

THE NATURE OF THE COMPONENT LAYERS OF  
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## ABSTRACT

Rectorite from the Fort Sandeman district, Baluchistan, Pakistan was examined in detail by x-ray, chemical, thermal and infra-red absorption methods. All of the experimental evidence supported Brown and Weir's conclusion that rectorite was made up of pairs of mica-like (non-expandable) and montmorillonite-like (expandable) layers. One-dimensional Fourier transform of glycerol-solvated Mg-rectorite gave a regular sequence with a mixing ratio of 1:1 and the mica-like layer thickness, 9.2 Å. Precession photographs and powder diffraction patterns produced the unit cell dimensions:  $a = 5.12$ ,  $b = 8.90$ ,  $c = 24.99$  Å and  $\beta = 99^\circ$ . The Greene-Kelly test indicated that the expandable layers were divided into beidellite-like and montmorillonite-like layers. Mixed Na- and Ca-rectorites gave a sharp discontinuity of the basal spacings at the approximate ratio  $\text{Na}_{26}\text{Ca}_{75}$ . Assuming that exchangeable Ca ions will tend to occupy interlayer sites over exchangeable Na ions and will tend to pre-empt those sites having higher energy, an approximate ratio of montmorillonitic and beidellitic layers was estimated to be 1:3. In the natural sample, the exchangeable cations Na, K, Mg, Ca and Sr were randomly distributed.

It was concluded, thus, that rectorite consisted of a regularly alternating sequence of paragonite-like layers and expandable layers having beidellitic and montmorillonitic compositions.

It was also emphasized that, because variations in the kind and population of interlayer cations were recognized among similar materials, the specific name rectorite should be confined to a regular interstratification of Na-mica and montmorillonite, judging from the chemical data of the original rectorite from Garland County, Arkansas.

## INTRODUCTION

Recently, Brown and Weir (1963) have concluded that rectorite (= allevardite) is made up of pairs of mica-like and montmorillonite-like layers. Many papers have been published on similar materials from various localities (Bradley, 1950; Caillère *et al.*, 1950; Hénin *et al.*, 1954; Brindley, 1956; Kodama, 1958; Korolev, 1960; Shimoda and Sudo, 1960; Shimoda, 1960; Brindley and Sandalaki, 1963; Sudo *et al.*, 1963). Even though the similarity among those materials is remarkable, minor variations are recognized, especially in the kind and population of their interlayer cations (Table 1). It is an important question whether such variations are allowable within a mineral species as the "individuality of the mineral" (Sudo, 1959) or essential for the definition of different mineral species. However, before the question can be answered, more precise information on the mineral is necessary to clarify substantial variations. In the present study, detailed investigations were conducted on the nature of rectorite from Pakistan, with special regard to the kind, population and

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distribution of the cations existing in the mineral. The material studied by the writer is similar to that described by Brown and Weir (1963) and in the present paper particular attention is given to the nature of the component layers.

TABLE 1. CHEMICAL ANALYSES OF RECTORITE, ALLEVARDITE AND SIMILAR MINERALS ON IGNITED WEIGHT BASIS

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Mineral discussed by the present writer	Mineral described by Brown and Weir	Rectorite	Allevar-dite	Hydrous complex of mica	Hydrous complex of mica	Hydrous complex of mica	Allevar-dite
SiO <sub>2</sub>	54.11	53.5	55.2	53.73	52.79	53.44	52.77	53.29
TiO <sub>2</sub>	0.01	—	—	0.36	—	1.81	0.62	0.02
Al <sub>2</sub> O <sub>3</sub>	40.38	40.6	38.7	38.22	39.93	39.24	41.00	37.72
Fe <sub>2</sub> O <sub>3</sub>	0.15	—	0.59	0.77	—	0.31	0.32	2.83
FeO	—	—	—	0.65	0.46	—	0.16	0.97
MnO	none	—	—	—	—	—	—	0.03
SrO	0.13	—	—	—	—	—	—	—
CaO	0.52	—	0.33	1.19	1.14	0.07	0.64	1.61
MgO	0.78	0.11	—	0.42	1.46	1.29	0.79	—
K <sub>2</sub> O	0.29	0.14	0.11	1.31	1.33	2.31	3.47	0.13
Na <sub>2</sub> O	3.87	5.31	4.40	2.67	2.22	0.76	0.46	0.72
P <sub>2</sub> O <sub>5</sub>	—	—	—	0.18	—	0.16	—	—
Total	100.24	99.66	99.33	99.50	99.33	99.39	100.23	97.32
CEC (meq /100 gm)	55.5	57	54					

- (1) Natural sample from Fort Sandeman district, Baluchistan, Pakistan. Analysis by H. Kodama (1965).
- (2) Na-saturated sample from Brunjkaki, Fort Sandeman district, Baluchistan, Pakistan. Brown and Weir (1963).
- (3) Na-saturated sample from Garland County, Arkansas, U.S.A. Brown and Weir (1963).
- (4) Allevard, France. Hénin, *et al.* (1954).
- (5) Goto mine, Nagasaki, Japan. Sudo *et al.* (1962).
- (6) Honami mine, Nagano, Japan. Sudo, *et al.* (1962).
- (7) Yonago mine, Nagano, Japan. Shimoda and Sudo (1960).
- (8) Dagestan, U.S.S.R. Korolev (1960).

## MATERIAL

The sample used was from Fort Sandeman district, Baluchistan, Pakistan, supplied as beidellite from Ward's Natural Science Establishment, Inc.

The sample is fibrous and matted-like papyrous with a pale green colour. It swells in water to form a gelatinous mass. The impurities were minute crystals of quartz, anatase and brookite, and small lumps of earthy materials consisting of chlorite, ankerite and fine quartz. They

could easily be removed under a binocular microscope. The purified sample was ground to less than 300 mesh.

