THE ALTERNATING LAYER SEQUENCE OF RECTORITE*

W. F. Bradley, *Illinois State Geological Survey, Urbana, Illinois.*

Abstract

Rectorite is a complex layer type hydrous alumino-silicate related to the better known mica-like minerals. The structural scheme of rectorite consists of contiguous pairs of pyrophyllite-like units separated by pairs of layers of water molecules. An equally apt description would be the alternation of one pyrophyllite unit with one vermiculite unit. The nature of the arrangement is confirmed by the preparation of the equivalent complex in which ethylene glycol proxies for water.

The recognition that random mixed layer growths occur in nature with considerable frequency among the clay and clay-like minerals (1, 2) has raised the question whether minerals might not exist which would be characterized by a specific regularly alternating epitactic intergrowth. In a sense this is precisely the case with well known minerals like the chlorites or the chrondrodite series. The present intention is to demonstrate that the principle extends to more complex instances.

Rectorite is included among the species of doubtful validity in *Dana's* Sixth Edition, and has since been omitted. A specimen of the original material (USNM #80607), obtained by R. E. Grim from W. F. Foshag of the United States National Museum, has been available for study. Analyses cited by Dana for material dried at 110° C. are:

	SiO_2	Al_2O_3	H_2O	Fe_2O_3	CaO	MgO	Na_2O	K_2O	H_2O (110° C.)
1.	52.72	36.60	7.76	0.25	0.45	0.51	2.83	0.26	8.78
2.	52.88	35.51	7.76						8.83

The specimen is preponderantly monomineral, having associated with it only a small proportion of a kaolinite group mineral. The weak kaolinite lines in the diagrams of Fig. 1 have simply been excluded from the analysis which follows. Excessive preferred orientation, occasioned by characteristic matted texture of the sub-parallel aggregates is also evident in the reproductions, and serves to emphasize the outstanding characteristic of the diagrams, which is the extended series of orders of diffraction from the basal periodicity.

The presence of a hexagonal array of prism diffraction lines reminiscent of those of clays immediately suggests that rectorite is some arrangement of the mica-type hydrous alumino-silicate layer, but the magnitude of the fundamental periodicity, about 25 Å, exceeds common values.

A valuable supplementary source of information in the study of layer silicates has been the observation that water layers (when present in

---

* Published with the permission of the Chief, Illinois State Geological Survey, Urbana, Illinois.

such structures) may be displaced by other liquids, as ethylene glycol, with production of a new sequence of diffraction orders for an altered fundamental periodicity (1). The pair of sequences is then more amenable to interpretation than is a single sequence.

In Table 1 are summarized the data employed in interpretation of the diagrams of Fig. 1. From an earlier study of a number of layered associations of montmorillonite with organic liquids (3), arbitrarily reduced *F*-factor estimates and signs were available as comparison standards which could be assumed to apply in this present case if it were true that one mica, montmorillonite, or pyrophyllite layer were involved in the present structure. The numbers in the *F* columns of Table 1 were chosen by comparison of the intensities of the rectorite diagrams with those of reflections at comparable angles for various montmorillonite-liquid complexes.

TABLE 1. *X*-RAY DIFFRACTION DATA FOR RECTORITE IN 00*l* SERIES

Order	Relative Intensity natural configuration $d_{001}=25.0$Å	Estimated relative *F* importance	Sign for octahedral origin	Sign for interlayer origin	Relative intensity glycol complex $d_{001}=26.6$Å	Estimated relative *F* importance	Sign for octahedral origin	Sign for interlayer origin
1	SSS	10	+	+	SSS	10	+	+
2	SSS	6	+	−	SS	4	+	−
3	W	1	+	−	M	2	+	−
4	W	1	−	−	W	1	−	+
5	S	4	−	−	M	2	−	−
6		0			M	3	−	−
7	coincident with kaolinite	2	omitted		W	1½	+	+
8	SSS	15	+	−	SS	10	+	−
9		0			S	6	+	−
10		0			W	1	+	+
11	M	2	−	−		0		
12	M	2	−	+	W	1	−	−
13	S	4	−	+	M	2	−	+
14	M	2	−	−	S	4	−	+
15		0			W	1	−	−
16		0				0		
17	W	1	+	−		½	+	omitted
18						½	+	
19							+	
20						½	+	

Figure 2 represents the results of one-dimensional Fourier synthesis based on the *F*-values and signs so chosen. The traces from $z=0.0$ to 0.2 are typical for a three-component layer. The intervening space is occupied in both cases by five lesser maxima which lose definition in the glycol reaction. One suggestion is that this space includes a second three-component unit unsymmetrically displaced with respect to the conven-

