

## Nekoite. I. Composition and Thermal Dehydration

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Dehydration studies confirm that the composition of nekoite is  $3\text{CaO} \cdot 6\text{SiO}_2 \cdot 8\text{H}_2\text{O}$  and that water is lost at 120, 200, 400, and 450°C with loss of  $2\text{H}_2\text{O}$  per formula unit at each stage. Loss of the first pair of water molecules is reversible between 40 and 120°C, loss of the second pair is reversible between 120 and 200°C, and loss of the fifth molecule is reversible below 250°C. Above 250°C only irreversible loss of the sixth and subsequent molecules occurs. Single-crystal studies show that topotactic reactions occur at each stage. The products corresponding to loss of 2 and 4 molecules give sharp X-ray reflexions with no streaking, but those corresponding to loss of 6 and 8 molecules show very marked Debye-Scherrer streaking. The anhydrous product appears to be closely similar to xonotlite, and transforms topotactically at 700°C to wollastonite. Dehydration appears to proceed initially by loss of water molecules, below 250°C, with minor repacking of the structure. At higher temperatures counter migration of  $\text{Ca}^{2+}$  and  $\text{H}^+$  may occur to give an inhomogeneous crystal in which regions with compositions  $4\text{CaO} \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  and  $6\text{CaO} \cdot 6\text{SiO}_2$  may recrystallize to form the observed products.

### Introduction

Nekoite is a hydrated calcium silicate mineral. In a paper dealing with the Crestmore, California, deposits Eakle (1917) described a mineral as okenite, on the basis of its chemical composition and optical properties. This description was accepted until Gard & Taylor (1956) reinvestigated the mineral, concluded that it was a new species, and named it nekoite. The mineral has since been rediscovered at Crestmore by Carpenter (1959) but it has not been reported from any other locality, nor has it been made synthetically.

Although nekoite has been identified as a separate mineral, its water content is in doubt, no exhaustive thermal dehydration studies have been made on it, and its crystal structure is unknown. This study was undertaken to determine the thermal weight-loss curve for nekoite, to investigate and describe the products formed at the various stages of the dehydration, and to determine the orientations, if any, of these products relative to the original nekoite. It was hoped that, if nekoite transformed topotactically to a compound of known structure, it would be possible to postulate a trial structure for the mineral based on the known structure, as was done by Gard & Taylor (1960) in the case of foshagite. The structure and its mode of determination will be described in part II of this series.

### Previous work

#### Optical data

Eakle (1917) originally described the mineral as long slender needles showing parallel extinction, low birefringence, and mean refractive index 1.535. Gard

& Taylor (1956) confirmed the crystal habit, birefringence, and refractive index, but pointed out that the needles showed repeated twinning of thin lamellae lying parallel to the needle axis. Single lamellae lying on the cleavage face had negative elongation and an extinction angle of 26°.

#### X-ray data

Gard & Taylor (1956) showed that the unit cell is triclinic with

$$\begin{array}{lll} a = 9.86, & b = 7.32, & c = 7.60 \text{ \AA} \\ \alpha = 103^\circ 54' & \beta = 86^\circ 12' & \gamma = 111^\circ 48' \end{array}$$

(Here  $a$  and  $c$ ,  $\alpha$  and  $\gamma$  have been reversed compared with those given by Gard & Taylor (1956) and Heller & Taylor (1956) to bring them into line with the naming of axes in other related calcium silicate minerals.) The elongation is along  $b$  and the cleavage is (100).

#### Composition

Eakle (1917) gave the specific gravity as 2.206 and the composition as  $\text{CaO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . Gard & Taylor (1956) accepted these values and calculated that the triclinic cell contents were  $3\text{CaO} \cdot 6\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ . Chalmers, Nicol & Taylor (1962) have reinvestigated the mineral and give the specific gravity as  $2.23 \pm 0.01$  and the composition as  $3\text{CaO} \cdot 6\text{SiO}_2 \cdot 8\text{H}_2\text{O}$ .

