

## ORDER AND DISORDER RELATIONS IN THE DISTRIBUTION OF THE SUBSTITUTIONS IN SMECTITES, ILLITES AND VERMICULITES

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(Received 4 February 1974)

**Abstract**—It is shown that order–disorder relations in the distribution of the isomorphous substitutions are important in the characterization of different 2/1 phyllosilicates and in the determination of their behavior. These order–disorder relations are shown by selected area diffraction patterns obtained from single crystals. The range of layer charges corresponding to smectites (charge per half-cell <0.6) is that for which phyllosilicates are stable with disordered substitutions. Phyllites with charge >0.6 show anomalous diffusions which indicate that the distributions of exchangeable Ba ions are partially ordered; this result is taken as evidence that the isomorphous substitutions also are partially ordered.

### INTRODUCTION

Ten years ago the International Committee of Classification and Nomenclature of Clay Minerals (A.I.P.E.A.) proposed a scheme for the classification of the 2/1 phyllosilicates (Table 1), based mainly on the criterion of the interlayer charge (Mackenzie, 1965; Brindley, 1966; Pedro, 1967). This classification allowed the characterization of different groups of 2/1 phyllosilicate and at the present time it is obvious that the charge constitutes an indispensable criterion in classifying phyllosilicates and in recognizing some of

their physico–chemical characteristics. Nevertheless, a single parameter is insufficient to explain or to foresee all the properties of the 2/1 phyllosilicates. For example, the existing classification does not permit us to distinguish clearly two phyllites with a charge very near 0.6 and with a very similar structural formula when one can be a beidellite or a saponite and can show the properties of a smectite, while the other can have the properties of an illite or of a vermiculite.

This failure in the criteria used for the classification has been observed by several authors, especially Mer-

Table 1. Classification of the phyllosilicates 2:1 based upon the structural formula and the sheet charge

Charge per 1/2 cell	Diocahedral	Triocahedral
0	Pyrophyllite $(Si_8)^{IV}(Al_4)^{VI}O_{20}(OH)_4$	Talc $(Si_8)^{IV}(Mg_6)^{VI}O_{20}(OH)_4$
		Smectites
0.2–0.6	Montmorillonite $(Si_8)^{IV}(Al_{4-y}Mg_y)^{VI}O_{20}(OH)_4.M_y^+$ Beidellite $(Si_{8-x}Al_x)^{IV}(Al_4)^{VI}O_{20}(OH)_4.M_x^+$	Hectorite $(Si_8)^{IV}(Mg_{6-y}Li_y)^{VI}O_{20}(OH)_4.M_y^+$ Saponite $(Si_{8-x}Al_x)^{IV}(Mg_6)^{VI}O_{20}(OH)_4.M_x^+$
0.6–0.9	Illites $(Si_{8-x}Al_x)^{IV}(Al_{4-y}M_y^{2+})^{VI}O_{20}(OH)_4.K_{x+y}^+$	Vermiculites $(Si_{8-x}Al_x)^{IV}(Mg_{6-y}N_y^{3+})^{VI}O_{20}(OH)_4.M_{x-y}^+$
		Micas
1	Muscovite $(Si_6Al_2)^{IV}(Al_4)^{VI}O_{20}(OH)_4.K_2$	Phlogopite $(Si_6Al_2)^{IV}(Mg_6)^{VI}O_{20}(OH)_4.K_2$
		Brittle micas
2	Margarite $(Si_4Al_4)^{IV}(Al_4)^{VI}O_{20}(OH)_4.Ca_2$	Clintonite $(Si_4Al_4)^{IV}(Mg_6)^{VI}O_{20}(OH)_4.Ca_2$

ing and Pedro (1969) who have hypothesized that, over and above the interlayer charge, an important part can be played by the localization and the distribution of the isomorphous substitutions. This hypothesis was based principally upon three considerations:

1. Studies of the synthesis of smectites by Roy (Koi-zumi and Roy, 1959; Iiyama and Roy, 1963) have shown that it is possible to obtain homogenous and stable phases only when the layer charge is less than 0.6. Now, particularly in the case of saponite, whose structural constitution is very similar to that of many vermiculites, it is impossible to explain by a mere difference in the formula this real discontinuity in the stability of these structures.

