ORDER OF MIXED-LAYERING IN ILLITE/MONTMORILLONITES

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ABSTRACT

A NUMBER of otherwise poorly understood compositional-structural relationships in mixed-layer illite/montmorillonites appear to be explained by ordered interlayering of 2:1 units. The ordering appears to be between high and low charge 2:1 units. The relationship between per cent expandable layers and mean lattice charge in natural materials shows a scatter that is nicely bracketed by hypothetical curves constructed assuming random or completely ordered interlayering for several types of 2:1 charge distribution. Natural samples with 30–50% expandable layers plotting near the "ordered" curves have diffraction peaks at 25 Å for two water layers in the expandable layers and 27 Å with two glycol layers; samples plotting near the "random" curves do not have these peaks and have poorly developed 001/001 reflections.

Some tentative conclusions are: (1) illites are virtually non-expandable at lattice charges significantly less than that of ideal mica because of ordering of high–low charge 2:1 units, (2) illites and mixed-layer illite/montmorillonites with the same mean lattice charge show a range of expandability because of varying degrees of ordering, (3) the highly variable CEC of samples with the same expandability also results from a varying degree of ordering.

An interesting petrological implication results when it is realized that a sample with a given bulk composition can have a wide range of expandability, depending on ordering. Low expandability, achieved by ordering, should be promoted by formation at high pressures. Glauconites, known to form largely at the time of sedimentation, appear to be dominantly randomly interstratified; illites and illite/montmorillonites, which may form on deep burial of argillaceous sediments, are dominantly ordered.

INTRODUCTION

AN UNDERSTANDING of the nature of mixed-layering in layer silicates—especially in the ubiquitously mixed-layered clay minerals—is important both in crystal chemical considerations of these structures and in their petrological significance. Some types of mixed-layering appear to be trivial and easily understood, namely those which involve no compositional changes in the basic lattice from layer to layer, but are determined by the interlayer material only. Some examples are: (1) a montmorillonite in which some interlayer spaces contain one and others two water layers, (2) a mixed-layer biotite/vermiculite prepared by partial exchange of interlayer K^+ with Mg^{2+}

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in an initially homogeneous biotite. A feature of "trivial" examples of mixed-layering is that they can be converted to either component simply by control of the interlayer material. The 1–2 H_2O layer montmorillonite can be made a homogeneous one—or two—water layer structure by controlling the relative humidity; the biotite/vermiculite can be converted into biotite or vermiculite by control of the interlayer Mg^{2+}/K^+ ratio. In contrast, non-trivial mixed-layer structures involve compositional changes in the 2:1 unit from layer to layer and the structure cannot be converted to either end member by control of the interlayer cation. For example, a mixed-layer illite/montmorillonite cannot be converted wholly to illite or to montmorillonite. Addition of potassium will not collapse the montmorillonite layers (as it did the vermiculite in the biotite/vermiculite); leaching of potassium results in a mixed-layer vermiculite/montmorillonite. Other non-trivial examples are some naturally occurring biotite/vermiculites and chlorite/montmorillonites.

The basic problem in the consideration of non-trivial mixed-layer structures and the alternative models possible to explain them will be outlined in this paper. These models will then be applied to the montmorillonite–mixed-layer illite/montmorillonite–illite series, the only group for which sufficient data are available to test the models.

It should be pointed out that the very real possibility of lateral changes in composition (and structure) (cf. Jackson, 1963) within layers will not be considered in this paper.

MODELS FOR NON-TRIVIAL MIXED-LAYER STRUCTURES

A mixed-layer structure such as illite/montmorillonite can be considered, from the point of view of first order X-ray diffraction results, as simply a mixture of a unit which remains at 10 Å independently of treatment and another unit of variable spacing which depends on treatment. Possible basal reflections can be calculated from the repeat distances of units which can be called *A* and *B* and from the manner in which these are interspersed (MacEwan *et al.*, 1961) i.e. randomly (*ABBAABAABBB* . . .), ordered (e.g. *ABABAB* . . .), or segregated (*AAAA* . . . , *BBBB* . . . , as in homogeneous crystals).

