining the C-Dimensions of Phyllosilicates

층상 규산염광물 C-축 결정에 있어서의 런던에너지 역할

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ABSTRACT: To examine how London energy controls the c-dimensions of phyllosilicates, London energy, as well as Coulomb and Pauli repulsion energy was calculated as a function of d (001) for 1M and d(002) for 2M1 phyllosilicates. London and Pauli repulsion energy calculation use a direct interaction calculation method and Coulomb energy calculation adopts Fourier synthesis method.

The energy calculations show that Coulmb and Pauli repulsion energy dominantly control the c-dimensions of phyllosilicates having the interlayer cations, i.e., the layer charges. On the other hand, if phyllosilicates have no interlayer cations, London energy is solely responsible for holding the layers and maintain the c-dimensions.

The significance of London energy in determining the c-dimensions of phyllosilicates decreases as the layer charge increases. when the layer charge is lower than one equivalent on the basis of $O_n(OH)_2$ formula, London energy plays an important role in determing the c-dimensions. However, if the layer charge is higher than one equivalent, London energy becomes insignificant in determining the c-dimension.

요약 : London 에너지가 어떻게 층상 규산염광물의 c축 길이를 결정하는가를 알아보기위해, 1M 층상 규산염광물의 d(001)과 2M1 층상 규산염광물의 d(002)의 변화에 따라 Coulomb 에너지, Pauli 반발에너지와 함께 London에너지를 계산하였다. London에너지와 Pauli반발에너지는 직접 상호작용법에 의해서 계산하였고, Coulomb에너지는 Fourier수열을 이용하여 계산하였다.

이와 같은 에너지 계산 결과, 층간 양이온을 가진 층상 규산염광물의 c축 길이는 주로 Coulomb에너지 및 Pauli 반발에너지에 의해 좌우되는 것으로 나타난 반면, 층간 양이온이 없는 층상 규산염광물의 c축 길이는 London에너지에 의해서 결정되는 것으로 나타났다.

층상 규산염광물의 c축 길이 결정에 있어서의 London에너지의 중요성은 충간전하 값이 증가할수록 감소한다. 만일, 충간전하 값이 $O_n(OH)_2$구조식을 기준으로 1당량 보다 적으면, 층상 규산염광물의 c축 길이를 결정하는에 있어서 London에너지가 중요한 역할을 하나, 충간전하 값이 그보다 크면, London에너지의 역할은 무시할 만 하게 된다.

INTRODUCTION

Different phyllosilicates have diferent c-dimensions. Pyrophyllite and illite respectively have about 9.2 (Brindley and Wardle, 1970; Wardle and Brindldy,1972) and 10.0Å (Soboleva and Zvyagin, 1969; Sidorenko et al., 1975) in terms of d (001). Muscovite, paragonite and margarite respectively have about 10.0 (Radoslovich, 1960; Zvyagin and Mishchenko, 1960; Güven, 1972). 9.6 (Sidorenko et al., 1977) and 9.5 Å (Takeuchi, 1965; Guggenheim and Bailey, 1975) in terms of d (002).The different c-dimensions for different phyllosilicates suggest that each phyllosilicate

has its own minimum binding energy as a function of its chemical composition and structure when it has such d-spacing. The binding energy consists of Coulmb (electrostatic), covalent, Pauli repulsion and van der Waals energy, but the author considers only Coulomb, Pauli repulsion and London energy.

A few researchers have investigated the interlayer bondings of phyllosilicates by calculating their electrostatic and/or van der Waals energies (Ward and Phillips, 1971; Giese, 1974, 1975 and 1978) based on a purely ionic model. However, most of these researcher's work has focused only on the electrostatic energy variation as a function of the silicate layer separation without any indication of possible c-dimension control of the binding energies. Ward and Phillips (1971) only suggested that van der Waals energy may have important role in holding the layers of pyrophyllite and talc.

The purpose of this study is to examine how Coulmb, Pauli repulsion and London energy control the c-dimensions of phyllosilicates. London energy, also called induced diploe-induced dipole interaction energy, is one of the van der Waals energies. The reason for excluding covalent energy in this study is that the covalent energy is short ranged and, thus, does not have an important role in determining the equilibrium distance between the silicate layers and the interlayer cations whose interactions are almost ionic.

