# BASELINE STUDIES OF THE CLAY MINERALS SOCIETY SOURCE CLAYS: LAYER-CHARGE DETERMINATION AND CHARACTERISTICS OF THOSE MINERALS CONTAINING 2:1 LAYERS

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## INTRODUCTION

The layer charge is perhaps the single most significant characteristic of 2:1 layer phyllosilicates. Layer charge affects cation-retention capacity and adsorption of water, and various polar organic molecules. The effects of layer charge on the sorptive properties of organo-clays were illustrated by Lee *et al.* (1990). It is generally agreed that the classification of 2:1 silicate clays, which is a continuing problem, may be resolved by taking into account the magnitude of the layer charge (Bailey *et al.*, 1971; Malla and Douglas, 1987). Studies on structural chemistry also confirm the importance of the layer charge for the characterization of the 2:1 phyllosilicates (Newman and Brown, 1987).

Layer charge involves charge per $[O_{20}(OH)_4]$ and the sum of the tetrahedral and octahedral charges. Cation exchange capacity (CEC) results not only from the layer charge, but also pH-dependent edge charges. If the molecular mass ($M$) or formula weight of the phyllosilicates and the layer charge are known, the CEC due to interlayer charge ($\xi$) can be calculated from the following equation:

$$\text{Interlayer CEC (cmol}_c\text{kg}^{-1}) = 10^5 \times \xi/M \quad (1)$$

The molecular mass (Table 1) is without dimension, because it is a relative property. The mean molecular mass of the 2:1 phyllosilicates varies from 370–390. The total CEC exceeds the interlayer CEC, because of charge at crystal edges. For smectites, the edge charge is between 10 and 30% and on average it is ~20% of the total CEC (Lagaly, 1981). Non-exchangeable cations such as $K^+$ in illite or mica are excluded from the total apparent CEC, but they are included in the layer charge.

## DETERMINATION OF LAYER CHARGE

Traditionally, the layer charge is calculated from the structural formula of homoionic pure clay mineral specimens (Ross and Hendricks, 1945). From the occupancy of elements in the tetrahedral and octahedral sheets, the charge distribution between these sheets may be estimated. Details of the calculation are given in Köster (1977) and Newman and Brown (1987). Hofmann and Klemen (1950) suggested that with Li saturation and heating at 200°C, the octahedral charge can be neutralized. Thus, the source of the dominant charge may be located (Ertem, 1972; Lim and Jackson, 1986; Jaynes and Bigham, 1987; Madejova *et al.*, 1996).

However, the structural formula technique is prone to large errors because of impurities, as is generally the case in soil clays. Lagaly and Weiss (1969), Lagaly *et al.* (1976) and Lagaly (1981, 1982) described a method to determine the layer charge based on the measurement of basal spacings after exchange with alkylammonium cations of varying chain lengths. Several simplifications and improvements of this technique have been made (Ruehlicke and Kohler, 1981; Ghabru *et al.*, 1989; Olis *et al.*, 1990; Stanjek *et al.*, 1992; Lagaly, 1994).

Expansion of soil clay minerals of the 2:1 layer type by means of the alkylammonium-intercalation technique provides greater insight into the nature of the charge characteristics of these clay minerals than other methods (Senkayi *et al.*, 1985). The most significant advantage of this method is that it can determine the layer charge of several 2:1 clay minerals in mixtures. In addition, layer charge heterogeneity within a clay mineral can be determined.

## ALKYLAMMONIUM METHOD

Alkylammonium ions are capable of expanding nearly all finely dispersed 2:1 clay minerals except unweathered mica, within 24 h. The kinetics of expansion with alkylammonium are probably related to the charge characteristics and size of the particles. In this technique, the 2:1 clay minerals are reacted with an aqueous solution of primary *n*-alkylammonium salts: $C_nH_{2n+1}NH_3^+Cl^-$, where $C_n$ is the carbon chain. They can be prepared according to Ruehlicke and Kohler (1981) and Lagaly (1994). The synthesis of the alkylammonium salts is represented by the following equation ($R$ represents the alkyl group):

$$R\text{-NH}_2 + \text{HCl} \rightarrow R\text{-NH}_3^+ + \text{Cl}^- \quad (2)$$

