Clays and Clay Minerals, Vol. 30, No. 3, 215–222, 1982.

LAYER CHARGE HETEROGENEITY IN VERMICULITES

GERHARD LAGALY

Institut für anorganische Chemie der Universität Kiel
Olshausenstraße 40/60, 23 Kiel, Germany

Abstract—The broad charge heterogeneity typical of nearly all smectites is not necessarily characteristic of vermiculites. In addition to vermiculites with pronounced heterogeneity, minerals with no or only limited charge heterogeneities are known. Layer charge and charge heterogeneity of 25 vermiculites were determined by alkylammonium ion exchange. The comparison of experimental basal spacings with d_L/n-plots provided a simple determination of the average charge density. The spacings of high-charged vermiculites ($\geqslant 0.8$ eq/$(Si,Al)_4O_{10}$) with paraffin-type interlayers follow a straight line in the d_L/n-plots. Lower-charged vermiculites were recognized by stepwise increasing spacings due to mono-, two-, or three-layer chain packings. Charge heterogeneity produced a superposition of the d_L/n-curves for different charges, and the basal reflections of some of the alkylammonium derivatives became nonintegral.

Key Words—Alkylammonium, Layer charge, Vermiculite, Weathering.

INTRODUCTION

Alterations of micas and mica-type layer silicates are solid state reactions. The layer structure is responsible for the anisotropy of the reaction course. In succeeding layers or interlayer spaces the reactions can proceed at different rates or to different extents. The consequence is a nonuniform distribution of the charges in the reaction products (charge heterogeneity). The heterogeneity depends not only on the degree of the alteration, but also on the cooperativity of the reactions. Cooperative reactions (Weiss *et al.*, 1970) are the cause of puzzling effects of particle size on potassium exchange in micas (Scott, 1968; von Reichenbach and Rich, 1969; cf. Norrish, 1973) and the occurrence of ordered phases during exchange reactions in vermiculites (Shawney, 1972; Gruner *et al.*, 1979).

Micas as starting materials in weathering series are thought to be homogeneous with nearly with same cation density in all interlayer spaces. Smectites as weathering products generally have heterogeneous charge distributions, similar to those found in mixed-layer minerals (Lagaly, 1979a, 1981a). Vermiculites may represent initial stages in the alteration sequence of micas, and the knowledge of their charge heterogeneity should enlighten our understanding of some of the fundamental processes of weathering.

EXPERIMENTAL PROCEDURES

Most of the vermiculites examined in this work were investigated by Norrish (1973). Those examined in detail here include vermiculites from (1) Texas Mines Magnesite, Llano County, Texas (Q 210), clear, white crystals; (2) Carl Moss Ranch, Llano County, Texas (Q 209), stop 11, 10th annual Clay Minerals Conference, 1961, clear, white crystals; (3) Beni-Buxera, Spanish Morocco (V 19), clear, white crystals; (4) Young River, Western Australia (V 20), donated by G. F. Walker; (5) Transvaal, South Africa (V 1), yellow and bronze colored crystals; (6) Moore-Williams Property of W. R. Grace & Company (Q206), nearly black, large crystals; and vermiculitized sheridanite, Brewster, New York, donated by H. Kodama.

Layer charges and charge heterogeneities were determined by alkylammonium ion exchange on small crystals, about 0.5 × 3 mm^2 in area and about 0.1 mm thick. The crystals were cut from larger flakes in directions parallel to sharp edges. About 20 mg of vermiculite crystals was treated with 5 ml of alkylammonium chloride solutions in sealed 10-ml ampules at 65°C. One or two weeks later the solution was poured off, and, after washing with 10–20 ml of an ethanol/water solution, the procedure was repeated. Excess alkylammonium chloride and alkylamine was removed by washing the crystals 12 times with the ethanol/water solution. Selected air-dried crystals were carefully slipped into Lindemann glass tubes and dried in high vacuo ($p \leqslant 0.01$ torr, 24 hr, 65°C). The specimens were investigated in Debye-Scherrer powder cameras (diameter $= 36/\pi = 11.46$ cm; CuKα radiation). Depending on the individual vermiculite sample, several or numerous basal reflections could be observed as sharp dots. In general, the exchange was quantitative after two procedures within two or three weeks.

Exchanged vermiculites that gave poorly developed X-ray powder diffraction (XRD) diagrams were reacted with alkylammonium chloride for 50 days or longer. In addition, some crystals or larger flakes were first allowed to stand in a large excess of a 1 M solution of LiCl for several days. After washing, the macroscopic swelling of the Li-exchanged vermiculites in pure water was examined. Most crystals were thickened or exfoliated by osmotic processes (cf. Sridhar and Jackson, 1973; Le Dred and Wey, 1978a, 1978b). The exfoliated crystals were cut into small specimens and then reacted

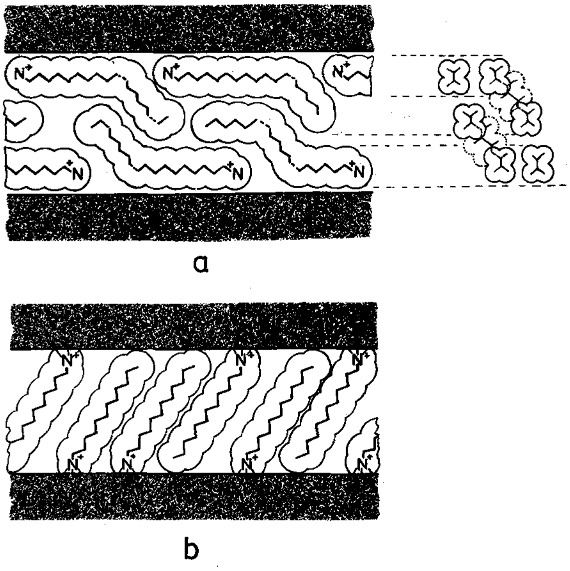

Figure 1. Pseudotrimolecular ("three-layer") (a) and paraffin-type (b) chain packing in alkylammonium vermiculites.

with alkylammonium chloride solution. However, for the main part, no improvement of the XRD pattern was achieved.