2. Gataineau and Mering's studies (Gataineau, 1964; Gataineau and Mering, 1966) have shown that in some 2/1 phyllosilicates (micas) an order exists in the distribution of Si-Al tetrahedral substitutions.

3. Mering and Glaser's studies (Glaser and Mering, 1954, 1958) on Na-Ca bi-ionic hectorites and montmorillonites have shown, indirectly, that in those minerals the distribution of octahedral substitutions was perfectly disordered.

The aim of the following studies is to show more precisely the part played by the localization and the distribution of isomorphous substitutions in different 2/1 phyllosilicates.

## 1. EXPERIMENTAL METHOD

In order to recognize order or disorder in the distribution of isomorphous substitutions, it is necessary to analyse the diffraction phenomena produced by a single crystal. For the past years, Alcover and Gataineau (Alcover *et al.*, 1973) have studied the order-disorder in the substitutions in macroscopic single crystals of vermiculites with the help of X-rays. A similar study of microcrystalline minerals, particularly smectites and illites, can be done only with the help of selected area electron diffraction.

An extra difficulty comes from the fact that the diffracting power of the substituant atoms is nearly always next to that of the substituted atoms. Thus one cannot expect to localize by diffraction the substituant atoms themselves. But it is plausible to think that, for a substituted phyllosilicate, the most stable electric balance corresponds to the case when the interlayer cations settle in the immediate neighbourhood of a local charge deficiency in the layer. It is then possible to show by diffraction, the more or less disordered distribution of the balancing cations by using a cation with a high scattering power and, later, to try to relate this distribution to that of the isomorphous substitutions themselves.

Lastly in order to confirm the validity of the use of electron diffraction, we have verified that the diagrams

Table 2. Origin, structural formula and charge of the studied minerals

Minerals	Structural formula	Charge per 1/2 cell
Montmorillonite (Wyoming)	$(\text{Si}_{7.78}\text{Al}_{0.22})(\text{Al}_{2.14}\text{Fe}_{0.34}^{3+}\text{Fe}_{0.04}^{2+}\text{Mg}_{0.54}^{2+})\text{O}_{20}(\text{OH})_4\text{Na}_{0.66}$	0.33
Beidellite (Synthetic)	$(\text{Si}_{7.34}\text{Al}_{0.66})(\text{Al}_4)\text{O}_{20}(\text{OH})_4\text{Na}_{0.66}$	0.33
Illite (Beavers Bend) < 2 $\mu\text{m}$	$(\text{Si}_{7.28}\text{Al}_{0.72})(\text{Al}_{2.74}\text{Ti}_{0.06}\text{Fe}_{0.64}^{3+}\text{Fe}_{0.14}^{2+}\text{Mg}_{0.44})(\text{OH})_4\text{O}_{20}\text{Na}_{0.10}\text{K}_{1.12}$	0.61
Illite (Puy)	$(\text{Si}_{6.96}\text{Al}_{1.04})(\text{Al}_{2.46}\text{Ti}_{0.66}\text{Fe}_{0.64}^{3+}\text{Fe}_{0.06}^{2+}\text{Mg}_{0.76})(\text{OH})_4\text{O}_{20}\text{Ca}_{0.14}\text{Na}_{0.06}\text{K}_{1.42}$	0.88
Hectorite (Hector)	$\text{Si}_8(\text{Mg}_{5.3}\text{Li}_{0.7})[(\text{OH})_2\text{F}_2]\text{O}_{20}\text{Na}_{0.55}\text{K}_{0.15}$	0.35
Saponite (Synthetic)	$(\text{Si}_{6.3}\text{Al}_{1.7})(\text{Mg}_{5.4}\text{Al}_{0.6})(\text{OH})_4\text{O}_{20}\text{Na}_{1.1}$	0.55
Vermiculite (Kenya)	$(\text{Si}_{5.52}\text{Al}_{2.48})(\text{Mg}_{4.94}\text{Fe}_{0.8}^{3+}\text{Fe}_{0.16}^{2+}\text{Ti}_{0.1})\text{O}_{20}(\text{OH})_4\text{Mg}_{0.70}\text{Ca}_{0.04}$	0.74

