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The structure of chloritoid.

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Two recent publications (Milne, 1949; Hietanen, 1951) on chloritoid prompt us to make a preliminary statement of a structure analysis on which we are engaged. The general properties of the mineral and its composition, ideally $4[(\mathrm{Fe''}, \mathrm{Mg})_2\mathrm{Al}_2(\mathrm{Al}_2\mathrm{Si}_2\mathrm{O}_{10})(\mathrm{OH})_4]$ for a monoclinic cell with $a = 9{\cdot}45$, $b = 5{\cdot}48$, $c = 18{\cdot}16$ Å, $\beta = 101°\ 30'$, and space group *Cc* or *C*2/*c* (Milne, 1949), suggest similarity to muscovite with cell composition $4[\mathrm{KAl}_2(\mathrm{AlSi}_3\mathrm{O}_{10})(\mathrm{OH})_2]$. Machatski & Mussgnug (1942), using 00*l* reflexions, put 1(Fe″, Mg) with 2(OH) in a close-packed arrangement where K occurs in muscovite, and 1(Fe″, Mg) with 2Al in the octahedral positions.

Using chloritoid from Île de Groix, France, (British Museum, 1908, 362), kindly supplied by Dr F. A. Bannister, we have verified Milne's cell dimensions and by a Wilson statistical treatment of (*h*0*l*) reflexions shown the space group to be *C*2/*c*.

Taking the chemical analysis quoted by Milne (1949, analysis 5) of chloritoid from the same locality, we could not explain satisfactorily the (00*l*) reflexions on the basis of Machatski & Mussgnug's structure or any simple variant of it. A Fourier synthesis using ten orders of (00*l*), when compared with similar syntheses for muscovite, vermiculite and penninite, showed the electron content of the 'Si' peak to be about one-half its usual value, namely, 2Si in place of the usual 4Si at this level in the structure. The peak heights also suggested 2(Fe″, Mg)+1Al within the silicate sheets and 3Al between the sheets where K normally occurs. *F*(00*l*)'s calculated on this basis agree well with observed values.

Patterson and Fourier projections on (010) have led to the structure depicted in Fig. 1(*a*). Observed and calculated *F*(*h*0*l*)'s have given a reliability index $R = (\Sigma|F_o - F_c|) \div \Sigma|F_c|$ of 34%. A structural arrangement viewed along the *a* axis, conforming to the space group and the (010) projection and reasonable on spatial grounds, is shown in Fig. 1(*b*). Observed and calculated *F*(*hk*0)'s give $R = 31\%$.

Although no discrimination between O and (OH) is possible by means of X-rays, a tentative designation of the anions has been attempted (Fig. 1(*a*)) on the basis of an optimum balancing of the electrostatic valencies. The (OH)'s labelled A_1 lie directly above or below O's labelled A_2, and hydrogen bonds would be expected to occur between them as shown by broken lines. The $A_1 \cdots A_2$ separation obtained from the (010) projection is about 2·5 Å, which though of limited accuracy agrees with OH ⋯ O distances in other ionic crystals (Davies, 1946). If the H is more closely associated with A_1 than A_2 then no ion in the structure has its electrostatic valency unbalanced by more than one-sixth of a unit.

It is seen that the structure is made up of two close-packed octahedral layers, L_1 and L_2, joined by Si atoms in tetrahedral coordination and by hydrogen bonds. Layer L_1 is essentially a hydroxide layer, 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 Å, Bragg, 1937, p. 94) agree closely 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, and the structural formula may now be written $[(\mathrm{Fe''}, \mathrm{Mg})_2\mathrm{Al}](\mathrm{OH})_4\mathrm{Al}_3[\mathrm{O}_2(\mathrm{SiO}_4)_2]$.

This departure from a normal mica arrangement offers an explanation for the increase of the *a* and *b* parameters over those of micaceous minerals with continuous silicate sheets and similar (Fe″, Mg) content (e.g. biotite and bavalite).

It must be emphasized that the present X-ray evidence for the structure is good agreement for (00*l*) reflexions and moderate agreement for (*h*0*l*) and (*hk*0) reflexions Confirmation will be sought by more accurate ex.

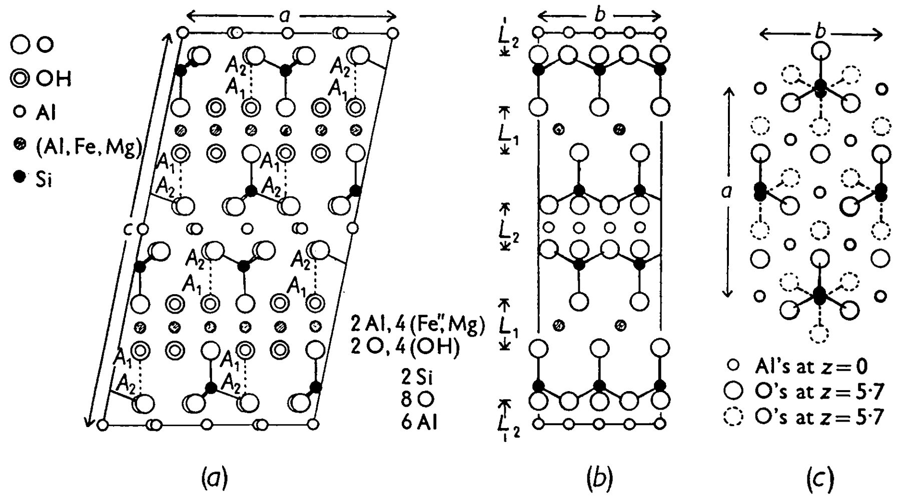

Fig. 1. (*a*) The structure of chloritoid projected on (010). (*b*) The structure viewed along the *a* axis. (*c*) Layer L_2 viewed normal to *a b*.

perimental work using Mo $K\alpha$ radiation to reduce the large absorption corrections involved in our work with Cu $K\alpha$ radiation.

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Diffuse scattering of sericite.

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Sericite is a mineral of the mica group, the structure of which is said to be of the muscovite type. As it always occurs in a powder state in nature, only the X-ray powder method has been used for the study of its crystal structure. Recently, however, we have obtained X-ray fibre diagrams of various Japanese sericites by passing the X-rays parallel to thin films formed by drying water suspensions of these minerals. These diagrams correspond to rotation photographs obtained by rotating a single crystal about the normal to the $a\,b$ plane.

With many sericites it was observed that considerable diffuse scattering took place along the innermost row lines (with indices $(11l)$, $(02l)$) and other similar row lines with $k \neq 3n$ (where n is integer), while those with $k = 3n$ were relatively sharp. These effects indicate that in sericite, as in many other clay minerals, there is considerable random displacement of layers by multiples of $\frac{1}{3}b$ parallel to the b axis.

Using many Japanese sericites, we have found a wide range of variation in the degree of disorder, as shown in the following scheme:

Nearly ordered
↓
Partially disordered
with random displacements of $\pm\frac{1}{3}b$
↓
Fully disordered
with random displacements of $\pm\frac{1}{3}b$
↓
Partially random layer structure

Details will be reported in the near future.

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