

LAYER CHARGE OF THE EXPANDABLE COMPONENT OF ILLITE/SMECTITE IN K-BENTONITE AS DETERMINED BY ALKYLAMMONIUM ION EXCHANGE

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Abstract—The charge of the expandable interlayers in a series of fourteen diagenetic illite/smectites (I/S) from lower Paleozoic K-bentonites was determined by the alkylammonium ion exchange method. The magnitude (<0.50 equivalents per half formula unit) and characteristic heterogeneous distribution of interlayer charges in eight samples with expandabilities from 70% to about 15% confirm the smectitic character of the expandable interlayers in this range. This result coupled with the lack of a correlation between expandability and interlayer charge is consistent with the hypothesis of a layer-by-layer transformation from a precursor smectite to highly illitic I/S clays during K-bentonite diagenesis. The charge of the expandable interlayers in I/S samples with about 10% or less expandabilities have been inferred to be vermiculitic rather than smectitic. The K-fixed interlayers and expandable interlayers in these samples appear to be similar in charge. The significantly higher charges inferred for the highly illitic samples can be consistent both with a layer-by-layer transformation and the neof ormation mechanisms proposed in the literature for the formation of illite.

Key Words—Alkylammonium, Bentonite, Clays, Diagenesis, Illite, Illite/smectite, Layer charge, Smectite.

INTRODUCTION

The structure of illite/smectite (I/S) clays can be interpreted on the basis of either of two models. The Markov model (MacEwan 1958, Reynolds and Hower 1970, Reynolds 1980), also called the MacEwan crystallite model (Moore and Reynolds 1987), postulates that I/S is composed of silicate layers about 10 Å thick that are separated by K-fixed illite and expandable smectite interlayers. The interlayers are stacked in the c-axis direction to form crystallites of various ordering types. These crystallites are commonly considered to consist of 5–15 silicate layers (50–150 Å thick). In contrast, the fundamental particle model (Nadeau *et al* 1984, 1985, Nadeau 1985), based on transmission electron microscopy (TEM) observations of dispersed I/S, proposes that I/S is composed of fundamental particles that are mainly 10–50 Å thick, considerably thinner than MacEwan crystallites, and that these particles can hydrate and expand at their interfaces and act as smectite interlayers. In effect, the fundamental particle model implies that materials yielding X-ray powder diffraction (XRD) patterns of I/S do not necessarily contain chemically distinct illite and smectite layers.

A direct way of testing whether or not the expanding, smectite-like component of I/S clays is actually smectite is to determine the magnitude and distribution of the layer charge of this component. Determining the layer charge is essential because smectite is defined, and distinguished from other expanding 2:1 clay minerals on the basis of its layer charge (Bailey 1980). Previous studies indicate that the mean layer charge of smectite is approximately 0.4 equivalents per half formula unit (Weaver and Pollard 1973), and that a

great majority of smectites have heterogeneous charge distributions across their silicate layers (Lagaly and Weiss 1976, Lagaly 1981). Due principally to this heterogeneity, smectite is described as having a charge range of 0.20–0.60 equivalents per half formula unit (Bailey 1980, Martin *et al* 1991). In view of this definition of smectitic charge, a positive identification of the expanding component in I/S clays as smectite entails a characterization of the layer charge of the expanding layers. The need for information on the layer charge was also noted by Nadeau *et al* (1985) who pointed out that their fundamental particle model had not considered the surface charge of the particles and that future research should look into this issue.

The layer charge of monomineralic clays may be estimated from structural formulas that are based on total elemental analyses or measured directly by various absorption methods. Due to the interstratified nature of I/S minerals, however, these methods provide average results that contribute little information about the layer charge of individual mineral components. Thus, other methods of characterizing the layer charge of I/S minerals have been sought. One that has received particular attention with expanding layer silicates has been the alkylammonium ion exchange method (Lagaly and Weiss 1969). This is a method that utilizes the quantitative relationships between the layer charge, the shape and area occupied by organic molecules in the interlayer space and their effects on the basal spacings of the clay-organic complexes. The layer charge is calculated based on the basal spacings of a clay mineral after treatment with alkylammonium ions of varying carbon chain length ($N_c = 6$ to 18, where N_c is the

number of carbon atoms in the alkyl chain), from a total of 13 clay-alkylammonium ion complexes. The attraction of this method is due primarily to the selective uptake of alkylammonium ions by expanding layers in the presence of non-expanding components such as kaolinite or micas. For example, it has been shown by Lagaly (1979) that the alkylammonium ion exchange method permits an extensive investigation of the layer charge of the expanding component in regularly interstratified 1:1 minerals with mica-like and smectitic or vermiculitic interlayers.

This paper reports the results of alkylammonium exchange experiments conducted on a suite of I/S clays whose XRD characteristics demonstrate widely varying expandability (=percentage of smectite layers) and interstratification ranging from random (R0) to long-range ordered (R3). The objective of the study is to obtain layer charge data on the expandable interlayers independent of chemical analyses, and evaluate the MacEwan and fundamental particle models and the smectite illitization schemes that are commonly associated with these models.