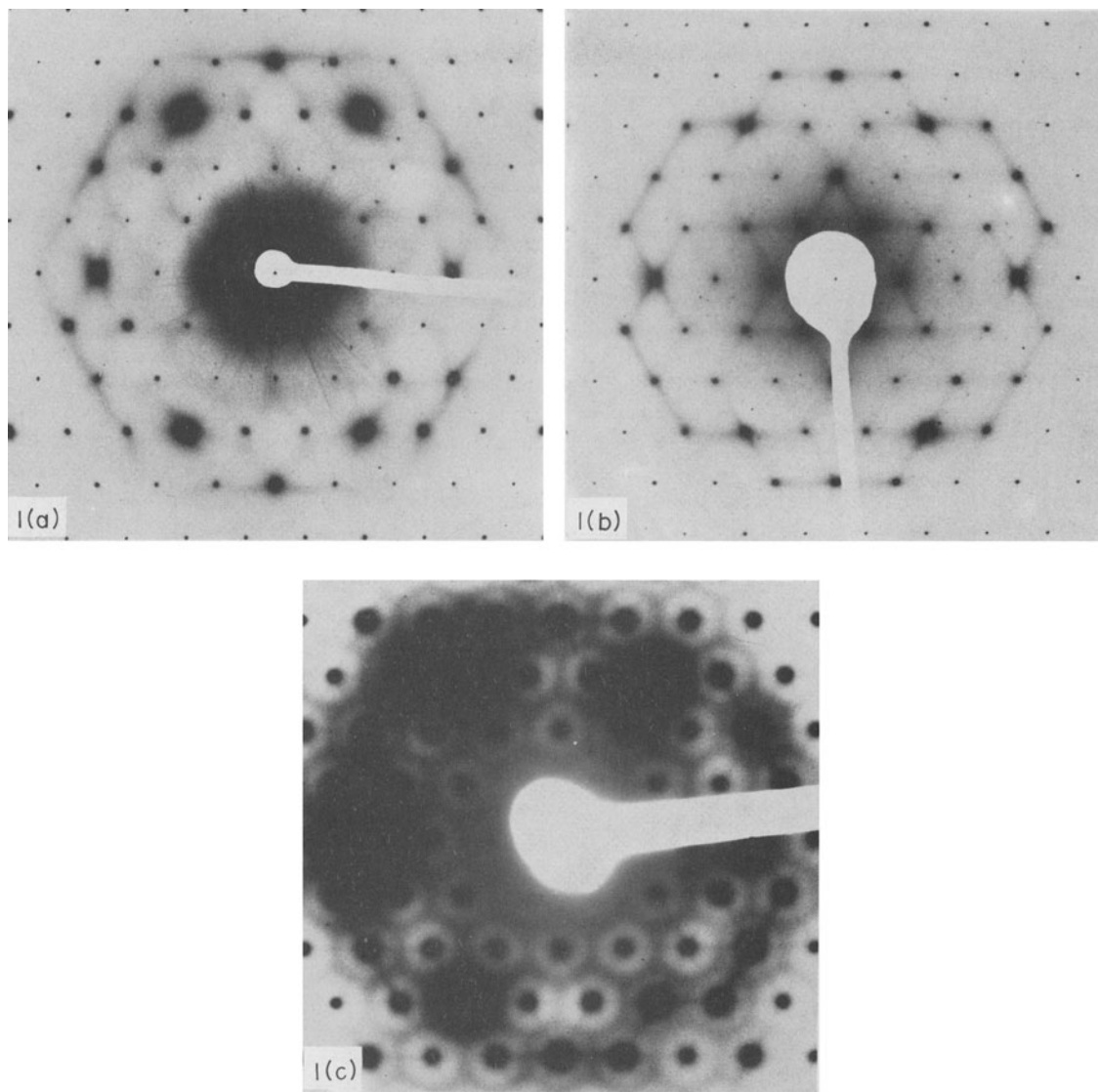


Fig. 1. Electron diffraction patterns of a single crystal of: (a) Ba-Montmorillonite. (b) Ba-Beidellite. (c) Ba-Illite. With the (001) plane perpendicular to the electron beam.

obtained from anhydrous Ba-vermiculite by X-ray diffraction are identical with those obtained by selected area electron diffraction (Besson *et al.*, 1974b). Figure 2(c) shows the appearance of such a pattern in the case of the Ba-vermiculite from Kenya; this pattern is similar in every respect to those obtained by X-ray diffraction (Alcover *et al.*, 1973).