The alkylammonium chlorides $C_nH_{2n+1}NH_3^+Cl^-$, where n ranges from 4 to 18, were used as aqueous solutions in the concentrations: 2 M for n = 4–6; 0.5 M for n = 7–9; 0.1 M for n = 10–15; and 0.05 M for n = 16–18. The solutions were prepared by dissolving pure alkylamine (Fluka, Switzerland) in small amounts of ethanol. Some water was added (avoiding an intense clouding), and the pH was adjusted to about 6 with HCl.

RESULTS

Alkylammonium ions in the interlayer spaces of vermiculite acquire distinct arrangements: monolayer and two-layer (bilayer) structures with the alkyl chains parallel to the surface (Brindley and Hofmann, 1962; Lagaly and Weiss, 1971), pseudotrimolecular layers[1] (Lagaly and Weiss, 1971; Lagaly *et al.*, 1976), and paraffin-type structures (Brindley and Ray, 1964; Brindley, 1965; Johns and Sen Gupta, 1967; Lagaly and Weiss, 1970).

High-charged vermiculites

High-charged vermiculites are recognized by spacings linearly increasing with n. Typical plots are shown in Figure 2. The spacings of two vermiculites from Llano County, Texas, follow the relations:

$d_L = 11.0 + 0.98$ n (Texas Mines Magnesite)
$d_L = 11.05 + 0.965$ n (Carl Moss Ranch)

The spacings indicate paraffin-type monolayers with a chain tilt of 51° and 50° (Figure 1b). This tilting allows an optimal interaction of the NH^+_3-groups by three hydrogen bonds to the surface oxygen atoms (Brindley, 1965; Lagaly and Weiss, 1970).

With a highly ordered interlayer structure odd/even alternating basal spacings should be observed and actually were observed for a batavite (Weiss, 1963) and some intercalation complexes of other host compounds (Lagaly, 1979b; Beneke and Lagaly, 1982). The odd/even alternation has led to controversies in the literature (cf. Walker, 1967; Lagaly and Weiss, 1970). In general, the odd/even alternation in vermiculites is not as pronounced as that derived from the ideal interlayer arrangement, but it is still detectable for the Llano vermiculite (Carl Moss Ranch, Figure 2b).

Vermiculites have paraffin-type interlayers if the layer charge is at least 0.75 eq/$(Si,Al)_4O_{10}$. Van Olphen (1965) reported a layer charge of 0.80 eq/$(Si,Al_4)O_{10}$ for the Llano vermiculite. Norrish (1973) gave values between 0.72 and 0.95 for vermiculites from the same locality in Llano County, clearly revealing the difficulties in comparing literature data even if the localities are reported as the same.

The optimal chain orientation and molecular packing makes the paraffin-type chain arrangement less sensitive to charge density variations. Thus, the interlayer structure and the d_L/n-relation scarcely change with increasing layer charge. The tilting angle increases to about 65° for a layer charge of 0.9 eq/$(Si,Al)_4O_{10}$ (Lagaly and Weiss, 1971). The limited influence of the layer charge on the chain tilt and the basal spacings renders difficult the detection of charge heterogeneities in the range 0.75–1.0 eq/$(Si,Al)_4O_{10}$.

Low-charged vermiculites

Vermiculite from Beni-Buxera (Spanish Morocco) is a low-charged vermiculite. Its basal spacings (Figure 3a) increase stepwise, and all alkylammonium derivatives showing integral basal reflections lie on the plateaus d_L = 17.6 Å and 22 Å. Between the plateaus the basal reflections are nonintegral (for n = 10, 11, 12, 16, and 17). The nonintegrality of the basal reflections indicates a random interstratification of two (or more) units with different identity periods (fundamental spacings). If several basal reflections are observed, the two fundamental spacings d_I and d_{II} can be recognized by comparing in a plot the integer multiples of the basal d-values of different alkylammonium derivatives. Coinciding values indicate the fundamental spacings d_I or d_{II} or very similar values (cf. the "visual inspection

---

[1] The term "pseudotrimolecular" was chosen because the alkylammonium ions actually are arranged in bilayers (Figure 1a). The ends of the chains are shifted one above the other, so that the thickness of three alkyl chains determines the spacing. This chain packing is made possible by formation of kinks or kink-like conformations (Lagaly, 1976, 1981b).

