Monodimensional Fourier Analysis of Some Vermiculite-l-Ornithine⁺ Complexes

Jose A. Rausell-Colom, and Vicente Fornés

Instituto de Edafologia y Biologia Vegetal, C.S.I.C. Madrid, Spain

Abstract

From vermiculite saturated with l-ornithine cations, three crystalline phases with basal spacings of 20.3 Å, 16.3 Å, and 14.63 Å were obtained, giving rational *001* X-ray reflections up to 2θ values of 140°. The structures have been determined by monodimensional Fourier syntheses normal to (001).

The first two phases contain monovalent ornithine cations and water molecules in the interlayer space (ten and six water molecules per cation, respectively). The third phase is dehydrated, and contains divalent peptide cations of the diketopiperazine type.

In the 20.3 Å phase the interlayer material (Fig. 3) is arranged in three layers. Ornithine cations lie flat on the vermiculite surfaces, with the plane of the zig-zag chain perpendicular to the layer and with the $-COO^-$ and $-NH^+_3$ groups directed toward the center of the structure, away from the silicate surface. None of the $-NH^+_3$ groups are keyed into the ditrigonal cavities of the tetrahedral sheet, due probably to intermolecular association with neighboring $-COO^-$ groups. Five water molecules per each ornithine cation cover the silicate surface. The rest of the water forms a bimolecular layer at the center of the structure.

The 16.3 Å phase has the interlayer material (Fig. 2) arranged in two layers. Organic cations and water molecules are adsorbed on each surface with the same disposition as before, but the crystal has lost the intermediate water layer.

The 14.63 Å phase has the peptide cations arranged in one layer. The plane of the cyclic ring is inclined 60° to the vermiculite layers, with the $>C = O$ groups at the center of the structure and the $>N-H$ groups each directed to one surface. Both lateral chains are on planes normal to the layers, resulting from a 60° rotation around the $>CH-CH_2-$ bonds.

Introduction

Since the early work on organic complexes of montmorillonite (Bradley, 1945; MacEwan, 1948), the nature and properties of clay-organic complexes have been extensively studied by X-ray diffraction, because the most obvious manifestation of the adsorption of organic molecules into the interlayer space is a modification of the basal spacing of the mineral. Reliable X-ray data will show if such complexes possess long range regularity or are formed by mixed-layer sequences. Accurate basal spacings, derived from at least a few integral diffraction maxima, place important restrictions on possible packing and orientation arrangements, which, combined with considerations of molecular geometry, may lead to probable molecular orientations (Brindley, 1970).

Complexes giving complete integral series of diffraction of the basal spacing, extending to 00l spacings of 1 Å or lower, may be studied by one-dimensional Fourier syntheses normal to 001, thus providing more rigorous information on the orientation of the organic molecules. Examples in which the method has been successfully applied are ethylene glycol complexes of smectites and vermiculites (Brindley, 1966; Brindley and Hoffmann, 1962; Bradley, Weiss, and Rowland, 1963; Reynolds, 1965), certain intercalation complexes of kaolinite (Weiss, Thielepape, and Orth, 1966), complexes of aliphatic amines and vermiculites (Johns and Sengupta, 1967) and of ϵ-aminocaproic acid and vermiculite (Kanamaru, Tsunashima, and Koizumi, 1969).
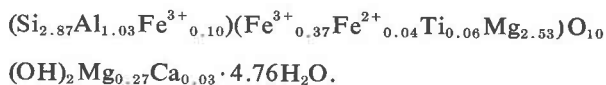
Mifsud, Fornés, and Rausell-Colom (1970) describe the formation of cationic complexes of vermiculite-ornithine-water, with basal spacings ranging between 42.2 Å (stable in the presence of amino acid solution) and 14.35 Å (fully dehydrated phase). We will refer in particular to three crystalline phases, with basal spacings of 20.3 Å, 16.3 Å, and 14.63 Å. These appear to be sufficiently stable under ambient atmospheric conditions and to pos-

sess sufficient long range regularity, as indicated by *00l* reflections up to 2θ values near 140°, to make their structural study by Fourier methods worthwhile.

Additional information by IR absorption spectroscopy, regarding the disposition and interaction of the functional groups of the amino acid molecules with the silicate layer and with themselves, has been obtained by Fornés *et al* (1974), and has been used advantageously for determining the orientation adopted by the organic molecules in interlayer space.

Experimental Materials

Vermiculite from Kapirikamodzi (Malawi) (mineral formula and C.E.C. supplied by Dr. G. F. Walker, Division of Applied Mineralogy, C.S.I.R.O., Melbourne, Australia) had the formula:

$$(Si_{2.87}Al_{1.03}Fe^{3+}_{0.10})(Fe^{3+}_{0.37}Fe^{2+}_{0.04}Ti_{0.06}Mg_{2.53})O_{10}$$

$$(OH)_2 Mg_{0.27}Ca_{0.03} \cdot 4.76H_2O.$$

Its cation exchange capacity was 150 meq/100 g (interlayer water-free material).

The l-ornithine hydrochloride is from Sigma Chemical Company, with purity grade Σ, molecular weight, 168.6.