The solution concentration of the alkylammonium ions depends on the chain length. Optimum concentrations, according to Ruehlicke and Kohler (1981), are given in Table 2. The solutions are stored at 65°C

Table 1. Approximate layer charge of 2:1 phyllosilicates.

| Mineral | Layer charge[1] per half unit-cell $[O_{10}(OH)_2]$ | Mean molecular mass $(M)$[2] $[O_{10}(OH)_2]$ | Interlayer CEC $cmol_c kg^{-1}$ |
|---|---|---|---|
| Hectorite | 0.20–0.25 | 380 | 50–65 |
| Montmorillonite | 0.25–0.40 | 360 | 70–110 |
| Vermiculite | 0.50–0.80 | 390 | 130–210 |
| Illite | 0.60–0.90 | 385 | 160–230 |
| Biotite | ~1.00 | 450 | ~220 |
| Muscovite | ~1.00 | 390 | ~260 |

[1] Without exchangeable cations and calculated for typical composition (Lagaly, 1994, corrected).
[2] Formula weight.

and can be used for 3–4 months. Due to increased decomposition, storing for a longer period of time at 65°C is not advised. Interaction between 2:1 clay minerals and alkylammonium ions is achieved by dispersing the clay samples in the solution and incubating overnight at 65°C. If the alkylammonium solution becomes turbid during storage, it can be heated to 65°C before use. Then samples are washed with a mixture of alcohol and water to remove excess alkylammonium salt (see Ruehlicke and Kohler, 1981; Lagaly, 1994). Oriented mineral-aggregate mounts are prepared on glass slides and analyzed by X-ray diffraction (XRD).

## LAYER-CHARGE DETERMINATION

In low-charge 2:1 clay minerals, the arrangement of alkylammonium depends on the chain length of the cations. Short chains are arranged in monolayers (Figure 1). The area of an alkylammonium ion, $A_c$, is determined (Lagaly and Weiss, 1969; Lagaly, 1981, 1994) by the following equation:

$$A_c = 1.27 \times 4.5 \; n_c + 14 \; (\text{Å}^2) \tag{3}$$

where $n_c$ is the number of the carbon atoms in the alkyl chain. The area for a half unit-cell of a given 2:1 phyllosilicate ($A_e$) is equal to $ab/2$ (Figure 1) where $a$ and $b$ are unit-cell parameters. When the monolayer of alkylammonium ions is close-packed, then $A_c$ will be equal to $A_e$ and the charge can be calculated from the following equation:

$$\text{layer charge} = \xi = \frac{A_e}{A_c} = \frac{ab/2}{5.67 n_c(\text{I}) + 14} \tag{4}$$

where $n_c$ (I) is the number of carbon atoms in a chain, which are close packed in the monolayer; ($ab$) is the unit-cell surface area of the clay mineral. Thus, for example, a dioctahedral montmorillonite will have a surface area of 46.5 Å$^2$ (half of which equals 23.25 Å$^2$) and the layer charge is:

Table 2. Optimum concentration for the *n*-alkylammonium chloride solutions.

| Chain length ($n_c$) | Molarity |
|---|---|
| 6 | 2.0 |
| 6 to 9 | 0.5 |
| 10 to 15 | 0.1 |
| 16 | 0.05 |
| 17 and 18 | 0.03 |

$$\xi = \frac{23.25}{5.67 n_c(\text{I}) + 14} \tag{5}$$

where I represents a monolayer alkylammonium arrangement. The $d$ value obtained from the XRD pattern is between 13.4 and 13.6 Å. When the chain length increases above $n_c$ (I) at the monolayer coverage, the alkylammonium ions will produce an incomplete bilayer and a shift in $d$ value from 13.6 to 17.6 Å (Figure 1). The nature of discontinuity of basal spacing, $d(001)$, depends on the homogeneity or heterogeneity of the layer charge of the silicate clay mineral. In the case of charge heterogeneity, the cation density varies from one interlayer to another, between the two limiting values calculated from the transition region.

