

alignment of low-resolution structural features such as solvent regions, helices, *etc.* It is interesting to note that many of the very strong reflections at about 12 Å are of the $0kl$ class. Thus, a 180° rotation about an axis in the $0kl$ photograph (and therefore lying in a reciprocal-lattice mirror plane) will cause a strong reflection to fall on its Friedel mate or on some other strong reflection in the same zone.

The most reasonable interpretation of the rotation function indicates that flavocytochrome b_2 has 222 symmetry. This is in agreement with chemical evidence that the four subunits are identical, or nearly so (Jacq & Lederer, 1974). Furthermore, powder diffraction studies of another crystal form of flavocytochrome b_2 indicate a tetragonal lattice in which the molecule is located on a point of crystallographic 222 symmetry (Monteilhet & Risler, 1970).

The rotation-function result will be useful in the structural analysis of flavocytochrome b_2 . First, it can be used to help locate heavy atoms in difference Patterson maps (Argos & Rossmann, 1974). Second, it can aid in the search for a cytochrome b_5 -like structure in the flavocytochrome b_2 crystal. If the b_5 and b_2 molecules are sufficiently alike, the three-dimensional cross rotation function should show peaks when the two molecules are aligned. These peaks should obey the same symmetry as the flavocytochrome b_2 molecule itself. We are presently continuing these studies along these lines.

This work has been supported by National Institutes of Health grant No. 5R01 GM 20530 and National Science Foundation grants Nos. BMS-74-03059 and PCM 76-82053.

References

ARGOS, P. & ROSSMANN, M. G. (1974). *Acta Cryst.* **A30**, 672–677.

Acta Cryst. (1979). **A35**, 416–421

CROWTHER, R. A. (1972). In *The Molecular Replacement Method*, edited by M. G. ROSSMANN. New York: Gordon and Breach.

CZERWINSKI, E. W., BETHGE, P. H., MATHEWS, F. S. & CHUNG, A. (1977). *J. Mol. Biol.* **116**, 181–187.

CZERWINSKI, E. W. & MATHEWS, F. S. (1974). *J. Mol. Biol.* **86**, 49–57.

GUIARD, B., GROUDINSKY, O. & LEDERER, F. (1974). *Proc. Natl Acad. Sci. USA*, **71**, 2539–2543.

GUIARD, B. & LEDERER, F. (1976). *Biochimie*, **58**, 305–316.

JACQ, C. & LEDERER, F. (1974). *Eur. J. Biochem.* **41**, 311–320.

JOHNSON, J. E., ARGOS, P. & ROSSMANN, M. G. (1975). *Acta Cryst.* **B31**, 2577–2583.

LABEYRIE, F., GROUDINSKY, O., JACQUOT-ARMAND, Y. & NASLIN, L. (1966). *Biochim. Biophys. Acta*, **128**, 482–503.

LENHERT, P. H. (1975). *J. Appl. Cryst.* **8**, 568–570.

MARSH, D. J. & PETSKO, G. A. (1973). *J. Appl. Cryst.* **6**, 76–80.

MATHEWS, F. S., ARGOS, P. & LEVINE, M. (1971). *Cold Spring Harbor Symp. Quant. Biol.* **36**, 387–395.

MATHEWS, F. S. & LEDERER, F. (1976). *J. Mol. Biol.* **102**, 853–857.

MONTEILHET, C. & RISLER, J. L. (1970). *Eur. J. Biochem.* **12**, 165–169.

OLIVE, J., BARBOTIN, J. N. & RISLER, J. L. (1973). *Int. J. Peptide Protein Res.* **5**, 219–228.

PAJOT, P. & CLAISSE, M. (1974). *Eur. J. Biochem.* **49**, 275–285.

RAE, A. D. (1965). *Acta Cryst.* **19**, 683–684.

ROSSMANN, M. G. & BLOW, D. M. (1962). *Acta Cryst.* **15**, 24–31.

ROSSMANN, M. G., FORD, G. C., WATSON, H. C. & BANASZAK, L. J. (1972). *J. Mol. Biol.* **64**, 237–249.

TOLLIN, P. & ROSSMANN, M. G. (1966). *Acta Cryst.* **21**, 872–876.