EXPERIMENTAL PROCEDURE

Samples

A suite of fourteen I/S clays from lower Paleozoic K-bentonite beds in Great Britain and North America was used in this study. XRD data interpreted using NEWMOD® (Reynolds 1985) indicate the I/S compositions range from randomly interstratified (R0) to long-range ordered (R3), and have expandabilities between 70% and 3% (Table 1).

Methods

The <0.2 μm fractions of the samples were separated from Na-saturated bulk sample suspensions by centrifugation. The preparation of thirteen alkylammonium chlorides from their commercially available amines and the treatment of clay samples with alkylammonium solutions were conducted according to the procedure of Rühlicke and Köhler (1981). Air-dried glass slides of treated samples were stored at 60°C in a desiccator under vacuum until X-rayed. A Siemens D-500 automated powder X-ray diffractometer using monochromated Cu-K α radiation was used to record the XRD patterns of alkylammonium derivatives.

Major elements were determined on pressed powder pellets of the 0.5 μm clay fraction separated from bulk samples by centrifugation (Table 1). Analyses were performed using a Rigaku 3070 X-ray fluorescence spectrometer. Structural formulas were calculated by assuming a theoretical structure containing 11 oxygens (Table 1). Samples SI-64 and NI-6 gave anomalously small values of octahedral occupancy (<1.90) and negative octahedral charges. This was caused by large amounts of P and S detected in these samples which,

due to the interdependency of each element in the multiple regression analysis used in calculating percent oxides, resulted in unbalanced structural formulas. Recalculation of structural formulas for these two samples, assuming less P and S gave acceptable octahedral occupancies and charge-balanced structural formulas. Sample SI-64 was corrected for 2% kaolinite and 2% quartz, and sample NI-6 was corrected for 2% quartz. Ti, Mn, P and S, not considered structurally held, were not included in the structural formulas.

Investigation of alkylammonium ion-I/S complexes

As a result of ion exchange reaction, alkylammonium ions in the clay interlayers may adopt either a monolayer (13.6 Å), a bilayer (17.7 Å), a pseudotri-molecular layer (21.7 Å), or a paraffin-type configuration depending on the magnitude of layer charges. The mean interlayer cation density (\approx interlayer charge density) and its distribution in alkylammonium exchanged smectites and low-charge vermiculites are commonly determined from monolayer-to-bilayer (MTB) transition during which a monolayer configuration of alkylammonium ions is replaced by a bilayer configuration in the interlayer in the interlayer spaces. If the mineral has a homogeneous charge distribution, the MTB transition occurs as a sharp jump from about 13.6 Å to about 17.7 Å between two successive values of Nc. However, the layer charge, especially for smectites and low-charge vermiculites, usually varies between interlayers such that MTB transitions occur over a certain range of Nc values. In other words, the layer charge heterogeneity leads to a transition where monolayers and bilayers coexist in the interlayers and give rise to non-integral basal spacings between 13.6 Å and 17.7 Å (Lagaly and Weiss 1969).

In the analysis of data, the convention is to plot basal spacings (d_{001}) versus alkylammonium ion chain length (Nc). The upper and lower limits of the cation density are determined from the Nc values that mark the start and end of the MTB transition by converting the Nc values to layer charges (Lagaly *et al* 1976). The mean layer charge is calculated by simple averaging of the upper and lower limits of charge in the case of a homogeneously-charged mineral; in the case of a heterogeneously-charged mineral, a weighted average charge is calculated using the non-integral spacings and MacEwan's peak migration curve.

In the present study, the principles of the conventional alkylammonium method outlined above were used to determine the layer charge of the expanding, smectite-like component in alkylammonium ion-I/S complexes. The basal spacings induced by alkylammonium ion exchange were plotted versus Nc values and the plots were examined for the presence or absence of MTB transition zones. In samples where the d-Nc plots displayed an identifiable MTB transition between approximately 13.7 Å and 17.7 Å plateaus,

Table 1. Chemical analyses (weight %), structural formulas (half cell), and mineralogical characteristics of illite/smectite samples. % Exp. = percent expandability; R = type of ordering.