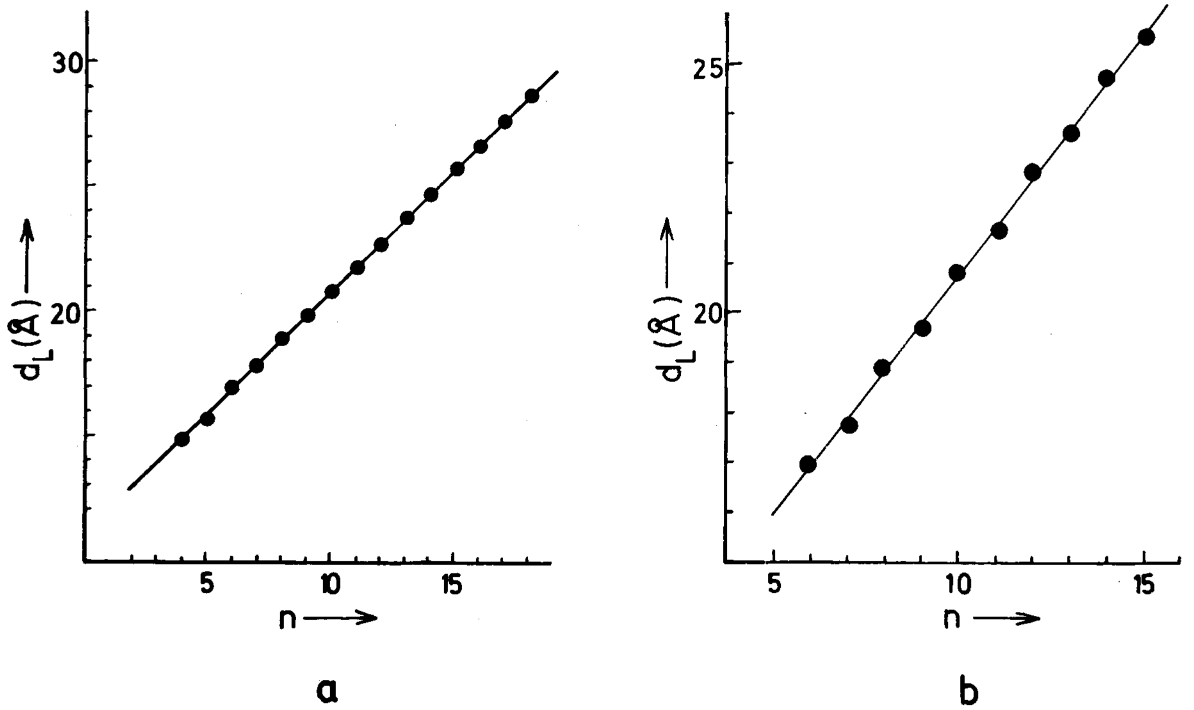

Figure 2. Basal spacings of high-charged alkylammonium vermiculites from Llano County, Texas (layer charge $\xi \geq 0.8$ eq/$(Si,Al)_4O_{10}$): (a) Texas Mines Magnesite, (b) Carl Moss Range.

method'' of Mering, 1949; Weaver, 1956; MacEwan *et al.*, 1961). For the Beni-Buxera vermiculite values of 17.8 Å and 21.5 Å are indicated as fundamental spacings d_I and d_{II} and correspond to the plateaus in Figure 3. It is evident from Figure 3 that the charge density in the Beni-Buxera sample varies between 0.57 and 0.70 and averages 0.63 eq/$(Si,Al)_4O_{10}$ (cf. Norrish, 1973; 0.65 eq/$(Si,Al)_4O_{10}$).

The d_L/n-diagrams (Figures 3–7) for low-charged vermiculites were constructed on the basis of geometrical considerations (Lagaly, 1981a). One-layer/two-layer and two-layer/three-layer transitions occur if the area per alkylammonium ion, A_c, is equal or twice the equivalent area, A_e:

$$A_c = \lambda A_e, \quad \lambda = 1, 2$$

or

$$(1.27)(4.50)n + 14 = \lambda[d(010)d(100)]/2\xi,$$

where ξ = interlayer cation density (= average layer charge in eq/$(Si,Al)_4O_{10}$) and $d(010)d(100) \approx 49$ Å^2. The transition of the three-layer structure into the paraffin-type arrangement occurs at $n \simeq 1.5\, n_{II}$, where n_{II} is the chain length for close packed two-layers.

At a first glance it might be advisable to calculate charge heterogeneity data from the transitions between the 13.7-, 17.7- and 21.7-Å plateaus as for montmorillonites. In most cases, however, the charge distribution deduced from the 13.6 Å/17.7 Å transition differs from that of the 17.7 Å/21.7 Å transition. One of the reasons is that the 17.7 Å/21.7 Å transition is more indicative of the charge density of the silicate layer with the highest charge density than of the average charge density in the interlayer (Lagaly *et al.*, 1976). Further, at charge densities $\geq$0.50 eq/$(Si,Al)_4O_{10}$ and at spacings below the 17.7-Å plateau, a denser chain packing can be achieved in the paraffin-type structure than in the two-layer arrangement (see below). Therefore, the spacing of 17.0 Å (n = 6, Beni-Buxera vermiculite) does not result from an interstratification of 70% two-layers and 30% one-layers, but simply follows from the paraffin-type chain arrangement. An indication is the pronounced rationality of the basal reflections up to ℓ = 13.

Vermiculite from Young River, Western Australia (Figure 3b) has a broad charge heterogeneity. From the 17.7 Å/21.7 Å transition a charge heterogeneity of 0.52–0.70 is obtained with an average of 0.61 eq/$(Si,Al)_4O_{10}$, in good agreement with analytical data (0.55 eq/$(Si,Al)_4O_{10}$, Walker, 1967; 0.65 eq/$(Si,Al)_4O_{10}$, Norrish, 1973, for the low-charged specimens). Analysis of the one-layer/two-layer transition by the usual procedure gives a mean layer charge of 0.44 eq/$(Si,Al)_4O_{10}$ which evidently is too low. It probably results from interstratification with interlayer spaces

