

THE HETEROGENEITY OF THE CHARGE DENSITY IN MONTMORILLONITES

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Abstract—The heterogeneity of the interlayer cation density and the corresponding mean layer charge density due to isomorphous substitution have been determined for six montmorillonite samples. This has been achieved by considering the transition of a monolayer to a double layer complex with alkylammonium ions. The transition is related to the interlayer cation density, together with the variation of the apparent spacings, which in turn is related to the composition of this two-component mixture.

All the samples showed a heterogeneous interlayer cation distribution and a differing mean charge density.

INTRODUCTION

Much attention has been paid to the charge density of clay minerals (see, e.g. Lagaly and Weiss, 1969; Mering and Pedro, 1969). Besides the mean value of the charge density, the distribution of charge is of utmost importance. There are several methods for determining charge density which generally give a biased mean value and do not yield information about the homogeneity of the isomorphous substitution. Chemical analysis and CEC contain the effect of the 'broken bonds', the percentage of which depends on the sample under consideration. The CEC further depends on the method of determination and varies to a large extent with the pH (Maes, 1973).

Lagaly and Weiss (1970a) have developed a method for the determination of the homogeneity of the layer charge. The samples are ion-exchanged with *n*-alkylammonium ions of different chain length, thus producing varying interlayer spacings. The transition from a monolayer to a double layer of organic cations depends on the charge density of the mineral and the size of the cation. A homogeneously charged mineral undergoes this transition in one sharp step while heterogeneously charged clay sheets show a gradual transition. The transition contains information on the relative frequency of higher and lower charged clay sheets, which may be recovered by the method described by Brown and MacEwan (1949).

Brown and MacEwan (1949) followed a method developed by Hendricks and Teller (1942) for the analysis of X-ray diffraction diagrams of a two-component interstratified assemblage. The analysis was based on curves of peak migration and applied strictly only to random interstratification. These curves showed the

variation of the apparent basal spacing as a function of the proportion of the two components. MacEwan's (1956) later method using Fourier transform techniques was not suitable for our case, since in our work only a limited number of basal reflections could be obtained.

EXPERIMENTAL

Six montmorillonites were studied: Marnia (M.A. Algeria), Camp Berteau (C.B., Morocco), Greek White (G.W., Greece), Moosburg (M.O., Germany), Wyoming Bentonite (W.B., U.S.A.) and Greek Yellow (G.Y., Greece). The clay samples were prepared in such a way to allow the application of the formula derived by Brown and MacEwan (1949), which meets the condition of a completely random succession of the phase changes determined by the interlayer spacings. The procedure is the one used by Cremers (1968) modified to some extent as described below.

The crude montmorillonite minerals were stirred in a 1 M NaCl solution for 2 hr. The supernatant was removed by decantation and renewed three times. Then the samples were washed with distilled water until spontaneous peptization occurred. The fraction <0.5 μm (e.s.d.) was separated by decantation. The peptized samples were concentrated by adding NaCl. Preferential reorganisation of flocculation is not likely to occur considering the velocity of the process (Lagaly and Weiss, 1972). The slurry was washed with an acidified (pH 3.4–4) 1 M NaCl solution for removing hydroxyaluminum compounds which may have resulted from clay decomposition. It was then immediately washed with a neutral 1 M NaCl solution and stored at 4°C in the dark. All the clays were investigated by

X-ray diffraction. Two were found to contain impurities; i.e. cristobalite (W.B.) and kaolinite (G.Y.). Salt-free samples prepared by dialysis were dried at 40°C and ground.

The alkylammonium samples were obtained by the method of Lagaly and Weiss (1970b). One hundred mg of clay were mixed with 4 ml of RNH_3^+ solution for 24 hr at 60°C. The concentration used varied with the chain length of the organic cation. For alkyl chains containing 6 carbon atoms ($n_c = 6$), the concentration was 2 N. For $6 < n_c < 10$ the solution was 0.5 N and for $n_c = 10$ it was 0.1 N. After two washings with pure ethanol the clay was exchanged a second time with the RNH_3^+ solution and was then washed 10–15 times with a 1:2 mixture of water:ethanol. The clay was dried for 1 day at 60°C and ground into particles less than 0.1 mm. Drying was then completed in high vacuum (10^{-6} Torr) for one day at 50°C. The clay was subsequently brought into a Lindemann capillary, submitted for another day to high vacuum, and the tube sealed off for X-ray investigation.