Sample Preparation

Single crystals of homoionic vermiculite (Sr), of ≃50 μ thickness, were cut to appropriate size (1 × 0.2 cm). They were treated repeatedly with a 0.5M solution of l-ornithine hydrochloride for several hours, washed slightly with distilled water to eliminate excess amino acid, and dried at room temperature for about 2 hours.

The resultant material has a 20.3 Å basal spacing (Mifsud *et al,* 1970) and is stable under normal atmospheric conditions for 2–3 hours. Dehydration of the above complex at 60°C overnight leads to a phase with $d_{001} = 16.3$ Å stable at room temperature for 6–7 hours. Finally, a stable phase with $d_{001} = 14.63$ Å is obtained by heating the former at 180°C for 20 hours.

Studies by IR absorption spectroscopy (Fornés *et al,* 1974) and by X-ray fluorescence spectrography (Mifsud, Fornés, and Rausell-Colom, 1970), show that, in the 20.3 Å and 16.3 Å phases, ornithine cations replace the interlayer inorganic cations of the vermiculite; in the 14.63 Å phase the amino acid adsorbed has reacted to form the cyclic peptide,

$$NH^+_3 - (CH_2)_3 -$$

$$- CH \Big\langle {CO - NH \atop NH - CO} \Big\rangle CH - (CH_2)_3 - NH^+_3$$
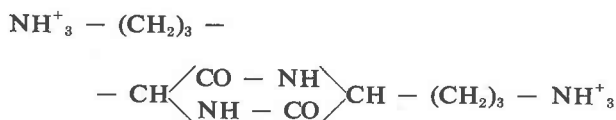
which contains a ring of the diketopiperazine type.

Carbon and Nitrogen Determinations

Determinations of C and N contents of these complexes were made with a F.M. Analyzer Model H185. Hydrogen contents determined with the same instrument are not significant since they depend on the degree of hydration of the complex at the moment that the sample is injected into the oxidation furnace. But the specimen has to remain for several minutes in the instrument prechamber at around 60°C, and a part of the total water content is thus lost before analysis.

C and N contents have been calculated relative to the weight of the original Mg-vermiculite crystal in equilibrium with an atmosphere of 80 percent R.H. (15 percent interlayer water). Results show that the organic matter content of the three complexes corresponds to the C.E.C. of mineral.

X-ray Diffraction Measurements

The X-ray diffraction measurements were made with a Philips Diffractometer type PW1010, equipped with goniometer, scintillation counter, linear amplifier, pulse height analyzer, rate meter, and recorder. With Cu$K\alpha$ radiation, a total of 24 orders were recorded for the 20.3 Å phase, of 19 orders for the 16.3 Å phase, and of 17 orders for the 14.63 Å phase.

The diffraction peaks were recorded using scanning speeds, time constants, and chart speeds compatible with the stability over time of the different complexes. Under optimum instrumental conditions, recording of all the *00l* diffraction orders of each crystal would take from 4 to 5 hours. Exposure of the crystal to ambient conditions for this length of time can produce irreversible structural changes, such as loss of interlayer water (even if these do not affect the basal spacing). Therefore, after completing the recording of all of the diffraction orders for each crystal, the first three orders were again recorded. If there were no variations in the position and intensity of these first three peaks during the time of recording, then the whole set of integrated intensities was accepted as reliable.

A slit system was chosen so that the specimen

TABLE 1. Integrated Diffraction Intensities

00l	20.3Å phase	16.3Å phase	14.63Å phase	00l	20.3Å phase	16.3Å phase	14.63Å phase
1	468.0	572.0	1404.0	13	59.0	120.0	18.0
2	92.0	32.0	36.6	14	84.0	31.0	29.0
3	2.0	40.0	256.0	15	86.0	36.0	17.0
4	20.0	15.0	805.0	16	46.8	39.1	55.0
5	2.0	1120.0	927.0	17	18.6	62.4	33.0
6	368.0	920.0	8.5	18	7.4	124.0	
7	256.0	245.0	780.0	19	14.8	55.5	
8	16.0	420.0	132.0	20	12.8		
9	36.0	130.0	104.0	21	22.0		
10	77.0	104.0	216.0	22	26.4		
11	26.0	240.0	110.0	23	29.0		
12	2.0	160.0	46.0	24	19.0		

was totally within the beam at all angles of incidence. The angular correction applicable is, thus, that defined by Brindley and Gillery (1956).

The crystal thickness was measured in all cases, in order to apply the corresponding absorption corrections.

Integrated diffraction intensities are given in Table 1.

Structural Analysis

Integrated intensities were converted into observed structure factors, F_{obs}, by applying the appropriate L-P, angular, and absorption corrections. A first set of signs for the F_{obs} was obtained by calculating the contribution of the atoms of the silicate layer alone, using the atomic coordinates and temperature factors of Shirozu and Bailey (1966) for Mg-vermiculite. With those signs, electron density functions $\rho(z)$ for the three phases were calculated to see if they were correct in their general features; that is, to see if the maxima corresponding to the silicate layer were in appropriate positions and that the areas under $\rho(z)$ in the z intervals of 0–2.05 Å (octahedral layer) and of 2.05–4.82 Å (tetrahedral layer) were proportional to 93.8 and to 102.6 electrons respectively. Then, the rest of the area under $\rho(z)$ gives the electron content, in interlayer space, that corresponds to the organic cations and adsorbed water molecules. This permits calculating by difference the approximate content of interlayer water in each phase.