From a crystal chemical point of view the situation is less simple, for now the units must be defined compositionally in such a manner that the composition of each unit determines whether it is a 10 Å (illite) or expandable (montmorillonite) layer. The behavior of a given layer depends on the negative charge (and thus composition) of adjacent 2:1 units. Layers can be considered as compositionally centered on the octahedral layer or on the interlayer position. Centering the structure on the octahedral layer (as is usually done) implies that the two tetrahedral layers within that 2:1 unit are compositionally identical and that adjacent 2:1 units share the interlayer space. Centering the structure on the interlayer position implies that adjacent

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tetrahedral layers have the same composition and that adjacent compositional units share an octahedral layer. Either assumption leads to problems on further consideration of the structure.

Each interlayer space can have uniquely a mica or a montmorillonite charge only in the interlayer space centered model. It is difficult, however, to see how octahedral compositions can be assigned in this model. If the compositional unit is centered on the octahedral layer, this means that an interlayer space will frequently be bounded by a low charge unit on one side and a high charge unit on the other. How this unit will behave in terms of expandability can only be guessed.

At this time, it seems preferable to the writer to consider the 2:1 unit as being compositionally homogeneous. This means that in any model for mixed-layering in illite/montmorillonite a decision must be made as to the behavior of a unit consisting of differing charges on either side of the interlayer position. The charge difference may be as much as two-thirds of an equivalent per $O_{10}(OH)_2$—the charge difference between "ideal" montmorillonite and mica. Forces tending to expand the structure are: (1) the hydration energy of the cation, (2) the adsorption energy of water, and (3) repulsion by locally uncompensated negative charge on the 2:1 lattice caused by ionization. When the sum of these forces exceeds the strength of the bonds between the interlayer cations and the negatively charged 2:1 units the structure expands. For sheets of a given size (Jonas, 1960), potassium as the exclusive interlayer cation, and equal charges on adjacent 2:1 units, expansion should take place at a specific value of layer charge. Although it may not be possible to calculate this charge, it may be approximated empirically by testing the fit of various models for mixed-layering to the data from natural samples. The section which follows shows the fit of several simple models to available data from natural samples.

MIXED-LAYERING MODELS FOR ILLITE/MONTMORILLONITES

Introduction

A number of variables must be defined in constructing a mixed-layering model. They are: (1) the charge distribution of the 2:1 units, (2) the manner of interlayering of the 2:1 units (random, ordered, etc.), (3) the layer charge necessary for non-expansion in water (which may depend on particle size). It is assumed that potassium is the interlayer cation.

The "models" outlined below are used to predict the relative amounts of expandable and non-expandable layers in mixed-layered illite/montmorillonites as a function of gross lattice charge, i.e. the charge obtained by calculating a homogeneous structural formula from the chemical analysis. Relationship between charge on the 2:1 units (in equivalents/$O_{10}(OH)_2$) and per cent expandable layers is shown in Fig. 1. The data come from Hower and Mowatt (1966). The charge is derived from structural formula calculations

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and the per cent expandable layers from X-ray diffraction data. The diffraction data were interpreted assuming random interstratification and are therefore subject to some error, for as will be shown below, most illites and illite/montmorillonites are almost surely ordered. Table 1 is a list of sample names for identification. As can be seen, there is considerable scatter and a

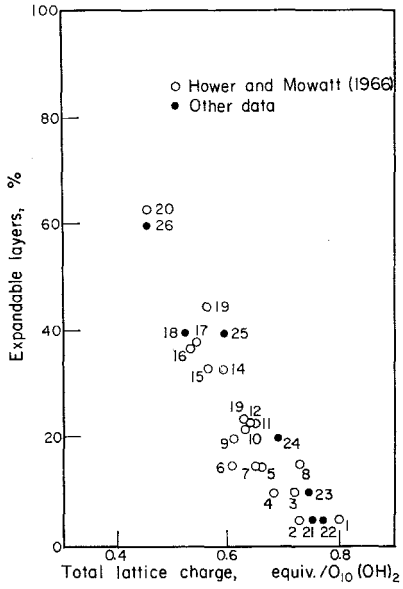


FIG. 1. The relationship between total lattice charge and per cent expandable layers in illites and illite/montmorillonites.