#### Dehydration

Gard & Taylor (1956) have shown that dehydration of nekoite at 900°C yields wollastonite. The nekoite  $b$ -axis becomes wollastonite  $b$ .

#### Starting material

Two samples were used in the investigation, both from the type locality at Crestmore, California:

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U.S.N.M. 95637

A portion of Eakle's original sample was very kindly lent by the United States National Museum. It was the sample which Gard & Taylor had used in identifying the mineral and its unit cell. There was insufficient material for a thermal weight-loss curve but an analysis (Chalmers, private communication) had showed the composition to be, apparently,



This water content will be discussed later in the paper.

Com. 230

Dr A. B. Carpenter of Harvard University rediscovered nekoite at Crestmore in 1959, and kindly made a portion available for this study. The nekoite was in the form of tufts of slender needles up to 0.5 mm by about 50 $\mu$  each on the surface of a rock section. The mineral was mixed with apophyllite, from which it could be easily separated manually under the microscope. Twinning was common but some crystals were found which showed an extinction angle of 26°. The mean refractive index, in white light, was 1.525 and the density, by the suspension method, was 2.23 ± 0.01 g.cm<sup>-3</sup>. The unit-cell dimensions were identical with those given by Gard & Taylor (1956).

### Real and pseudo-cells

Gard & Taylor (1956) showed that the intensities of reflexions in layers with odd  $k$  values, in rotation photographs about  $b$ , are much less than those in layers with even  $k$ , indicating a pseudo-symmetry which involves pseudo-halving of  $b$ . The pseudo-cell, obtained by ignoring the weak layers, is monoclinic with:

$$\begin{array}{lll} a = 9.15, & b = 3.66, & c = 14.78 \text{ \AA} \\ \alpha = 90^\circ 00' & \beta = 91^\circ 30' & \gamma = 90^\circ 00' \end{array}$$

All reflexions, including those in the odd layers, could, however, be indexed on a 'large monoclinic cell' derived from the 'small monoclinic cell' by doubling  $a$ ,  $b$  and  $c$ , *i.e.*

$$\begin{array}{lll} a = 18.30 & b = 7.32 & c = 29.56 \text{ \AA} \\ \alpha = 90^\circ 00' & \beta = 91^\circ 30' & \gamma = 90^\circ 00' \end{array}$$

Gard & Taylor further showed that the  $a^*$  and  $c^*$  reciprocal axes coincide in direction for the triclinic and monoclinic cells and are normal to the fibre axis, which contains the common  $b$  axis.

Fig. 1 shows the (100) and (001) faces of nekoite with the lattice points pertaining to the triclinic cell superimposed on the monoclinic axes. It can be seen that these occur, in terms of the 'large monoclinic cell', at (000),  $[0(b/4) (c/4)]$ ,  $[0(b/2) (c/2)]$ ,  $[0(3b/4) (3c/4)]$  on (100) and at (000) and  $[(a/2) (b/2)0]$  on (001). Such an arrangement of lattice points suggests that the overall structure of nekoite may conveniently be described in terms of a small monoclinic-shaped unit with dimensions

$$\begin{array}{lll} a = 9.15 & b = 7.32 & c = 7.39 \text{ \AA} \\ \alpha = 90^\circ 00' & \beta = 91^\circ 30' & \gamma = 90^\circ 00' \end{array}$$