## 2. MATERIALS AND SAMPLE PREPARATION

In order to verify the part played by the more or less disordered distribution of the isomorphous substitutions, we have chosen to compare:

On the one hand, smectites whose substitutions are localized in the tetrahedral layer (beidellite and saponite) with montmorillonites and hectorites.

And on the other hand, vermiculites and illites with saponites and beidellites.

In Table 2 we give a list of the studied minerals.

The interlayer cations initially present in the natural samples have been exchanged by barium which has a high scattering power. For the smectites and the vermiculites, the exchange has been done using a 1 N solution of  $\text{BaCl}_2$  at  $50^\circ\text{C}$ . The obtaining of the total exchange has been checked by adding to the  $\text{BaCl}_2$  solution a known proportion of  $^{133}\text{BaCl}_2$  and deter-

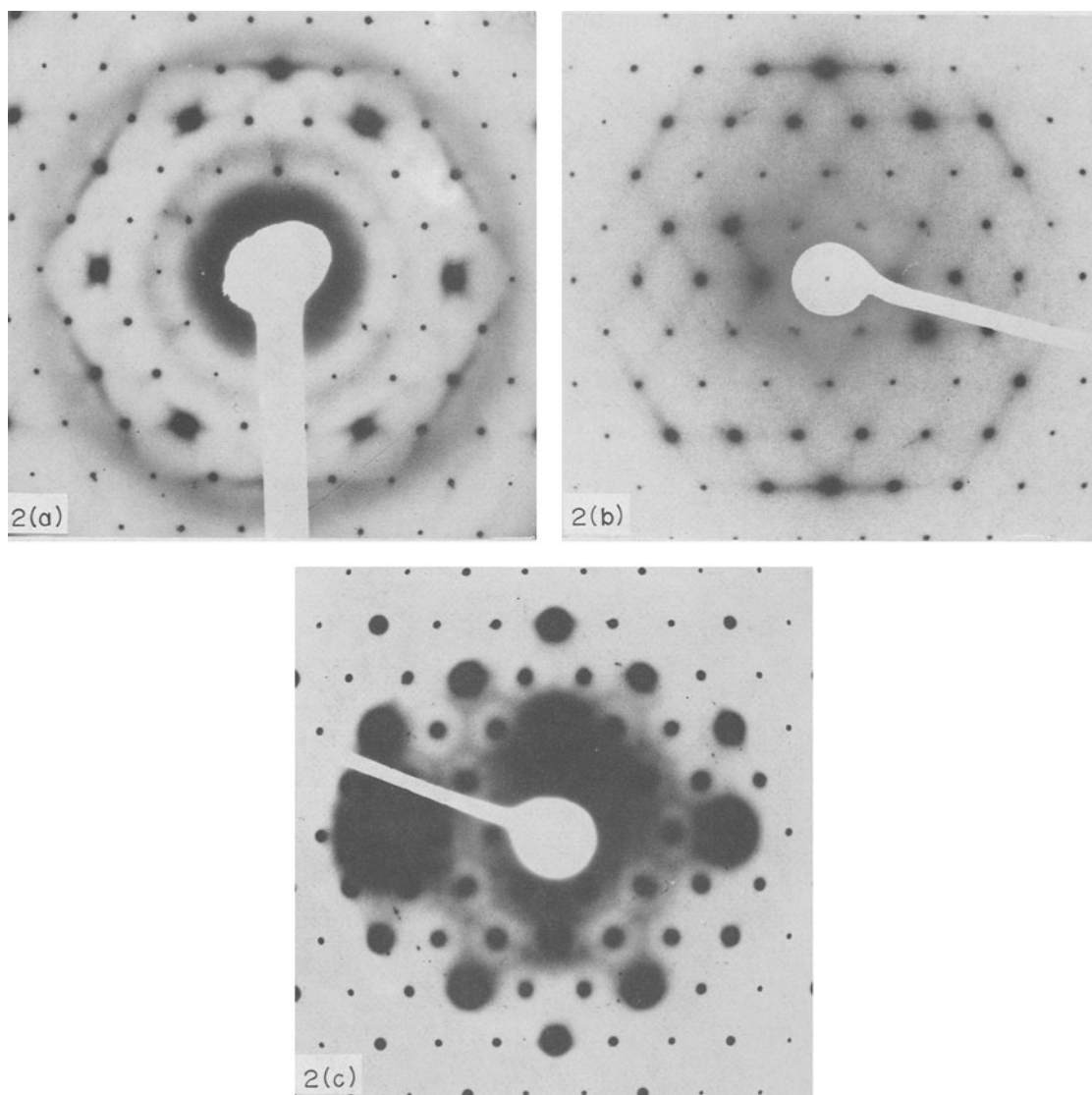


Fig. 2. Electron diffraction patterns of a single crystal of: (a) Ba-Hectorite. (b) Ba-Saponite. (c) Ba-Vermiculite. With the (001) plane perpendicular to the electron beam.