TABLE 1.—IDENTIFICATION OF SAMPLES USED
(Basic data in Hower and Mowatt [1966])

Sample no.	Name	Sample no.	Name
1	Interlake	14	High Bridge
2	Silver Hill	15	Two Medicine
3	Clinton	16	Kinnekulle A–1
4	Eau Claire	17	Kinnekulle A–2
5	New Albany	18	Wilcox No. 1
6	Sylvan (coarse)	19	Colorado
7	Lowville	20	Kinnekulle B
8	Gros Ventre	21	Morrison
9	Sylvan (fine)	22	Burnt Bluff
10	Salona KB	23	Steamboat Springs
11	Martinsburg KB	24	Nealmont
12	Onondage KB	25	Kinnekulle No. 8
13	Kg KalkberB	26	Kinnekulle No. 15

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best fit curve extrapolates to about 0.8 equivalents/$O_{10}(OH)_2$ at zero per cent expandable layers. Another way of looking at it is that the ratio of fixed charge to total charge is not simply related to increasing total charge. A related phenomenon is the relatively poor relationship between CEC and per cent expandable layers in illite/montmorillonites (Hower and Mowatt, 1966). Both phenomena appear to be explainable by the models described below.

Some Preliminary Models

Although the charge distribution in real structures is undoubtedly more complicated (Roberson and Jonas, 1965), it is assumed in the first, and simplest, models that the 2:1 units have charges only of -1 (mica) or $-1/3$ equivalent (montmorillonite) per $O_{10}(OH)_2$. In this model the charges of the pair of 2:1 units on either side of an interlayer space will be $(-1/3, -1/3)$, $(-1, -1)$, or $(-1, -1/3)$. The behavior of the first two pairs is clear: the $(-1/3, -1/3)$ pair will expand with water, the $(-1, -1)$ pair will not. The behavior of the $(-1/3, -1)$ pair is questionable, but because of the simplicity of the model either situation (expansion or none) can be tested. Note that for this model we do not have to choose a specific value for non-expansion.

The remaining variable to be chosen is the manner of interlayering. Several types are applied to this model. They are:

1. Random.
2. Complete order, the ordering requirement being that each mica charge 2:1 unit is faced on either side by a montmorillonite charge 2:1 unit.
3. Partial order of the type described in 2 $(-1/3, -1, -1/3)$.

The equations to describe the probability of the three possible combinations of layers are as follows. Let P_A=probability of occurrence of a 2:1 unit of charge -1 equiv/$O_{10}(OH)_2$. P_B=probability of occurrence of a 2:1 unit of charge $-1/3$ equiv/$O_{10}(OH)_2$. Then for the random case:

$$P_{AA} = \text{probability of a } (-1, -1) \text{ pair} = P_A \times P_A.$$
$$P_{AB} = \text{probability of a } (-1, -1/3) \text{ pair} = P_A \times P_B.$$
$$P_{BA} = \text{probability of a } (-1/3, -1) \text{ pair} = P_B \times P_A = P_{AB}.$$
$$P_{BB} = \text{probability of a } (-1/3, -1/3) \text{ pair} = P_B \times P_B.$$

The $(-1, -1/3)$ and $(-1/3, -1)$ pairs are structurally equivalent. Note that for equal numbers of mica and montmorillonite charge 2:1 units the probability of a mica–montmorillonite contact is twice that of a mica–mica or a montmorillonite–montmorillonite contact. For this case $P_A=0.5$, $P_B=0.5$, $P_{AA}=0.25$, $P_{BB}=0.25$, $P_{AB,BA}=0.5$. The mean structural charge is $-2/3$ equivalent. In this structure there will be 25% non-expandable layers (P_{AA}), 25% expandable layers (P_{BB}), and 50% indeterminate layers ($P_{AB}+P_{BA}$). If a mica–montmorillonite contact expands with water, this structure will contain 75% expandable layers; if this contact does not expand, it will contain 25% expandable layers. The per cent expandable layers for mean lattice charges varying from that of montmorillonite to that of mica are

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listed in Table 2. As can be seen from the calculations, the assumption of expansion of a $(-1/3, -1)$ contact does not come close to the relationship shown by real structures. However, the curve plotted from the per cent expandable layers using the non-expansion of the $(-1, -1/3)$ pair borders closely the actual relationship, on the high charge side as shown in Fig. 2.