	Sample ¹													
	SI-59	SI-64	SI-55	SI-44	SI-53	SI-9	MLH	SI-47	WDH-62	WDH-64	WDH-60	WDH-68	WDH-25	NI-6
SiO ₂	55.41	58.39	53.44	52.81	51.54	52.52	53.50	51.11	48.97	47.16	48.74	52.37	49.84	54.29
Al ₂ O ₃	19.16	18.45	20.12	20.66	24.88	21.74	21.35	23.45	26.49	29.35	27.44	23.70	26.07	23.85
Fe ₂ O ₃	1.89	1.89	1.81	1.52	1.25	1.29	1.10	1.40	1.45	1.04	1.33	1.85	1.64	2.60
MgO	3.64	3.64	3.41	3.86	3.10	3.95	4.45	3.32	2.52	1.93	2.49	1.86	2.47	3.39
K ₂ O	2.43	4.22	3.92	4.79	5.38	5.57	6.80	6.73	7.67	7.69	7.90	7.84	7.15	7.93
CaO	1.81	1.97	1.75	1.49	0.76	1.48	0.99	1.08	0.52	0.18	0.36	0.10	0.19	1.45
Na ₂ O	0.16	0.76	0.24	0.32	0.26	0.17	0.25	0.10	0.26	0.11	0.18	0.83	0.20	0.08
LOI	12.23	9.51	13.99	13.73	12.07	11.40	10.00	10.70	9.49	9.02	8.95	9.49	9.03	7.11
Total	96.73	98.83	98.68	99.17	99.24	98.12	98.44	97.89	97.37	96.48	97.39	98.04	96.59	100.70
Tetrahedral														
Si	3.91	3.95	3.81	3.76	3.60	3.70	3.72	3.61	3.46	3.34	3.42	3.66	3.51	3.61
Al	0.09	0.05	0.19	0.24	0.40	0.30	0.28	0.39	0.54	0.66	0.58	0.34	0.49	0.39
Charge	-0.09	-0.05	-0.19	-0.24	-0.40	-0.30	-0.28	-0.39	-0.54	-0.66	-0.58	-0.34	-0.49	-0.39
Octahedral														
Al	1.50	1.42	1.50	1.49	1.65	1.51	1.47	1.56	1.66	1.79	1.69	1.61	1.67	1.48
Fe ⁺³ (Total)	0.10	0.10	0.10	0.08	0.07	0.07	0.06	0.07	0.08	0.06	0.07	0.10	0.09	0.13
Mg	0.38	0.37	0.36	0.41	0.32	0.42	0.46	0.35	0.27	0.20	0.26	0.19	0.26	0.34
Sum	1.98	1.89	1.96	1.98	2.04	2.00	1.99	1.98	2.01	2.05	2.02	1.90	2.02	1.95
Charge	-0.44	-0.70	-0.48	-0.47	-0.20	-0.42	-0.49	-0.41	-0.24	-0.05	-0.20	-0.49	-0.20	-0.49
Net charge	-0.53	-0.75	-0.67	-0.71	-0.64	-0.72	-0.77	-0.80	-0.78	-0.71	-0.78	-0.83	-0.69	-0.88
Interlayer														
K	0.22	0.37	0.36	0.44	0.48	0.50	0.60	0.61	0.69	0.69	0.71	0.70	0.64	0.67
Na	0.02	0.10	0.03	0.04	0.03	0.02	0.03	0.01	0.04	0.02	0.02	0.11	0.03	0.01
Ca	0.14	0.14	0.13	0.11	0.06	0.11	0.07	0.08	0.04	0.01	0.03	0.01	0.01	0.10
Charge	0.52	0.75	0.65	0.70	0.63	0.74	0.77	0.78	0.81	0.73	0.79	0.83	0.69	0.88
% Exp.	70	55	48	45	43	40	30	17	11	11	10	10	5	3
R	0	0	0/1	0/1	0/0.5	0/0.5/1	1	1.5	2.5	3	3	3	3	3

¹ SI-59 = Silurian, Overbury Quarry, Shropshire, UK; SI-64 = Silurian, Sleaves Oak Quarry, Shropshire, UK; SI-55 = Silurian, Woolhope Quarry, Woolhope Inlier, UK; SI-44 = Silurian, Perton Quarry, Woolhope Inlier, UK; SI-53 = Silurian, Haugh Wood Section, Woolhope Inlier, Shropshire, UK; SI-9 = Silurian, Mortimer Forest near Ludlow, UK; MLH = Middle Ordovician, Hickman Creek at Wesley Chapel, Jessamine County, Central Kentucky, USA; SI-47 = Silurian, Bagpiper's Trump, Westwood, Woolhope Inlier, Shropshire, UK; WDH-62, WDH-64, WDH-60, WDH-68 = Silurian, Dob's Linn, Southern Uplands, UK; WDH-25 = Silurian, Newtown, UK; NI6 = Silurian, County Down, Northern Ireland.

the conventional alkylammonium method was used (Lagaly and Weiss 1969, Lagaly *et al* 1976). For samples with progressively smaller expandabilities whose d-Nc plots showed plateaus taking place at smaller spacings than 13.6 Å and 17.7 Å, the presence of transitions were confirmed by calculated basal spacings (i.e., weighted average basal spacings for an I/S of known expandability were calculated both for a monolayer and a bilayer configurations of alkylammonium ions in the expandable interlayers). Consider, for example, an I/S sample which has an expandability of 50%. When each smectite-like interlayer in this clay has alkylammonium ions arranged in monolayers, the average basal spacing for this monolayer alkylammonium-smectite/illite complex would be:

$$d = 11.8 \text{ \AA} = (13.6 \text{ \AA}) \cdot (50\% \text{ S}) + (10.0 \text{ \AA}) \cdot (50\% \text{ I}),$$

where the thickness of the alkylammonium ion-layer silicate complex is 13.6 Å. Similarly, the average basal spacing for a bilayer alkylammonium-smectite/illite complex would be:

$$d = 13.9 \text{ \AA} = (17.7 \text{ \AA}) \cdot (50\% \text{ S}) + (10.0 \text{ \AA}) \cdot (50\% \text{ I}),$$

where the thickness of the alkylammonium ion-layer silicate complex is 17.7 Å. If the presence of plateaus at or near 11.8 Å and 13.9 Å is confirmed on the d-Nc plot, the Nc's that correspond to the start (11.8 Å) and the end (13.9 Å) of the transition can be converted to layer charges. The mean layer charge and its distribution can then be determined as in the conventional method.