so stacked as to be displaced by  $b/2$  along the  $a$  direc-

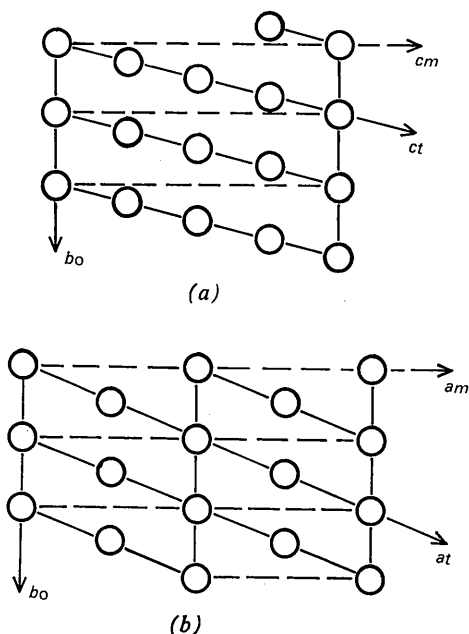


Fig. 1. Crystal lattice points for nekoite plotted on (a) the (100) plane and (b) the (001) plane. Note the common  $b$  axis and the relative orientations of the monoclinic ( $a_m$  and  $c_m$ ) and triclinic ( $a_t$  and  $c_t$ ) axes.

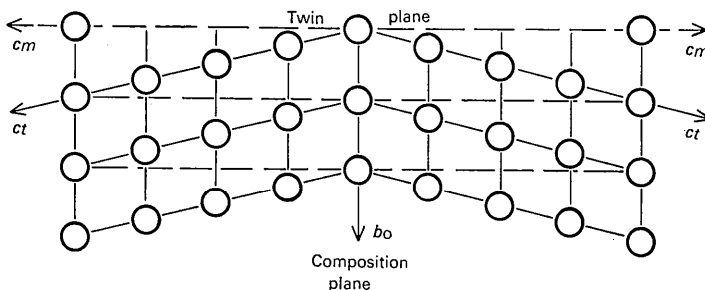


Fig. 2. Mode of twinning in nekoite due to change in stacking order along the  $c$  direction. The twin plane is the monoclinic (010) and the composition plane is (001).

tion and by  $b/4$  in the  $c$  direction. This type of stacking of small units to produce more complex structures or to generate polymorphic variations on a basic structure has been discussed by Gard (1960) and by Gard & Taylor (1960). All the work in this study will be referred to this 'basic monoclinic cell'.

Fig. 2 shows how this type of stacking readily explains the repeated twinning in the  $c$  direction seen in crystals lying on the cleavage face, which is (100). The twinning mechanism reduces to a simple stacking error with (001) as the composition plane.

### Thermal dehydration curve

About 40mg of nekoite was removed from the surface of Com. 230, the apophyllite was picked out manually under the microscope to leave a sample containing not more than 5% impurity, and then crushed to  $-250$  mesh size. A portion was carefully dehydrated stepwise in a tube furnace of standard design, using a current of dry,  $\text{CO}_2$ -free nitrogen as the carrier gas. Fibre bundles were heated simultaneously and the products formed at various temperatures identified using X-ray diffraction methods.

Fig. 3 shows the results of the thermal dehydration experiment. The sample lost weight when heated to