TABLE 2.—PER CENT EXPANDABLE LAYERS FOR DIFFERING MEAN 2:1 CHARGES CALCULATED FOR SEVERAL ILLITE/MONTMORILLONITE MODELS

Model			Per cent expandable layers					
			1/3, 1 equiv. 2:1 units				2:1 charge dist. normal; $T=0.15$, collapse chg. $=0.60$ equiv.	
			Random		AB ordered	Partial AB ordering $F=0.5$		
PA	PB	Mean charge (equiv.)	1/3, 1 expands	1/3, 1 collapses			Random	High-low ordered
—	—	0.35	—	—	—	—	92	84
0.1	0.9	0.40	99	81	80	80	—	—
—	—	0.45	—	—	—	—	80	60
0.2	0.8	0.47	96	64	60	61	—	—
—	—	0.50	—	—	—	—	72	44
0.3	0.7	0.53	91	49	40	43	—	—
—	—	0.55	—	—	—	—	61	22
0.4	0.6	0.60	84	36	20	27	50	0
—	—	0.65	—	—	—	—	39	—
0.5	0.5	0.67	75	25	0	13	—	—
0.6	0.4	0.73	64	16	—	3	—	—
—	—	0.75	—	—	—	—	20	—
0.7	0.3	0.80	51	9	—	—	—	—
—	—	0.85	—	—	—	—	8	—
0.8	0.2	0.87	46	4	—	—	—	—
0.9	0.1	0.93	19	1	—	—	—	—
—	—	0.95	—	—	—	—	2	—

A different relationship results if one imposes an ordering condition on the interlayering. For an ordering condition that every -1 unit is faced on either side by a $-1/3$ unit, the equations become:

$$P_{AA}=0 \text{ (from ordering condition)}$$
$$P_{AB}=1_A=P_{BA}$$
$$P_{BB}=1-2P_A$$

For equal amounts of -1 and $-1/3$ 2:1 units $P_{AB}+P_{BA}=1$, and if $(-1, -1/3)$ contacts are non-expandable, the structure contains no expandable layers. Per cent expandable layers calculated from this model appear in Table 2. The relationship is shown in Fig. 2 along with data from real samples and the random interlayering relationship. As can be seen, the "ordered" curve borders the data for real samples on the low charge side. Together

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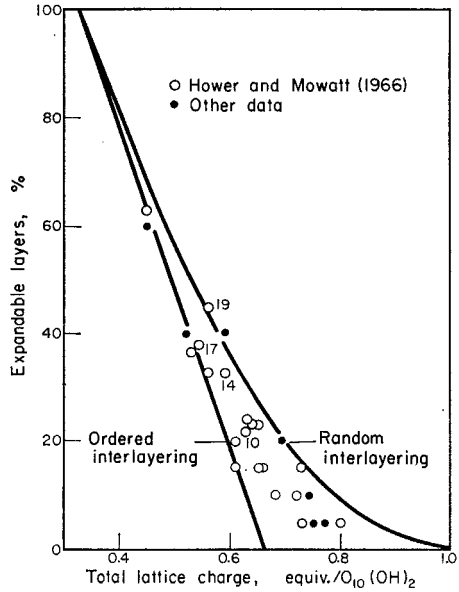


FIG. 2. Fit of calculated curves of per cent expandable layers vs. mean lattice charge in illite/montmorillonites assuming 2:1 units of charges $-1/3$ and -1 equivalents/$O_{10}(OH)_2$ and either random or ordered interlayering.

the per cent expandable layers versus mean charge curves for random and for ordered interlayering neatly bracket the relationship for real samples. The remarkably good fit of this simple model suggests that most natural illites and illite/montmorillonites have at least partially ordered interlayering. Further tentative conclusions are (1) that illites can attain a mica-type structure (no expandable layers) at a mean charge lower than that of a mica because of ordered interlayering, and (2) the spread of points in the per cent expandable layers vs. mean lattice charge relationship shown in Fig. 1 is caused by a varying amount of order in natural materials.