The value of $n_c$ at $d(001)$ of 13.6 Å gives the upper value of $\xi$, whereas the lowest value of $n_c$ at the spac-
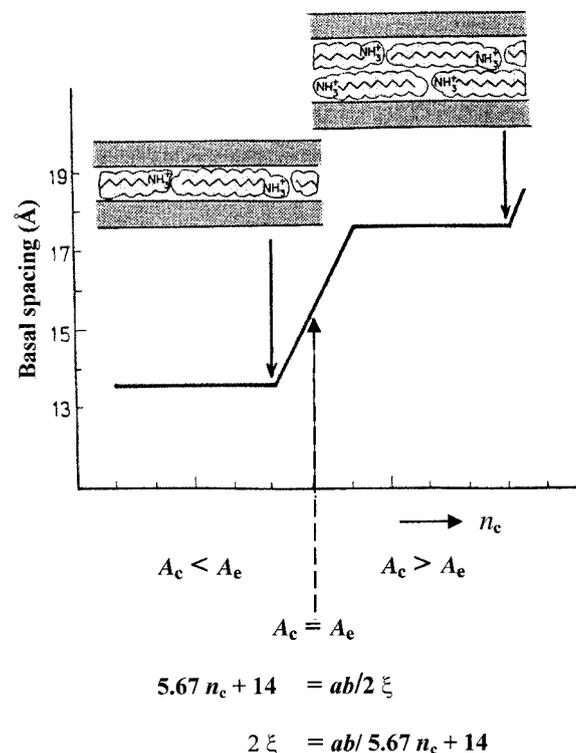


Figure 1. Alkylammonuim monolayers and bilayers in low-charge 2:1 clay minerals and calculation of the cation density from $n_c$ at the monolayer-bilayer transition (from Lagaly, 1981).
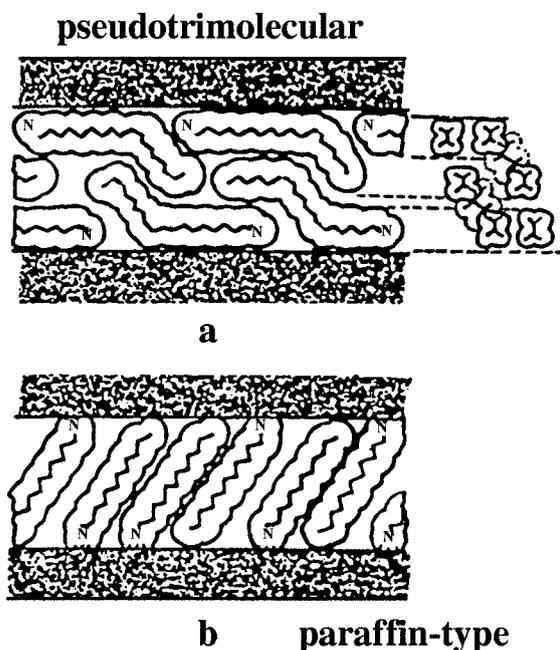
## pseudotrimolecular



**a**



**b        paraffin-type**

Figure 2.   Arrangements of *n*-alkylammonium ions; (a) pseudotrimolecular and (b) paraffin-type structure (from Lagaly, 1982).



Figure 3.   Dependence of tilt angle ($\alpha$, in degrees) of alkylammonium cations on layer-charge density of high-charge 2:1 phyllosilicates. Curve 1 is from Lagaly and Weiss (1969), curve 2 from Ghabru *et al.* (1989), and curve 3 is from Mermut and St. Arnaud (1990).

ing of 17.7 Å provides the lower limit of the charge distribution ($\xi$). The average of both values is often close to the mean layer charge. Mean layer charge and the charge distribution can be calculated from the basal spacing in the transition range, *i.e.* between 13.6 and 17.7 Å (for details, see Lagaly, 1981, 1994; Rengasamy *et al.*, 1976; for particle size corrections, see Lagaly, 1994; for an improved method by curve fitting, see Stanjek and Friedrich, 1986). Studies show that smectites commonly have charge heterogeneity.