Atomic scattering factors were taken from the *International Tables of Crystallography* (1962). The atoms of the silicate layer were assumed to be totally ionized (Radoslovich, 1960), but the atoms of the organic cation and water molecules were assumed to be in a neutral state.

The 14.63 Å Phase

The profile of the electron density function $\rho(z)$ shows (1) an electron content in interlayer space of 80 e^-, corresponding to $0.6(N_4C_{10}O_2H_{22})$ molecules per unit cell; (2) a one layer disposition of the organic matter; and (3) an accumulation of electron density near $z = 0.5$ and $z = 0.425$.

A disposition for the organic cations, compatible with the basal spacing of the complex and with the electron density profile, has been deduced with the aid of molecular models, using the values of bond distances and bond angles of Degeilh and Marsh (1959) for the diketopiperazine structure. Such disposition (Fig. 1) consists of (1) the cyclic peptide symmetrically arranged with respect to the plane $z = 0.5$; (2) the electronegative groups $>C = O$ in $z = 0.5$; (3) the unit $-HN-\overset{|}{C}H-CH_2-$ in a plane parallel to the silicate layer, in $z = 0.43$; and (4) the rest of the molecule, that is, the unit $-CH_2-CH_2-NH^+_3$ with the zig-zag chain on a plane normal to the silicate layer.
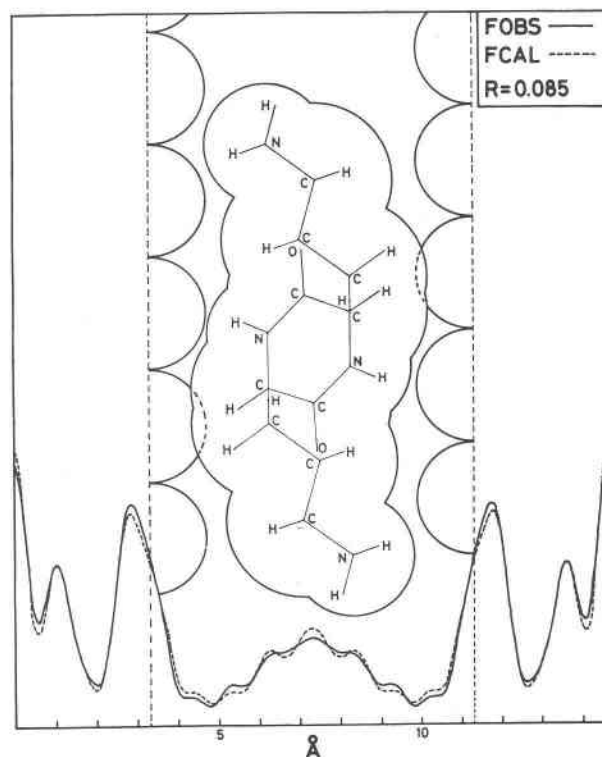
The plane of the peptide ring is inclined 60° to

FIG. 1. 14.63 Å phase
$(Si_{2.87}Al_{1.03}Fe^{3+}_{0.10})(Fe^{3+}_{0.37}Fe^{2+}_{0.04}Ti_{0.06}Mg_{2.53})$
$O_{10}(OH)_2(N_4C_{10}O_2H_{22})^{2+}_{0.3}$

Electron density function (ρ) and structural model.

the silicate plane, resulting from the double tendency of the >NH groups to approach the silicate surfaces while the >C=O groups remain equidistant between the layers. A 60° rotation around the >CH–CH₂– bond places each lateral chain on a plane normal to the layers. Coordinates z_i for the atoms of the organic molecule were obtained and the corresponding structure factors were calculated using the above disposition. A temperature coefficient of $B = 2.85$ was obtained by the method of Wilson (1942).

Table 2 gives the final values of F_{obs} and F_{calc}. The R factor equals 0.085 for the 17 observed 00l reflections and 0.06 for the first nine orders. Figure 1 (lower part) shows the electron density profiles $\rho(z)$ obtained with F_{obs} (continuous line) and with F_{calc} (broken line).

The 16.3 Å Phase

The profile of the electron density function shows (1) an electron content in interlayer space of 156 e-

TABLE 2. Structure Factors

L	14.63Å phase		16.3Å phase		20.3Å phase	
	F_{obs}	F_{calc}	F_{obs}	F_{calc}	F_{obs}	F_{calc}
1	152.0	150.7	122.8	128.1	197.0	194.2
2	24.7	24.6	29.2	46.2	87.6	81.2
3	66.0	−61.8	32.9	−29.4	5.5	5.5
4	119.2	125.7	9.3	9.3	41.4	−47.8
5	130.9	120.9	179.9	176.7	5.5	25.4
6	2.5	2.5	89.2	89.3	181.3	159.4
7	77.4	−65.9	51.3	−44.7	153.3	136.5
8	35.9	−31.7	74.2	−59.3	38.9	25.5
9	35.2	34.6	45.4	−29.5	59.4	−43.3
10	55.8	63.6	44.5	22.3	88.5	−78.1
11	42.3	47.7	73.6	89.3	52.4	−23.4
12	29.9	47.6	64.6	65.7	14.8	−9.8
13	19.6	19.9	59.7	64.1	57.6	71.7
14	25.2	27.0	31.8	51.1	72.5	75.8
15	18.8	17.9	35.2	21.5	77.0	75.2
16	31.7	34.8	36.6	39.1	58.9	61.5
17	21.6	22.2	44.6	45.7	38.4	57.8
18			58.5	57.3	24.7	35.6
19			34.8	44.5	34.9	23.4
20					32.0	39.4
21					40.5	44.1
22					41.8	54.3
23					40.3	56.1
24					29.0	34.4

F_{obs} corrected for absorption

F_{calc} corrected for temperature, $B = 2.85$Å² for 14.63Å phase; B(silicate) from Shirozu and Bailey (1966), B(organic) of 4Å², and B(water) of 6Å² for the 20.3Å and 16.3Å phases.