To measure the basal spacing, a Debye–Scherrer camera (ϕ 114,6) was used and the Straumanis method (Peiser *et al.*, 1955) applied. The radiation was Cu K_α ($\lambda = 1.5418 \text{ \AA}$). The accuracy of the d_{001} value lies within $\pm 0.04 \text{ \AA}$ (for $d = 13.6 \text{ \AA}$) and $\pm 0.07 \text{ \AA}$ (for $d = 17.6 \text{ \AA}$). Decisions on the existence of an integral series of basal reflections were based on only three reflections (d_{001} , d_{002} and d_{003}).

METHOD OF INVESTIGATION

(a) *Relation between critical chain length, critical cation density and the particle radius*

Combining the method of Brown and MacEwan (1949) with that of Lagaly and Weiss (1970a), we were able to determine the percentage of clay particles with a given interlayer space, corresponding to a given cation density. The latter may not always correspond to the charge densities of the individual clay sheets (Lagaly and Weiss, 1970a). However, the mean charge density of the clay sheets due to isomorphous substitution must equal the mean of the interlayer cation densities.

The transition between a monolayer and a double layer of organic cations depends on the surface of the cation $A_c (= 5.67 n_c + 14)$. It depends also on the 'equivalent area', i.e. the area available for each monovalent interlayer cation calculated as $A_c = a \times b/2\xi$ (Lagaly and Weiss, 1970a). The number of monovalent interlayer cations per formula unit ($\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$) is ξ and is called the "interlayer cation density"; a (5.3 Å) and b (9.05 Å) are unit cell parameters. For an infinitely large crystal, the critical cation density is reached when

$A_c = A_c$. This equivalency is realised for $\xi = 23.25/(5.67 n_c + 14)$ (Lagaly and Weiss, 1971). However, for finite crystals the outer interlayer cations may not occupy an entire equivalent surface A_c of the layer. This results in an increased interlayer space inducing slight displacements of the interlayer cations. These displacements may certainly be assumed for octahedrally substituted clays, and octahedral substitution has been proved experimentally for Camp Berteau and Wyoming bentonite (Glaeser *et al.*, 1972). We assume that statistically these particular cations are lying only with half of their surface between the layers (Lagaly and Weiss, 1971). As a first approximation, we may write for the surface of the cations: $A_c = A_c$. The area between the layers is then increased by the number of external interlayer cations (N) multiplied by $A_c/2$. This number may be estimated as a function of the particle radius (r) and is given by $N = 2\pi r/4.5$.

The method we follow here differs somewhat from that of Lagaly and Weiss (1971). We make a correction for the critical A_c after expansion of the interlayer volume and write A'_c as the corrected A_c .

$$A'_c = \frac{\pi r^2 + (2\pi r/4.5)A_c/2}{\pi r^2/A_c} = A_c(1 + A_c/4.5r) = A_c \times Q$$

where $\pi r^2/A_c$ is the number of interlayer cations. A_c is multiplied by a factor Q which equals 1 for an infinite crystal. However, the surface gain was estimated only by assuming that the critical chain length was still determined by A_c . A more realistic approximation of the increase in surface is given by $(2\pi r/4.5)A'_c/2$, which, when introduced into the above expression, gives a second approximation for A_c , i.e. A''_c :

$$A''_c = A_c[1 + A_c/4.5r + (A_c/4.5r)^2].$$

This iteration may be maintained until convergence and gives for Q :

$$Q = 1 + \sum_{i=1}^n (A_c/4.5r)^i.$$

We may obtain the critical chain length from $A_c = A_c \cdot Q$, or

$$n_c = (A_c \cdot Q - 14)/5.67.$$

Figure 1 gives the relation between n_c and r with $A_c = 71 \text{ \AA}^2$ ($\xi = 0.33$): (1) according to Lagaly and Weiss (1971); (2) after three iterations for Q ($n = 3$); (3) for a one term approximation in Q ($n = 1$). With this formula we then obtain the critical ξ values for the transition between a monolayer and a double layer for a given particle radius and a given chain length of the interlayer cations.