WYCKOFF, H. W., DOSCHER, M., TSENOGLOU, D., INAGAMI, T., JOHNSON, L. N., HARDMAN, K. D., ALLEWELL, N. M., KELLY, D. M. & RICHARDS, F. M. (1967). *J. Mol. Biol.* **27**, 563–578.

Topotactical Dehydration of Chloritoid

BY D. A. JEFFERSON AND J. M. THOMAS

Department of Physical Chemistry, University Chemical Laboratories, Lensfield Road, Cambridge, CB2 1EP, England

(Received 15 November 1978; accepted 21 December 1978)

Abstract

The dehydration of the silicate mineral chloritoid in air and *in vacuo* has been investigated by single-crystal X-ray methods and high-resolution electron microscopy.

0567-7394/79/030416-06\$01.00

Vacuum dehydration yields an amorphous product, but the reaction in air produces a topotactical transformation to an anhydrous structure with an alteration in the stacking arrangement and symmetry. To be consistent with these observed facts, considerable

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modification to one component of the structure is necessary, a structural model being proposed for the anhydrous variant.

Introduction

Chloritoid is an unusual orthosilicate, having more in common with the layer silicates, such as the micas, than the more conventional orthosilicates, typified by the olivines. The structure of chloritoid (Harrison & Brindley, 1957) is shown in Fig. 1. The central feature of one layer, namely an infinite two-dimensional network of edge-sharing metal-oxygen/hydroxyl octahedra, designated L_1 by the above authors, is analogous to the corresponding component of the mica layer. However, whereas the cation site occupancy of this component in micas ranges from two-thirds to complete filling, in chloritoid all available sites are occupied. The principal difference between the two structures, however, lies in the arrangement of the SiO_4 tetrahedra. In micas these constitute an infinite array of six-membered rings, complete layers being bonded to one another (except in talc and pyrophyllite) by large cations (Na^+ , K^+ , Ca^{2+}) lying between the six-membered rings on adjacent layers, whereas in chloritoid the tetrahedra are completely isolated, individual layers being linked by a second network of octahedra, designated L_2 , having Al^{3+} ions in only three-quarters of available sites. Octahedral vacancies in the L_2 component are arranged such that the SiO_4 tetrahedra share faces only with unoccupied octahedra. Hydrogen bonds between O atoms on L_2 and OH groups on L_1 provide a secondary form of inter-layer binding.

Chloritoid exhibits polytypism, the determined structure being a two-layer monoclinic variant, but a simpler, one-layer triclinic polytype has been reported by Halferdahl (1956). More recently, a second two-layer monoclinic form and a three-layer structure have

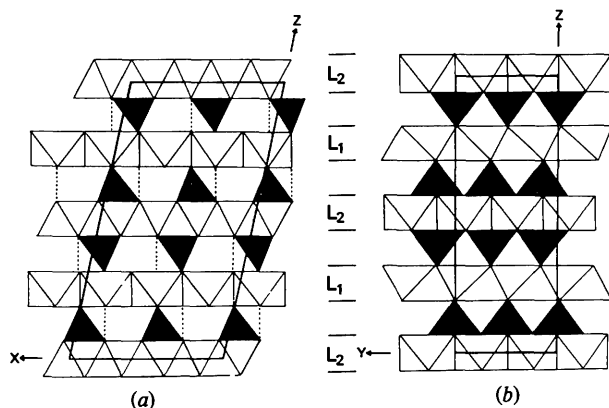
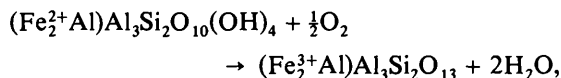


Fig. 1. The structure of $2M_2$ chloritoid, indicated in terms of coordination polyhedra. (a) Projection on to (010). (b) Projection along [100].

been noted during an electron-optical investigation (Jefferson & Thomas, 1978). The possibility of further, more complex polytypes cannot be ruled out. The phenomenon of polytypism in chloritoid has also been discussed by von Bachmann (1956) in the context of a dehydration study. Using X-ray powder diffraction methods, von Bachmann found that, upon dehydration, a sample of the two-layer monoclinic polytype of chloritoid appeared to undergo a structural transformation to a one-layer variant with a slightly increased interlayer spacing. von Bachmann proposed a reaction to explain this dehydration in air,



and suggested that the increase in interlayer spacing arose from the destruction of the hydrogen bonds between layers. He also proposed a tentative structure for the air-dehydrated structure (Fig. 2). Although the basic features of this structure appeared to be correct, the reliance upon X-ray powder diffraction measurements made determination of the exact unit cell somewhat difficult, and there were many unexplained lines in the diffraction diagram of the anhydrous form, largely due to the fact that the second two-layer monoclinic structure, which was at that time unsuspected, was the principal polytype present. To investigate the reaction more fully, single-crystal studies were required, and such an examination, together with electron-optical observations, is described.