FIG. 2. 16.3 Å phase
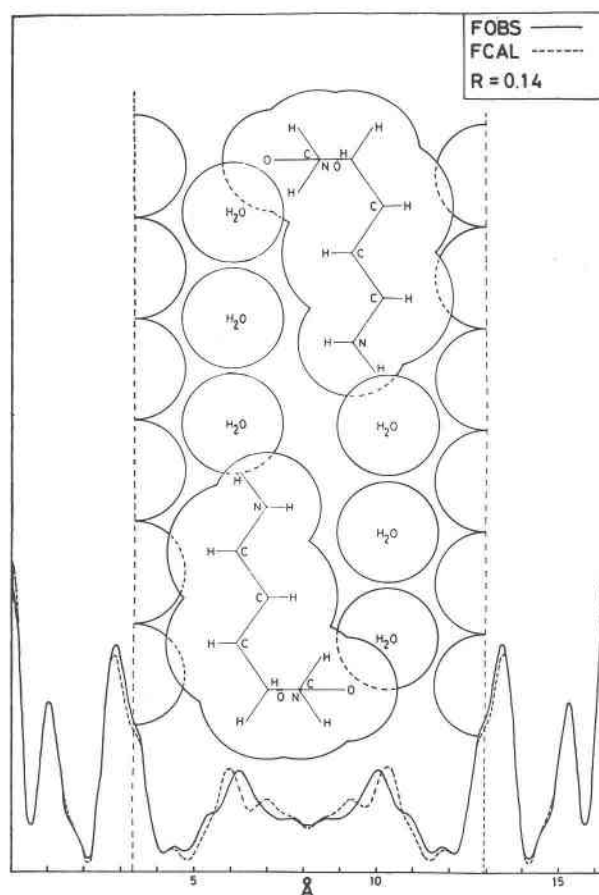
$(Si_{2.87}Al_{1.03}Fe^{3+}_{0.10})(Fe^{3+}_{0.37}Fe^{2+}_{0.04}Ti_{0.06}Mg_{2.53})$

$O_{10}(OH)_2(N_2C_5O_2H_{13})^+_{0.6} \cdot 3.4H_2O$-

Electron density function (ρ) and structural model.

corresponding to $1.2(N_2C_5O_2H_{13}) + 6.8\ H_2O$ molecules per unit cell; (2) a disposition of the interlayer material in two layers; and (3) an accumulation of electron density in $z = 0.5$. An appropriate disposition for the organic cation and water molecules in interlayer space was deduced as before, using the values of bond distances and bond angles of Marsh and Donohue (1967) for the amino acid structure. Such disposition (Fig. 2) has the following characteristics: (1) The amino acid cation, in all TRANS conformation is parallel to the oxygen surfaces of the silicate, with the zig-zag chain in a plane normal to the layer. Two C atoms occur at $z = 0.37$ and two C atoms and the terminal N atom at $z = 0.43$. (2) The α-NH⁺₃, the CH, and the COO⁻ groups are in a plane perpendicular to the chain plane. The C atom of the carboxyl group and the N atom in $z =$

0.48. (3) A total of 3.4 water molecules is next to each silicate surface, in $z = 0.37$; and (4) layers of water molecules alternate with layers of organic cations.

With the above disposition, coordinates z_i for the atoms of the amino acid cation and water molecules were obtained, and the corresponding structure factors were calculated. The temperature coefficients used were $B = 6$ for the interlayer water, $B = 4$ for the atoms of the organic cations, and the B values of Shirozu and Bailey (1966) for the atoms in the silicate layer. Table 2 gives the final values of F_{obs} and F_{calc}. The agreement factor is $R = 0.14$ for the 19 reflections observed, and $R = 0.10$ for the first nine orders. Figure 2 shows the electron density profiles obtained with F_{obs} (continuous line) and with F_{calc} (broken line).

The 20.3 Å Phase

The profile of the electron density function shows (1) an electron content in interlayer space of 208 e^- corresponding to $1.2(N_2C_5O_2H_{13}) + 12\ H_2O$ molecules per unit cell; (2) a disposition of interlayer material in three layers; and (3) an accumulation of electron density in $z = 0.32$ and in $z = 0.5$. An appropriate disposition of the organic cation and water molecules in interlayer space (Fig. 3) is: (1) the organic cation with the same disposition as in the 16.3 Å phase; (2) three water molecules next to each silicate surface, in $z = 0.295$; (3) six water molecules symmetrically arranged with respect to the plane $z = 0.5$, in coordinates $z = 0.46$ and $z = 0.54$, occupying the remaining interlayer space.