## CHEMICAL DATA

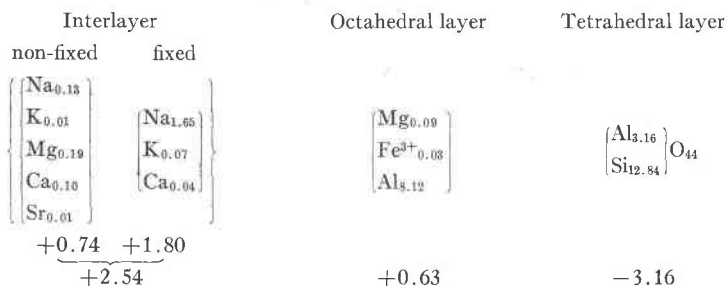
*Chemical composition and exchangeable cations.* Chemical analyses except Na were made on the natural sample ignited at 1000° C. by the  $\alpha$ -ray

TABLE 2. CHEMICAL COMPOSITION AND CALCULATION OF STRUCTURAL FORMULA

(1) Wt. % (based on 1000° C. ignited material)		(2) Atom ratio (Over-all layer)		(3) Non-expandable layer (Paragonitic comp.)	(4) (2)-(3) Mean expandable layer
SiO <sub>2</sub>	54.11	Si	12.84	6.00	6.84
TiO <sub>2</sub>	0.01				
Al <sub>2</sub> O <sub>3</sub>	40.38	Al	11.28	6.00	5.28
Fe <sub>2</sub> O <sub>3</sub>	0.15	Fe <sup>3+</sup>	0.03	0.02	0.01
MnO	0.00				
SrO	{ fixed 0.04 exch. 0.09	Sr	{ fixed 0.00 exch. 0.01		0.01
CaO	{ fixed 0.15 exch. 0.37	Ca	{ fixed 0.04 exch. 0.10	0.04	0.10
MgO	{ fixed 0.24 exch. 0.54	Mg	{ fixed 0.09 exch. 0.19	0.07	0.02 0.19
K <sub>2</sub> O	{ fixed 0.24 exch. 0.05	K	{ fixed 0.07 exch. 0.01	0.07	0.01
Na <sub>2</sub> O	{ fixed 3.59 exch. 0.28	Na	{ fixed 1.65 exch. 0.13	1.65	0.13
Total	100.24				

spectrochemical method (Rose *et al.*, 1963; Kodama *et al.*, 1966). Exchangeable cations such as K, Mg, Ca and Sr were estimated in comparison with analyses of Sr- and Ca-saturated samples. Total and fixed Na contents were determined on the natural and Ca-saturated samples respectively by a flame photometric method. Cation exchange capacity was determined by the method of Clark (1965). These results are listed in column 1 of Table 2. The CEC value of 55.5 meq/100 gm was as expected from a 1:1 interstratification of expandable and non-expandable layers (Brown and Weir, 1963).

*Over-all structural formula.* The calculation of structural formula was based on the total anionic charges  $O_{44}=88$  because analytical data were obtained from the ignited samples. From the calculated atom ratios (col. 2, Table 2), the over-all layer formula of the mineral was constructed as follows:



This formula agreed basically with the formula given by Brown and Weir (1963).

#### X-RAY INVESTIGATION

*Basal reflections.* The spacings of the basal (001) reflections were measured at about 50% relative humidity with a Philips diffractometer using oriented aggregates of the specimens after various treatments. The compiled data for  $d(001)$  spacings are listed in Table 3 together with corresponding data by Brown and Weir (1963). The  $d(001)$  spacing of the natural sample is intermediate between those of monovalent cation- and divalent cation-saturated specimens. This indicated that exchangeable cations in the natural sample were not mono-ionic. The best sequence of the basal reflections was obtained with a divalent cation-saturated specimen. Its  $d(001)$  spacing was evaluated to be  $24.61 \pm 0.03 \text{ \AA}$  when air-dry and  $27.33 \pm 0.02 \text{ \AA}$  on glycerolation. The difference ( $2.72 \text{ \AA}$ ) was almost the same as that of a divalent cation-saturated montmorillonite.

*Type of interstratification.* A good integral sequence of the basal reflections suggests a regular interstratification. The Fourier transform (MacEwan, 1956) of the basal reflections (col. 1, Table 4) from the glycerolated Mg-saturated specimen showed that the alternate layers were composed of two units of  $9.2 \text{ \AA}$  and  $18.3 \text{ \AA}$  in thickness with a mixing ratio of 0.49:0.51 (Fig. 1). This result was essentially consistent with earlier conclusions (Brown and Weir, 1963) that the structure was made up of pairs of mica-like and montmorillonite-like layers. Because of the high content of fixed Na, the layer thickness of  $9.2 \text{ \AA}$  suggested that the non-expandable mica-layer was similar to paragonite ( $9.6 \text{ \AA}$ ; Zen and Albee, 1964) rather than muscovite ( $10.0 \text{ \AA}$ ).

TABLE 3. BASAL SPACINGS,  $d(001)$ , OF RECTORITE FROM BALUCHISTAN, PAKISTAN  
( $\text{CoK}\alpha$ ) = 1.7902 Å  
Relative humidity  $50 \pm 2\%$

Condition of specimen	$d(001)$ Å	
	Present Work	Brown and Weir (1963)
Air-dry, natural state	$23.87 \pm 0.17$	24.9
Air-dry, after saturated with $\text{Na}^+$	$22.22 \pm 0.07$	22.0
Air-dry, after saturated with $\text{K}^+$ , $\text{Rb}^+$	$22.3^1$	
Air-dry, after saturated with $\text{Cs}^+$	$22.12 \pm 0.10$	
Air-dry, after saturated with $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$	$24.61 \pm 0.03$	24.9
Glycerol+natural state specimen	$27.39 \pm 0.05$	27.2
Glycerol+K- or Rb-saturated specimen	$26.3^1$	
Glycerol+Cs-saturated specimen	$27.13^1$	
Glycerol+Mg- or Ca-saturated specimen	$27.33 \pm 0.02$	27.4
After Greene-Kelly's test	$27.64 \pm 0.20$	
After heating at $600^\circ \text{C}$ . for 3 hours	$19.3^1$	19.6
After heating at $700^\circ \text{C}$ . for 3 hours	$19.4^1$	
After heating at $800^\circ \text{C}$ . for 3 hours	$19.4^1$	
After heating at $900^\circ \text{C}$ . for 3 hours	$19.5^1$	
After heating at $1100^\circ \text{C}$ . for 3 hours	mullite reflections	

<sup>1</sup> Less rational series of diffuse reflections.