To examine how Coulomb, Pauli repulsion and London energy controls the c-dimensions of phyllosilicates, one must separately calculate the above energies as a function of various d(001) for 1M and d(002) for 2M1 phyllosilicate. The d-spacing which produces the minimum sum of the above energies must represent the sum of silicate layer thickness and the equilibrium distance bewteen the layers. Comparing the energies around minimum energy producing d-spacing may suggest how each energy relatively controls the minimum energy d-spacing of phyllosilicates. Following sections discuss details of the energy calculation theory, study method and the results from this study.

ENERGY CALCULATION THEORY

Coulomb Energy

The Coulomb energy between two charged body A and B is generally represented by the following equation:

$$E_C = \frac{q_A q_B}{r_{AB}} , \qquad (1)$$

where E_C is Coulomb energy between A and B, q_A and q_B are respectively the electrical charges on A and B, and r_{AB} is the distance between A and B. For a phase having N-charged bodies, its total Coulomb energy becomes

$$E_C = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=i+1}^{N-1} \frac{q_i q_j}{r_{ij}} , \qquad (2)$$

where q_i and q_j are the charges of ith and jth body, respectively and r_{ij} is the distance between ith and jth body in the phase. Minerals usually have so many constituent atoms, which may be charged bodies that we can assume their numbers are infinite. If a mineral has N atoms in its unit cell, the Coulomb energy for one mole of its unit cell is

$$E_C = \frac{1}{2} N_A \sum_{i=1}^{N} \sum_{j=i+1}^{\infty} \frac{q_i q_j}{r_{ij}} , \qquad (3)$$

where N is the number of the atoms in the unit cell and N_A is Avogadro's number. Practically speakng, however, Coulomb energy calculation by equation (3) is too tedious and often inaccurate, especially when small energy difference is important. To resolve these problems, one can use Fourier synthesis for the energy calculation (Slaughter, 1966; Yu, 1990)

The energy calculation using Fourier synthesis is relatively fast and precise. Based on the assumption of the Gaussian distribution of charge density around an atom, Fourier synthesis represents the electric potential on an atom with a Fourier series and calculates the Coulomb energy by multiplying the charge to the potential on an atom, i.e.,

$$E_C = \frac{1}{2} N_A \sum_{i=1}^{N} q_i U_i , \qquad (4)$$

where U_i is the electric potential on the ith atom. U_i is expressed with a Fourier series as the below:

$$U_i = \frac{1}{4\pi V} \sum_{hkl} (\sin^2\theta)^{-1} F'(hkl) e^{-2\pi i (hx + ky + lz)}$$

$$-U_s + U_o ,\qquad (5)$$

where V is the unit cell Volume, h, k and l are the miller indices, θ is the Bragg angle, $F'(hkl)$ is the "pseudo-structure factor" for the (hkl) plane, x, y and z are the atomic coordinates in the unit cell, U_s is the self potential and U_o is the overlap potential. The "pseudo-structure factor", F' (hkl), is represented by

$$F'(hkl) = \sum_{i=1}^{N} q_i e^{(-4\frac{\pi^2}{\eta}\sin^2\theta)} e^{(-2\pi i(hx_i + ky_i + lz_i))} ,\qquad (6)$$

where η is the width parameter of the ith Gaussian distribution. The self potential, U_s, and the overlap potential, U_o, respectively become

$$U_s = 4q_i\sqrt{\frac{\eta}{4\pi}} \qquad (7)$$

and

$$U_o = 4\sqrt{\frac{\eta}{4\pi}} \sum_{j=1 \neq i}^{N-1} \frac{q_i}{r_{ij}} \int_0^\infty r_{ij} e^{(-\eta r^2)} dr. \qquad (8)$$

The Coulomb enerhgy of a mineral can be obtained by substituting equations (5), (6), (7) and (8) into (4). Note that the potential calculated by equation (5) should converge as a function of h, k and l.