A typical *d* value for bilayer arrangements is 17.6 Å. Beidellite has higher charge (charge deficits exist both in tetrahedral and octahedral sheets) and alkylammonium ions can form densely packed bilayers. In a complete bilayer occupancy (Figure 2), $A_c = 2A_e$; in this case, the charge can be calculated from the following simple equation:

$$\xi = \frac{ab}{5.67n_c(\text{II}) + 14} \tag{6}$$

where II indicates a bilayer arrangement.

If the area required for the flat-lying alkylammonium cation is more than twice the area available for each monovalent cation ($A_c > 2A_e$), the transition from a bilayer to a pseudotrimolecular layer occurs (Figure 2). This transition, if observed, gives further information on the charge distribution (see Lagaly, 1994). At still higher charge densities, alkylammonium cations will form paraffin-type structures (Figure 2) (Lagaly and Weiss, 1969). In this type of structure, the angle ($\alpha$)
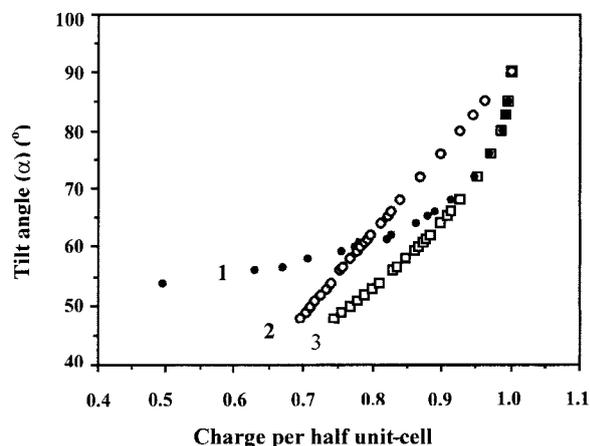
of the cations is controlled by the layer charge density:

$$\alpha = \sin^{-1}\frac{\Delta d}{1.27} \tag{7}$$

Where $\Delta$ represents a slight increase in *d* spacing.

Based on experimental evidence, a linear relationship between the tilt angle ($\alpha$) and the layer charge was suggested by Ghabru *et al.* (1989). Further studies by Mermut and St. Arnaud (1990) and Mermut (1994) suggested that the layer charge of high-charge 2:1 phyllosilicates can be best calculated using the sin $\alpha$ curve (Figure 3, curve 3). Studies on phlogopite and high-charge vermiculite by Vali *et al.* (1992) confirmed the validity of the sin $\alpha$ curve as suggested by Mermut and St. Arnaud (1990) (Figure 3, curve 3). The tilt angles ($\alpha$) of most highly charged phyllosilicates are <65°. Above this point, as seen in the sin $\alpha$ curve, the change in the curve is very sensitive to layer charge. Using this curve, $\alpha = 65°$ shows a 0.91 charge per $[O_{10}(OH)_2]$ and angles between 65 and 90° will contribute only small additional fractions to the potential charge.

Vertical arrangements (*i.e.* $\alpha = 90°$) of alkylammonium ions were also reported and evidence of these orientations were shown by high-resolution transmission electron microscopy (HRTEM; Marcks *et al.*, 1989). However, XRD data for these arrangements seem to result in a lower degree of tilt angle. Laird *et al.* (1989) and Laird (1994) found that the layer charge determined by the alkylammonium and structural-formula methods were linearly correlated; however, the values that were determined by the alkylammonium method were 20–30% lower than those by the structural formula method.

Table 3. Measured *d* values and derived parameters of the 2:1 Source Clays of the Clay Minerals Society.