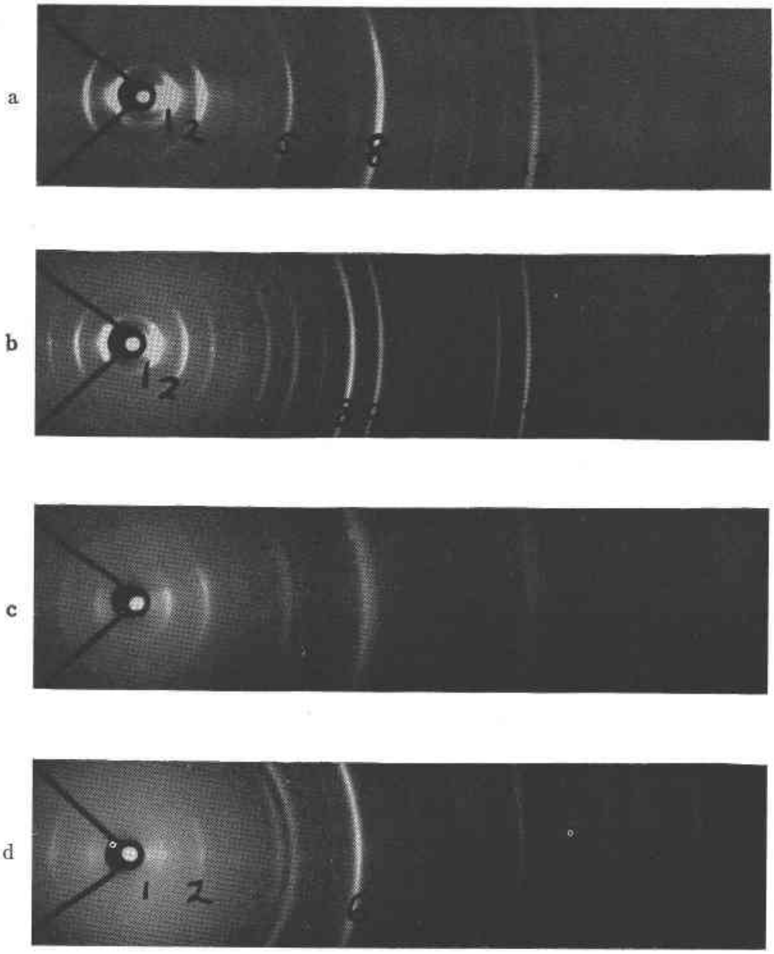

Fig. 1. X-ray powder diffraction diagrams of rectorite; (*a*) natural material, (*b*) complex with ethylene glycol, (*c*) natural material dried at 200° C, (*d*) natural material roasted at 600° C. Several important $00l$ orders are marked for reference.

tional origin. Rearrangement of signs to conform to an origin at the trough near $z=0.2$ affords the second pair of syntheses illustrated in Fig. 3. These traces are readily interpreted as contiguous pairs of three component, pyrophyllite-type layers, interleaved in the one case by double layers of water and in the other by double layers of ethylene glycol.

Rectorite does not swell or disperse in water. Specimens irradiated while bathed in water exhibit the same 25 Å periodicity as does the natural material. The molecular water layers are however removed by oven drying, after which a pyrophyllite-like dehydration product remains.

The condition of the dehydration product can be discussed in some

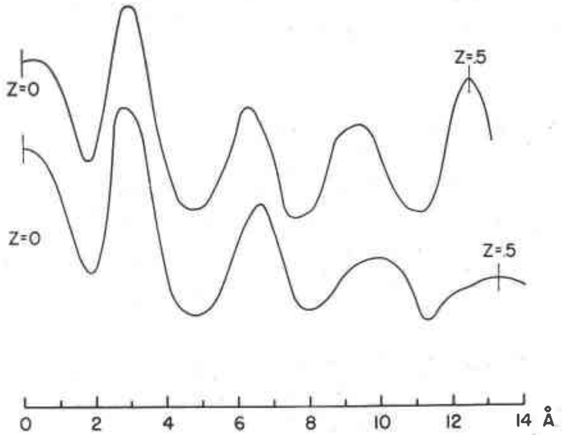

FIG. 2. Preliminary electron density projections from $z=0$ to $z=.5$ for rectorite (upper) and for the rectorite glycol complex (lower). The origin lies in an octahedral layer.