TABLE 4. X-RAY DATA FOR THE GLYCEROLATED MG-SATURATED SPECIMEN AND THE SPECIMEN AFTER GREENE-KELLY TEST

$l$	(1) Glycerolation		(2) Greene-Kelly test	
	$d(\text{Å})$	$I^1$	$d(\text{Å})$	$I^1$
1	27.31	57880	27.36	57880
2	13.65	13420	13.86	39577
3	9.10	3400	9.33	50684
4	6.83	600	6.85	5944
5	5.46	580	5.48	5944
6	4.55	1700	4.65	36762
7	3.90	420	3.95	6570
8	3.41	1750	3.43	28001
9	3.04	1780	3.07	43958
10	2.73	14	2.79	782
11	2.48	34	2.51	2190
12	2.28	67	—	—
13	2.10	10	—	—

<sup>1</sup> Represented as peak area in an arbitrary unit.

*Lattice constants.* A small thin flake was cut from the unground original sample and used for *x*-ray crystallographic work. The precession photograph taken with the incident *x*-ray beam normal to the plane of the flake, gave a diffraction pattern consisting of several rings. When the incident *x*-ray beam was parallel to the plane, the photograph (Fig. 2) showed a diffuse pattern characteristic of a fibrous texture giving a long identity period of 24.4 Å along the  $c^*$ -axis and giving two identity periods of about 2.6 Å and 4.5 Å in the direction perpendicular to the  $c^*$ -axis. The

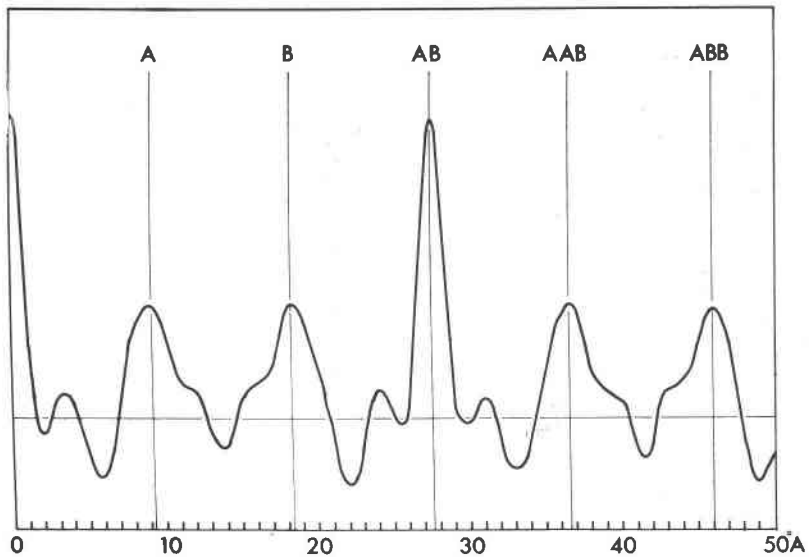


FIG. 1. Fourier transform of the glycerol-solvated Mg-rectorite.

two periods agreed well with the *d*-spacings for two strong lines from the Debye-Scherrer diffraction pattern of a powder sample, which were obviously related to the (200) and (020) reflection indices of micaceous minerals, respectively. Consequently, it was revealed that the skin-like specimen in the original state consisted of exceedingly fine platy crystals and that the *a*- and *b*-axes were randomly oriented around  $c^*$ -axis. As seen in Fig. 2, vertically diffuse lines at the periodicity of 2.6 Å contained two maxima which did not lay on the zero layer line. This indicated that the crystal of the mineral could be monoclinic and with the aid of the geometry of the reciprocal lattice, the angle was evaluated to be 99°. If it is assumed that the *a* and *b* dimensions of the mineral approximate those of mica, then the fibrous-texture photograph, the diffraction data for the oriented specimen, and the Debye-Scherrer camera pattern may be inte-

grated and the lattice constants for divalent cation-saturated specimen can be tabulated as follows:  $a = 5.12$ ,  $b = 8.90$ ;  $c \sin \beta = 24.61$  Å,  $\beta = 99^\circ$  and  $c = 24.99$  Å. Since the  $a$  and  $b$  dimensions of paragonite, montmorillonite and muscovite are 5.13 and 8.89 Å (Deer *et al.*, 1962), 5.17 Å and 8.94 Å (Pinsker, 1953), and 5.189 and 8.995 Å (Yoder and Eugster, 1955) respectively, the obtained  $a$  and  $b$  dimensions supported the existence of paragonite-like layers.

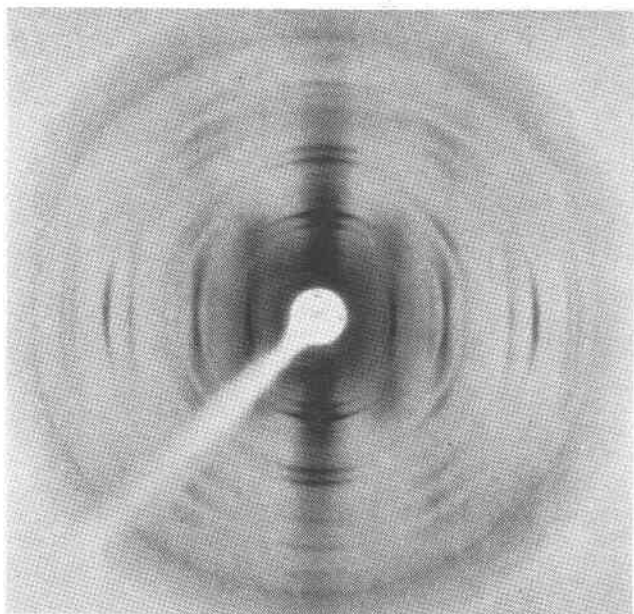


FIG. 2. Zero level photograph with precession on an axis normal to  $c^*$ -axis.  
 $\bar{\mu} = 20^\circ$ , MoK, 50KV, 20mA, 16 hrs.