RESULTS

Based on their XRD characteristics upon treatment with various alkylammonium chlorides, two groups of I/S samples were recognized. XRD patterns for eight I/S samples with about >15% expandabilities show basal reflections that migrated to lower 2θ positions with increasing chain length (Nc) for which both monolayer and bilayer and MTB transition arrangements could be identified. XRD patterns for six I/S samples with approximately 10% or less expandabilities, on the other hand, exhibit a basal illite reflection stable at about 10 Å, in addition to low-angle reflections that become apparent only with the longer-chain alkylammonium derivatives. XRD patterns for three samples, two representative of the former group, and one representative of the latter, are presented in Figure 1. The basal spacings observed on the XRD patterns of fourteen I/S samples plotted versus alkylammonium chain length are shown in Figures 2 and 3.

I/S samples with about >15% expandabilities show basal reflections that migrate progressively from the 10.5–13 Å region for the short-chain alkylammonium derivatives (Nc = 6–8) to the 11.5–18 Å region for the longer-chain alkylammonium derivatives (Nc = 10–14). Although some of the long-chain derivatives show

>18 Å basal spacings (e.g., Nc = 17, Figure 1a), MTB transitions are identified consistently between Nc = 6 and Nc = 14 as described below.

Alkylammonium derivatives of three randomly interstratified samples exhibit distinct MTB transitions similar to that of pure smectite (Figures 2a–2c). For each of these three samples, two or more basal reflections forming plateaus at about 13 Å and 18 Å, which represent monolayer and bilayer forms, respectively, are observed. For sample SI-59, the transition starts at Nc = 7, and is completed at Nc = 10 as indicated by the plateaus for both monolayer and bilayer arrangements at about 13 Å and 18 Å, respectively (Figure 2a). From the transition Nc's, it can be calculated (Lagaly 1981) that the layer charge density in the expanding interlayers of this sample varies between lower and upper limits of 0.36 and 0.46 equivalents per half formula unit, respectively. The mean layer charge is calculated to be 0.40 equivalents per half formula unit. The lower and upper charge density limits, and the mean layer charge densities for samples SI-64 and SI-55 are similarly calculated from MTB transitions. The MTB transitions taking place over a range of Nc values and calculated mean layer charges show that samples SI-59, SI-64, and SI-55 all have heterogeneous interlayer charge densities which are indistinguishable from pure smectite (Table 2).

In five samples with various degrees of I/S ordering and 45% to 17% expandability, plateaus resembling monolayer and bilayer plateaus are observed in the basal spacing ranges 10.5–12 Å and 11.5–14 Å, respectively. These values are significantly smaller than those for pure smectites and indicate that the total average contribution from the expanded layers to the diffracted X-ray beam becomes smaller at progressively higher illite proportions. The short-chain derivatives of SI-44, SI-53, and SI-9 are characterized by basal spacings of about 11.7 Å, forming plateaus in d-Nc plots (Figures 2d–f). In order to determine whether 11.7 Å represents a monolayer arrangement of alkylammonium ions in the expandable layers, percent expandability (=percent smectite) was used to calculate a basal spacing for an I/S mineral that has alkylammonium ions arranged in monolayers in its expandable interlayers. Calculated powder XRD patterns indicate that samples SI-44, SI-53, and SI-9 have between 45 and 40% expandability (Table 1). If all the expandable interlayers are occupied by alkylammonium ions arranged in monolayers, then the basal reflections for the expandability range 45–40% would have spacings of 11.6 Å to 11.4 Å, respectively. These calculated spacings agree with the observed spacing of 11.7 Å reasonably well. Because the differences between the observed and calculated basal spacings fall within the confidence level with which expandability can be estimated in I/S by XRD methods, ±5–10% for most I/S (Reynolds 1980), it is likely that the 11.7