Curves can be calculated for models with partial ordering by the equations shown below. These equations are simple generalizations of the random and completely ordered equations used above. F = fraction of layers involved in ordering; for random interlayering $F=0$, for complete order $F=1$.

$$P_{AA}=\frac{[(1-F)P_A]^2}{(1-2F)P_A+P_B}$$

$$P_{AB}=FP_A \quad \frac{(1-F)+P_A\times(P_B-FP_A)}{(1-2F)P_A+P_B}=P_{BA}$$

$$P_{BB}=\frac{[P_B-FP_A]^2}{(1-2F)P_A+P_B}$$

Data calculated for $F=0.5$ are listed in Table 2.

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As mentioned above, the model assuming that 2:1 units have charges of only $-1/3$ or -1 equivalent per $O_{10}(OH)_2$ is almost certainly too simple. A more complicated—and possibly more realistic model—is one in which it is assumed that the charge obtained from the "homogeneous" structural formula is the mean charge of a normal distribution of charges on the 2:1 units. In such a model it is necessary to specify the charge at which the layers will no longer expand, the standard deviation of the distribution, and, for ordered models, the nature of the order. An example of the results of this model is shown in Fig. 3. It is assumed that the "non-expansion" charge

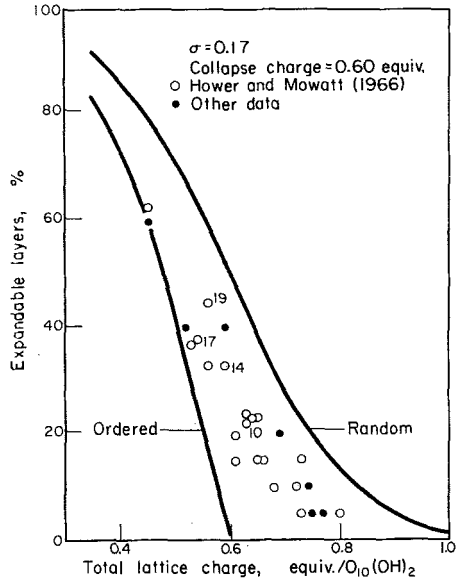


FIG. 3. Fit of calculated curves to illite/montmorillonite data assuming a normal charge distribution of the 2:1 units.

is 0.60 equivalents per $O_{10}(OH)_2$, that the standard deviation of the charge distribution is 0.17, and that the ordering is high–low charge (much the same as in the previous model), which results in twice the number of non-expandable layers as random interlayering. Again the random and ordered models bracket the data for natural samples. More complicated models could be devised by assuming non-normal distributions and other types of order. It is of interest to note that no model assuming random interlayering and a reasonable standard deviation of the charge distribution devised by the writer did more than approach the real data on the high expandable side. This again indicates strongly that it is necessary to assume a certain amount of order of the mixed-layering to explain the structural–compositional

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relationship in natural samples. Reynolds (in press), has also concluded that it is necessary to assume ordering to fit calculated diffraction patterns to those of real samples in mixed-layer illite/montmorillonites.

Diffraction Patterns

It must be pointed out first, that the ordering discussed in the above section is ordering of 2:1 unit charges (and thus compositions)—not (00*l*) repeat distances. Ordering of 2:1 charges does not necessarily give rise to ordering of mica–montmorillonite repeat distances. For example, in the simplest model described above when $P_{-1}=0.2$ and $P_{-1/3}=0.8$ with the ordering requirement that every (-1) is flanked by a $-1/3[(-1/3, -1, -1/3)]$, then $P_{(-1,-1/3;-1/3,-1)}=-0.4$. There are, therefore, 40% non-expandable layers. To have ordering of 10 Å and expandable layers we can further require that the 2:1 charge sequence is $(-1/3, -1/3, -1, -1/3, -1/3)$. According to the model this results in the repeat distances (for two water layers in the interlayer spaces flanked by $-1/3$ equiv 2:1 units) of 15, 10, 10, 15 Å, and uses up 80% of the 2:1 units. If, however, repeat units such as these are randomly interspersed with the remaining $(-1/3, -1/3)$ or 15 Å contacts, the structure is not ordered with respect to diffraction effects. Following the same reasoning, when $P_{-1/3}=0.25$, then $P_{(-1/3,-1;-1;-1/3)}=0.5$ and, of necessity the (00*l*) repeat distances are 15, 15, 10, 10, 15, 15, 10, 10, 15, 15, . . . and the repeat unit is 50 Å. The mean structural charge is 0.5 equivalents and there are 50 per cent expandable layers. Increasing the structural charge—and thus P_{-1}—more necessarily breaks down the possible ordering or repeat distances until, when $P_{-1}=0.5$, the structure is completely non-expandable.