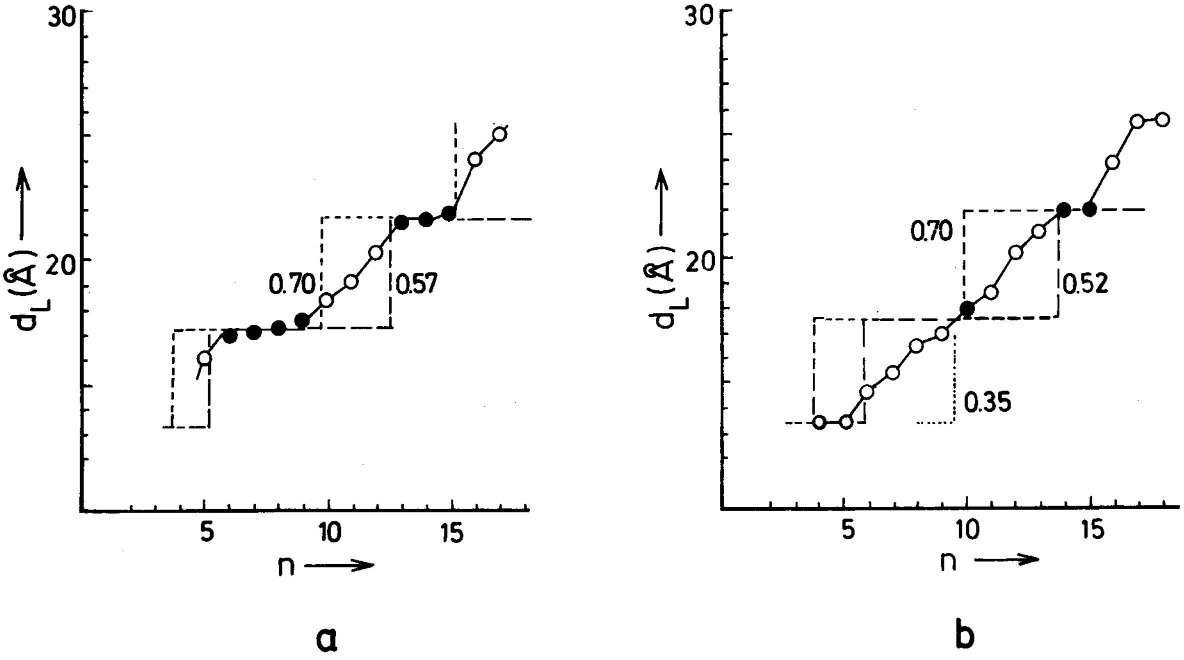

Figure 3. Basal spacings of low-charged alkylammonium vermiculites: (a) Beni-Buxera, Spanish Morocco, charge heterogeneity = 0.57–0.70; mean layer charge ξ = 0.63 eq/$(Si,Al)_4O_{10}$. (b) Young River, Australia, broad charge heterogeneity = 0.52–0.70; mean layer charge ξ = 0.61 eq/$(Si,Al)_4O_{10}$. Solid and open circles = integral and nonintegral basal reflections ($d_L = d_1$); dashed lines = theoretical spacings, charge density indicated.

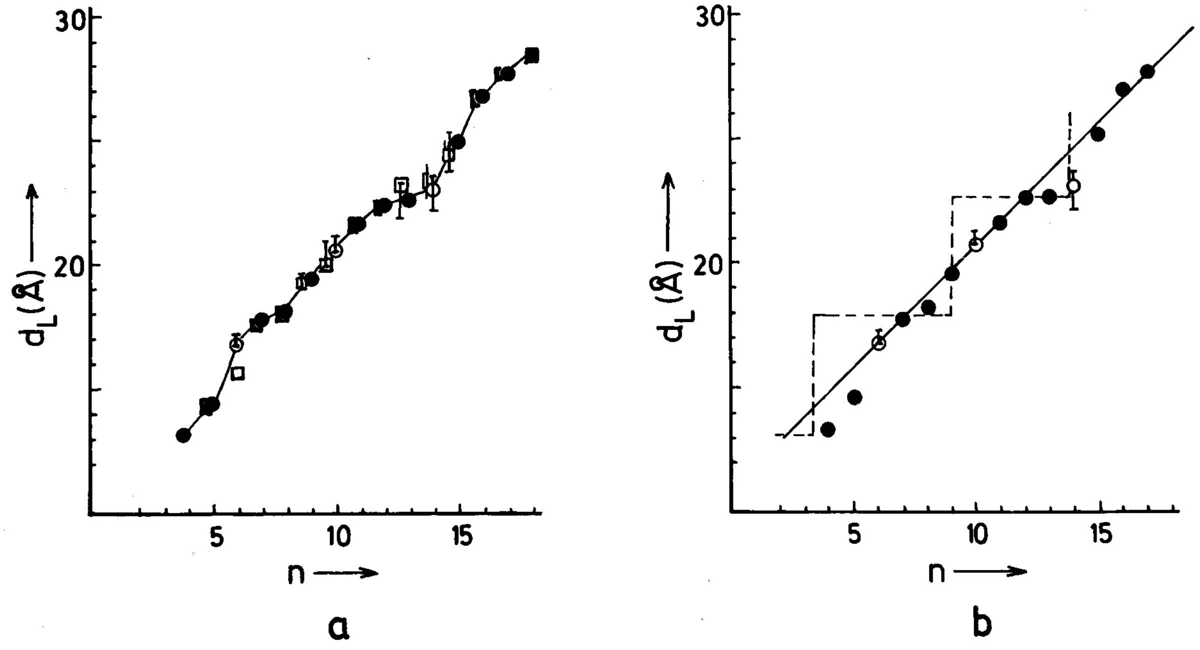

Figure 4. Basal spacings of a medium charged alkylammonium vermiculite from South Africa. (a) Spacings of different crystals. Circles = light yellow-bronze crystals; squares = dark bronze crystals; solid circles or squares = integral; circles or squares = nonintegral basal reflections ($d_L = d_1$). The bars indicate the variations of the products 1d(001), 2d(002) . . . $\ell d(00\ell)$. (b) Interpretation of the spacings (light crystals) by alternating layer-type and paraffin-type chain packings. Broken line = layer-type structure; charge density ξ = 0.75 eq/$(Si,Al)_4O_{10}$; full line = paraffin-type structure, charge density $\xi \geq 0.8$ eq/$(Si,Al)_4O_{10}$).