*Indexing of non-basal reflections.* Indexing of non-basal reflections was carried out in order to check the lattice constants. The non-basal reflection data were obtained from the Debye-Scherrer powder pattern of an air-dry Mg-saturated specimen with reference to the pattern of a glycerolated Mg-saturated specimen. Conversion of the  $d$ -spacings to the observed  $Q$ -values ( $Q = 1/d^2 = (4 \sin^2 \theta) / \lambda^2$ ) was made with the table prepared by Azaroff and Buerger (1958). The calculation of  $Q$ -values was carried out with an IBM Model 1620 computer using the program for a monoclinic system (World No. 279) written by Dr. H. M. Haendler (1962, 1965). Table 5 shows the comparison of the observed  $Q$ -values with the calculated ones for the possible indices. The agreement was satisfactory.

TABLE 5. INTERPLANAR SPACINGS, RELATIVE INTENSITIES AND POSSIBLE INDICES OF NON-BASAL REFLECTIONS FROM RECTORITE, IN COMPARISON WITH OBSERVED AND CALCULATED Q-VALUES

$d_{\text{obs}}$	I	$Q_{\text{obs}}$	$Q_{\text{calc}}$	$\Delta Q^1 \times 10^4$	hkl	
4.45	band	0.0505	0.0505	0	020	
4.41		0.0514	0.0510	+4	11 $\bar{1}$	
4.37		0.0514	0.0514	0	102	
		0.0523	0.0520	+3	110	
		0.0522	0.0522	+1	021	
3.93	vw br	0.0647	0.0640	+7	112	
			0.0656	-9	023	
2.560	band	vs	0.1526	0.1529	-3	130
			0.1530	-4	117	
2.542			0.1548	0.1544	+4	13 $\bar{2}$
2.518			0.1577	0.1572	+5	131
			0.1573	+4	200	
2.235	vw	0.2002	0.1995	+7	109	
			0.2010	-8	213	
2.154	w vbr	0.2155	0.2154	+1	217	
1.683	m	0.3530	0.3539	-9	15 $\bar{1}$	
1.652	vbw br	0.3664	0.3662	+2	241	
			0.3666	-2	310	
1.484	s	0.4541	0.4544	-3	060	
1.283	m br	0.6075	0.6074	+1	20 $\bar{1}$ 8	
1.264	vw br	0.6259	0.6253	+6	41 $\bar{3}$	
			0.6263	-4	13, 16	
1.239	m	0.6514	0.6507	+7	13, 1 $\bar{8}$	
			0.6523	-9	408	
1.169	ms br	0.7318	0.7313	+5	267	
1.112	m br	0.8087	0.8084	+3	360	

<sup>1</sup>  $\Delta Q = Q_{\text{obs}} - Q_{\text{calc}}$ .

*Nature of the expandable layer.* Williams, *et al.* (1953) showed that Ca-montmorillonite had a double water layer, while Na-montmorillonite had a single water layer at room temperature and 50% relative humidity. The



d(001) spacings of Ca- and Na-saturated montmorillonites under these conditions are generally given as 15.4 and 12.4 Å, respectively. The difference,  $15.4 - 12.4 = 3.0$  Å, corresponds to the thickness of a single water layer. Almost the same difference was obtained between d(001) spacings of the Ca- and Na-saturated specimens, indicating that the expandable layer of the mineral is montmorillonitic.

The *b* dimension and the chemical data suggested that the mineral was dioctahedral and that the expandable layer had characteristics of the minerals belonging to the montmorillonite-beidellite series. Consequently the Greene-Kelly test (1953) was applied to evaluate the layer charge distribution. The result (col. 2, Table 4) showed the expansion to 27.64 Å ( $\pm 0.20$  Å) which obviously indicated that the expandable layers were beidellitic. However, the change in the intensity ratio such as the enhancement of intensities of the basal reflection with their indices  $l = 3n$ , suggested that some of the expandable layers collapsed irreversibly. The results indicated, therefore, that the expandable layers contained both montmorillonitic and beidellitic layers.

Chemical data indicated that exchangeable monovalent and divalent cations were both present in the natural specimen. Its basal reflection data gave an intermediate d-spacing and less rationality, which suggested the random distribution of the exchangeable monovalent and divalent cations.

*Unmixing of exchangeable Na and Ca ions.* Méring and Glaeser (1954) mentioned the unmixing phenomenon of Na and Ca ions in a bi-ionic montmorillonite and explained it on the basis of crystallo-chemical aspects. Glaeser (1958) confirmed the same phenomenon in hectorite and proposed an *x*-ray technique for detection of the unmixing. This technique was applied to the present study.

The experimental procedure was as follows: Na- and Ca-saturated specimens were mixed in various proportions. 40 mg of the mixed specimen was placed in a small centrifuge tube, 5 ml of water was added and then shaken with a "wrist-action" shaker for 16 hours. After centrifuging, 3 ml of the supernatant solution was removed and the specimen was resuspended by a small stirrer. One ml of the suspension was pipetted onto a glass slide to prepare oriented aggregates for *x*-ray analysis. The analysis was carried out with  $\text{CoK}\alpha$  radiation and the low scanning speed of  $\frac{1}{2}^\circ$  ( $2\theta$ ) ranging the diffraction angle  $2^\circ$  to  $36^\circ$  using a Philips diffractometer. Figures 3 a, b, c illustrate characteristics of the results. The observed peak migration of basal reflections clearly indicated a formation of the randomly interstratified sequence of Na-saturated ( $d_1 = 22.8$  Å) and Ca-saturated ( $d_2 = 24.7$  Å) layers. Although the method of Méring (1949)

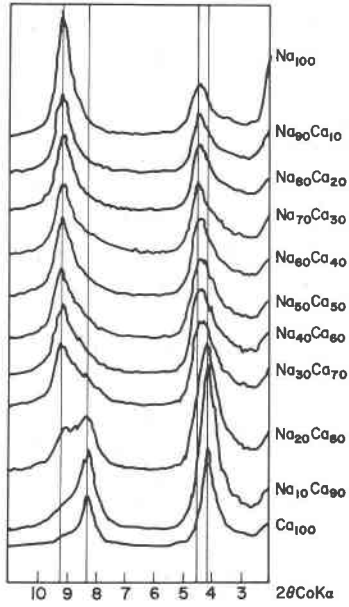


FIG. 3a. X-ray diffraction patterns of oriented specimens of the mixed Na- and Ca-rectorites,  $2\theta = 2^\circ$  to  $11^\circ$ .