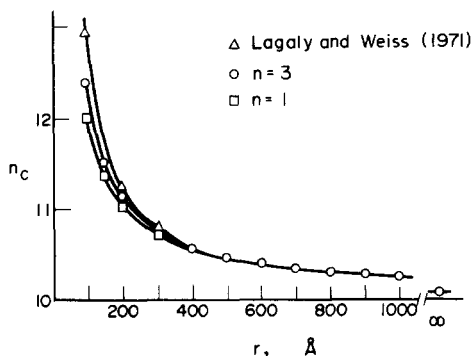


Fig. 1. Variation of the critical chain length n_c with the particle radius r , calculated for $\xi = 0.33$.

(b) Interpretation of the apparent basal spacings

The transition between a monolayer and double layer of organic cations ($d_{001} = 13.6$ and 17.6 \AA respectively) is a discontinuous process for which no intermediates are allowed. However, for natural samples the transition extends over a certain number of n_c values due to the inhomogeneous charge distribution. This transition is characterized on the X-ray diffraction pattern by a number of 'apparent spacings'. Apparent spacings may result from a mixing of two phases and/or of the particle thinness (Tettenhorst and Roberson, 1973). The latter was neglected since in all cases of a pure monolayer and double layer intercalation, we obtained integral reflections. This apparent spacing d' varies with the fraction (f) of higher spacings (d_1) and the fraction ($1 - f$) of lower spacings (d_2). The intensity formula for the diffraction pattern of a mixture of two

randomly interstratified phases is then given by the Hendricks-Teller equation (see Brown and MacEwan, 1949).

The structure factor was

$$F_c = \sum_r n_r f_r \cos(2\pi z_r/d')$$

where r is the number of atoms of type r , f_r the atomic scattering factor for that ion, and z_r the z coordinate measured from the supposed symmetry center of the one-dimensional projection of the silicate layer. In this approximation it is assumed that all layers have the same structure factor. For the silicate layer, the coordinates of muscovite (Radoslovich, 1960) were used. Since the influence of the interlayer material may also be important (McAtee, 1958), a 50 per cent occupancy of each layer by alkylammonium ions was adopted. The intensity function reveals that the apparent spacing d_{001} varies between 13.6 and 17.6 \AA following the composition of the mixture. From that plot the fraction of higher spacings may be derived for each apparent spacing between 13.6 and 17.6 \AA . This may be calculated for each n_c value. It allows us to distinguish several classes of interlayer cation densities, characterized by the mean value between two critical ξ values.

To illustrate the method: if for $n_c = i$ the apparent spacing indicates a fraction p of higher spacings and for $n_c = i + 1$ a fraction q , then $q - p$ is the fraction of all silicate layers which have an interlayer cation density lying between the critical ξ values determined by $n_c = i$ and $n_c = i + 1$. The mean charge density is then derived as the weighted mean of the interlayer cation densities.

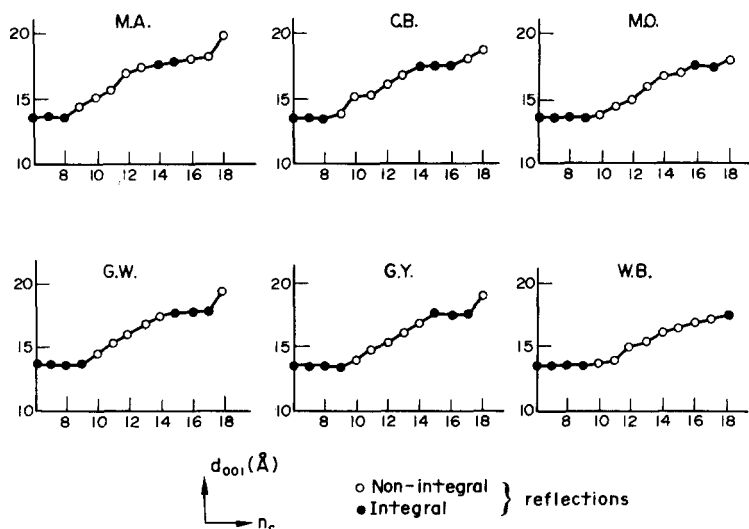


Fig. 2. Basal spacings of the n -alkylammonium complexes of the different montmorillonites; n_c indicates the number of carbon atoms.