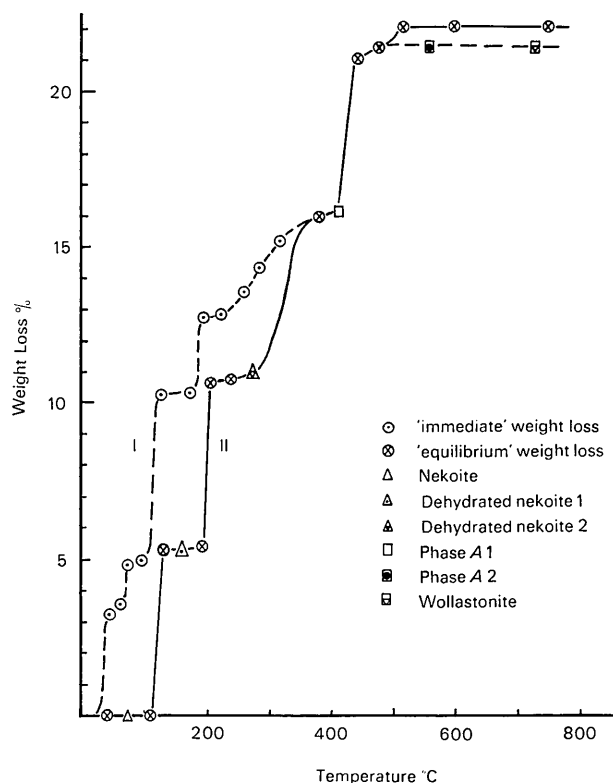


Fig. 3. Weight loss curves for nekoite, showing I the 'immediate' and II the 'equilibrium' weight losses along with the dehydrated phases found by X-ray diffraction after heating to different temperatures.

temperatures above  $40^\circ\text{C}$  but, at temperatures below  $260^\circ\text{C}$ , it regained weight while on the balance pan during weighing at each step in the dehydration. The regain in weight was complete within 30 minutes after heating to temperatures below  $120^\circ\text{C}$ . Between  $120$  and  $210^\circ\text{C}$  the regain was only partial but the 'equilibrium weight-loss' (see below), attained after four hours, was the same after each heating and cooling cycle. Between  $210$  and  $260^\circ\text{C}$  a second 'equilibrium weight-loss' was obtained, this time after the sample had been on the balance pan for three hours. Above  $260^\circ\text{C}$  the extent of the regain in weight gradually diminished and became undetectable above  $350^\circ\text{C}$ .

Curve I in Fig. 3 was constructed from the weight-losses measured immediately after removal of the sample from the furnace, the 'immediate weight-loss', whereas curve II was constructed from the weight-losses measured after the sample had come to equilibrium, at room temperature, with the ambient water vapour pressure in the balance case, probably  $5$ – $10$  mmHg at  $20^\circ\text{C}$ , *i.e.* the 'equilibrium weight-loss'. Curve I thus approximates to the water content of the sample at the temperature of dehydration in equilibrium with the water vapor in the furnace, the partial pressure of which was probably very low since pure, dry nitrogen was used as the carrier gas. Curve II, on the other hand, appears to represent the maximum easily attainable water contents of the phases formed in the early stages of the dehydration, at the relatively high water pressure obtaining in the balance case.

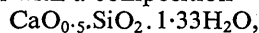
It is possible that the assumption implied above, that the regain in weight is due to re-absorption of water lost at high temperature, is wrong and that the regain is due to absorption of just enough of some other gas, such as  $\text{CO}_2$ , to balance the weight of water lost at each stage. Such a process was thought to be highly unlikely, but an experiment was carried out to check the possibility. If water were being re-absorbed, it is to be expected that it would occupy the same sites in the structure as before dehydration, but if some other gas were being absorbed it would be held quite differently and probably would not be so easily lost on reheating. Accordingly, the sample was heated to  $140^\circ\text{C}$  and the 'immediate' and 'equilibrium' weight-losses recorded. It was then reheated to  $110^\circ$  and again to  $140^\circ\text{C}$ . The 'immediate' and 'equilibrium' weight-losses were identical with the original values in both subsequent heating cycles, strongly suggesting that re-absorption of water was, in fact, occurring during the regain in weight.

Fig. 3 also shows the results of the study of the heated fibre bundles plotted against the 'equilibrium weight-loss' curve. It can be seen that the phases formed are closely related to specific regions of the curve, and the fact that nekoite persists up to  $120^\circ\text{C}$  unchanged, and that dehydrated nekoite 1 and dehydrated nekoite 2 persist in the ranges  $120$ – $210$  and  $210$ – $250^\circ\text{C}$ , can be taken as further evidence that the regains in weight are regains in water. The nature of

the phases formed will be detailed in subsequent paragraphs.