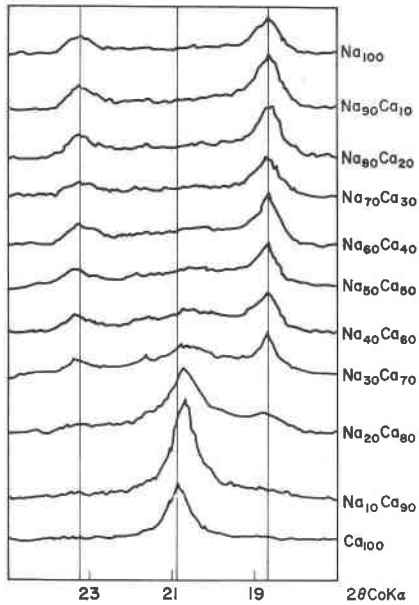


FIG. 3b. X-ray diffraction patterns of oriented specimens of the mixed Na- and Ca-rectorites,  $2\theta = 18^\circ$  to  $24^\circ$ .

predicted seven diffraction regions where basal reflections may shift, the present consideration was restricted to four regions, where diffraction peaks  $d_1(001)/d_2(001)$ ,  $d_1(002)/d_2(002)$ ,  $d_1(004)/d_2(005)$  and  $d_1(007)/d_2(008)$  were observed, since the other peaks were very weak. Figures 4 a, b, c show the peak migrations in the three regions as a function of  $\text{Ca}/(\text{Na} + \text{Ca})$  ratio. The figure for the migration of peak  $d_1(004)/d_2(005)$  was omitted because of its similarity to that of the peak  $d_1(007)/d_2(008)$

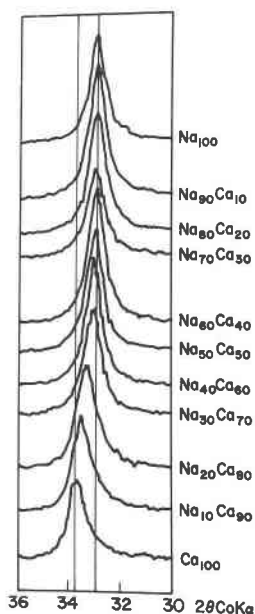


FIG. 3c. X-ray diffraction patterns of oriented specimens of the mixed Na- and Ca-rectorites,  $2\theta = 30^\circ$  to  $36^\circ$ .

(Fig. 4c). A sharp discontinuity occurred where the exchangeable cation ratio is between  $\text{Na}_{30}\text{Ca}_{70}$  and  $\text{Na}_{20}\text{Ca}_{80}$ . The appearance of two peaks with open circle representing the weaker peak in the diagram for  $d_1(002)/d_2(002)$  (Fig. 4b) was interpreted to mean a tendency to the formation of a zonal structure. Another discontinuity with less sharpness was observed only in the diagram for  $d_1(001)/d_2(001)$  (Fig. 4a). It occurred where the exchangeable cation ratio is between  $\text{Na}_{70}\text{Ca}_{30}$  and  $\text{Na}_{60}\text{Ca}_{40}$ , approximately corresponding to the ratio obtained by Mering and Glaeser(1954). It was considered, therefore, that the major unmixing at the approximate ratio  $\text{Na}_{25}\text{Ca}_{75}$  might be characteristic of the expandable layers.

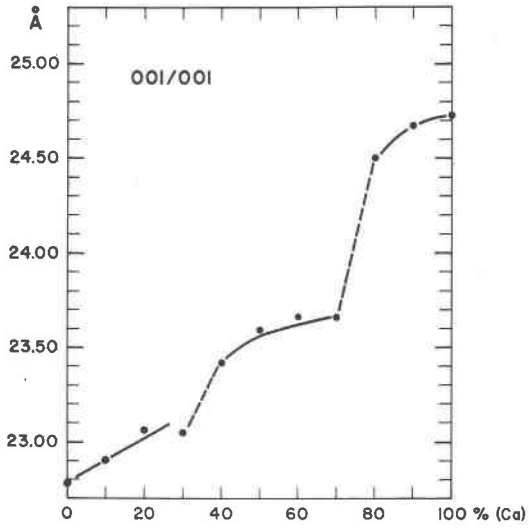


FIG. 4a. Peak migration of the  $d_1(001)/d_2(001)$  reflections of the mixed Na- and Ca-rectorites as a function of Ca/(Na+Ca) ratio.

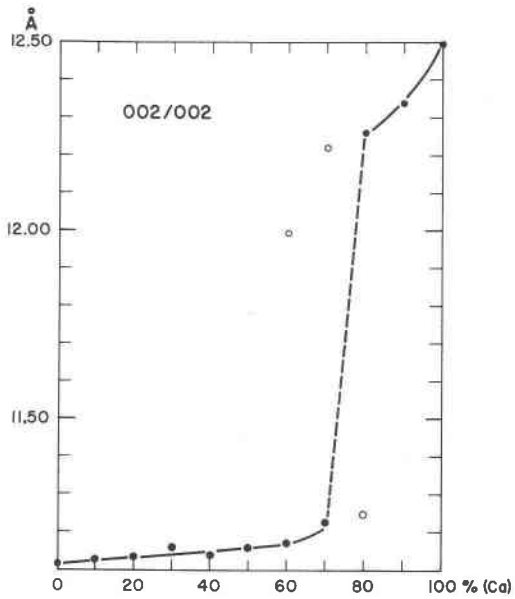


FIG. 4b. Peak migration of the  $d_1(002)/d_2(002)$  reflections of the mixed Na- and Ca-rectorites as a function of Ca/(Na+Ca) ratio.