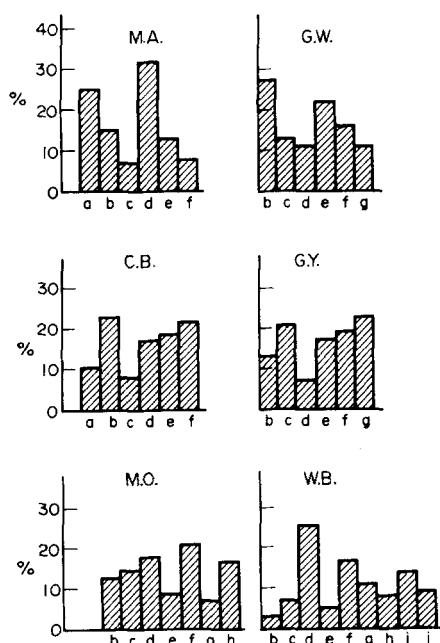


Fig. 3. Interlayer cation density distribution in different classes.

RESULTS

The varying apparent spacings d_{001} of the six montmorillonite samples saturated with alkylammonium ions of different length are given in Fig. 2. The interlayer cation distribution over the several classes was derived as described in the former section (Fig. 3). The classes were determined by the critical ξ value for the given length of the organic cation. The mean interlayer cation density of each class was calculated for various particle radii (i.e. $r = \infty$, 500, 225 and 150 Å respectively). The results are presented in Table 1. The radii of the samples, derived by De Bock and Pleyrier (1971) from electrical conductivity measurements, are given in Table 2. For the calculation of the critical ξ value the following particle radius was used: M.A., C.B. and M.O.: 150 Å; G.Y.: 225 Å; G.W. and W.B.: 500 Å. On the basis of the interlayer cation densities for the different classes (Table 1) the mean charge for those samples was calculated and also are given in Table 2.

Table 1. Classes of interlayer cation densities with varying particle radius

Class	$r = \infty$ Å	Interlayer cation density (electron/(Si,Al) ₄ O ₁₀)		
		$r = 500$ Å	$r = 225$ Å	$r = 150$ Å
a	0.375	0.385	0.398	0.409
b	0.344	0.354	0.366	0.378
c	0.317	0.327	0.340	0.351
d	0.294	0.304	0.317	0.328
e	0.274	0.284	0.297	0.308
f	0.257	0.267	0.280	0.291
g	0.242	0.252	0.265	0.276
h	0.229	0.239	0.252	0.263
i	0.217	0.226	0.239	0.250
j	0.206	0.215	0.228	0.239

DISCUSSION

The interlayer cation density in this series of montmorillonites extends over several classes for each sample (Fig. 3). From the point of view of the range of cation densities, Wyoming Bentonite is the most heterogeneous (9 classes), followed by Moosburg (7 classes) and finally, the samples Marnia, Camp Berteau, Greek White and Greek Yellow (6 classes each). There is no sample having a class which could predominantly influence the physicochemical properties of the sample. Only for the Marnia sample is there one class which contains about one third of the interlayer spaces. Furthermore, there is no sample for which the isomorphous substitution is continuous so that every degree of isomorphous substitution occurs in equal amounts.

The average charge density due to isomorphous substitution is also shifted from sample to sample, and decreases in the following order: Marnia > Camp Berteau > Moosburg > Greek White = Greek Yellow > Wyoming Bentonite. This sequence is not entirely that of the CEC for the samples (Maes, 1973), determined at a pH of approximately 6. These values, given in the same sample order as the above series, are 1.039; 1.050; 0.965; 0.975; —; and 0.911 m-equiv/g. The difference could be assigned to the influence of the broken bonds.

The impact of the broken bonds on the CEC can be estimated fairly well for the sample Camp Berteau.

