THE STRUCTURE OF CHLORITOID[1]

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ABSTRACT

A summary is given of a structure analysis of chloritoid. The structure contains continuously linked octahedral sheets cross-linked by discrete SiO_4 units. Comparisons are made with mica structures and with corundum.

INTRODUCTION

The presentation of a paper on chloritoid in a symposium on clay minerals requires justification. Physically and chemically, chloritoid closely resembles the mica minerals and it is commonly placed by mineralogists in the category of brittle micas. In a recent note (Brindley and Harrison, 1952) it has been pointed out that chloritoid appears to have a new type of layer lattice structure and subsequent work has confirmed this conclusion. Since the majority of clay minerals have layer lattice structures, it is not altogether out of place to draw the attention of clay mineralogists to this new type of structure and to suggest that other layer lattices may still remain to be discovered. So far as the writers are aware, chloritoid has not yet been discovered as a clay mineral.

The first x-ray study of the mineral was carried out by Machatski and Mussgnug (1942), who made rough measurements of the lattice dimensions. They proposed a structural arrangement on the basis of the $00l$ reflections which has not been confirmed by the present measurements. Milne (1949) has given a comprehensive summary of geological, optical, and chemical data for chloritoid and from a careful x-ray analysis has established the unit cell dimensions and probable space group; these are confirmed by the present work. A further recent paper (Hietanen, 1951), summarizes data on the orientation of the optic axes and lists a table of x-ray powder spacings.

The unit cell dimensions and compositions of muscovite, margarite (a typical member of the brittle mica group), and chloritoid are compared in Table 1. For convenience of comparison the composition of chloritoid is expressed in a form similar to that of the other two.

It will be seen that whereas the composition of margarite differs from that of muscovite only in that 1Ca + 1Al occurs in place of 1K + 1Si,

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

TABLE 1. — COMPARISON OF COMPOSITIONS AND CELL DIMENSIONS OF SOME MICA MINERALS

Composition	a	b	c	β	Space group
Muscovite $KAl_2(AlSi_3O_{10})(OH)_2$	5.18 A	9.02 A	20.04 A	95°30′	C2/c
Margarite $CaAl_2(Al_2Si_2O_{10})(OH)_2$	5.12 A	8.90 A	(9.73) A	100° 8′	....
Chloritoid $(Fe^{2+},Mg)_2Al_2(Al_2Si_2O_{10})(OH)_4$	9.52 A	5.47 A	18.19 A	101°39′	C2/c

in chloritoid there are *two* divalent (Fe^{2+}, Mg) cations + 1Al in place of 1K + 1Si and an additional 2(OH) to maintain the neutrality.

The *a* and *b* parameters of chloritoid are considerably greater than the corresponding values in muscovite and margarite, and are interchanged. Indeed the increase is so great that on the assumption of a mica-like structure it would necessitate a considerable distortion of the usual Si-O framework. The *c* parameter of chloritoid is, however, considerably diminished.

The structure proposed for chloritoid by Machatski and Mussgnug (1942) was based on that of muscovite, K being replaced by 1(Fe^{2+}, Mg) together with 2(OH) forming a close-packed arrangement between the silicate layers. The remaining 1(Fe^{2+}, Mg) joined 2Al in the octahedral positions within the silicate layers. This structure was postulated on the basis of the 00*l* intensities alone, and was not tested in detail.

THE STRUCTURE DETERMINATION

The investigation was carried out using single-crystal oscillation and Weissenberg photographs of a sample of chloritoid from Point des Chats, Île de Groix, France, kindly supplied by Dr. F. A. Bannister of the British Museum, catalogue no. B.M. 1908, 362.

The cell dimensions obtained are those of Table 1 and agree with the values of Milne to within the limits of experimental error.

Structure amplitudes for the 00*l* reflections calculated from the structure of Machatski and Mussgnug gave poor agreement with the observed values. However, the signs of the amplitudes were assumed to be correct and a one-dimensional Fourier projection of the electron density on the normal to the (001) plane, or basal cleavage plane, was carried out. This, when compared with the one-dimensional projection for muscovite given by Jackson and West (1930) showed the electron content of the "Si" peak to be about one-half its usual value, namely, 2Si in place of the usual 4(Si, Al) at this level in the structure.

The peak heights also suggested 2(Fe^{2+}, Mg) + 1Al within the silicate sheets, in the octahedral positions, and 3 Al between the sheets, where K occurs in muscovite. $F(00l)$'s, the structure amplitudes for the 00*l* reflections, calculated on this basis, agreed well with the observed values.

A Patterson projection, and Fourier projections of the electron density on the (010) plane, using the observed *h0l* reflections, led to the idealized structure shown in Figure 1(a).