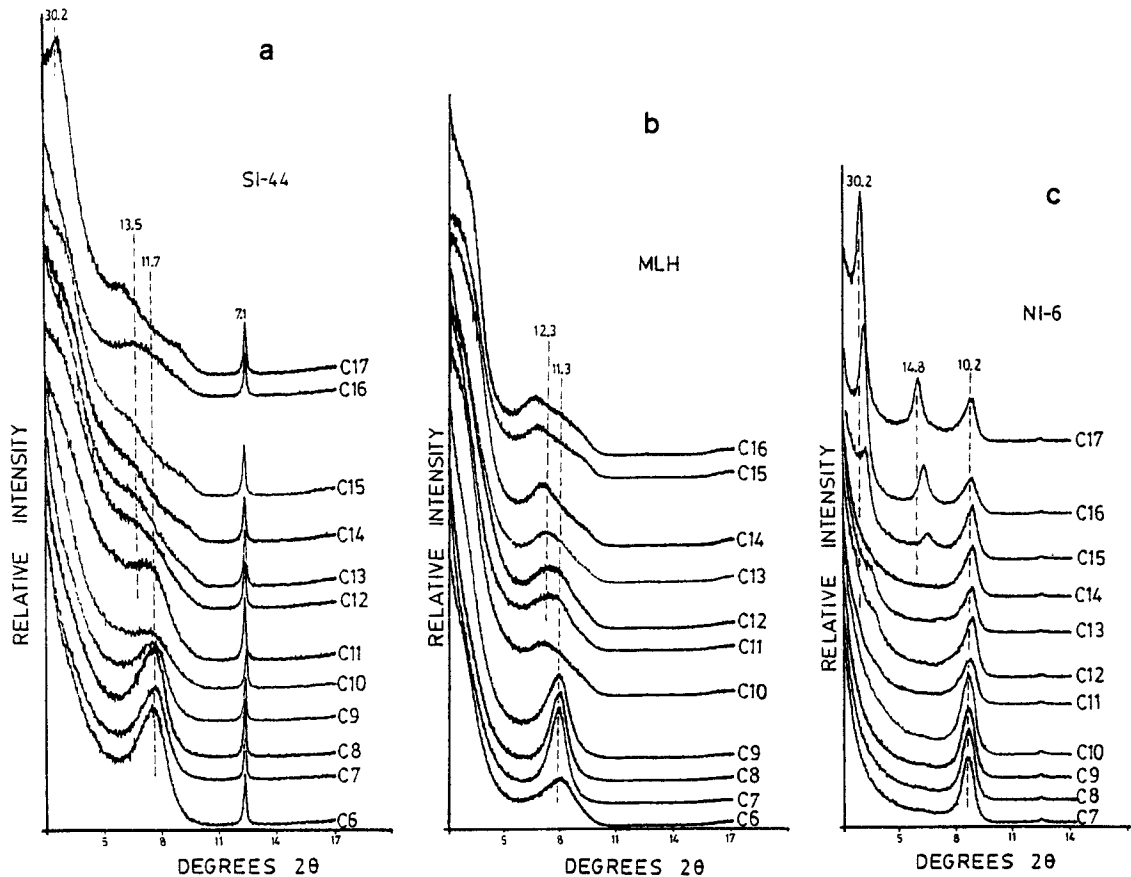


Figure 1. XRD patterns of three representative samples, SI-44 (a), MLH (b), and NI-6 (c), treated with alkylammonium chloride ions (carbon chain length specified at right).

A plateau is indeed due to a monolayer arrangement of alkylammonium ions. The 13.5 Å, 13.9 Å, and 12.6 Å plateaus observed in the respective d-Nc plots of SI-44, SI-53, and SI-9 are believed to represent a bilayer arrangement in the expandable layers as they are similar to the basal spacings of 13.5 Å, 13.3 Å and 13.1 Å, respectively, calculated for a bilayer arrangement using I/S expandabilities.

For sample MLH, which contains 30% expandable layers, the plateaus that form at 11.3 Å and 12.3 Å are considered to represent monolayer and bilayer arrangements, respectively, on the basis of their good agreement with the calculated spacings of 11.1 Å and 12.3 Å. The sharp MTB transition taking place over only one chain length category between $N_c = 9$ and $N_c = 10$ (Figure 2g) suggests a homogeneous layer charge distribution for this sample (Lagaly and Weiss 1976). Sample SI-47, which has only about 17% expandables, produces even smaller spacings (Figure 2h). The $N_c = 6$, and $N_c = 9$ –10 derivatives of this sample with 10.5 Å and 11.4 Å basal reflections represent monolayer and bilayer formations in the expandable interlayers,

respectively. Calculated basal spacings for an I/S with 17% expandability are 10.6 Å for a monolayer arrangement and 11.3 Å for a bilayer arrangement, and are in good agreement with the observed spacings. The MTB transitions taking place over two or more chain length categories, and the calculated values of mean layer charge ranging between 0.32 and 0.45 (Table 2) indicate that the expandable interlayers in samples SI-44, SI-53, SI-9, and SI-47 are also smectitic and possess a heterogeneous charge distribution. Only sample MLH, which also has a smectitic charge, possesses a homogeneous charge distribution.