## THERMAL ANALYSES

*Differential thermal analysis.* The DTA curve recorded with a heating rate of  $11.5^{\circ}\text{C./min}$  on the specimen diluted 50:50 with alumina is given in Fig. 5. There are four endotherms including a shoulder-like one with peak temperatures of  $140^{\circ}\text{C.}$ ,  $200^{\circ}\text{--}205^{\circ}\text{C.}$ ,  $570^{\circ}\text{C.}$ , and  $960^{\circ}\text{C.}$  The first two endotherms were considered to be due to dehydration of absorbed and interlayer water and the third due to dehydroxylation of structural hydroxyl groups. X-ray data on the fired product showed that

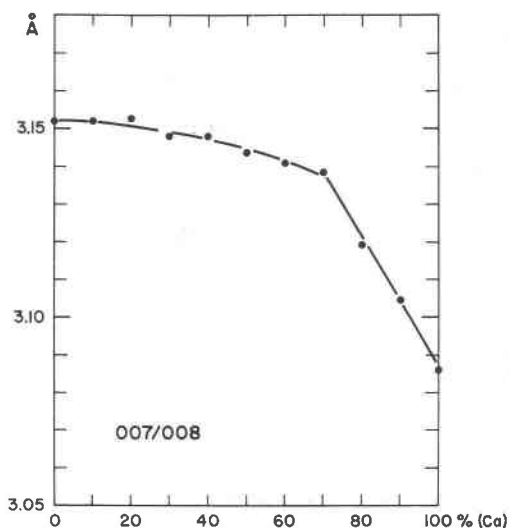


FIG. 4c. Peak migration of the  $d_1(007)/d_2(008)$  reflections of the mixed Na- and Ca-rectorites as a function of Ca/(Na+Ca) ratio.

the fourth endotherm and the following exotherm at  $1030^{\circ}\text{C.}$  were connected with the recrystallization to mullite.

*Thermogravimetric analysis.* Thermogravimetric data were obtained with a Stanton Recording Thermobalance having a constant heating rate of  $3^{\circ}\text{C./min}$ . Figure 6 gives the thermogravimetric curve obtained by replotting the data as weight loss per cent against temperature. The curve showed two main steps which were not sharply differentiated as is generally the case in curves of montmorillonitic clays.

Assuming that the inflexion of the curve between the two steps divides the weight loss into two contributions due to dehydration and dehydroxylation, each contribution may be evaluated by mathematical treatment.

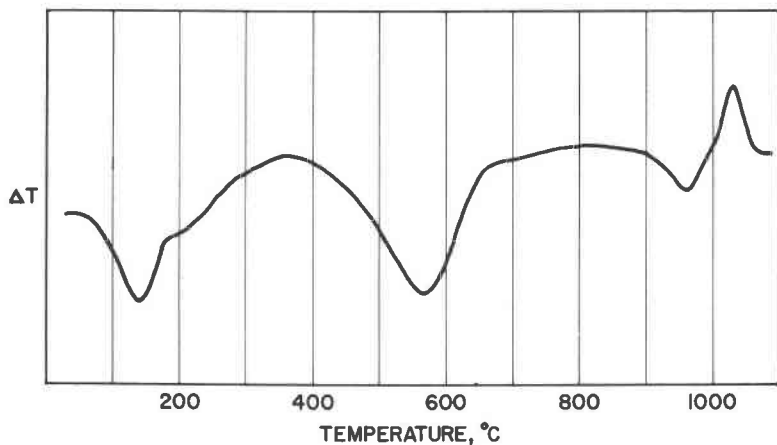


FIG. 5. Differential thermal analysis of rectorite.

The curve between 250° C. and 500° C. is expressed by the following power series,

$$W(\%) = 0.0175t^5 - 0.547t^4 + 5.94t^3 - 29.20t^2 + 67.14t - 52.05$$

where  $W$  is the per cent of weight loss and  $t$  is the temperature in one hundredth unit (° C./100). Differentiating the equation, the inflexion was calculated to be at 331° C. and the corresponding weight loss was 6.92%. Since the total weight loss is 12.10%, the expected weight loss due

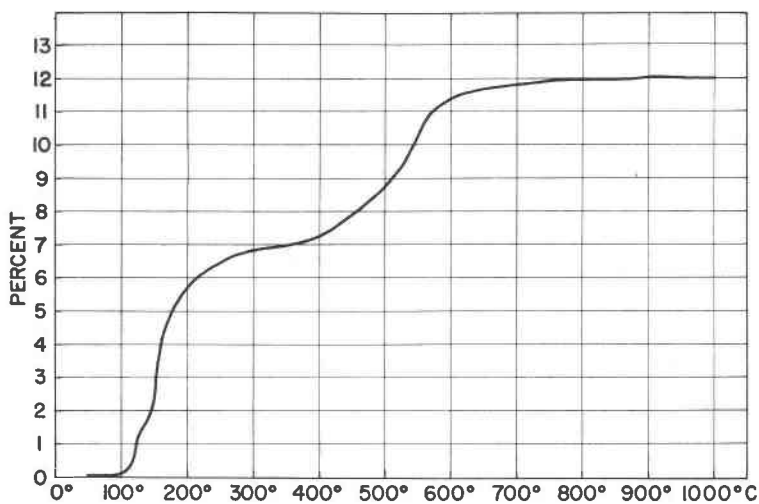


FIG. 6. Thermogravimetric analysis curve of rectorite.

to dehydroxylation is  $12.10 - 6.92 = 5.18$  (%). In view of the difficulty in evaluating the content of structural water, the value seems reasonable since it is only slightly higher than the theoretical values, 4.71% (paragonite) and 4.93% (montmorillonite).

#### INFRA-RED ABSORPTION SPECTRA

*General features.* The absorption spectra in the region  $400-700\text{ cm}^{-1}$  were obtained with a potassium bromide disk containing 0.25% of the natural sample, using a Perkin-Elmer Model 21 spectrophotometer with a sodium chloride prism. The general pattern agreed well with that of rectorite from Arkansas given by Brown and Weir (1963). Table 6 lists the wavenumbers of the absorption maxima in comparison with the published data for some related minerals. The spectra appear to be almost identical to the composite ones of montmorillonite and illite except for a few very weak maxima. The faint absorption peak at  $1388\text{ cm}^{-1}$  was considered to be due to a slight trace of  $\text{NH}_4^{1+}$  absorbed in the sample.