Experimental

The specimen was from Ile de Groix, France, the same as that studied by Harrison & Brindley (1957). Two groups of single crystals were examined by X-ray precession methods, six levels of reciprocal space, namely ($h0l$), (hhl), ($hh'l$), ($0kl$), ($3h,h,l$) and ($3h,\bar{h},l$) being recorded. These confirmed the original unit cell of Harrison & Brindley (Table 1), the polytype exhibited

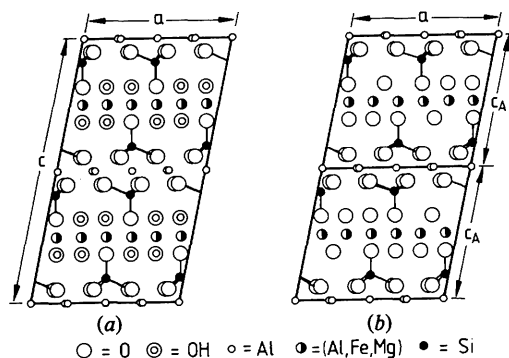


Fig. 2. (a) Structure of $2M_2$ chloritoid, projected on to (010) compared with (b) the structure of the anhydrous variant (after Bachmann).

being designated $2M_2$ (Jefferson & Thomas, 1978). ($h0l$) and ($0kl$) levels are illustrated in Fig. 3. Both sets of crystals were then subjected to dehydration treatment. One set was heated in an open crucible in air at approximately 973 K for several hours, to ensure

Table 1. Cell constants of the parent $2M_2$ chloritoid and the triple hexagonal cell in the dehydrated variant

Untreated chloritoid type $2M_2$	$a = 9.47 \pm 0.03 \text{ \AA}$ $b = 5.48 \pm 0.03$ $c = 18.14 \pm 0.05$ $\beta = 101^\circ 39' \pm 06'$
Dehydrated chloritoid type $3R$ (X-ray)	$a = 5.79 \pm 0.08 \text{ \AA}$ $c = 28.09 \pm 0.08$
Dehydrated chloritoid type $3R$ (electron diffraction)	$a = 5.81 \pm 0.05 \text{ \AA}$ $c = 28.06 \pm 0.06$

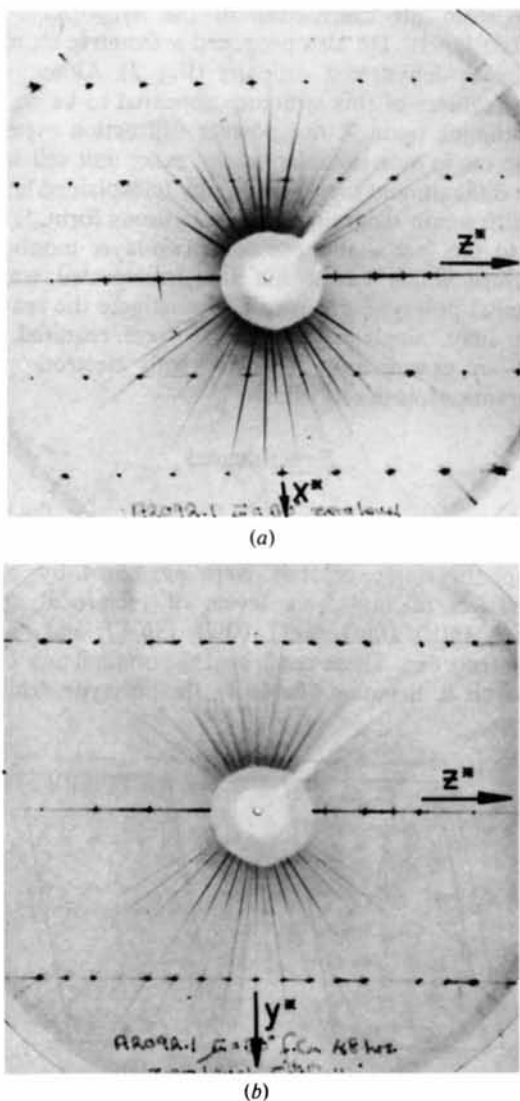


Fig. 3. (a) ($h0l$) precession photograph of an unreacted chloritoid crystal. (b) ($0kl$) level of the same crystal. (Ni-filtered Cu radiation, $\mu = 30^\circ$, $F = 60 \text{ mm.}$)