Following from the above argument, we would expect any ordering reflections to be present in mixed-layer illite/montmorillonites with mean structural charges of about 0.5 equivalents and having about 50% expandable layers. The ordering reflection, detectable using CuKα radiation, would be the 002 and should appear at 25 Å (one-half of 10+15+15+10) for two water layer and 27 Å (one-half of 10+17+17+10) for two glycol layer expandable layers. Of the nineteen samples plotted in Fig. 2 available to the writer, four have detectable low angle peaks—numbers 14, 15, 16, and 17. These range in expandability from 33–38% montmorillonite layers and have structural charges ranging from 0.53 to 0.59 equivalents/$O_{10}(OH)_2$. Figures 4 and 5 show a sequence deduced to be decreasing order from Figs. 2 and 3 from samples 17–14–19. Sample 17 has obvious low angle peaks at 29 Å for two water layers and 31 Å for two glycol layers. These shift to 25 and 27 Å, respectively, when corrected for the Lorentz and polarization factors. Sample 14 shows a shoulder at about the same positions; sample 19, which is closest to the "random" curves in either model, shows no low angle peak. In addition, the 001/001 and 001/002 peaks are poorly defined in the glycoled sample—a feature of random interlayered structures (Reynolds, pers. comm., 1966). Sample 10, with 20+ per cent expandable layers, is typical of the less expandable samples in showing no hint of a low angle reflection.

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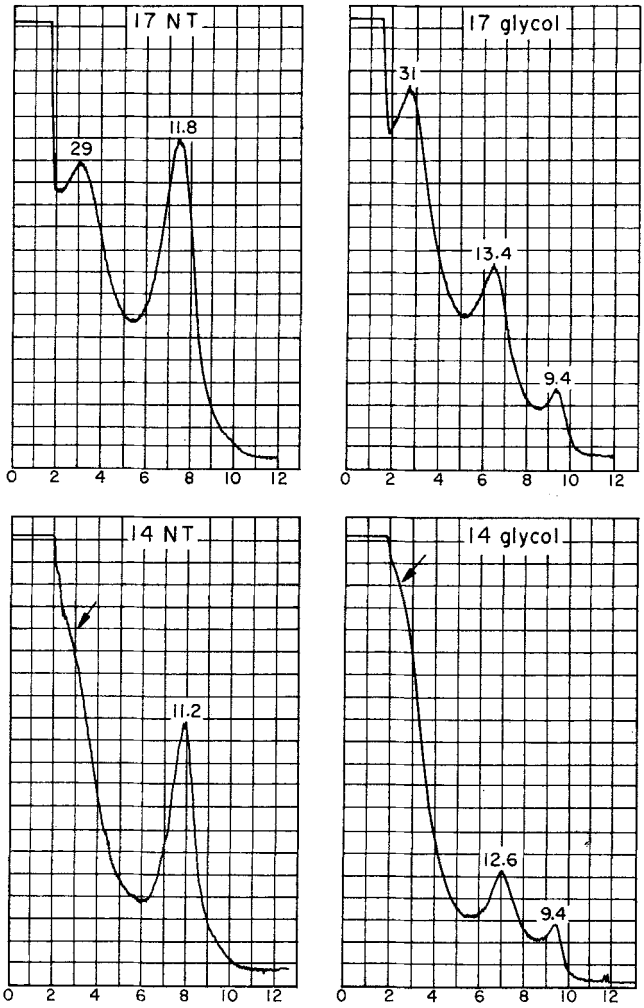


FIG. 4. X-ray diffraction patterns of the Kinnekulle A-2 K-bentonite (17) and the High Bridge K-bentonite (14) with two H_2O layers (NT) and two glycol layers. Low angle peaks in 17 shift to 25 Å for two H_2O layers and 27 Å for two glycol layers on correcting for the Lorentz and polarization factors for single crystals.