All six I/S samples with about 10% or less expandabilities respond to the alkylammonium treatment in a similar fashion. The XRD patterns of alkylammonium derivatives of these samples show (Figure 1c): 1) an illite peak at about 10 Å which persists and is more or less unaffected over the whole range of alkylammonium chain lengths; and 2) low-angle reflections with >24 Å spacings that become apparent only with longer-chain alkylammonium derivatives. The persistence of the illite peak and the absence of identifiable

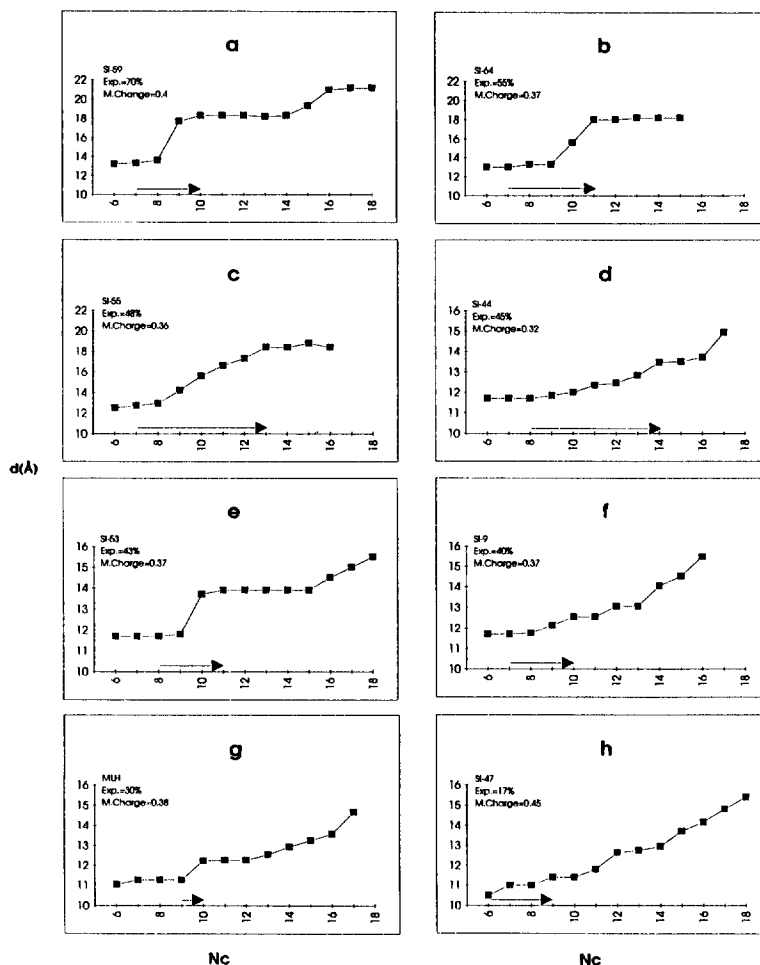


Figure 2. Variation of basal spacing (d) in eight I/S clays with more than about 15% expandabilities, treated with alkylammonium chloride ions of various chain length (N_c).

MTB transitions precludes a quantitative estimation of interlayer charges for these samples. The low-angle peaks observed with long-chain derivatives indicate the presence of apparently discrete or segregated packets of layers that expand upon alkylammonium exchange. The spacings observed for this expanded component, when plotted versus N_c (Figure 3), show a more or less linear relationship between the two variables. Greater than 20 Å spacings and near linearity of this relationship suggest a paraffin-type arrangement of the alkylammonium ions in the expanded interlayers and point to a homogeneous and high-charge distribution, comparable to that of a vermiculite (Lagaly 1981, Ghabru *et al* 1989). The layer charge density of this component was calculated using the empirical relationship of Ghabru *et al* (1989), developed to quantitatively estimate the interlayer charge density in vermiculites. The layer charge densities calculated for the expanded component (Table 3) in four of the six sam-

ples are vermiculitic (for sample WDH-64 charge density was not calculated due to inadequate number of data points). For sample NI-6 with only 3% expandables, however, the charge density of the expanded component is 0.93, a charge even higher than vermiculite, and very close to that of an ideal dioctahedral mica (Bailey 1980).

DISCUSSION

The XRD patterns and d - N_c plots for eight I/S samples with >15% expandabilities provide evidence for the formation of monolayer, bilayer and MTB transition arrangements in the expandable interlayers upon alkylammonium treatment. The occurrence of well-defined plateaus on the d - N_c plots and good agreement between observed and calculated basal spacings indicate that all of the eight samples have a monolayer configuration of short-chain alkylammonium ions (N_c

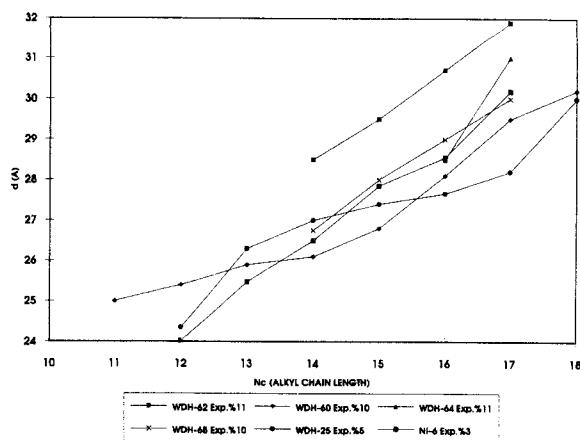


Figure 3. Variation of basal spacing (d) with alkylammonium chain length (N_c) of the expanded component observed in six I/S samples with about 10% or less expandabilities. Note that $N_c = 6$ through $N_c = 10$ alkylammonium derivatives whose XRD patterns show an illite peak but do not exhibit a reflection for the expanded component are not shown for the sake of clarity.