Coordinates z_i for all the atoms were obtained and structure factors were calculated. Values for the temperature coefficients were taken as before (16.3 Å phase). Table 2 gives the final values of F_{obs} and F_{calc}. The agreement factor was $R = 0.175$ for the 24 orders observed, and 0.16 for the first 12 orders. Figure 3 shows the electron density profiles obtained with F_{obs} (continuous line) and with F_{calc} (broken line).

Discussion

In discussing the structural models for the vermiculite complexes, it should be verified that the amino acid cations are disposed so that positively charged groups approach negative charge sites as closely as other factors will permit, while negatively charged groups are located apart from negative sites. The organic cations adopt identical dispositions

in both the 20.3 Å and the 16.3 Å crystalline phases. The aliphatic chain lies parallel to the layer and the COO^- group is directed towards the center of the structure, away from the silicate surface. The two $-NH^+_3$ groups, however, are at 6.95 Å and at 7.85 Å from the octahedral Mg plane, apparently in contradiction with the general trend of minimizing charge separations. By analogy with vermiculite-alkylammonium complexes, one would have expected to find $-NH^+_3$ groups "keyed" into the ditrigonal cavities formed by the surface oxygens of the silicate. In such complexes the position of the N atom has been determined to be at 4.65 Å from the central Mg plane (Johns and Sengupta, 1967), and there is evidence, from IR spectroscopy data, of strong H-bonding of the $-NH^+_3$ to the surface oxygens and of a disposition of the N-C bond normal to the layer (Serratosa, Johns, and Shimoyama, 1970; Martin-Rubi, Rausell-Colom, and Serratosa, 1974).

In the case of the present complexes, IR spectra have been obtained by Fornés *et al* (1974), and none of the above features is evident from the data. Here, the $-NH^+_3$ symmetric deformation band appears at 1505 cm^{-1} and is not dichroic (C_3 axis not directed normal to the layer). This result agrees well with the coordinates found for the $-NH^+_3$ groups, and excludes the possibility of association of these groups with the surface oxygens of the silicate. Moreover, displacements of $+18$ cm^{-1} and of -14 cm^{-1} were observed by Fornés *et al* (1974) for the positions of the $-NH^+_3$ symmetric deformation band and of the COO^- symmetric stretching band, relative to the positions of the corresponding absorptions in ornithine Cl$^-$. This result, coupled with the coordinates found for the O atoms of the carboxyl groups (at 7.37 Å and 9.12 Å from the octahedral Mg plane), suggests the possibility of intermolecular association through carboxyl and amino groups, either by coulombic interaction or by H-bonding.

It seems, then, that intermolecular interaction is energetically more favorable than the tendency of the $-NH^+_3$ groups to enter into association with the surface oxygens of the silicate, thus determining the configuration adopted by the organic cations in interlayer space.

The manner in which organic cations and water molecules are packed together in the complex should be directly related to the available surface area in the vermiculite. The *ab* projection of the adsorbed ornithine molecule is shown in Figure 4A, enclosed for convenience into a T-shaped surface
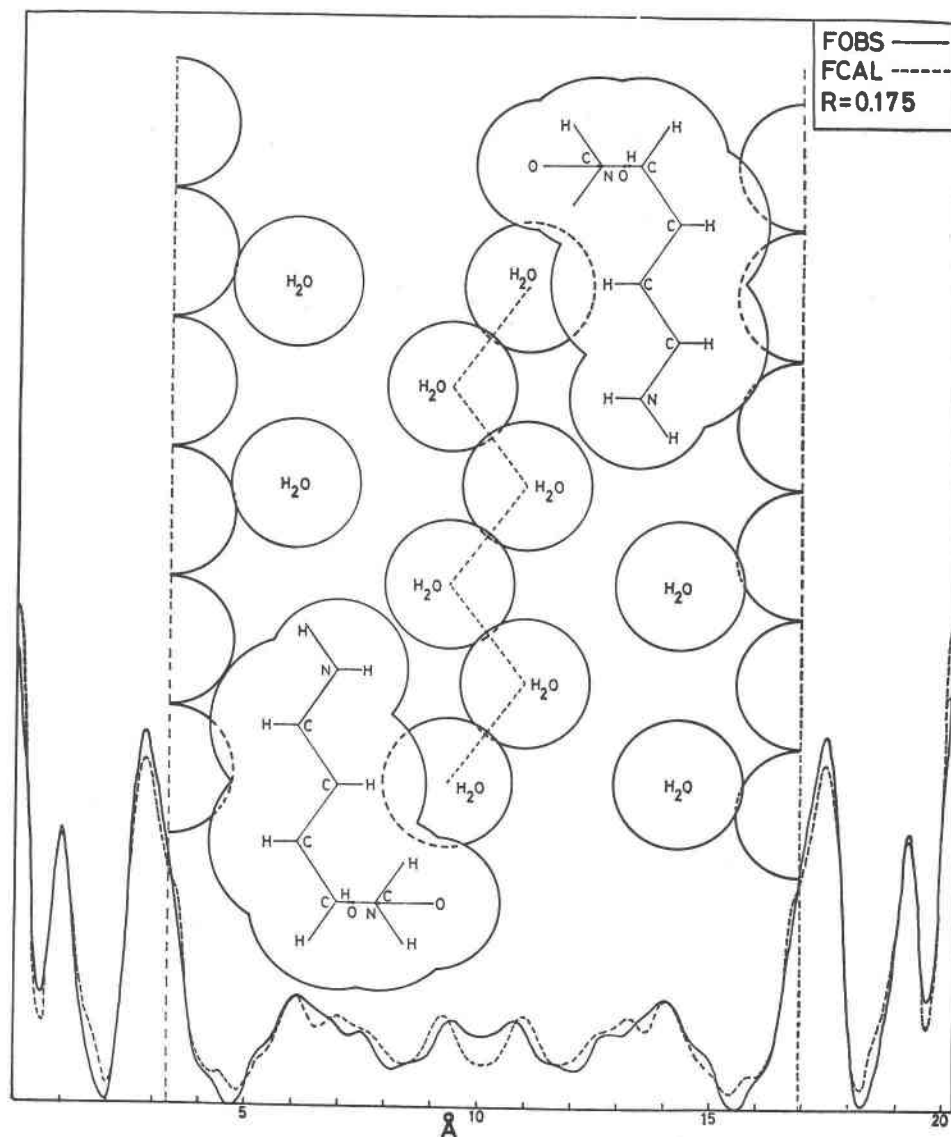
FIG. 3. 20.3 Å phase