Pauli Repulsion Energy

There are two types of Pauli repulsion energy representation: a normal reciprocal and an exponential form (Moelwyn-Huges, 1961). In this study, the exponential form was used. For two charged bodies, A and B, their Pauli repulsion energy becomes

$$E_r = b\left(1 + \frac{q_A}{n_A} + \frac{q_B}{n_B}\right) \exp\left(\frac{r_{PA} + r_{PB} - r_{AB}}{\rho}\right) ,\qquad (9)$$

where b and ρ are the empirical constants, n_A and

n_B are respectively the number of the electrons in the outermost closed shell, r_{PA} and r_{PB} are respectively the pauli radii of A and B, and r_{AB} is the distance between A and B. Thus, for a mineral having N atoms in its unit cell, the Pauli repulsion energy for its one mole of unit cell is calculated by the following direct interaction calculation method:

$$E_r = \frac{1}{2} N_A \sum_{i=1}^{N} \sum_{j=1 \neq i}^{\infty} b\left(1 + \frac{q_i}{n_i} + \frac{q_j}{n_j}\right)$$

$$\exp\left(\frac{r_{pi} + r_{pj} - r_{ij}}{\rho}\right) .\qquad (10)$$

The Pauli repulsion energy is approximately inversly proportional to the sixth power of the interatomic distance and, thus, fastly converge.

London Energy

London energy, E_1, between a cation and an anion is calculated by

$$E_1 = -3\alpha^+\alpha^- \frac{(I.E.)(E.A.)}{2r^6(I.E + E.A.)} ,\qquad (11)$$

where α^+ and α^- are the polarizabilities of the cation and anion, respectively, I E. is the ionization energy of the cation, E.A. is the electron affinity of the anion (Sebera, 1964). London energy is always positive regardless of whether the interactions are berween cations, between anions or between a cation and an anion. For a mineral, its London energy for one mole of the unit cell becomes

$$E_1 = -\frac{3}{4} N_A \sum_{i=1}^{N} \sum_{j=1 \neq i}^{\infty} \alpha^i \alpha^j \frac{(I.E.)_i (E.A.)_j}{r_{ij}^6 ((I.E.)_i + (E.A.)_j)}$$

$$(12)$$

METHOD OF STUDY

To calculate the Coulomb, Pauli repulsion and London energy of a phyllosilicate, we must know details of its crystal structure and chemical composition. Moreover, for the purpose of this study, we need to know the structural details, such as the cell dimensions, the interaxial angles and the atomic positions

in the unit cell, as a function of the c-dimension variations. Few structural reports on phyllosilicates are available in this respect. The author made a computer program, namely CLAYSEC, which can simulate the crystal structures of dioctahedral phyllosilicates with given chemical compositions and d(001) for 1M and d(002) for 2M1 phyllosilicates(Yu, 1990). CKLYSEC has been proved fairly accurate (Yu and Slaughter, 1991). Thus, the author obtained all the necessary structural details of the phyllosilicates with CLAYSEC for this study. Table 1 compares the computer simulated structural data of pyrophyllite having 9.0 Å to those having 9.2 Å d(001).

The binding energy calculation in this study is based on partly ionic model, that is, Coulomb and Pauli repulsion energy calculation use effective ionic charges rather than formal valence charges of the constituent atoms. The effective ionic charge, q_e, of an atom is estimated by multiplying the ionicity, I, of the bond between the atom and another to its formal valence charge q:

$$q_e = q I .\qquad (13)$$

The ionicity between two atoms is calculated by a modified Hannay and Smyth's empirical equation (Hannay and Smyth, 1946):

Table 1. Comparison of the computer simulated structural parameters of pyrophyllite, having 9.0 Å and 9.2 Å d(001). The space group is C2/m.

	Pyrophyllite, 9.0 Å d(001)			Pyrophyllite, 9.2 Å d(001)		
Atomic Coordinates:						
	x	y	z	x	y	z
Si	.4254	.3276	.2942	.4231	.3276	.2878
Al	.0000	.3333	.0000	.0000	.3333	.0000
O1	.1903	.2526	.3593	.1874	.2526	.3515
O2	.4615	.5000	.3426	.4587	.5000	.3352
O3	.3488	.3091	.1079	.3480	.3091	.1055
OH	.4216	.0000	.1079	.4207	.0000	.1281

Cell—Dimensions and Interaxial Angles:

a	5.2218	5.2218
b	9.0444	9.0444
c	9.2034	9.3991
β	102.0688	101.8139

$$I = \frac{N}{M}[0.16(x_A - x_B) + 0.035(x_A - x_B)^2] + (1 - \frac{N}{M}) ,\qquad (14)$$

where N is the number of the valence electrons, M is the coordination number of the cation and X_A and X_B are the electronegativities of the bond forming atom A and B, respectively. This study uses Pauling's electronegativities (Huheey, 1978). Table 2 lists the calculated effective ionic charges of the atoms in muscovite.