Table 2. Mean charge density and radius of the different montmorillonites

Clay sample	MA	CB	MO	GW	GY	WB
Mean charge density (electron/46.5 Å ²)	0.352	0.339	0.314	0.305	0.305	0.270
Particle radius (Å)*	148	140	138	500	225	490

* Derived from conductivity measurements (De Bock and Pleyrier, 1971).

Maes (1973) investigated the pH dependence of the CEC of a Na Camp Berceau montmorillonite. In the pH range 3.9–5.8, he found that the CEC varies as follows: $CEC = 79.9 + 5.04 \text{ pH}$ (m-equiv/100 g). Eeckman and Laudelout (1961) stated that a CEC of 0.85 m-equiv/g corresponds to the isomorphous layer charge of the Camp Berceau montmorillonite. In this way Maes (1973) found a zero point of charge for the broken bonds at a pH of about 2, which is in a good agreement with values known for silica–water interfaces. Thus, it is reasonable to accept 0.85 m-equiv/g as the isomorphous layer charge. From the specific surface for that sample ($764 \text{ m}^2/\text{g}$; De Bock and Pleysier, 1971) we may then derive the mean charge density due to isomorphous substitution: 6.70×10^{-3} electrons/ \AA^2 . Multiplying this value by the average surface per formula unit we can obtain the charge density per formula unit at zero charge of broken bonds. This average surface, taking into account the particle radius (cylindrical layer), is given by $(2\pi r^2 + 2\pi r \times 9.6) 46.5/2\pi r^2$ or $46.5(1 + 9.6/r)$. Therefore, the charge density arising from layer substitution, derived from the specific surface and the CEC is 0.333 electron/formula unit. This value is in very close agreement with the mean charge density for this sample (0.339) as determined by our method. Since, at a pH of 6, with a CEC of 1.101 m-equiv/g, the average charge density is 0.431 electron/(Si,Al)₄O₁₀, the contribution of the isomorphous substitution (0.339 electron/(Si,Al)₄O₁₀) is only 79 per cent of the CEC for this montmorillonite sample.

CONCLUSIONS

A method is proposed to determine the heterogeneity of the interlayer cation density in octahedrally substituted smectites. Application to a series of six montmorillonites shows the interlayer cation density extending over several classes for each sample. The charge density due to isomorphous substitution shifts from sample to sample and for the Camp Berceau montmorillonite it constitutes only 79 per cent of the CEC.

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Résumé—On a déterminé pour six montmorillonites l'hétérogénéité de la densité de cation interfeuillet et la densité de charge moyenne du feuillet correspondante, due aux substitutions isomorphes.

Ceci a été effectué en utilisant la transition d'un état monocouche à un état deux couches pour des complexes formés avec des ions alkylammonium. La transition est reliée à la densité de cation interfeuillet ainsi qu'à la variation des espacements apparents qui est à son tour reliée à la composition de ce mélange de deux composants.

Tous les échantillons montrent une distribution hétérogène des cations interfeuillets et une densité de charge moyenne différente.

Kurzreferat—Die Heterogenität der Zwischenschichtkationendichte und die entsprechende mittlere Schichtladungsdichte als Folge isomorphen Ersatzes wurden für sechs Montmorillonitproben bestimmt. Dies wurde erreicht, indem der Übergang von Einschicht- in Zweischichtkomplexe mit Alkylammoniumionen verfolgt wurde. Der Übergang weist eine Beziehung zur Zwischenschichtkationendichte in Verbindung mit der Veränderung der scheinbaren Schichtabstände auf, die ihrerseits zur Zusammensetzung dieser aus zwei Komponenten bestehenden Mischung in Beziehung steht. Alle Proben wiesen eine heterogene Zwischenschichtkationenverteilung und eine unterschiedliche mittlere Ladungsdichte auf.

Резюме — На шести образцах монтмориллонита определяется неоднородность плотности катионов промежуточных слоев и соответствующая средняя плотность заряда слоев вследствие изоморфного замещения. Определение достигли учитывая переход монослоя в двухслойный комплекс с алкиламмониевыми ионами. Переход связан с плотностью катионов промежуточных слоев, вместе с вариацией очевидных параметров, которые в свою очередь связаны со строением этой двухкомпонентной смеси.

Все образцы выявили неоднородное размещение межслойных катионов и различную среднюю плотность заряда.