complete dehydration, and subsequently re-examined, all six reciprocal-lattice levels being again recorded. Examples of the second set were given identical heat treatment, but in a vacuum furnace at a partial oxygen pressure of approximately $1.3 \times 10^{-5} \text{ Pa}$. In each case, no change in the crystal morphology was noted, although a pronounced colour change from transparent pale green to nearly opaque black-brown was observed. In addition, finely powdered samples were given the same treatment and examined, after deposition on to holey carbon support films, in a Philips EM300 electron microscope fitted with a goniometer stage. Lattice images and electron diffraction patterns were observed and recorded.

Results

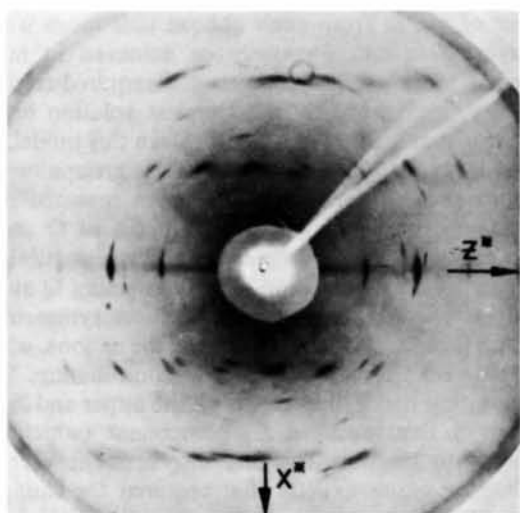
Both single-crystal X-ray and electron-optical studies of the vacuum-dehydrated chloritoid indicated a complete absence of crystallinity, the product appearing, even at the highest resolution, completely amorphous. Further heat-treatment studies of the products of this vacuum dehydration will form part of a later publication. In contrast, the single-crystal X-ray studies of the air-dehydrated product indicated a topotactic dehydration/oxidation reaction, as inferred by von Bachmann, although the reciprocal lattice maxima corresponding to the product phase were somewhat diffuse, suggesting only short-range order. ($h0l$) and ($0kl$) precession photographs of an air-dehydrated crystal are illustrated in Fig. 4. Although some maxima resulting from misoriented fragments are present, those corresponding to the main reaction product clearly predominate, but traces of the $2M_2$ monoclinic reciprocal lattice remain, indicating that the reaction within this particular crystal had not quite proceeded to completion.

In the air-dehydrated product, the increase in inter-layer spacing reported by von Bachmann was readily noted, the measured value being 9.36 \AA , compared with 8.88 \AA in the untreated chloritoid. Owing to the extremely diffuse nature of the reciprocal lattice maxima, it was difficult to ascertain whether the spacing of reciprocal lattice rows parallel to z^* had altered, but within the limits of experimental error, a slight decrease in this spacing was noted, corresponding to an expansion within the plane of the layers. The most obvious change, however, lay in the alteration of symmetry. Whereas the initial $2M_2$ structure gives a clearly definable monoclinic pattern of maxima, with an apparent halving of c evident only in the ($h0l$) section, in the air-dehydrated product the apparent c spacing exhibited in all reciprocal lattice sections corresponded to only a single layer. Furthermore, the product displayed trigonal symmetry, and measurement of reciprocal lattice maxima indicated a rhombo-

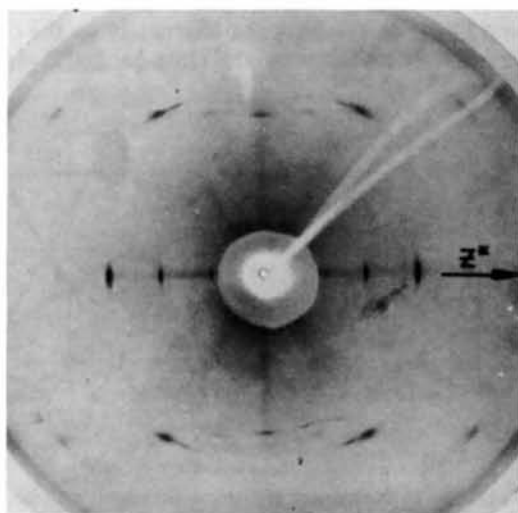
hedral unit cell containing three of the dehydrated layers. Lattice constants for this unit cell are listed in Table 1.