Thus the diffraction data also indicate ordering of 2:1 units of the type described above.

Petrological Implications

As can be seen from Figs. 2 and 3, a mixed-layer illite/montmorillonite of given bulk composition can have a wide range of expandability, depending

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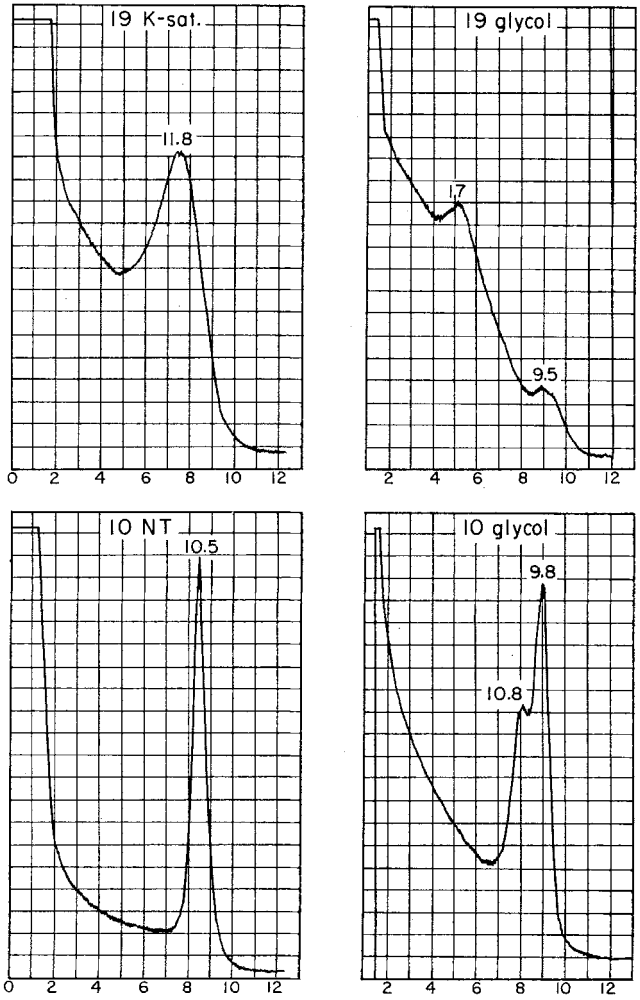


FIG. 5. X-ray diffraction patterns of Colorado I/M and Salona K-bentonite.

on the amount of ordering. Random interstratification of 2:1 units results in significantly greater expandability than an ordered structure of the same composition. One might expect, therefore, that illite/montmorillonite structures forming at high pressures—with H_2O a mobile constituent—should tend to be ordered. It is therefore very interesting that glauconites, which form at the time of sedimentation and therefore low pressures, appear to be dominantly randomly interlayered (cf. diffraction patterns of Burst, 1958, and Hower, 1961). In contrast, illites and illite/montmorillonites, which appear to form by pre-metamorphic reactions on deep burial of argillaceous

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sediments (Burst, 1959; Dunoyer de Segonzac, 1964) are dominantly ordered —a result which should follow from the above argument.

CONCLUSIONS

Their structural–compositional relationships and X-ray diffraction characteristics indicate strongly that there is an ordering of high–low charge 2:1 units in illites and illite/montmorillonites. The amount of ordering is variable, accounting for the variability in expandability and cation exchange capacities of illite/montmorillonites with the same structural formula. Ordering of 2:1 units also explains how illites can achieve a non-expandable structure at lower lattice charges and potassium contents than true dioctahedral micas.

Formation at high pressures should promote ordering in illite/montmorillonites. Glauconites, which form at low pressures, appear to be dominantly randomly interstratified; illites and illite/montmorillonites are predominantly ordered, indicating formation in a high pressure environment, i.e. on deep burial of argillaceous sediments.

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The origin of the writer's consideration of illite and illite/montmorillonites as ordered interlayer structures came from discussions with Robert C. Reynolds.

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