*Thermal effect on the OH bands.* Further investigations were made on the OH absorption spectra by determining the effect of consecutive heat treatments. Up to  $200^\circ\text{ C}$ ., spectra were recorded with a Perkin-Elmer Model 621 grating spectrophotometer equipped with a heating stage<sup>1</sup> using a Na-saturated specimen. Figure 7 illustrates the absorption spectra of the samples at room temperature and heated at intervals of  $50^\circ\text{ C}$ . from  $50^\circ\text{ C}$ . to  $200^\circ\text{ C}$ . The unheated Na-saturated specimen gave absorption bands at  $3645\text{ cm}^{-1}$ ,  $3420\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$ , which were attributed to free OH stretching ( $\nu\text{OH}$ ), H-bonded OH stretching ( $\nu\text{OH}\cdots\text{O}$ ) and H-bonded OH in-plane bending ( $\delta\text{OH}\cdots\text{O}$ ) respectively. With increasing temperature the intensities of the bands at  $3420\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  weakened gradually and the former band shifted to higher frequencies reaching a maximum of  $3450\text{ cm}^{-1}$ . Upon heating at  $200^\circ\text{ C}$ . both bands disappeared. On the other hand, the free OH band at  $3645\text{ cm}^{-1}$  remained unchanged during this treatment. Consequently, the absorption bands at  $3420\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  were attributed to absorbed water and interlayer water molecules. There was the additional result that the bands at  $3420\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  of the unheated Na-saturated specimen were also slightly different from those of the natural sample (Table 6). Since the free OH band remained unchanged, the observed shift suggests that  $\nu\text{OH}\cdots\text{O}$  and  $\delta\text{OH}\cdots\text{O}$  frequencies are dependent on the kinds of interlayer cations.

In order to determine the spectra after heating to temperatures near

<sup>1</sup> Through the courtesy of Perkin-Elmer Corporation, Montreal.

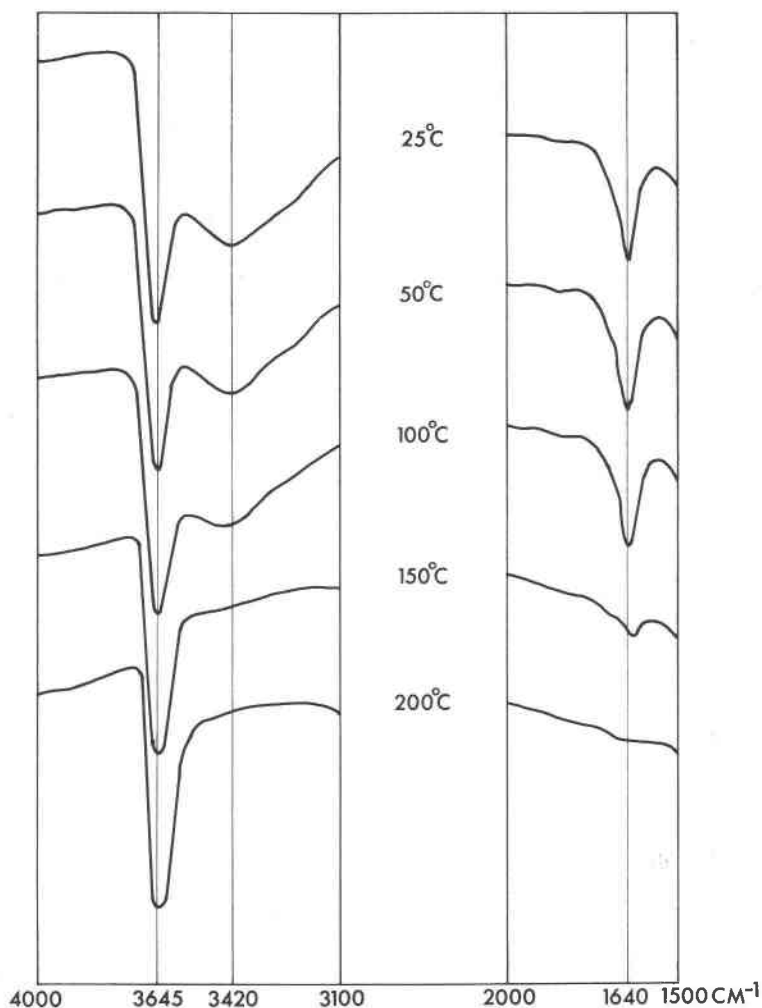


FIG. 7. The OH absorption spectra of rectorite at 25° C. to 200° C.

and after dehydroxylation, the natural samples were heated at 600° C. and 900° C. for three hours, cooled to room temperature in a desiccator and then subjected to infra-red study with a Beckman IR7 grating spectrophotometer using the Nujol mull technique. After heating at 600° C., the OH band shifted from 3645 cm<sup>-1</sup> to 3660 cm<sup>-1</sup> and became much weaker. The band completely disappeared upon heating at 900° C., which indicated the completion of dehydroxylation. The cause of the shift to higher frequency was not clear from this study. However, the higher



frequency should mean a higher energy state of residual hydroxyl groups, since an increase of  $1 \text{ cm}^{-1}$  corresponds to an increase of 2.859 cal/mol.

## DISCUSSION

*Summary of the mineral data.* The mineral from Pakistan was a dioctahedral regularly interstratified mixture of mica (non-expandable) and montmorillonite-(expandable) type layers. Fourier transform gave their

TABLE 6. POSITIONS OF INFRA-RED ABSORPTION MAXIMA OF RECTORITE IN COMPARISON WITH THOSE OF SOME RELATED CLAY MINERALS FROM PUBLISHED DATA<sup>1</sup> ( $\text{cm}^{-1}$ )

Rectorite (Baluchistan, Pakistan)	Montmorillonite (Togo, Japan)	Vermiculite (Uzumine, Japan)	Illite (Shiraishi Japan)	Pyrophyllite (Honami, Japan)
3645 s	3644 s		3630 s	3680 s
3400 s br	3416 s br	3140 s br		
1650 m	1650 m	1650 m		
1388 vvw				
1125 vvw	1128 m			1125 s
1080 w			1070 m	1070 s
1050 s				1050 s
1023 s	1030 s		1025 s	
995 vw		985 s		
920 vw	915 m		933 m	946 s
875 vw	883 w			
	845 w			850 w
823 vw			827 w	832 m
810 w			803 w	812 w
730 m			755 m	

s—strong; m—medium; w—weak; vw—very weak; vvw—very very weak; br—broad.