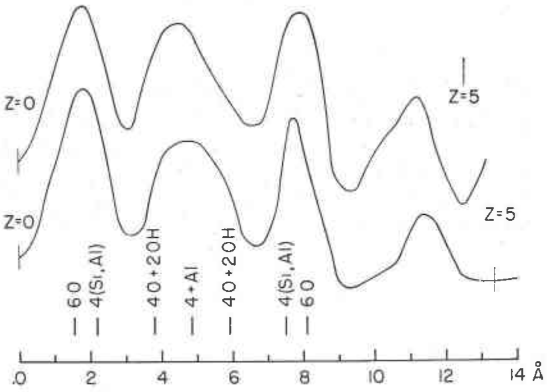

FIG. 3. Electron density projections from $z=0$ to $z=.5$ using interlayer origin for rectorite (upper) and for its glycol complex (lower). Levels of constituent atoms for the ideal structural model are marked.

detail. Thermal analysis (4) indicates that the molecular water is removed in three fractions. Two rather large unresolved endothermal effects center around 100° and 150° C., and a lesser ill defined trend extends to about 300° C. This character, together with the absence of swelling just noted, is suggestive of the vermiculite type of water layer rather than the montmorillonite type. Diffraction diagrams of partially dehydrated material, of which one is illustrated in Fig. 1, show distinct lack of homogeneity. Low orders are relatively sharp and at least approximately rational. Higher orders are complex and appear to consist of relatively sharp rational components with which there are associated more or less diffuse scattering maxima. For parallel to sub-parallel aggregates such as those with which we are here concerned, penetration of radiation into the aggregates is less for low angle diffraction than for the higher orders. The conclusion may therefore be made that for the par-

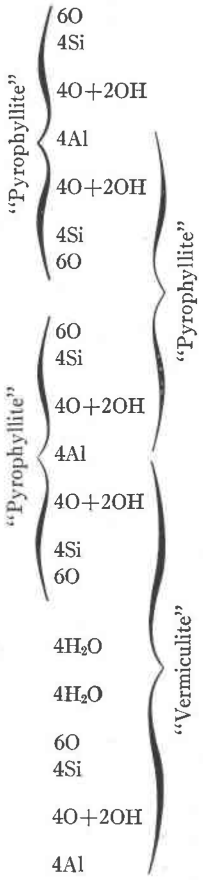

FIG. 4. Schematic representation of the sequence of atomic layers in rectorite.

tially dehydrated aggregates a surface skin of a certain number of dehydrated layers encloses interior layers with which water either may or may not still be associated, the interior sequence being a random array. The surface layer periodicity is about 19.5 Å and the interior average periodicity about 21 or 22 Å. Specimens heated to 600° C. have again become homogenous, and differ for the anhydrides prepared from montmorillonite or related minerals only in the persistence of a weak first order line for the doubled periodicity; that is about 19.5 Å. This order apparently signifies that the "pyrophyllite" neighbors which were originally together continue to stand closer to each other than to those neighbors which were previously separated by water, and are probably still separated by the not inconsiderable number of Na^+ ions of the cited analysis which were presumably associated with this water.

Chemically, this assemblage is in agreement with the analyses quoted by Dana if allowance be made for the 10 or 15 per cent of kaolinite which was probably present in the analyzed specimens. Optically, the refractivities are essentially the same as for Na-montmorillonite. The mean index would be about 1.50–1.52 with birefringence low. No observed index is cited by Dana.

In coordinating the *x*-ray diffraction information with the thermal character it can probably best be said that both alumino-silicate layers resemble pyrophyllite and that the water is in a condition comparable with that of the vermiculites. The structure then amounts to alternate piling of one pyrophyllite unit on one vermiculite unit. The schematic sequence is illustrated in Fig. 4. Alternative braces illustrate the ambiguity of origin which arises accordingly as one considers the layers to be geometrical or chemical entities.

The question of whether a study such as this can be said to validate the specific rank of rectorite as a mineral is probably one which should be deferred. The number of incompletely characterized doubtful species and variety names is too great to fairly estimate how many might be intergrowths of simpler systems.

REFERENCES

1. BRADLEY, W. F., Diagnostic criteria for clay minerals: *Am. Mineral.*, **30**, 704–713 (1945).
2. GRIM, R. E. & BRADLEY, W. F., The illite clays: *International Geological Congress*, vol. of titles and abstracts, London, pp. 127–128 (1948).
3. BRADLEY, W. F., Molecular associations between montmorillonite and some polyfunctional organic liquids: *J. Am. Chem. Soc.*, **67**, 975–981 (1945).
4. GRIM, R. E. & ROWLAND, R. A., Differential thermal analysis of clay minerals and other hydrous materials: *Am. Mineral.*, **27**, 811 (1942).