A MIXED-LAYER KAOLIN-CHLORITE STRUCTURE[1]

By

G. W. BRINDLEY and F. H. GILLERY
The Pennsylvania State University

ABSTRACT

A mineral of chlorite-type composition, classified as a daphnite, is shown to give a series of basal x-ray reflections which are incompatible with the normal chlorite structure. Fourier analysis indicates a modified distribution of Si and O atoms. A model is suggested in which some Si atoms are displaced and linked to the adjacent brucite-type layer, producing in effect kaolin-type structural units within the chlorite structure.

During the x-ray investigation of some iron-bearing chlorites, a mineral classified as a "daphnite" from Cornwall, England, was singled out as showing certain peculiarities. Both the positions and the intensities of the x-ray reflections were not those to be expected from a chlorite, and although a 14 A reflection was observed (which is characteristic of the layer-structure of chlorites) the general pattern resembled more closely that of an orthorhombic (or hexagonal) chamosite (Brindley, 1951). Chamosite and daphnite are scarcely distinguishable on chemical grounds (see Hallimond et al., 1939) but structurally chamosite belongs to the kaolinite-antigorite group of layer structures. The experimental observations, if restricted to finely powdered material, could have been interpreted superficially as arising from a chamosite-like mineral with a chlorite impurity. The material available for investigation, however, (which was kindly supplied by Dr. F. A. Bannister of the British Museum, cat. no. A.G.4) contained individual crystals suitable for single-crystal analysis. The rotation diagrams obtained were of a poorer quality than was expected from the appearance of the crystals under the microscope, but the existence of a 14 A basal 001 reflection was clearly confirmed, together with a number of higher odd-order reflections. The following cell dimensions were obtained:

$$a = 5.38_6, \quad b = 9.32_9, \quad c = 14.0_8 \text{ A}$$

The relative weakness of the odd-order as compared with the even-order reflections agrees qualitatively with the intensities to be expected from an iron-bearing chlorite, but difficulties were encountered when a quantitative evaluation was attempted. A chemical analysis of the mineral by Mr. R. F.

---

[1] This investigation was carried out in the Physics Laboratories, The University of Leeds, England.

Youell (University of Leeds, England), see Table 1, showed comparable percentages of FeO and Al_2O_3, whereas considerably more iron appeared to be necessary in the structure to account for the weak odd-order $00l$ reflections.

TABLE 1. — CHEMICAL ANALYSIS OF A MIXED-LAYER KAOLIN-CHLORITE TYPE MINERAL

(Analyst, Mr. R. F. Youell: Analysis made on 0.8 g of Material)

SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	H_2O+	H_2O-	Total
22.0	27.6	4.7	30.2	4.7	10.6	0.1	99.9

To investigate the problem in detail, structure factors $F(00l)$ were determined from both single-crystal and powder data, and one-dimensional Fourier syntheses were carried out. The signs of the Fourier coefficients were based in the first place on those calculated for a normal chlorite-type layer structure with the composition given in Table 1. The observed F values, obtained from the measured intensities in relative units, were scaled to the calculated F values by making $\Sigma F^2(00l)$ the same for the observed and calculated data. The agreement between these "observed" F values and those calculated for the normal chlorite-type structure, [see columns (2) and (3) of Table 2], is no more than qualitative, and is distinctly poor when considered quantitatively.

TABLE 2. — OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CHLORITE AND MIXED KAOLIN-CHLORITE TYPE STRUCTURES. THE VALUES GIVEN CORRESPOND TO THE HALF UNIT CELL.

1	2	3	4	5
	Chlorite structure		Mixed-layer structure	
$00l$	F. obs.	F calc.	F obs.	F calc.
001	7	+ 25	5	+ 7
002	123	+ 89	94	+ 79
003	20	— 59	15	— 16
004	130	+107	99	+111
005	21	+ 59	16	+ 15
006	12	+ 32	9	+ 7
007	13	— 33	10	— 8
008	9	— 14	7	— 2
009	8	+ 4	6	0
0010	42	+ 45	32	+ 35
0011	9	+ 10	7	+ 3
0012	30	+ 48	23	+ 22
0013	6	— 7	5	— 1
0014	21	+ 44	16	+ 15
0015	5	— 4	3	— 3
ΣF^2	36590		21160	

By applying the method of differential Fourier analysis, the source of the poor agreement was shown to arise not from the electron density produced by the octahedral cations Fe and Al, but from the distribution of the atoms in the Si-O hexagonal networks. In particular, the combined Si-O peak [which in one-dimensional syntheses of chlorites is never resolved, c.f. Brindley and Robinson (1951, p. 180)] was seen to be considerably lower and broader than is customary and to be partially filling the "gap" between the mica- and brucite-like components.

It is shown in Figure 1 how this displacement of the Si-O sheet may occur. Si atoms are moved from the centers of tetrahedral oxygen groups to corresponding positions on the opposite side of the oxygen sheet and are then linked to oxygen atoms in the adjacent brucite layer. In order that the new Si-O bonds shall be of the correct length, some displacement of the oxygen sheet is also required. The net result of these displacements is that a chlorite layer is converted to two kaolin-type[1] layers. Moreover, the kaolin-type layers, which have a polar structure, may point with equal probability in either direction along the *c*-axis. The resulting structure retains, therefore, a statistical symmetry center as regards the sequence of layers parallel to (001).