### Composition of nekoite

The overall water loss, from the curve, appears to be  $22.1 \pm 0.1\%$  by weight, which gives  $H_2O:SiO_2 = 1.39:1$ . The shape of the upper portion of the curve, however, suggests that the true course of dehydration of pure nekoite should follow the dashed curve in Fig. 3, and the last, very small step in the curve is due to loss of water from the apophyllite, which is known to be present as an impurity. Lacy, Nicol & Tarney (1970) have shown that apophyllite loses water at about  $550^\circ C$ . If this is so, the weight-loss now becomes about  $21.5\%$  and the value of  $H_2O:SiO_2$  falls to  $1.33:1$ . This agrees very well with a composition



or  $3CaO \cdot 6SiO_2 \cdot 8H_2O$ , for nekoite, in comparison with  $3CaO \cdot 6SiO_2 \cdot 6H_2O$  reported by Eakle (1917), and  $3CaO \cdot 6SiO_2 \cdot 7.5H_2O$  given by Chalmers.

A further distinction can be made between the proposed composition and that of Eakle by considering certain physical parameters, as used by Buckle, Gard & Taylor (1958) in checking the composition of tricalcium silicate hydrate. Howison & Taylor (1957) have shown that the molar refractivity of a calcium silicate hydrate is an additive function of the composition, if certain empirical values are taken for the atomic refractivities, and hence that the Lorentz-Lorenz equations can be applied to these compounds. Table 1 compares the values of the molecular weight and molar refraction of the unit-cell contents calculated from the observed refractive index ( $1.525$ ) and density ( $2.23 \text{ g.cm}^{-3}$ ), using the Lorentz-Lorenz equations, with those calculated from the two compositions using the equations of Howison & Taylor.

Table 1. Comparison of observed and calculated values of  $M$  and  $R$

	Observed	$C_3S_6H_8$	$C_3S_6H_6$
$M$	665	672	636
$R$	91.4	93.7	86.4
$M_{obs}/M_{calc}$		99.0%	104.5%
$R_{obs}/R_{calc}$		97.5%	106.0%

The accuracy of the calculated value from the formula  $3CaO \cdot 6SiO_2 \cdot 8H_2O$  is within common experimental error, since the specific gravity is correct to  $\pm 1\%$ , and the unit-cell volume to  $\pm 2\%$ . The values calculated from Eakle's composition lie outside the limits of experimental error.

The above results all indicate a composition  $3CaO \cdot 6SiO_2 \cdot 8H_2O$  for nekoite. The apparent lower water content of sample U.S.N.M. 95637 may be explained by the fact that this sample had been lying unprotected for some time in a warm, dry atmosphere and may have partially converted to the first dehydrated form. The fresher Com. 230 sample has not had the same opportunity to lose water.

### Dehydration of single crystals

Studies were made of the behaviour of single crystals of nekoite on dehydration, to characterize fully the phases formed on heating and to investigate the occurrence of topotactic relationships between these products. The technique used involved choosing an untwinned single crystal of easily recognized outline and with a clearly defined cleavage face, finding the orientation of its crystallographic axes relative to this face by oscillation or Weissenberg X-ray diffraction methods, removing the crystal from its mount and heating it to the required temperature in a furnace, replacing it on its mount in the same orientation as before, and finding the orientations, if any, of the product phases again relative to the cleavage face. By this method, the orientation of the product phase relative to the original nekoite could be defined to within  $\pm 2^\circ$ , particularly when Weissenberg methods could be used. In addition, one crystal was held in a pair of copper tweezers while the free end was heated in a Bunsen flame, so that the treated crystal contained high temperature phases at one end and unchanged nekoite at the other.