To calculate Pauli repulsion energy by equation (10), one must determine the empirical constants, b and ρ, and the Pauli radii of the constituent atoms. After several energy calculations, it is found that the optimum values for phyllosilicates are b=0.038, ρ=0.13 and the Pauli radii listed in Table 3.

Table 2. Calculated effective inoic charges of the constituent atoms of muscovite.

Atoms	Effective Ionic Charge	Atoms	Effective Ionic Charge
K	0.943243	O3	−0.755761
Si+Al	1.302006	O4	−1.109180
Al	2.115018	O5	−1.109180
O1	−0.755761	OH	−0.705006
O2	−0.755761		

Table 3. Pauli radii used in the binding energy calculation.

Element	Layer	Radii (Å)
Si	Tetrahedral	0.3600
Al	Tetrahedral	0.4500
Fe^{3+}	Tetrahedral	0.5670
O	Tetrahedral	0.9680
Al	Octahedral	0.6075
Fe^{3+}	Octahedral	0.7065
Fe^{2+}	Octahedral	0.8280
Mg	Octahedral	0.7740
O	Octahedral	0.9920
K	Interlayer	1.4850
Na	Interlayer	1.3140
Ca	Interlayer	1.3200
O	Interlayer	0.8000
H	Interlayer	0.1500

London energy calculation requires the polarizabilites and ionization energies (or electron affinities) of the constituent atoms. The polarizabilities of the constituent atoms of phyllosilicates are obtained by interpolation between the theoretical polarizabilities of ions from Pauling (1926) as a function of the atom's effective ionic charges (Yu, 1990). Table 4 lists the calculated polarizabilities of the constituent atoms of paragonite. The ionization energies or electron affinities of the atoms are estimated from parabolic relations between the charges and energies. The parabolic equations are

$$E = 143.56q_e + 109.9q_e^2 ,\qquad (15)$$

$$E = 93.365q_e + 94.344q_e^2 ,\qquad (16)$$

$$E = -9.926q_e + 147.86q_e^2 ,\qquad (17)$$

$$E = 90.979q_e + 85.084q_e^2 ,\qquad (18)$$

$$E = 85.561q_e + 95.656q_e^2 ,\qquad (19)$$

where equation (15) is for O, equation (16) is for Si, equation (17) is for Al, equation (18) is for Mg and equation (19) is for Fe. Table 5 shows the calculated ionization energies and electron affinities of the constituent atoms of margarite according to their effective ionic charges.

After optimizing the empirical constants and other parameters in the energy calculation equations as the above, the Coulomb, Pauli repulsion and London energies were calcualted with a computer program, called CPLEC (Yu, 1990), based on the simulated crystal structures of pyrophyllite, illite, muscovite, paragonite and margarite with CLAYSEC. CPLEC is written in FORTRAN -77 and executable on VAX-8600a and CYBER-205. Table 6 summarizes the structural chemical formulae of the minerals.

Table4. The calculated polarizabillties (Å^{-3}) of the constituent atoms of paragonite.

Atoms	Polarizability	Atoms	Polarizability
Na	0.1790	O3	1.9646
Si+Al	0.1533	O4	2.5085
Al	0.0892	O5	2.5085
O1	1.9646	OH	1.8870
O2	1.9646		

RESULTS AND DISCUSSION

Tables 7, 8, 9, 10 and 11 respectively list the calculated Coulomb, Pauli repulsion and London energies of pyrophllite, illite, muscovite, paragonite and margarite as a function of d(001) (or d (002)). As d(001) or d(002) increases, the Coulomb and London energy increase and Pauli repulsion energy decreases. The phyllosilicates should have the minimum sum of the energies with their optimum d-spacings. If the d-spacing is shorter than the optimum one, the amount of Pauli repulsion energy increase is greater than the amount of Coulomb and London energy decrease, and consequently, make the total energy more positive. Similarly, if the d-spacing is longer than the optimum one, the amount of Coulomb and London energy increase is greater than the Pauli repulsion energy decrease, and consequently, make the total energy more positive again.

Many mineralogists, crystallographers and soil scientists think that the Coulomb and Pauli repulsion interactions among silicate layers and interlayer cations play a very important role, while London force among them has a negligible role, in determining the d(001) or d(002) of a phyllosilicate. Is London energy really negligible, compared with Coulomb and Pauli repulsion energy? If not, how much does London energy contribute to determining the d-spacings, especially as a function of the layer charges of the phyllosilicates? To answer these questions, we may plot the sums of the Coulomb and Pauli repulsion energies (C+P) and the sums of the Coulomb, Pauli repulsing and London energies (C+P+L) against d(001) or d(002) of pyrophyllite (Fig. 1), illite (Fig. 2), muscovite (Fig. 3), paragonite (Fig. 4) and margarite (Fig. 5).