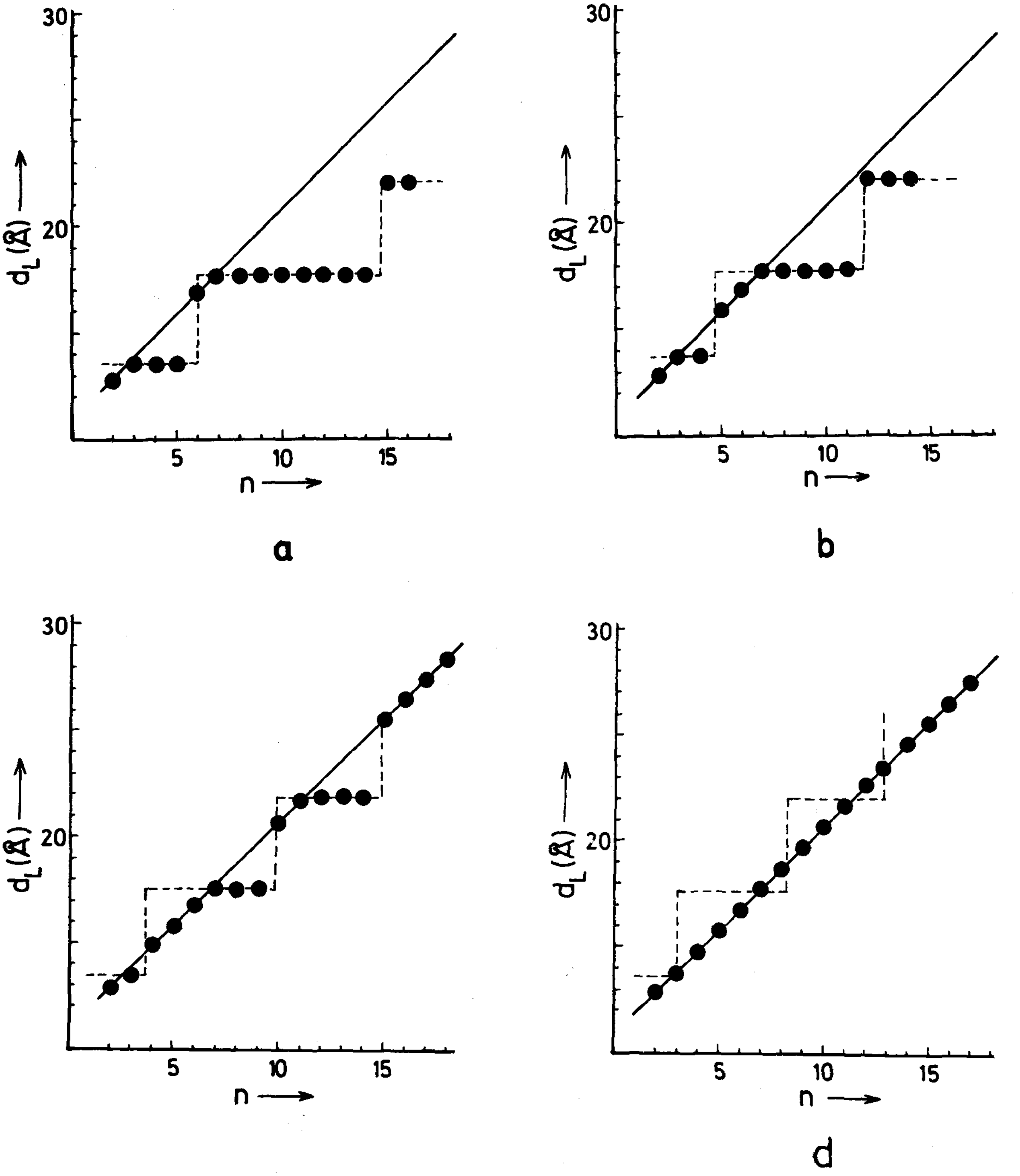

Figure 5. Theoretical d_L/n-plots for homogeneously charged vermiculites; charge densities ξ (a) 0.50, (b) 0.60, (c) 0.70, and (d) 0.80 eq/(Si,Al)$_4$O$_{10}$. Solid line = paraffin-type chain packing; broken line = layer arrangements, solid circle = theoretical spacings.

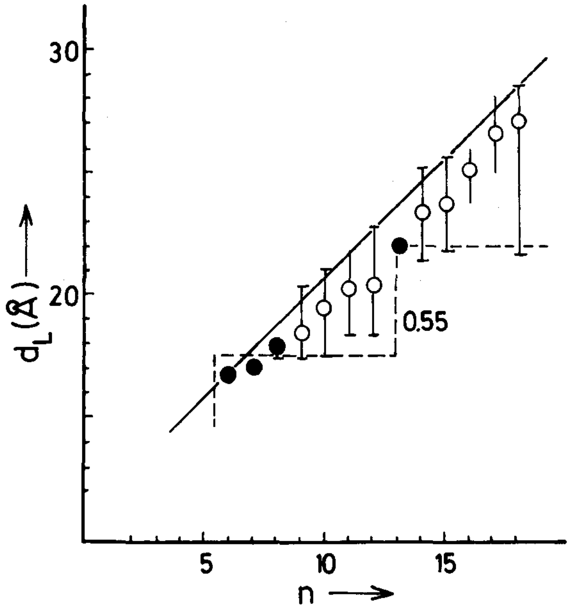

Figure 6. A medium charged vermiculite with broad charge heterogeneity. (Sample Q 206, Moore Williams, W. R. Grace & Company, USA). Solid circles = integral or nearly integral basal reflections; open circles = large deviations from integrality. "Fundamental" spacings as estimated by visual inspection method are indicated by bars.