mining the quantity of fixed  $^{133}\text{Ba}$  with the help of a multichannel analyser.

The extraction of the interlayer potassium from an illite is more difficult. To do so we have used Graf's method (Graf *et al.*, 1968) slightly modified. We put in a 21. Nalgene polypropylene bottle 1 l. of a solution of 0.5 N  $\text{BaCl}_2$ . Dialysis tubes containing 20 mg of illite (fraction  $< 2 \mu\text{m}$ ) were placed in this solution. The exchange was carried out at  $90^\circ\text{C}$ . The solution was renewed every day for a total duration of approx. 3 weeks. After the last exchange, the solution was filtered, and the illite washed several times with distilled water till complete disappearance of  $\text{Cl}^-$  ions.

The calculated exchange capacity of this illite, according to its structural formula, is 162 m-equiv per 100 g of calcined sample. Experimentally, thanks to the method of the radio tracers (Besson *et al.*, 1974a), we have found 126 m-equiv per 100 g of calcined sample. Thus, we have exchanged 77 per cent of the potassium cations by barium.

### 3. RESULTS

#### 3.1 Study of illite and vermiculite

Comparison of the electron diffraction patterns of the illite and vermiculite with those of the smectites has

shown a fundamental difference between these phyllosilicate groups. The electron diffraction patterns of Ba-vermiculite and Ba-illite present, apart from the Bragg reflections, abnormal diffusions situated half way between these reflections which have the shape, on the photographs, of diffuse segments forming honey comb-like patterns (Figs 1(c) and 2(c)). For a given illite or a given vermiculite, the existence of such 'honey combs' depends upon the nature of the interlayer cations.

The existence of these anomalous diffusions allows us to affirm that the distribution of barium ions in vermiculite and illite obeys a linear correlation law (the precise study of this correlation law has been previously done by Alcover *et al.* (1974) and by Besson *et al.* (1974b). Therefore, assuming that the  $Ba^{2+}$  ions are localized in the immediate neighbourhood of a local charge defect in the layer, a partially ordered distribution of the interlayer cations must indicate that the isomorphous substitutions also are partially ordered.

### 3.1 Study of the smectites

All the smectites that we have studied are characterized by the same type of electron diffraction patterns in which the only intensity strengthenings, situated outside Bragg areas, are diffusions which link certain reflections together. In Fig. 1(a, b) and 2(a, b) are examples of such patterns. In changing the nature of the interlayer cation, we find that these abnormal diffusions are independent of the balancing cation. Furthermore, their existence does not depend on the substitution ratio, and in particular they appear even in such non-substituted phyllosilicate as pyrophyllite and talc. In that case they are thermal diffusions.

The absence of localization in reciprocal space of the intensity diffused by  $Ba^{2+}$  ions can be explained only by a totally disordered distribution of the interlayer cations (in that case, these cations give a distribution of intensity, continuously variable with the scattering angle, of the type of Laue's diffusion). Such an absence of localization of the intensity scattered by the  $Ba^{2+}$  ions, which is observed with smectites having a turbostratic structure (montmorillonite and hectorite) as well as with smectites having a three-dimensional periodic structure (beidellite and saponite), can be interpreted only by a totally disordered distribution of the isomorphous substitutions.

Nevertheless the difference in the  $Ba^{2+}$  ion distribution between smectites and illite-vermiculite can be also interpreted owing to the fact that, in smectites, a small number of  $Ba^{2+}$  cations are located in a weak interlayer electrical field, the fluctuation of which being smooth. Therefore the  $Ba^{2+}$  ions can easily go to the best places each to satisfy two ionic replacements. An interpretation based only on the mutual repulsions of

the interlayer cations, cannot explain the disorder in the  $Ba^{2+}$  ions distribution for synthetic saponite. In this studied saponite the charge (localized in the tetrahedral layer) is rather like that of Kenya-vermiculite.