$(Si_{2.87}Al_{1.03}Fe^{3+}_{0.10})(Fe^{3+}_{0.37}Fe^{2+}_{0.04}Ti_{0.06}Mg_{2.53})O_{10}(OH)_2(N_2C_5O_2H_{13})^+_{0.6} \cdot 6H_2O$

Electron density function (ρ) and structural model.

of 44 Å². The area available per monovalent ex-change cation in the vermiculite can be computed from the structural formula as 82 Å². A scheme for the disposition of the organic cations relative to the exchange sites[1] is illustrated in Figure 5A, and it

[1] An idealized distribution of negative charge sites is represented in Figure 5 (black dots) corresponding to a surface charge density of 6.5×10^4 esu/cm². Since the actual charge density in the vermiculite used is 10 percent lower, the areas covered in the diagram by the organic cations are reduced in the same proportion.

may be appreciated that each occupied position alternates with a site of identical shape and area in which five water molecules can be accommodated to complete surface coverage (assuming water mole-cules as spheres of $r = 1.34$ Å, Evans, 1964).

The 20.3 Å phase of the complex consists of a stacking of vermiculite layers having their surfaces covered in the above manner and separated by two monolayers of water molecules (six molecules per structural unit, symmetrically distributed with respect to $z = 0.5$, at $z = 0.46$ and $z = 0.54$) which are
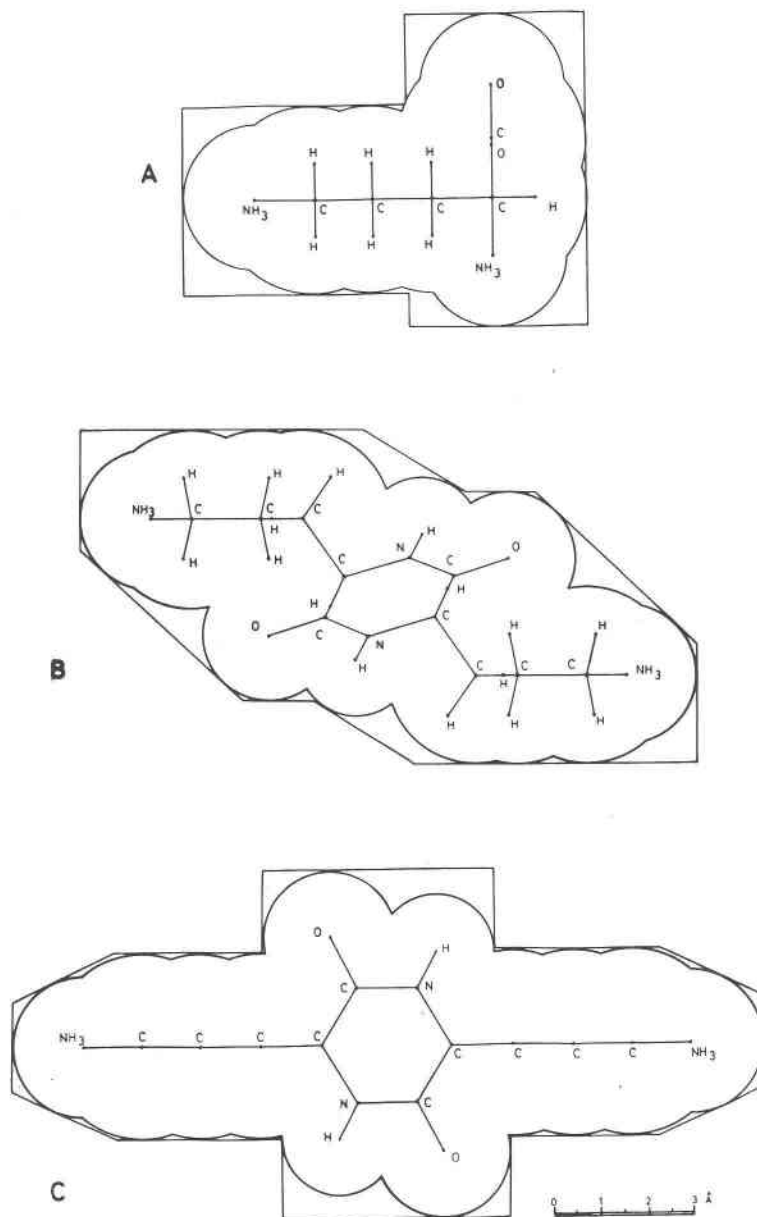
FIG. 4. Projection on the *ab* plane of vermiculite, of adsorbed species
A. L-ornithine cation (20.3 Å and 16.3 Å phases); B. Peptide cation
(14.63 Å phase); C. Peptide cation in all TRANS configuration.