= 6–8) in their expandable interlayers. The start of MTB transitions in these samples can clearly be observed to take place mostly at $N_c = 7$ and $N_c = 8$ (Table 2). The formation of monolayers with such short-chain alkylammonium ions, rather than bilayers or pseudotrimolecular layers, or paraffin-type structures, provides compelling evidence of interlayer charge densities of <0.5 equivalents per half formula unit which are characteristic of smectitic clays. Several workers have previously observed that short-chain alkylammonium ions form bilayers and pseudotrimolecular layers with high-charged smectites (0.5–0.6), and paraffin-type structures with vermiculites (0.6–0.9) (Lagaly and Weiss 1969, Lagaly 1982, Ghabru *et al* 1989, Olis *et al* 1990). Therefore, it would appear that expandable interlayers in I/S with $>15\%$ expandability range are smectitic in terms of their charge.

Table 2. Interlayer charge density and its distribution in I/S minerals with expandabilities between 70% and about 15%.

Sample	Transition range (Nc classes)	Charge range	Mean charge ¹	Nature
SI-59	7–10(3)	0.46–0.36	0.40	Heterogeneous
SI-64	7–11(4)	0.46–0.34	0.37	Heterogeneous
SI-55	7–13(6)	0.46–0.29	0.36	Heterogeneous
SI-44	8–14(6)	0.42–0.28	0.32	Heterogeneous
SI-53	8–11(3)	0.42–0.29	0.37	Heterogeneous
SI-9	7–10(3)	0.46–0.29	0.39	Heterogeneous
MLH	9–10(1)	0.40–0.35	0.38	Homogeneous
SI-47	6–9 (2)	0.51–0.36	0.45	Heterogeneous
Average = 0.38 ± 0.03				

¹ Expressed as equivalents per half formula unit.

Table 3. Estimated interlayer charge of the expanded component observed in six I/S samples with about $\leq 10\%$ expandabilities.

Sample	Interlayer charge	
	AE	SF
WDH-60	0.70	0.73
WDH-64	NE	0.79
WDH-68	0.81	0.83
WDH-25	0.69	0.69
NI-6	0.93	0.88

AE = Interlayer charges from alkylammonium exchange estimated using the linear regression expression of Ghabru *et al* (1989).

SF = Interlayer charges from structural formulas shown in Table 1.

NE = Layer charge is not estimated due to few data points.

The average interlayer charge density estimated by the alkylammonium ion exchange method for the eight I/S samples with $>15\%$ expandabilities is 0.38 ± 0.03 (Table 2). This value is about 25% lower than the total (or net) layer charge density of about 0.50 determined for an "initial" smectite composition (100% expandable) by extrapolation of total charge from structural formulas and XRD expandability for I/S (Cetin 1992). This result conforms to the observation that the alkylammonium exchange method estimates interlayer charge density which, for smectites, represents about 80% of the total charge as inferred from structural formula method (Lagaly 1981). Most of the differences may be attributable to broken-bond effects, cations adsorbed on the lateral edges of particles, which would be included in the total charges by structural formulas. Laird *et al* (1989) also showed that interlayer charges from alkylammonium exchange are 20 to 30% lower than those from structural formulas calculated for monomineralic smectites and vermiculites. Their results, furthermore, indicated that a systematic underestimation of charges by alkylammonium exchange contributes, in addition to the broken-bond effects, to the discrepancy between the values from the two methods. This systematic error appears to account for up to about a third of the differences between the total layer charge from structural formulas and interlayer charges from alkylammonium exchange (Figure 3, Laird *et al* 1989).

On the other hand, interlayer charge densities determined by alkylammonium exchange of these same eight I/S samples (Table 2) are, on average, about 45% lower than the interlayer charge densities determined by their respective structural formulas (Table 1). Such low values by the alkylammonium exchange method are unlikely to be a result of the broken-bond effects and underestimation by alkylammonium exchange, since these two effects combined may account for up to 20 to 30% lower charges as noted above. It is con-

ceivable, however, that much larger interlayer charges by the structural formula method reflect its averaging effect for two-component minerals such as I/S, in addition to broken-bond effect and underestimation by alkylammonium exchange. On this basis, the comparison of interlayer charges from the two methods appears to reveal the two-component nature of I/S clays with >15% expandabilities.

It has been noted above that expandable interlayers in I/S with >15% expandabilities retain a smectitic character, even after particles have been disturbed and resedimented during alkylammonium treatments. Another notable feature of the alkylammonium ion exchange data is that the interlayer charges do not show an identifiable correlation with expandability as they vary around an average of 0.38 (Table 2). Furthermore, smectitic character of the interlayer charges prevails with ordered I/S samples with as low as about 17% expandability. An implication of these observations, with regard to the smectite-to-illite conversion during bentonite diagenesis, is that present data are more consistent with the layer-by-layer transformation mechanism (Hower *et al* 1976, Srodon *et al* 1986) wherein expandable interlayers retain much of their charge characteristics rather than a neof ormation mechanism (Nadeau *et al* 1985).