<sup>1</sup> Kodama and Oinuma (1963) and Oinuma and Kodama (1964).

mixing ratio 1:1 and the mica-type layer thickness,  $9.2 \text{ \AA}$ . Integrating the chemical and *x*-ray data, the mica-type layers were paragonite-like. Based upon the Greene-Kelly test, the expandable layers were divided into beidellite-like and montmorillonite-like layers. In the natural sample, exchangeable cations such as Na, K, Mg, Ca and Sr were randomly distributed.

*Interpretation of the unmixing in Na-Ca system.* An interpretation of the unmixing phenomenon may be given on the basis of the following considerations: (1) the expandable layers consist of two kinds of layers, (2) exchangeable Ca (divalent) ions will tend to occupy interlayer sites over

exchangeable Na (monovalent) ions and will tend to pre-empt those sites having the higher energy (Marshall, 1954). If all exchangeable sites of beidellitic layers are occupied by Ca ions, unmixing would take place. This assumption seems reasonable because the layer charge density of beidellite is higher than that of montmorillonite (Weir and Greene-Kelly, 1962). Consequently, the ratio  $\text{Na}_{25}\text{Ca}_{75}$  would give an approximate ratio of montmorillonitic and beidellitic layers. On the basis of the discontinuity mentioned above, three quarters of the expandable layers are considered to be beidellitic.

*Expandable layer formula.* Since the ratio of non-expandable and expandable layers was nearly 1:1, and with the assumption that the non-expandable layer formula was similar to dehydrated paragonite  $\text{Na}_2\text{Al}_6\text{Si}_6\text{O}_{22}$ , a separation of the expandable layer formula from the over-all layer formula was attempted. The charge deficiency due to the low population of interlayer cations of the paragonite was balanced by adding some octahedral cations (col. 3, Table 2). The results of the correction (col. 4) gave the mean formula of the expandable layers;  $(\text{Na}_{0.13}\text{K}_{0.01}\text{Mg}_{0.19}\text{Ca}_{0.10}\text{Sr}_{0.201}) (\text{Mg}_{0.02}\text{Fe}^{3+}_{0.01}\text{Al}_{4.12}) (\text{Si}_{6.84}\text{Al}_{1.16})\text{O}_{22}$ . As indicated by x-ray data, there were two kinds of expandable layers which may be represented as beidellitic and montmorillonitic layers having higher and lower negative tetrahedral charges respectively, and whose mixing ratio is 3:1 or 0.75:0.25. Accordingly, the relation  $0.75\text{X} + 0.25\chi = 6.84$  could be obtained from the Si atom proportion of the mean expandable layer formula and another relation  $6.00 < \text{X} < \chi \leq 8.00$  could be obtained from the ideal proportions of paragonite and montmorillonite and by the definition, where X and  $\chi$  are the Si atom proportions of beidellitic and montmorillonitic tetrahedral layers, respectively. The relations resulted in the inequality,  $6.45 \leq \text{X} < \chi \leq 8.00$ . Taking the extreme condition of each proportion, the tetrahedral layer of the mean expandable layer formula,  $(\text{Si}_{6.84}\text{Al}_{1.16})$ , could be rewritten by

$$[0.75 \times (\text{Si}_{6.45}\text{Al}_{1.35})] + [0.25 \times (\text{Si}_{8.00})].$$

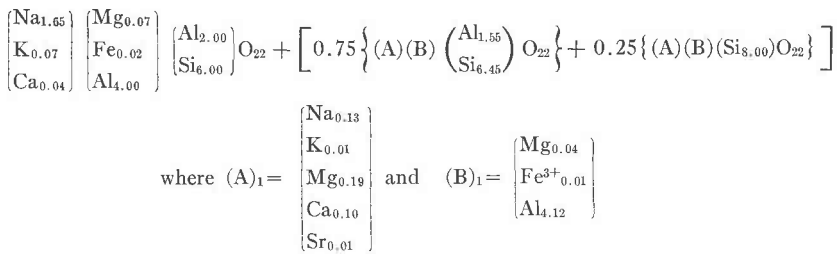
In general, chemical-analysis data supported the structural scheme derived from other data.

*Definition and nomenclature of rectorite.* It must be emphasized that, although the present study reveals only one example of the layer charge distribution, the kind and population of interlayer cations, especially those of non-exchangeable cations are very significant because they may define a type of mica-like layer. For instance, in the mineral having a high K content, its mica-like layer is expected to be muscovite-type

instead of paragonite-type. Using similar arguments, the montmorillonite-like layers can also be determined more specifically as described above. Thus, the interstratified mica-montmorillonite minerals should be divided into more individual mineral species. Judging from chemical data of the original rectorite, it seems to be suitable at the present stage that the specific name rectorite should be confined to a regular interstratification of Na-mica and montmorillonite rather than that of mica in the broad sense and montmorillonite.

### CONCLUSIONS

From this series of experiments, then, it may be concluded that: (1) rectorite consists of non-expandable and expandable layers with a mixing ratio 1:1 in the regularly interstratified manner, (2) the non-expandable layer is paragonite-like, (3) the expandable layers are divided into beidellitic and montmorillonitic ones with their mixing ratio 3:1 and (4) the kind, population and distribution of layer charges is given schematically in the following structural formula as one possible example;



The existence of two different types in the expandable layers excluded the concept of solid solution between both end members. The expandable layers, thus, have either a beidellitic or montmorillonitic composition and, in the rectorite from Pakistan, are regularly interstratified with paragonite-like layers.

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