## 4. CONCLUSIONS

The results allow us to make more precise the part played by substitutions in various 2/1 phyllosilicates.

(1) For a long time it was agreed that all smectites possessed a turbostratic structure. Later studies, especially by Weiss *et al.* (1955), Weir (1960) and Glaser *et al.* (1967), have shown that only smectites with octahedral substitutions were turbostratic whereas smectites with tetrahedral substitutions were characterized by a triperiodic organization.

Our study shows that in the smectite group it is not possible to connect the bi or triperiodic character of the mineral to a difference of order in the distribution of the substitutions whether they are octahedral or tetrahedral: we have actually found that those substitutions in any case are distributed in totally disordered way.

(2) In the introduction we have indicated that, when the layer charge is near to 0.6 it is difficult to foresee with no ambiguity whether the mineral belonged to the smectite group or to the illite-vermiculite group. The results obtained show that a fundamental difference exists in the distribution of the isomorphous substitutions in these two groups. The charge range of smectites (charge per half-cell < 0.6) corresponds to that of the stability of phyllosilicates with disordered substitutions; on the contrary, the illite-vermiculite group seems characterized by a partially ordered distribution of substitutions.

Thus, in agreement with the hypothesis of Mering and Pedro (1969), this investigation of the order-disorder relations of the substitutions seems to provide an extra criterion which allows a more precise characterization of some 2/1 phyllosilicates and whose use is rather easy.

*Acknowledgements*--The authors wish to thank Dr. G. W. Brindley for many helpful discussions and suggestions during the preparation of this manuscript. Acknowledgement is also made to Dr. Iiyama, Dr. Robert, and Dr. Kodama for the samples and chemical analysis results.

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**Résumé**—On montre que les relations ordre-désordre dans la distribution des substitutions isomorphes sont importantes pour caractériser les différents phyllosilicates 2/1 et pour déterminer leur comportement.

Ces relations ordre-désordre sont mises en évidence au moyen de diagramme de microdiffraction électronique obtenus à partir de monocristaux. Le domaine des charges de feuillet correspondant aux smectites (charge par demi maille  $<0,6$ ) est celui pour lequel les phyllosilicates sont stables avec des substitutions désordonnées. Les phyllites ayant une charge supérieure à 0,6 montrent des diffusions anormales qui indiquent que les distributions des ions Ba échangeables sont partiellement ordonnées; ce résultat est considéré comme un argument démontrant que les substitutions isomorphes sont aussi partiellement ordonnées.

**Kurzreferat**—Es wird gezeigt, daß das Ordnungs-Fehlordnungsverhältnis in der Verteilung der isomorphen Substitutionen für die Charakterisierung der verschiedenen 2/1-Schichtsilikate und die Bestimmung ihres Verhaltens von Bedeutung ist. Diese Ordnungs-Fehlordnungsverhältnisse werden durch Feinbereichsbeugungsmuster nachgewiesen, die an Einkristallen erhalten wurden. Im Bereich von Ladungsdichten, die denen der Smectite entsprechen (Ladung je Halbzelle  $<0,6$ ), sind Schichtsilikate mit Substitutionsfehlordnung stabil. Phyllite mit einer Ladung  $>0,6$  weisen Diffusionsanomalien auf, die anzeigen, daß die Verteilung austauschbarer Ba-Ionen teilweise geordnet ist. Dieses Ergebnis wird als Nachweis dafür angesehen, daß die isomorphen Substitutionen ebenfalls teilweise geordnet sind.

**Резюме** — Нашли, что отношение порядок-беспорядок в распределении изоморфных замещений имеет значение при установлении характеризующих факторов 2/1 листовых силикатов и при определении их поведения. Это отношение порядок-беспорядок показано на дифракционных картинах выбранных поверхностей монокристаллов. Предел заряда слоев, соответствующий сульфатной глине (заряд на полуячейку  $<0,6$ ), является для листовых силикатов устойчивым с беспорядочными замещениями. Филлиты с зарядом  $>0,6$  показывают аномальные диффузии указывающие, что распределение обменных Ва ионов частично регулярное и этот результат принимают как доказательство, что изоморфные замещения также являются частично регулярными.