Some difficulties were encountered in heating the crystals through the initial dehydration steps. Several crystals 'exploded' at this stage, possibly owing to a build-up of excessive pressure at grain boundaries as the water left the crystalline lattice. Slow and careful heating avoided this, and it was found that all crystals which survived intact were exact polymorphs after the originals and contained product phases with marked topotactic orientations. Table 2 lists the results of the dehydration of single crystals after various heating treatments. The temperatures at which the dehydration products are formed appear to show some relationship to the results of heating fibre bundles but dehydration temperatures are generally higher for the single crystals, a result which is to be expected. Phase  $A 1$  does appear at abnormally low temperatures in two cases and this is not so easily explained, but it may depend on the defect structures of the crystals involved. The orientations of the phases relative to nekoite are shown in Fig. 4 and Table 3 lists their unit-cell parameters.

Table 2. Dehydration products

Crystal No.	Temperature	Time	Products
N 1	$600^\circ C$	$\frac{1}{2}$ hr	Ph $A 2$
N 2	600	18 hr	Ph $A 2$
N 3	1050	2 hr	Woll.
N 4	180	2 hr	Ph $A 1$
N 5	280	15 hr	D.N. 2
N 6	280	15 hr	Ph $A 1$
N 7	260	20 hr	{ Nekoite D.N. 2 Ph $A 1$
N 8	173	82 hr	Nekoite
N 9	216	16 hr	Ph $A 1$

Table 2 (cont.)

Crystal No.	Temperature	Time	Products
N 10	205	48 hr	{D.N. 1 Ph A 1
N 11	Bunsen flame	5 min	{Nekoite Ph A 2 Woll.
N 12	200	5 min	{Nekoite D.N. 2

Table 3. Unit-cell parameters for nekoite and product phases

Phase	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$
Nekoite	9.15 Å	7.32 Å	7.49 Å	91° 30'
D.N. 1	9.15	7.32	6.68	84° 30'
D.N. 2	9.15	7.32	6.13	84° 30'
Ph A 1	{7.2 8.1	7.32	7.3	70° 90°
Ph A 2	8.56	7.32	7.03	90°
Woll.	15.4	7.32	7.03	95° 16'

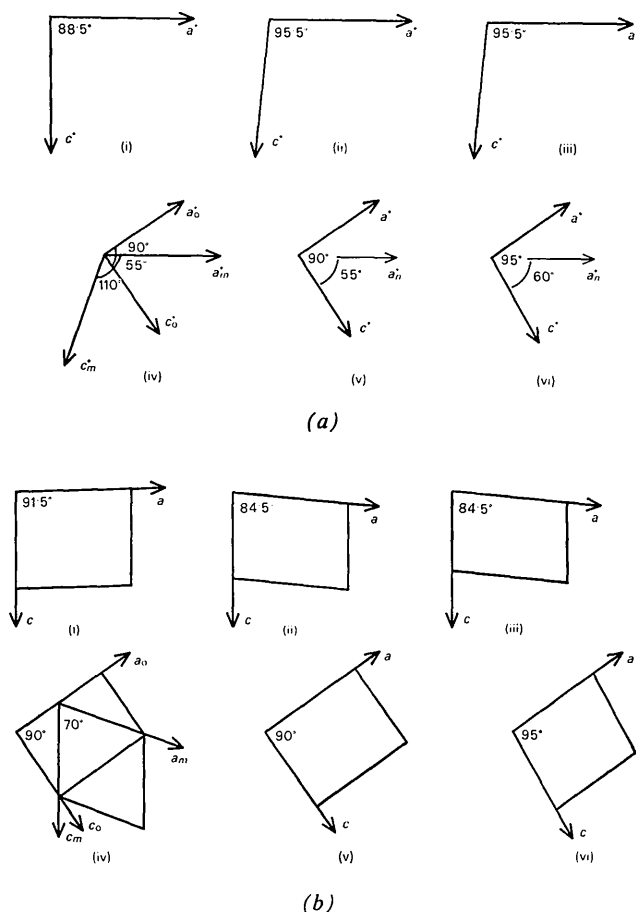


Fig. 4. Experimentally observed relative orientations of (a) the reciprocal axes and (b) the unit cells of nekoite and its dehydration products. The phases are (i) nekoite, (ii) dehydrated nekoite 1, (iii) dehydrated nekoite 2, (iv) phase A 1, (v) phase A 2, and (vi) Wollastonite.