probably bonded to the amino groups and to the carboxyl groups of the ornithine cations (Fig. 3). The 16.3 Å phase results from the former by removal of the intermediate water layer at a temperature of 60°C, and with the stacking of the vermiculite layers such that the ornithine cations of one surface are positioned against the water molecules of the adjacent surface (Fig. 2). Furthermore, both the COO⁻ and the α-NH$^+_3$ groups from each ornithine

cation on one layer are mutually faced against the α-NH$^+_3$ and COO⁻ groups of each ornithine cation on the adjacent layer and, with such disposition, condensation of the amino acid into a cyclic peptide of the diketopiperazine type is favored upon dehydration at 180°C.

The configuration of the peptide cations in the 14.63 Å phase offers characteristics which are worth discussing. Relative to the cyclic ring, the two lateral

chains are in the TRANS configuration, but modified by a 60° rotation around each of the two >CH–CH2– bonds. A CIS peptide ought to be obtained, instead, from the l-isomer of ornithine; therefore, it must be concluded that at the temperature of the reaction the amino acid is racemiced prior to condensation, or else that the CIS peptide is converted to the more stable TRANS peptide after condensation. Which of the two mechanisms is operative cannot be inferred from the present data, but it is known that amino acids are racemiced in clay-water suspensions (Kraepeling and Koust, 1968), so it seems quite probable that, in an electronegative environment and at elevated temperature, l-ornithine will be racemiced readily.

If the peptide cations had adopted the more stable all-TRANS configuration, then a crystalline phase of 13.2 Å basal spacing would be formed which would be energetically more favorable than the observed 14.63 Å phase. With such configuration, however, the surface area covered per cation amounts to 85 Å (Fig. 4C), which is just greater than the surface available in the vermiculite, *i.e.*, 82 Å² per divalent cation, for a monolayer complex. Space will not accommodate the dimers if exchange capacity is to be balanced unless exclusion from the crystal as neutral molecules of some ornithine cations from the preceding phase could provide protons to the >C = O or even to the amide N during the heat treatment to increase the charge per pair. The need for exclusion is avoided with the disposition adopted in the 14.63 Å phase, where rotation of the –(CH2)n– reduces surface requirements to 71 Å² per dimer (Fig. 4B). Molecular packing in the *ab* plane is accomplished as illustrated in the scheme of Figure 5B, showing almost complete surface coverage.

Conformational changes of the type described have been proposed by Lagaly and Weiss (1973) to explain shorter than expected d_{001} spacings in vermiculite complexes with long chain alkylammonium ions. The activation energy required is small, of the order of 3 – 4 kcal/mole (Hägele and Pechhold, 1970). Confirmation of their existence has been obtained by Martin-Rubi *et al* (1974) in butylammonium complexes of low charge vermiculites, where surface requirements were appropriate.

For both the 16.3 Å phase and the 20.3 Å phase, attempts to obtain an isotropic temperature coefficient by the method of Wilson (1942) were unsuccessful. Plots of ln (F_{calc}/F_{obs}) *vs* sin²θ failed to give a linear correlation. The *B* values chosen for the
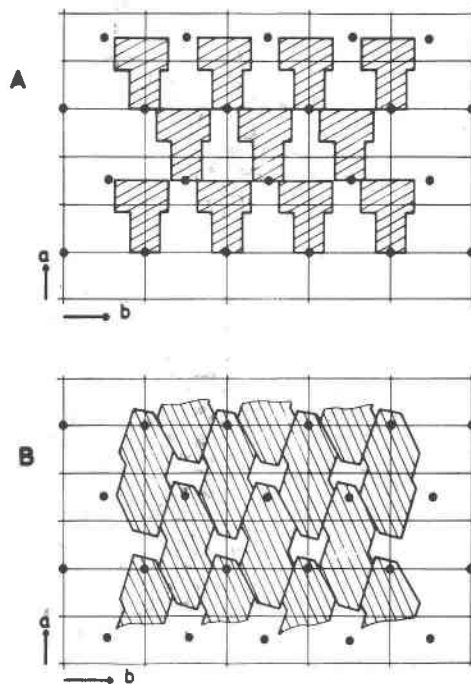

FIG. 5. Surface coverage and interlayer packing of adsorbed species A. Vermiculite — 1-ornithine complexes; B. Vermiculite — peptide complex.

different atoms were considered to be the most appropriate but, with these, the final agreement factors could not be dropped below 0.15 and 0.17 respectively. This, in turn, may reflect uncertainties in the structure determination, mainly in the location and number of H_2O molecules present. In the case of the 14.63 Å phase, however, the Wilson plot yielded a straight line from which an isotropic temperature coefficient, *B*, of 2.85 *A*² was obtained. It represents an average root mean square vibrational amplitude parallel to (001) of 0.19 Å, which is high for a layer silicate. Comparable values are *B* = 3.75 Å² for complexes of vermiculite with cyclic amine cations (Moll, 1963) and *B* = 3.75 – 5 Å² for complexes with aliphatic amine cations (Johns and Sengupta, 1967). They are all higher than the isotropic temperature coefficient for Mg-vermiculite (Mathieson and Walker, 1954), indicating that, in organic complexes, layers are more poorly held together than in the mineral itself.