Attention was then turned to the *y* parameters of the atoms. In particular it was necessary to postulate a satisfactory arrangement of the atoms forming layer L_2 (Fig. 1,a). Figure 1(c) shows an arrangement of L_2 which conforms to the space group and the (010) projection and is reasonable on spatial grounds. From this it was possible to build up a structure which fitted the unit cell and was in agreement with the (010) projection. This structure viewed along the *a*-axis is shown in Figure 1(b).

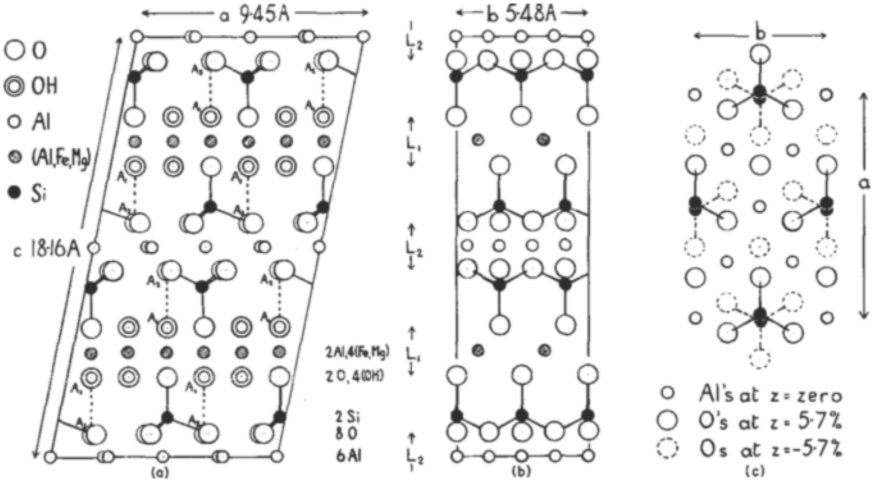

FIGURE 1. — (a) — The structure of chloritoid projected on (010). (b) The structure viewed along the *a* axis. (c) Layer L_2 viewed normal to *ab*.
(From Acta Cryst. v. 5, p. 698, 1952)

Refinement of the structure was carried out by means of Fourier projections parallel to *b* using the *h0l* reflections, and parallel to *a* using the *0kl* reflections. The ultimate agreement obtained between observed and calculated structure amplitudes for 118 *0kl* reflections, 215 *h0l* reflections, and 90 *hk0* reflections was very satisfactory, the values of the reliability index $R = (\Sigma|F_o\text{-}F_c|)/\Sigma|F_o|$ for the three zones being 0.143, 0.201, and 0.250 respectively.

Although no discrimination between O and (OH) is possible by means of x-rays, designation of the anions as in Figure 1(a) has been carried out on the basis of an optimum balancing of the electrostatic valencies. The (OH)'s labelled A_1 in the octahedral layer lie directly above or below O's labelled A_2 at the center of the hexagonal rings of O's forming the bases of the Si-O tetrahedra, and hydrogen bonds would be expected to occur between them as shown by the broken lines. The $A_1 \ldots A_2$ separation obtained from the (010) projection is about 2.6 A which accords with OH . . . O distances in other ionic crystals.

Though the mineral structure has been approached from the standpoint of a mica, it is more convenient to consider the structure as made up of two close-packed octahedral layers, L_1 and L_2 (Fig. 1(a) and (b)) joined by Si atoms in tetrahedral coordination and by hydrogen bonds. Layer L_1 is of the trioctahedral type found in brucite, whilst layer L_2 (Fig. 1(c)) resembles that found in corundum, for which the repeat dimensions within an Al-O sheet (9.50 and 5.48 A; Bragg, 1937, p. 94) are almost identical with the corresponding dimensions for chloritoid. The Si atoms do not form continuous silicate sheets as in the micas, but occur within distinct (SiO_4) groups.

We thus have an explanation of the increase in the *a* and *b* dimensions when compared with the micas, for, whereas in the micas the continuous silicate sheets set the scale of the dimensions, in chloritoid it is the corundum-type layer which does this. The decrease in *c* is a result of the close-packing of the O atoms at the bases of the Si-O tetrahedra to provide spaces with 6-fold coordination for the reception of the Al ions. This is in contrast to the direct superposition of the hexagonal rings of O's in muscovite to give spaces with 12-fold coordination in which the K ions are located.

As regards the cleavage of the mineral, it would hardly be expected to take place within the corundum-type layer. It might possibly occur within the brucite layer, where the bonding forces are weaker, but the most probable position would seem to be between the layers L_1 and L_2, where there are only 2 Si-O bonds + 2 H-bonds per unit cell level.

SUMMARY

The crystal structure of chloritoid has been determined using the intensities of reflections occurring on single crystal x-ray photographs. Progressive refinement of the structure by Fourier syntheses has led to good agreement between observed and calculated structure amplitudes for over 400 *0kl, h0l,* and *hk*0 reflections.

Chloritoid is seen to be a layer silicate structure of a new type.

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