In Fig. 1, for pyrophyllite, C+P continuously decreases as d(001) increases while C+P+L is showing a minimum at 9.2 Å d(001). The reason for continuous decrease of C+P is that the interlayer space of pyrophyllite is bound by the oxygens of silicate layers without any interlayercation. The oxygens exerts Coulomb repulsion

Table 5. The calculated ionization energies and electron affinities (kcal/mole) of the constituent atoms of margarite.

Atoms	Ionization Energy	Electron Affinity
Ca	237.3715	
Si+Al	388.7998	
Al	641.9785	
O1		−42.9696
O2		−42.9696
O3		−42.9696
O4		−16.9401
O5		−16.9401
O6		−46.6931

Table 6. Structural chemical formulae of the phyllosilicates used in this study.

Mineral	Structural Chemical Formula
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$
Illite	$K_{.80}Al_{1.88}Fe^{3+}_{.30}Mg_{.17}(Si_{3.82}Al_{.18})O_{10}(OH)_2$
Muscovite	$KAl_2(Si_3Al)O_{10}(OH)_2$
Paragonite	$NaAl_2(Si_3Al)O_{10}(OH)_2$
Margarite	$CaAl_2(Si_2Al_2)O_{10}(OH)_2$

Table 7. Calculated binding energies (kcal/mole) of pyrophyllite as a function of d(001) (Å).

d(001)	C*	P	L	C+P	C+P+L
9.0	−3401.714	46.069	−39.168	−3355.645	−3394.813
9.1	−3402.049	45.954	−38.831	−3356.095	−3394.927
9.2	−3402.304	45.898	−38.559	−3356.406	−3394.964
9.3	−3402.488	45.869	−38.334	−3356.619	−3394.954
9.4	−3402.682	45.868	−38.150	−3356.814	−3394.964

* : C = Coulomb energy.
P = Pauli repulsion energy.
L = London energy.
C+P = Sum of Coulomb and Pauli repulsion energy.
C+P+L = Sum of Coulomb, Pauli repulsion and London energy.
(The above notations will be also used in Tables 8, 9, 10 and 11).

Table 8. Calculated binding energies (Kcal/mole) of illite as a function of d(001) (Å).

d(001)	C	P	S	C+P	C+P+L
9.5	−3450.210	52.855	−39.349	−3397.355	−3436.703
9.7	−3449.901	49.817	−38.885	−3400.084	−3438.968
9.8	−3449.689	48.701	−38.689	−3400.988	−3439.677
9.9	−3449.445	47.794	−38.514	−3401.651	−3440.165
10.0	−3449.159	47.059	−38.354	−3402.100	−3440.454
10.1	−3448.862	46.468	−38.209	−3402.394	−3440.603
10.2	−3448.536	45.996	−38.078	−3402.540	−3440.618
10.3	−3448.192	45.617	−37.964	−3402.575	−3440.538
10.5	−3447.484	45.086	−37.754	−3402.398	−3440.153

Table 9. Calculated binding energies (Kcal/mole) of muscovite as a function of d(002) (Å).

d(002)	C	P	L	C+P	C+P+L
9.6	−3692.422	52.271	−36.840	−3640.151	−3678.214
9.8	−3689.947	48.087	−36.403	−3641.860	−3678.263
9.9	−3688.578	46.455	−36.217	−3642.123	−3678.340
10.0	−3687.199	45.149	−36.048	−3642.050	−3678.094
10.1	−3685.746	44.100	−35.893	−3641.646	−3677.539
10.2	−3682.703	42.600	−35.637	−3640.103	−3675.730

Table 10. Calculated binding energies (Kcal/mole) of paragonite as a function of d(002) (Å).

d(002)	C	P	L	C+P	C+P+L
9.3	−3695.087	52.556	−36.576	−3642.531	−3679.107
9.5	−3692.660	48.108	−36.094	−3644.552	−3680.646
9.6	−3691.243	46.460	−35.899	−3644.783	−3680.682
9.7	−3689.841	45.129	−35.732	−3644.712	−3680.443
9.9	−3688.322	44.045	−35.584	−3644.277	−3679.860