References

BRADLEY, W. F. (1945) Molecular associations between montmorillonite and some polyfunctional organic liquids. *J. Am. Chem. Soc.* 67, 975.

———, E. J. WEISS, AND R. A. ROWLAND (1963) A

glycol-sodium vermiculite complex. *Clays Clay Minerals,* **10,** 117.

BRINDLEY, G. W. (1966). Ethylene glycol and glycerol complexes of smectites and vermiculites. *Clay Mineral.* **6,** 237.

———— (1970) Organic complexes of silicates, mechanisms of formation. *Proc. Reunion Hispano-Belga de Minerales de la Arcilla,* J. M. Serratosa, Ed., Madrid, p. 55–67.

————, AND F. H. GILLERY (1956) X-ray identification of chlorite species. *Am. Mineral.* **41,** 169.

————, AND R. W. HOFFMAN (1962) Orientation and packing of aliphatic chain molecules on montmorillonite. *Clays Clay Minerals,* **9,** 546.

DEGEILH, R., AND R. E. MARSH (1959) Structure of diketopiperazine (2, 5-piperazinedione). *Acta Crystallogr.* **12,** 1007.

EVANS, R. C. (1964) *An Introduction to Crystal Chemistry.* Cambridge University Press, Cambridge.

FORNÉS, V., J. A. RAUSELL-COLOM, J. M. SERRATOSA, A. HIDALGO (1974) Estudio por espectroscopia infrarroja de los complejos vermiculita-ornitina. *Opt. Pur. y Apl.* **7** (in press).

HÄGELE, P. C., AND W. PECHHOLD (1970) Struktur-und konformations-berechnungen in Polymeren. *Kolloid Z. Z. Polymere,* **241,** 477.

JOHNS, W. D., AND P. K. SENGUPTA (1967) Vermiculite-alkyl ammonium complexes. *Am. Mineral.* **52,** 1706.

KANAMARU, F., A. TSUNASHIMA, AND M. KOIZUMI (1969) Preparation and structure of clay-organic complexes of aminoacid and vermiculite. *Mem. Inst. Sci. Ind. Res. Osaka Univ.* **26,** 165.

KRAEPELING, H., AND T. KOUST (1968) Racemisierung von Aminosauren am Silikaten. *Z. Naturforschung,* **23b,** 1266.

LAGALY, G., AND A. WEISS (1973) Conformational changes of chain molecules in the interlayer space of swelling mica-type layer silicates. *Proc. Int. Clay Conf. Madrid,* **3,** 637–649.

MACEWAN, D. M. C. (1948) Complexes of clay with organic compounds. I) Complexes formation between montmorillonite and halloysite and certain organic liquids. *Trans. Faraday Soc.* **44,** 349.

MARSH, R. E., AND J. DONOHUE (1967) Crystal structure studies of aminoacids and peptides. *Ad. Protein Chem.* **22,** 235.

MARTIN-RUBI, J. A., J. A. RAUSELL-COLOM, AND J. M. SERRATOSA (1974) Infrared absorption and X-ray diffraction study of butylammonium complexes of phyllosilicates. *Clays Clay Minerals,* **22,** (in press).

MATHIESON, A. McL., AND G. F. WALKER (1954) Crystal structure of Mg-vermiculite. *Am. Mineral.* **39,** 231–255.

MIFSUD, A., V. FORNÉS, AND J. A. RAUSELL-COLOM (1970) Cationic complexes of vermiculite with L-ornithine. *Proc. Reunión Hispano-Belga de Minerales de la Arcilla,* J. M. Serratosa, Editor, Madrid, p. 121.

MOLL, W. F. (1963) *The Orientation of Some Cyclic Amine Cations on Vermiculite.* Ph.D. Thesis, Washington University.

RADOSLOVICH, E. W. (1960) The structure of muscovite. *Acta Crystallogr.* **13,** 919.

REYNOLDS, R .C. (1965) X-Ray study of an ethylene glycol-montmorillonite complex. *Am. Mineral.* **50,** 990.

SERRATOSA, J. M., W. D. JOHNS, AND A. SHIMOYAMA (1970) Infrared study of alkyl-ammonium vermiculite complexes. *Clays Clay Minerals,* **18,** 107.

SHIROZU, H., AND S. W. BAILEY (1966) Crystal structure of two-layer Mg-vermiculite. *Am. Mineral.* **51,** 1124.

WEISS, A., W. THIELEPAPE AND H. ORTH (1966) Neue Kaoliniteinlagerungsverbindungen. *Proc. Int. Clay Conf. Jerusalem,* **1,** 277.

WILSON A. J. C. (1942) Determination of absolute from relative X-ray intensity data. *Nature,* **150,** 152.