The neof ormation mechanism, as detailed in Nadeau *et al* (1985), involves dissolution of smectite and thin illite synchronously with precipitation of progressively thicker illite particles. The dissolution of smectite and thin illite particles should conceivably result in progressive erasal of smectitic character of expandable interlayers. Furthermore, precipitation of new thin illite nuclei and their subsequent growth would be expected to produce particles with significantly higher and more homogeneous charges than that of smectite, as in the case of neof ormed illites (e.g., Rotliegend illite, Nadeau and Bain 1986) with charges well over 0.6. Present data for random through ordered I/S with >15% expandability do not support such implications of the neof ormation mechanism considered above. It is important to note, however, that the layer charge data presented here do not preclude the existence of the interparticle diffraction proposed by Nadeau *et al* (1984, 1985), but rather they substantiate the smectitic charge of the illite particle surfaces in I/S with >15% expandability.

The appearance of low-angle peaks in the XRD patterns of the long-chain derivatives of six samples with about 10% or less expandabilities may be attributable to the presence of packets of an expandable, vermiculite-like charged component, in addition to illite. This observation, that the expanding layers exist in packets, is most notable in that it conflicts with the current models of I/S. For illite-rich I/S, both the fundamental particles and MacEwan crystallite models predict only a small number of expandable interlayers separated by

illite packets (or particles), but not packets of expandable interlayers (Altaner and Bethke 1988, Nadeau *et al* 1984). An alternative explanation for the presence of these packets is an exchange reaction between interlayer K^+ and alkylammonium ions. Some workers (Mackintosh *et al* 1971, 1972, Laird *et al* 1987) have reported that alkylammonium ions displace K^+ from mica-like interlayers giving rise to low-angle reflections on XRD patterns. On the other hand, some other reports do not exhibit any evidence for expansion of mica-like interlayers in regularly ordered clays (Lagaly 1979) or in biotite (Ghabru *et al* 1989). From these studies, it is apparent that the extent to which alkylammonium ions exchange for K^+ depends on several factors such as particle size, sample re-treatment (e.g., grinding, Na-saturation), temperature, severity of the treatment, properties of the mineral, and the reactivity and size of the alkylammonium ions: Grinding samples in sample preparation, for example, may damage crystal structure and result in K-exchange from the damaged edges; repotassified samples may be more susceptible to K-exchange and to reexpansion upon alkylammonium treatment (Ghabru *et al* 1989); a mild alkylammonium treatment, on the other hand, even with the long-chain and highly reactive octadecylammonium ($N_c = 18$) ions, may result in no significant K-exchange (Laird and Nater 1993). In this study, an alkylammonium- K^+ exchange was considered unlikely to have taken place because 1) reaction times as long as a week in some test samples produced no identifiable changes in XRD patterns, and 2) 10 Å illite peak intensities remained more or less unchanged throughout much of alkylammonium chain lengths. However, in view of the results of Laird *et al* (1987) that illite samples may lose significant amounts of K^+ with no associated loss of illite peak intensity, it is possible that low-angle peaks observed with long-chain alkylammonium derivatives may be illite interlayers that expand due to loss of their interlayer K^+ . Nonetheless, the persistence of the 10 Å illite peak and absence of low-angle peaks indicate that majority of illite interlayers remain unexpanded with short-chain alkylammoniums ($N_c = 6-12$). Such non-expansion behavior of illite interlayers with short-chain alkylammoniums is also supported by good to excellent agreement of observed and calculated basal spacings for samples of >15% expandabilities, as previously noted. The contracted nature of the illite peak with short-chain alkylammoniums and the similarity of interlayer charge densities for the expanding packets both from alkylammonium ion exchange method and structural formulas (Table 3) ought to be interpreted as evidence: 1) that K-fixed illite interlayers and expandable surfaces in I/S are similarly charged; and 2) that the charges are vermiculitic in terms of magnitude (>0.6), and may even be higher than vermiculite (>0.9) for I/S with very few expandables (e.g., sample NI-6).

SUMMARY

As estimated from alkylammonium ion exchange, the layer charge of expandable interlayers in I/S with more than about 15% expandabilities are smectitic both in terms of charge magnitude and its characteristic heterogeneity. Expandable interlayers in I/S with about 10% or less expandabilities are inferred to have a vermiculitic rather than smectitic charge; both expandable and K-fixed interlayers appear to be identical in layer charge. A smectitic charge in the expandable interlayers coupled with the lack of any identifiable correlation between interlayer charge and expandability is consistent with the hypothesis of a layer-by-layer transformation from a smectite precursor to highly illitic I/S during diagenesis. On the other hand, significantly higher charges inferred for the expandable interlayers are consistent with both the continuation of layer-by-layer transformation and the neof ormation mechanism in the very illitic end of I/S series in K-bentonites.

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