Table 11. Calculated binding energies (Kcal/mole) of margarite as a function of d(002) (Å).

d(002)	C	P	L	C+P	C+P+L
9.2	−4108.331	83.709	−34.100	−4024.622	−4058.713
9.4	−4098.293	67.543	−33.280	−4030.750	−4064.030
9.5	−4092.985	61.538	−32.945	−4031.447	−4064.393
9.6	−4387.528	56.646	−32.649	−4030.882	−4063.532
9.7	−4081.862	52.673	−32.387	−4029.189	−4061.576
9.9	−4070.228	46.899	−31.942	−4023.329	−4055.271

and Pauli reapulsion.force to each other and these forces decreases as the interlayer space expands. It suggests that if the layers of pyrophyllite have only Coulomb and Pauli repulsion interactions, they should be separated infinitely. However, London force holds the layers and maintain a stable distance between the layers as shown by C+P+L in Fig. 1. Thus, London energy has major responsibility for determining the c-dimension of pyrophyllite. Fig. 1 shows the energy decrease of C+P+L from 9.35 A to 9.4 Å d(001). After several energy calculations of pyrophyllite with various calculation parameters, it turned out that 9.4 Å d (001) is a local minimum (Yu, 1990).

Fig. 2 shows the C+P and C+P+L variations against the d(001) of illite whose layer charge is 0.5 e-quivalents on the bases of $O_0(OH)_2$ formula. Both curves show mnimums, but they are at different d (001): 10.3 Å for C+P and 10.1 Å for C+P+L. For illite, the London force plays relatively less important role in holding the silicate layers than that for pyrophyllite. This is because illite has interlayer cations, and consequently, Coulomb atrractions between the oxygens and the interlayer cations, However, the contribution of London energy is still significant in determining the c-dimension of illite, because London force make the d(001) collapse to 10.1 Å which is very close to that of natural illite from 10.3 Å which is the d(001)

of the minimum C+P.

Figs. 3, 4 and 5 show the C+P and C+P+L variations as a function of d(002) of muscovite, paragonite and margarite. Muscovite shows the minimums at 9.93 and 9.91 Å d(002) of C+P and C+P+L respectively (Fig. 3). Paragonite shows the minimums at 9.62 and 9. 56 Å d(002) of C+P and C+P+L, respectively (Fig. 4). Margatite shows the minimums at 9.50 and 9.49 Å d (002) of C+Pand C+P+L, respectively. The difference of the minimums between C+P and C+P+L of margarite is the least, because margarite has the highest layer charge, two equivalents on the basis of O_0 $(OH)_2$ formula, and consequently, the most dominant Coulomb and Pauli repulsion interactions between the oxygens and the interlayer cations. The difference of the minimums between C+P and C+P+L of muscovite is less than that of paragonite, because the interlayer cation of muscovite, K, is more ionic than that of paragonite, Na, even though they have the same layer charge of one equivalent on the basis of O_0 $(OH)_2$ formula. On the contrary to the cases of pyrophyllite and illite, however, the minimums of C+P of these minerals show slight difference from the minimums of C+P+L. Thus, London energy may little contribute to determining the c-dimensions of these minerals, compared with the contribution of Coulomb and Pauli repulsion energy.
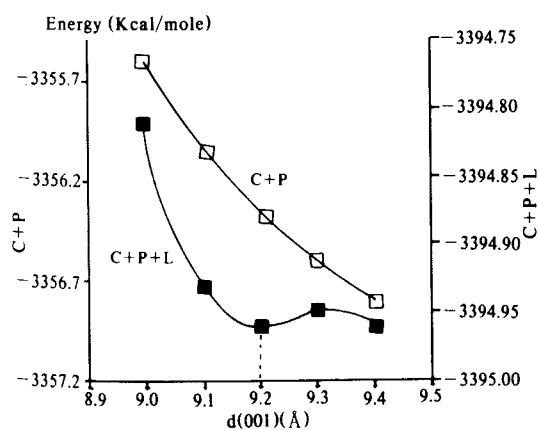