| $n_c$ | SHCa-1 | SAz-1 | STx-1 | SWy-1[5a] | SWy-2 | SWy-1[5] | Syn-1 |
|---|---|---|---|---|---|---|---|
| | | | | *d* values (Å)[6] | | | |
| 5 | — | — | — | — | 13.4 | — | 11.8 |
| 6 | 13.1 | 13.3 | 13.3 | — | 13.4 | 13.3 | 11.8 |
| 7 | 13.3 | 13.5 | 13.4 | — | 13.6 | 13.4 | 11.8 |
| 8 | 13.3 | 13.7 | 13.5 | 13.7 | 13.6 | 13.4 | 11.8 |
| 9 | 13.4 | 14.9 | 13.7 | 14.3 | — | 13.4 | — |
| 10 | 13.4 | 15.2 | 14.5 | 15.0 | 14.9 | 13.4 | 11.9 |
| 11 | 13.5 | 16.1 | 15.1 | 15.6 | 15.4 | 13.6 | 12.1 |
| 12 | 13.6 | 17.0 | 15.6 | 16.3 | 16.0 | 13.9 | 12.7 |
| 13 | 13.6 | 17.3 | 16.2 | 17.0 | 16.6 | 14.7 | 13.5 |
| 14 | 13.7 | 17.3 | 16.7 | 17.1 | 17.2 | 15.2 | 14.1 |
| 15 | 13.7 | 17.7 | 17.2 | 17.8 | 17.6 | 15.5 | 14.3 |
| 16 | 14.0 | 18.0 | 17.5 | 18.0 | 17.6 | 17.3 | 14.6 |
| 17 | 15.0 | 19.0 | 17.7 | — | — | 17.3 | — |
| 18 | 15.9 | 19.4 | 17.9 | — | 18.6 | 17.7 | 15.1 |
| | | | | Derived parameters[7] | | | |
| [1] | 0.20 | 0.24 | 0.24 | 0.26 | 0.26 | 0.23 | 0.29 |
| [2] | 0.31 | 0.46 | 0.42 | 0.42 | 0.42 | 0.33 | <0.24 |
| [3] | 0.23 | 0.35 | 0.31 | 0.33 | 0.32 | 0.27 | 0.24 |
| [4] | 0.64 | 0.97 | 0.86 | 0.89 | 0.87 | 0.75 | 0.63 |

[1] Minimum limit of layer charge: charges unit $(Si,Al)_4O_{10}$ (eq/mol) calculated from the charge distribution.
[2] Maximum limit of layer charge: charges unit $(Si,Al)_4O_{10}$ (eq/mol) calculated from the charge distribution.
[3] Mean layer charge.
[4] Charge calculated as cmol/kg.
[5] Analyzed by Lagaly, 5a by Mermut.
[6] From XRD pattern *d*(001).
[7] Calculated by Lagaly.

## CHARGE DISTRIBUTION IN TETRAHEDRAL AND OCTAHEDRAL SHEETS

As mentioned above, Hofmann and Klemen (1950) suggested that Li$^+$ can migrate from the interlayer to vacant octahedral sites, which results in the neutralization of the negative charge originating in the octahedral sheet owing to cation substitution. Greene-Kelly (1953) utilized this technique to differentiate montmorillonite from beidellite. Malla and Douglas (1987) extended the method using alkylammonium-ion exchange to estimate the layer charge located in both the tetrahedral and octahedral sheets of the 2:1 phyllosilicates. Malla and Douglas (1987) suggested that low-charge phyllosilicates having tetrahedral charge of <0.24 per $[O_{10}(OH)_2]$ cannot be completely characterized by alkylammonium exchange.

## CHARGE DENSITY AND MEAN LAYER CHARGE

As seen in Table 3 (cols. 5 and 6), spacings calculated from the short alkylammonium ions for SWY-1 are slightly larger than other data. Changes in this order are often observed from sample to sample. For instance, Lagaly (unpublished data) measured the charge distribution of several samples of Wyoming bentonites and arrived at the mean layer charges shown in Table 4.

Table 4. The charge distribution of several samples of Wyoming bentonites.

| Sample name, date and number | Layer charge eq/mol |
|---|---|
| Upton, 1975, M26 | 0.31 |
| Greenbond, 1976, M40 | 0.31; 0.30; 0.30 |
| Greenbond, 1976, M40 | 0.28 |
| Greenbond, 1976, M40[1] | 0.27 |
| Greenbond, 1976, M40[2] | 0.28 |
| Greenbond, 1976, M40A | 0.29 |
| Volclay, 1976, M40B | 0.27 |
| Volclay, 1976, Muller Vonmoos | 0.28 |

[1] Particles 2–63 μm (Lagaly, 1994, Table 7).
[2] Particles < 0.06 μm (Lagaly, 1994, Table 7).
M indicates clay-mineral sample.

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