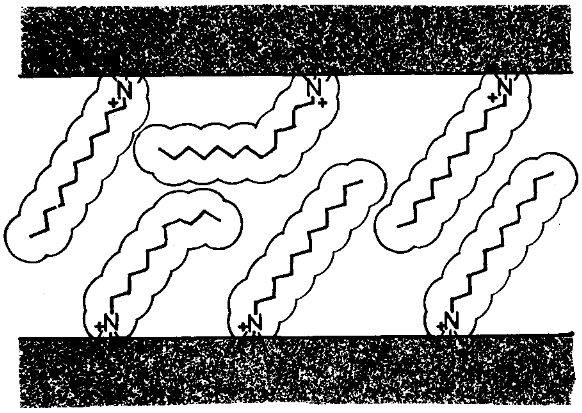

Figure 7. Formation of nonequilibrium forms of alkylammonium vermiculites by kinked alkyl chains during washing and drying sequences. The kinking impedes the interpenetration of the chains to the paraffin-type arrangement (cf. Figure 1).

which do not react with short-chain alkylammonium ions.

Vermiculitized chlorites

Ross and Kodama (1974) described the transformation of an orthochlorite (sheridanite) into a vermiculite by dehydroxylation at 610°C and subsequent HCl/NaCl treatment to dissolve the dehydroxylated hydroxide sheet. A sample of this vermiculitized chlorite (supplied by Dr. Kodama) gave basal spacings similar to those of Beni-Buxera vermiculite and with a pronounced three-layer plateau. The charge varies between 0.57 and 0.70 eq/$(Si,Al)_4O_{10}$; the mean value is 0.62 eq/$(Si,Al)_4O_{10}$ (from two-layer/three-layer transition). The analytical layer charges of Ross and Kodama (1974) are slightly lower (0.55 or 0.56 eq/$(Si,Al)_4O_{10}$). The one-layer/two-layer transition indicates a lower value of the average charge density (about 0.48 eq/$(Si,Al)_4O_{10}$), which may be attributed to an extreme unsymmetrical charge distribution (interlayers between very high-charged layers and very low-charged layers) or to the presence of interlayers nonreacting with short chain alkylammonium ions.

Medium charged vermiculites

The d_L/n-plot of a typical medium charged vermiculite (South Africa, Figure 4) shows at a first inspection spacings irregularly increasing. Figure 4b suggests that this is by no means indicative of broad charge heterogeneity. The full line corresponds to paraffin-type chain packing (layer charge ≥ 0.80), and the dashed curve gives the spacings for the layer-type arrangements and a layer charge of 0.75 eq/$(Si,Al)_4O_{10}$. The experimental points follow the theoretical spacings which belong to the structure with the closest packed chains. A slight nonintegrality of some reflections indicates a small charge heterogeneity (limiting values about 0.75 and $\geq$0.8 eq/$(Si,Al)_4O_{10}$).

Comparison of experimental spacings with theoretical d_L/n-plots (Figure 5) provides a rapid and reliable determination of the charge density of medium charged vermiculites. A pronounced charge heterogeneity makes the basal reflections of most alkylammonium derivatives nonintegral. An example is reported in Figure 6. The bars give the fundamental spacings obtained by the visual inspection method, and evidence that the nonintegrality results from interstratification of paraffin-type interlayers with two-layer (n = 9–12) or three-layer arrangements (n $\geq$ 14). The mean layer charge is about 0.65 eq/$(Si,Al)_4O_{10}$), and the structure contains interlayers of about 0.8 and 0.55 eq/$(Si,Al)_4O_{10}$ in random distribution.

DISCUSSION

The layer charge ξ of vermiculites with moderate heterogeneity can easily be determined using Figure 5. High-charged vermiculites ($\xi \geq 0.8$ eq/$(Si,Al)_4O_{10}$) are recognized by linearly increasing spacings after alkylammonium ion exchange (Figure 2). The spacings of medium charged samples ($0.6 < \xi < 0.75$) (Figure 4) reveal alternating layer-type and paraffin-type chain packings. Low-charged vermiculites have more or less extended 13.6-, 17.7-, and 21.7-Å plateaus (Figure 3).

One source of difficulty in obtaining reproducible basal spacings is that crystals of alkylammonium vermiculites with differing spacings form as a result of particular washing and drying sequences (Weiss and Kantner, 1960; Johns and Sen Gupta, 1967; Walker, 1967). Weiss and Kantner (1960), studying powdered materials, emphasized the importance of slightly grinding the exchanged vermiculites before drying. Sporadically, some crystals with too high spacings were obtained in course of our investigations. The occurrence of such forms presented no severe difficulties for layer charge determinations because several alkylammonium derivatives were investigated, and crystals with "false" spacings were easily recognized. Using clay-size particles the problems are avoided by carefully grinding the washed and air-dried vermiculites before the final drying in vacuo.

Walker (1967) suggested that expanded forms of alkylammonium vermiculite crystals result from a sticking of the chains which impedes their complete interpenetration to the monolayer. The molecular packing of chains is too low to sustain a stable sticking of the chains. The reason is the denting of the chains (Figure 7) as a result of trans-gauche-isomerizations (Lagaly, 1976).

In principle, the average charge density may also be obtained from the spacings of the alkylammonium derivatives under long-chain alkanols (Weiss and Kantner, 1960; Weiss and Lagaly, 1967). The formation of nonequilibrium phases with too high spacings commonly affects the accuracy of this procedure and pretends a lower charge density.

CONCLUSION

The broad charge heterogeneity typical of nearly all smectites is not necessarily typical of vermiculites. In addition to vermiculites with pronounced heterogeneity, specimens can be found with no or only a narrow charge heterogeneity.