In contrast to the diffuse reciprocal lattice maxima observed in the X-ray studies, electron diffraction patterns recorded from the dehydrated chloritoid appeared remarkably sharp, indicating a relatively high degree of crystallinity, although overall crystallite dimensions were comparatively small, few being >1000 Å across. Rhombohedral cell dimensions deduced from patterns of this type (Fig. 5*a*) are also listed in Table 1, and are probably more reliable than those resulting from the X-ray study. In addition to selected-area diffraction patterns, lattice images were recorded from selected flakes, one of which is illustrated in Fig. 5(*b*). All images of this type showed perfectly sharp fringes, extending throughout the crystals with, somewhat

surprisingly, no indications of any point defects, dislocations or stacking faults so frequently found in the untreated chloritoid. Indeed, the only departure from true crystal perfection observed in these lattice images was a slight mis-orientation of the layers at the periphery of some crystals, as shown circled in Fig. 5(*b*), but these were comparatively few. The marked differences in the crystallinity of specimens examined by single-crystal X-ray methods and electron diffraction probably arose from the extremely fine-grained nature of the latter specimens, which could be expected to facilitate a more complete dehydration reaction than that in the macroscopic crystals used for the X-ray work. Indeed, in the specimens used for electron diffraction, the dehydration mechanism appeared to proceed so rapidly that it proved impossible to find any partially dehydrated crystals, even with greatly reduced heating times.

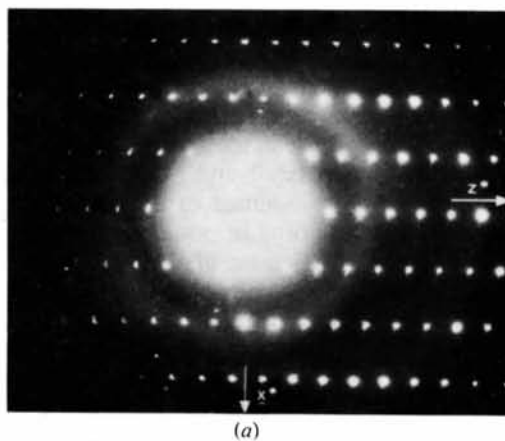


(a)

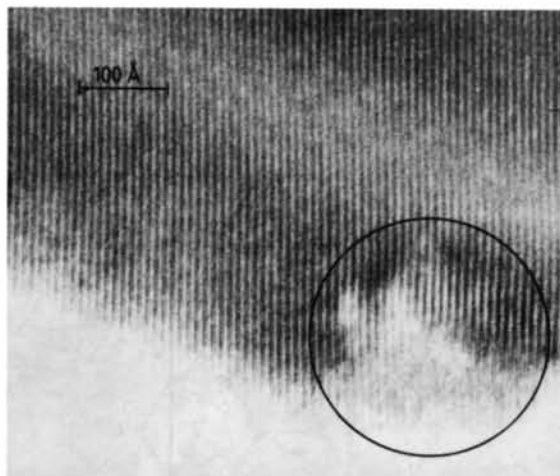


(b)

Fig. 4. (a) and (b). The same reciprocal lattice levels as in Fig. 3 after dehydration in air at 973 K.



(a)



(b)

Fig. 5. (a) Selected-area electron diffraction pattern from a small fragment of dehydrated chloritoid. (b) The corresponding high-resolution image, indicating near-perfect structural regularity. A slight misorientation of the layers at the margin of the crystal is circled.