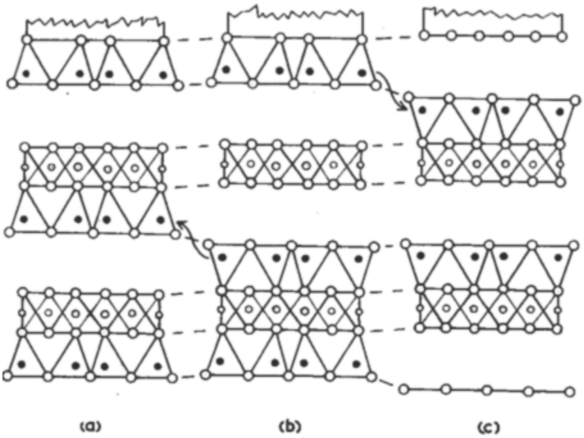

FIGURE 1.—Relation of chlorite structure (b) to kaolin-type structures (a) and (c); the arrows indicate the movements of the Si atoms required to change (b) into (a) or (c).

Structure factors calculated for a mixed-layer structure of this kind, in which the proportion of displaced to undisplaced Si atoms in any one layer is 1.4:2.6, are compared with the observed structure factors in columns (4) and (5) of Table 2; the observed factors are again scaled so that ΣF^2 has the same value as for the calculated factors. [It is for this reason

---

[1] The term signifies a layer comprising one tetrahedrally- and one octahedrally-coordinated sheet.

that the "observed" data in columns (2) and (4) have different values.] The agreement between columns (4) and (5) is markedly better than that between columns (2) and (3), especially as regards the lower odd-order reflections.

The model now suggested for a mixed-layer kaolin-chlorite structure differs from earlier suggestions which pictured single kaolin-type layers randomly interstratified with chlorite-type layers. The present model shows how the one type of layer may transform into the other laterally and may offer an explanation of the transformation of 7 A to 14 A layers discussed in this symposium by Nelson and Roy. Further details of this work will be published elsewhere.

We wish to thank Dr. F. A. Bannister for the material used in this investigation and the Department of Scientific and Industrial Research (Great Britain) for a grant to one of us (F. H. G.).

REFERENCES

Brindley, G. W. (1951) *The crystal structure of some chamosite minerals:* Min. Mag., v. 29, p. 502-525.

Brindley, G. W., and Robinson, K. (1951) *The chlorite minerals:* In *"X-ray identification and crystal structures of clay minerals,"* Mineralogical Society of Great Britain Monograph, chap. 6, p. 173-198.

Hallimond, A. F., Bannister, F. A., and Harvey, C. O. (1939) *On the relation of chamosite and daphnite to the chlorite group:* Min. Mag., v. 25, p. 441-465.

DISCUSSION

W. F. Bradley. — This mineral exemplifies a departure from the ideal chlorites which is encountered frequently among the chloritic sediments. A difference synthesis of the intensity deficiencies of the odd-order terms indicates that some silica tetrahedra point the wrong way, — just as the authors have deduced in this case.

R. A. Rowland. — (1) With low Mg content, of what does the "brucite" layer consist? (2) From the diagram this is essentially a lateral variation. Do you consider it also an 00*l* mixing?

G. W. Brindley. — The composition of the mineral deduced from its chemical analysis is as follows: —

$$(Mg_{0.76}Fe^{2+}_{2.74}\ Fe^{3+}_{0.38}\ Al_{2.12})\ (Si_{2.39}Al_{1.41})\ O_{10.33}\ (OH)_{7.68}$$

We have assumed the cations to be equally distributed among the octahedral positions, so that the cations in the brucite-type layer are: —

$$Mg_{0.38}\ Fe^{2+}_{1.37}\ Fe^{3+}_{0.19}\ Al_{1.06}$$

We consider that the mixing of kaolin-type and chlorite-type layers probably occurs both laterally and in the *c*-direction.

L. D. Swindale. — Brindley and Ali (1950, Acta Cryst.) have shown that Al-bearing chlorites have a higher temperature transformation chlorite→olivine; i.e., the Al stabilizes the chlorite layer. As this mineral has 30 percent FeO and as the specimen shows considerable stability in that the first order spacing does not show an increase in intensity even at 800°C is it possible that Fe^{2+} occurring in octahedral layers and in brucite layers would be sufficient to give F values of similar nature to those observed?

G. W. Brindley. — The calculations take account of the Fe^{2+} in the octahedral layers and show that the intensities of the odd order reflections cannot be interpreted quantitatively solely in terms of the Fe content of these layers.

The fact that on heating this mineral to around 800°C no enhancement of the 001 reflection is observed such as is commonly found with chlorites (including iron-bearing chlorites) may perhaps be attributed to the large proportion of kaolin-type layers in place of the usual regular alternation of brucite and mica-type layers.