From charge determinations of vermiculites, the transformation of micas into vermiculites and finally into smectites (Schwertmann, 1964; Tributh, 1976) probably proceeds by two reaction sequences. One reaction path first leads to relatively homogeneous vermiculites which alter to heterogeneous smectites. In the other sequence, initially heterogeneous hydromicas and vermiculites are formed which transform to smectites with comparable or different charge heterogeneity.

Two different types of vermiculites were recognized by Schwertmann and Politz (1967) and Schwertmann (1966) by potassium-fixation experiments. Their investigations provided some evidence that the soil vermiculites studied were more homogeneous than the reference vermiculites from South Carolina and Transvaal. One cannot generalize these observations at present. The method for determining charge heterogeneities in vermiculites outlined in the present paper should aid in studying the properties of vermiculites, especially the changes during alteration processes.

ACKNOWLEDGMENTS

Sincere thanks are due to Winfried Schreieck, who started the alkylammonium ion exchange of numerous vermiculite crystals. The financial support of the "Deutsche Forschungsgemeinschaft" (Schwerpunktsprogramm "Tonmineralogie") is acknowledged.

REFERENCES

Beneke, K. and Lagaly, G. (1982) The brittle mica-like $KNiAsO_4$ and its organic derivatives: *Clay Miner.* **17,** 177–185.

Brindley, G. W. (1965) Complexes of primary amines with montmorillonite and vermiculite: *Clay Miner.* **6,** 91–96.

Brindley, G. W. and Hofmann, R. W. (1962) Orientation and packing of aliphatic chain molecules on montmorillonite: in *Clays and Clay Minerals, Proc. 9th Natl. Conf., West Lafayette, Indiana, 1960,* Ada Swineford, ed., Pergamon Press, New York, 546–556.

Brindley, G. W. and Satyabrata Ray (1964) Complexes of Ca-montmorillonite with primary monohydric alcohols: *Amer. Mineral.* **49,** 106–115.

Gruner, L., Le Dred, R., and Wey, R. (1979) Obtention de minéraux interstratifiés sodium-alkylammonium de type 1/1 réguliers à partir de vermiculite: *C.R. Acad. Sci. Paris* **D 288,** 661–663.

Johns, W. D. and Sen Gupta, P. K. (1967) Vermiculite-alkylammonium complexes: *Amer. Mineral.* **52,** 1706–1724.

Lagaly, G. (1976) Kink-block and gauche-block structures of bimolecular films: *Angew. Chem. Int. Ed. Engl.* **15,** 575–586.

Lagaly, G. (1979a) The "layer charge" of regular interstratified 2:1 clay minerals: *Clays & Clay Minerals* **27,** 1–10.

Lagaly, G. (1979b) Crystalline silicic acids and their interface reactions: *Adv. Colloid Interface Sci.* **11,** 105–148.

Lagaly, G. (1981a) Characterization of clays by organic compounds: *Clay Miner.* **16,** 1–21.

Lagaly, G. (1981b) Inorganic layer compounds—phenomena of interface reactions with organic compounds: *Naturwissenschaften* **68,** 82–88.

Lagaly, G. and Weiss, A. (1970) Anordnung und Orientierung kationischer Tenside auf Silicatoberflächen. Teil III: paraffinähnliche Strukturen bei n-Alkylammonium-Schichtsilicaten mit mittlerer Schichtladung (Vermiculite): *Kolloid Z. Z. Polymere* **238,** 485–493.

Lagaly, G. and Weiss, A. (1971) Anordnung und Orientierung kationischer Tenside auf Silicatoberflächen. Teil IV: Anordnung von n-Alkylammoniumionen bei niedrig geladenen Schichtsilicaten: *Kolloid Z. Z. Polymere* **243,** 48–55.

Lagaly, G., Fernandez Gonzales, M., and Weiss, A. (1976) Problems in layer charge determination of montmorillonites: *Clay Miner.* **11,** 173–187.

Le Dred, R. and Wey, R. (1978a) Formation and applications de complexes mica-vermiculite-chlorure de sodium: *Clay Miner.* **13,** 177–186.

Le Dred, R. and Wey, R. (1978b) Formation de complexes mica-vermiculite-halogenure de metal alcalin: *Clay Miner.* **13,** 187–197.

MacEwan, D. M. C., Ruiz Amil, A., and Brown, G. (1961) Interstratified clay minerals: in *The X-ray Identification and Crystal Structures of Clay Minerals,* G. Brown, ed., Mineralogical Society, London, 393–445.

Mering, J. (1949) Factors in the weathering of mica to vermiculite: in *Proc. Int. Clay Conf., Madrid, 1972,* J. M. Serratosa, ed., Div. Ciencias C.S.I.C., Madrid, 417–432.

Norrish, K. (1973) Factors in the weathering of mica to vermiculite: in *Proc. Int. Clay Conf., Madrid, 1972,* J. M. Serratosa, ed., Div. Ciencias C.S.I.C., Madrid, 417–432.

von Reichenbach, H. Graf and Rich, C. I. (1969) Potassium release from muscovite as influenced by particle size: *Clays & Clay Minerals* **17,** 23–29.

Ross, G. J. and Kodama, H. (1974) Experimental transformation of a chlorite into a vermiculite: *Clays & Clay Minerals* **22,** 205–211.

Schwertmann, U. (1964) Neuere Ergebnisse auf dem Gebiet der Tonmineralogie von Böden: *Landw. Forschung, Sonderheft* **18,** 33–42.

Schwertmann, U. (1966) Das Verhalten von Vermiculiten gegenüber Kalium, Aluminium und anderen Kationen. II. Chemische Untersuchungen: *Z. Pflanzenern. Bodenk.* **115,** 200–209.

Schwertmann, U. and Politz, U. (1967) Das Verhalten von Vermiculiten gegenüber Kalium, Aluminium und anderen Kationen. I. Röntgenographische Untersuchungen: *Trans. Int. Congr. Soil Sci. Bucarest 1964,* Acad. Soc. Rep. Romania, 455–463.