Discussion

The possibilities for polytypism in chloritoid have been enumerated by Jefferson & Thomas (1978), and only a brief discussion will be given here. As with the structures, polytypism in chloritoid shows similarities to that in micas, but with distinct differences. The principal offset or displacement of structural layers with respect to their predecessors occurs at the upper and lower surfaces of the L_1 octahedral component. Owing to the close-packed nature of the O atoms and OH groups in L_1 , SiO_4 tetrahedra above and below it cannot superimpose, and one of six possible lateral displacements must exist between them. Vectors corresponding to these displacements are illustrated in Fig. 6. Various combinations of displacements give rise to different polytypes, as in micas. One complicating factor in chloritoid which does not occur in micas arises from the slight lateral displacement existing at the level of the L_2 component, thus precluding the possibility of having certain rows in reciprocal space which are identical for various polytypes, as found in micas unless 180° rotation of successive octahedral components takes place. However, when considering the various polytypes possible in chloritoid, the second source of lateral displacement is very small and can consequently be neglected, or at least assumed to be the same for all layers. It should be borne in mind, nevertheless, that variations in the arrangement of these minor displacements could give rise to subtle variations in the unit-cell dimensions of apparently identical polytypes.

Owing to the monoclinic or triclinic symmetry displayed by previously studied varieties of chloritoid, all structures have been described in terms of a centred rectangular lattice mesh within the plane of the layers (Fig. 7a). Where it is necessary to describe trigonal or rhombohedral symmetry, as in the air-dehydrated material, such a mesh can no longer be used unless

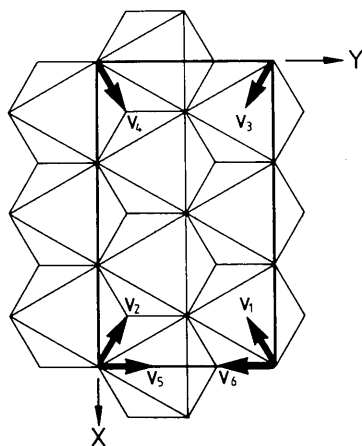


Fig. 6. The six possible layer displacement vectors in the unit cell of untreated chloritoid.

additional reciprocal lattice rows appear parallel to z^* , and the smaller, oblique mesh indicated in Fig. 7(a) must be employed. This immediately poses problems in describing the rhombohedral stacking observed in the dehydration product in terms of the accepted displacement vectors in chloritoid, as comparison of Figs. 6 and 7(a) indicates that none of the accepted displacement vectors corresponds to a displacement of $(2a/3, b/3)$ in the small oblique mesh. In structural terms, rhombohedral stacking corresponds to a vector displacement equivalent to that between anions on the *same* side of the central L_1 component, rather than *opposite* sides, and to produce this form of stacking, some drastic reorganisation of the L_1 component is required.

According to the dehydration/oxidation equation given by von Bachmann, one O atom and four protons are lost from each $(\text{Fe}_2\text{Al})(\text{Al}_3\text{Si}_2\text{O}_{10})(\text{OH})_4$ unit of chloritoid, and this is equivalent to the removal of this number of atoms from each oblique unit mesh within the layer. This can obviously be achieved in many ways, but most will not produce the required trigonal symmetry, and probably the simplest solution to the problem is that indicated in Fig. 7(b). In this model, the double layer of O atoms and OH groups which constitute the L_1 component have been replaced by a single, approximately close-packed plane of O atoms with the cations in the *same* plane. Two possibilities then exist for the disposition of the remaining O atoms in this modified L_1 component, the most symmetrical being to place these above and below the cations, which then assume a trigonal-bipyramidal coordination. Vector separation between O atoms on the upper and lower surfaces of this modified L_1 component (which are equivalent to possible stacking displacement vectors) can then be either exactly that required for rhombohedral stacking or, alternatively, zero. Fig. 7(b), however, indicates a second arrangement, in which the remaining O atoms are disposed alternately on the upper and lower surfaces of the central close-packed layer, but

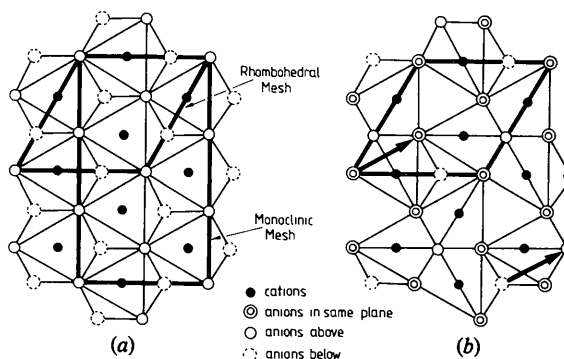


Fig. 7. (a) An L_1 component of natural chloritoid, indicating the lattice meshes used for the monoclinic and rhombohedral unit cells. (b) The corresponding component in the anhydrous structure, showing the only possible vector displacement between O atoms on the upper and lower surfaces.