Fig. 1. The binding energy variation of pyrophyllite as a function of d(001). The right and left ordinate represent C+P and C+P+L, respectively. The open squares are for C+P values and the solid squares are for C+P+L values. The broken line represents the minimum.
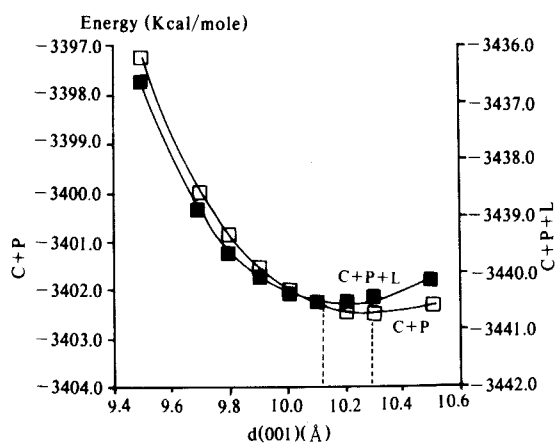

Fig. 2. The binding energy variation of illite as a function of d(001). All the notations and symbols are the same as in Fig. 1.
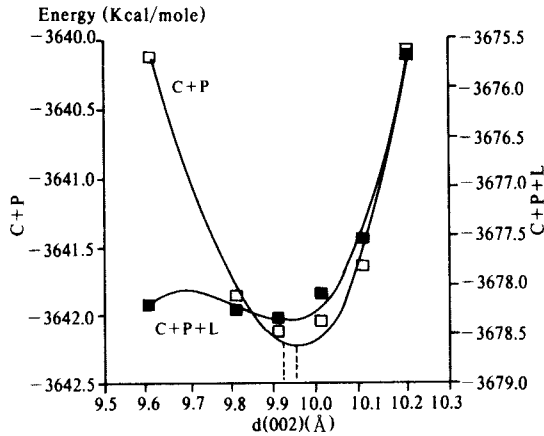
Energy (Kcal/mole)

Fig. 3. The binding energy variation of muscovite as a function of d(002). All the notations and symbols are the same as in Fig. 1.

Energy (Kcal/mole)
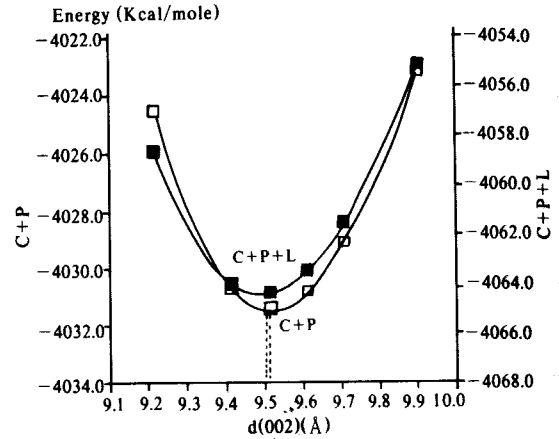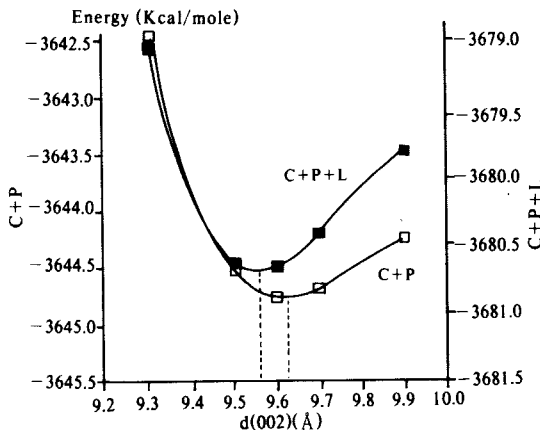

Fig. 4. The binding energy variation of paragonite as a funcion of d(002). All the notations and symbols are the same as in Fig. 1.

Energy (Kcal/mole)

Fig. 5. The binding energy variation of margarite as a function of d(002). All the notations and symbols are the same as in Fig. 1.

CONCLUSIONS

The binding energy calculation showed that Coulomb and Pauli repulsion energy play a major role in determining the c-dimension of the phyllosilicates having the interlayer cations, such as illite, muscovite, paragonite and margarite. On the other hand, London energy is a major factor in maintaining the c-dimensions of the phyllosilicates without any interlayer cation, such as pyrophyllite. As in the case of pyrophyllite, illite and smectite, however, when the layer charge of phyllosilicates are less than one equivalent, London energy is significant in determining the c-dimensions, even though they have the interlayer cations. The significance of the London energy in the c-dimension control decreases as the layer charges of phyllosilicates increase.

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