Scott, A. D. (1968) Effect of particle size on interlayer potassium exchange in micas: *Trans. 9th Int. Congr. Soil Sci.* **11,** 649–660.

Shawney, B. L. (1972) Selective sorption and fixation of cations by clay minerals: A review: *Clays & Clay Minerals* **20,** 93–100.

Sridhar, K. and Jackson, M. L. (1973) Fixing cation interaction with blister-like osmotic swelling on vermiculite cleavages: *Clays & Clay Minerals* **21,** 369–377.

Tributh, H. (1976) Die Umwandlung der glimmerartigen Schichtsilicate zu aufweitbaren Dreischicht-Tonmineralen: *Z. Pflanzenern. Bodenk.* **1976,** 7–25.

van Olphen, H. (1965) Thermodynamics of interlayer adsorption of water in clays. I—sodium vermiculite: *J. Colloid Interf. Sci.* **20,** 824–837.

Walker, G. F. (1967) Interactions of n-alkylammonium ions with mica-type layer lattices: *Clay Miner.* **7,** 129–143.

Weaver, C. E. (1956) Mixed-layer clays in sedimentary rocks: *Amer. Mineral.* **41,** 202–221.

Weiss, A. (1963) Mica-type layer silicates with alkylammonium ions: in *Clays and Clay Minerals, Proc. 10th Natl. Conf., Austin, Texas, 1961,* Ada Swineford and P. C. Franks, eds., Pergamon Press, New York, 191–224.

Weiss, A. and Kantner, I. (1960) Über eine einfache Möglichkeit zur Abschätzung der Schichtladung glimmerartiger Schichtsilicate: *Z. Naturforsch.* **15b,** 804–807.

Weiss, A. und Lagaly, G. (1967) Ein einfaches Verfahren zur Abschätzung der Schichtladung quellungsfähiger Schichtsilicate: *Kolloid Z. Z. Polymere* **216/17,** 356–361.

Weiss, A., Becker, H. O., Orth, H., Mai, G., Lechner, H., and Range, K. J. (1970) Particle size effects and reaction mechanism of the intercalation into kaolinite: in *Proc. Int. Clay Conf., Jerusalem, 1969, Vol. 2,* L. Heller, ed., Israel Prog. Sci. Transl., Jerusalem, 180–184.

(Received 19 May 1981; accepted 17 September 1981)

Резюме—Широкая разнородность заряда, типичная для почти всех смектитов, не является характерной для вермикулитов. В дополнение к вермикулитом со значительной разнородностью известны также минералы с нулевой или ограниченной разнородностью заряда. Слоевой заряд и разнородность заряда 25 вермикулитов определялись путем обмена ионов алкиламмония. Сравнение величин экспериментальных промежутков с графиками d_L/n позволило определить очень просто среднюю плотность заряда. Расстояния сильно заряженных вермикулитов ($\geq 0{,}8$ экв/(Si,Al_4O_{10}) с внутренными слоями типа парафина составляют прямую линию на графиках d_L/n. Слабее-заряженные вермикулиты были распознаны на основании увеличивающихся шагами промежутков в результате моно-, двух-, или трех-слойных цепных упаковок. Разнородность заряда вызывала наложение кривых d_L/n для разных зарядов и основные отражения некоторых дериватов алкиламмония становились неинтегральными. [E.C.]

Resümee—Im Gegensatz zu den Smectiten, für die eine mehr oder weniger breite Ladungsverteilung typisch ist, kommen neben Vermiculiten mit ausgeprägter Ladungsheterogenität auch Vermiculite mit recht gleichmäßig verteilten Ladungen vor. Schichtladung und Ladungsverteilung von 25 Vermiculiten wurden durch die Alkylammonium-Methode bestimmt. Der Vergleich der Schichtabstände mit theoretischen d_L/n-Diagrammen bietet eine sehr einfache Möglichkeit zur Schichtladungsbestimmung. Hochgeladene Vermiculite (≥ 0.8 eq/$(Si,Al)_4O_{10}$) mit paraffinartigen Zwischenschichtstrukturen sind an dem linearen Anstieg des Schichtabstandes mit der Alkylkettenlänge zu erkennen. Bei niedriger geladenen Vermiculiten ändert sich der Schichtabstand infolge der Anordnung der Alkylammoniumionen in mono-, bi-, und pseudotrimolekularen Schichten stufenweise. Ladungsheterogeneität führt zur Überlagerung der für homogene Vermiculite geltenden d_L/n-Kurven und dem Auftreten nicht-integraler Basisreflexe bei bestimmten Kettenlängen.

Résumé—La grande hétérogénéité de charge typique de presque toutes les smectites n'est pas nécessairement caractéristique des vermiculites. En plus des vermiculites à hétérogénéité prononcée, des minéraux n'ayant aucune hétérogénéité de charge, ou une hétérogénéité de charge limitée sont connus. La charge de couche et l'hétérogénéité de charge de 25 vermiculites ont été déterminées par échange des ions alkylammonium. La comparaison d'espacements de base expérimentaux avec des diagrammes d_L/n a permis une détermination simple de la densité de charge moyenne. Les espacements de vermiculites à charge élevée ($\geq 0{,}8$ eq/$(Si/Al)_4O_{10}$) avec des interfeuillets de type paraffine suivent une droite dans les diagrammes d_L/n. Les vermiculites à charge plus basse ont été reconnues par des espacements croissant par étape à cause de structures en chaines à une, deux, ou trois couches. L'hétérogénéité de charge a produit une superposition des courbes d_L/n pour différentes charges, et les réflections de base de certains dérivatifs alkylammonium sont devenues nonintegrales. [D.J.]