never above or below the cations. This second arrangement would again produce five-coordinated cations, but the disposition of O atoms would be of a distorted, square-pyramidal type. In addition, in this latter model, the *only* vectors between O atoms on the upper and lower surfaces of the modified L_1 component would correspond to rhombohedral stacking. As the more symmetrical first model, in theory, could give rise to two possible displacement vectors and hence the potential for stacking mistakes to be developed, and owing to the fact that such mistakes were never observed in practice, experimental evidence would favour the second of these two models. Both models would give rise to an increase in the interlayer spacing, in addition to any such increase resulting from the destruction of hydrogen bonds, although any increase could more readily be accepted in the second model where the cation coordination in L_1 was less symmetrical, and where the projecting O atoms were not situated immediately above or below the cations. As regards a change in dimensions within the plane of the layers, this is more difficult to predict, as any increase in the dimensions of a triangle of O atoms around a particular cation could, to some extent, be absorbed by a contraction of the equivalent triangle around one of the triad axes. Once again, however, experimental evidence, namely a slight overall expansion in the plane of the layers, is more readily in agreement with the second model for the dehydrated structure, for if the projecting O atoms within the L_1 component in this model were pushed towards the centre of this component (to minimize expansion normal to the layers), the central sheet of O atoms would become less closely packed and an expansion would result. In the more symmetrical model this could not occur, as the L_1 cations would presumably resist any attempt to force the projecting O atoms into the L_1 component in this manner.

Conclusion

Apart from the fivefold coordination of the L_1 cations after dehydration, which is not unknown in layer silicates, having been observed in dehydrated pyrophyllite (Brindley, 1978), the proposed model for the structure of the dehydrated chloritoid, although in agreement with experimental evidence, raises some interesting questions. In terms of structural transformations, the transition from a $2M_2$ chloritoid to a rhombohedral anhydrous variant involves considerable structural change, and one might therefore speculate whether an oxygen-deficient structure more

closely related to the $2M_2$ form, and retaining the same stacking sequence, might not be kinetically more probable. The experimentally observed preference for a rhombohedral stacking is, however, in accordance with the behaviour of certain layered silicates where considerable strain exists within the layers, such as the complex silicates zussmanite (Lopes-Vieira & Zussman, 1969) and stilpnomelane (Eggleton, 1972). Both of these minerals display a tendency to adopt a rhombohedral or near-rhombohedral symmetry when strain, in the form of K^+ ions, is introduced into the layers (Jefferson, 1976; Crawford & Jefferson, 1979), and in many respects, chloritoid resembles these minerals, particularly in possessing strong bonds (resulting from the presence of the L_2 component) between structural layers. In addition, the loss of oxygen and the reduction in cation coordination number in the L_1 component must introduce appreciable strain, and of all stacking arrangements, the rhombohedral variety is most suited to distributing this strain evenly throughout the lattice. This must therefore compensate for the considerable structural rearrangement necessary, but the rapidity with which the transformation appears to proceed is surprising, and further studies are required to determine the exact mechanism of dehydration.

The sample of chloritoid used in this investigation was provided by Dr A. C. Bishop, Keeper of Minerals at the British Museum, to whom we are grateful. The Philips EM300 electron microscope was provided by the Science Research Council and this support is acknowledged.

References

- BACHMANN, H. G. VON (1956). *Z. Kristallogr.* **108**, 145–156.
 BRINDLEY, G. W. (1978). Personal communication.
 CRAWFORD, E. S. & JEFFERSON, D. A. (1979). In preparation.
 EGGLETON, R. A. (1972). *Mineral. Mag.* **38**, 693–711.
 HALFERDAHL, L. B. (1956). *Carnegie Inst. Washington, Annu. Rep. Dir. Geophys. Lab.* 200.
 HARRISON, F. W. & BRINDLEY, G. W. (1957). *Acta Cryst.* **10**, 77–82.
 JEFFERSON, D. A. (1976). *Am. Mineral.* **61**, 470–483.
 JEFFERSON, D. A. & THOMAS, J. M. (1978). *Proc. R. Soc. London Ser. A*, **361**, 399–411.
 LOPES-VIEIRA, A. & ZUSSMAN, J. (1969). *Mineral. Mag.* **37**, 49–60.