Let us consider the phases formed in more detail.

#### D.N.1 and D.N.2

The diffraction patterns in rotation photographs about **b** obtained from dehydrated nekoite 1 (D.N.1) and dehydrated nekoite 2 (D.N. 2), the first and second dehydration products of nekoite, are very similar to the original pattern of nekoite. Both show quite sharp spots with little or no associated streaking, moderately strong pseudo-halving of **b**, and an intensity distribution very reminiscent of nekoite. There have, however, been contractions along the common **c** direction and a change in the  $\beta$  angle, and it should be particularly noted that the  $\mathbf{a}^*$  direction, *i.e.* the real **c** direction, has been preserved to within  $\pm 2^\circ$  and that it is the  $\mathbf{c}^*$  direction, the real **a** direction, which has moved relative to the original nekoite. The occurrence of residual nekoite in crystals N7 and N12, and a comparison of the orientations of D.N. 1, D.N. 2, and phase A 1 in crystals N7 and N10 have permitted these orientations to be worked out accurately.

D.N.1 and D.N.2 correspond to overall compositions  $3\text{CaO}\cdot 6\text{SiO}_2\cdot 6\text{H}_2\text{O}$  and  $3\text{CaO}\cdot 6\text{SiO}_2\cdot 4\text{H}_2\text{O}$  respectively. Crystals containing these phases were quite transparent under the microscope with little reduction in their apparent perfection, and their refractive indices were 1.543 and 1.540 respectively. The compositions calculated from these values by the Howison & Taylor method correlate exactly with those given by the weight-loss curve. Furthermore, both D.N. 1 and D.N. 2 can lose and regain water in a manner completely analogous to that shown by nekoite. The low temperatures at which these phases form, the retention of the microscopic crystal perfection, and the spot patterns produced by both phases all suggest that water is lost by a relatively simple mechanism in the first two stages of dehydration, and that there is probably little change in the major features of the crystal structure, although its constituent parts will have undergone a certain amount of repacking.

#### Phase A 1

When fibre bundles of nekoite are heated to temperatures between 200 and 250°C water is lost reversibly, the apparent limiting water content of the crystal from the 'immediate weight-loss' curve corresponding to the composition  $3\text{CaO}\cdot 6\text{SiO}_2\cdot 3\text{H}_2\text{O}$ . No separate phase corresponding to this composition has been detected by X-ray diffraction methods, however. The reversible water loss again suggests a relatively simple loss mechanism, as in the previous two stages, and the structure is probably little affected thereby. On heating to temperatures above 260°C the water loss becomes progressively less reversible until, at 350°C, no regain in weight can be detected, even after several hours on the balance pan.

Phase A 1 appears to be formed preferentially at temperatures between 350 and 500°C, although it can occur in single crystals heated to temperatures around

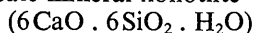
200°C. It gives an X-ray diffraction pattern which is quite different from that of nekoite, with marked streaking along Debye-Scherrer directions but none along radial directions in reciprocal space, indicating that the phase is much less well ordered than either D.N. 1 or D.N. 2 in the sense that the randomness of the mosaic structure of the crystals has increased. Under the microscope the crystals are no longer transparent, confirming the increase in randomness of the orientations of the mosaic blocks in the crystal. The evidence suggests that a much more complicated process accompanies the loss of water at this stage in dehydration.

The Weissenberg photographs obtained from phase *A* 1 could be indexed in terms of either a monoclinic or an orthorhombic unit cell, as shown in Fig. 3 and Table 2. Once again the sets of axes have been chosen to illustrate the relative orientations of the product phases and neither defines a conventional cell. The monoclinic cell has a  $\beta$  angle less than 90° and is *B* face centred, but it emphasizes the constancy of the  $a^*$  direction, the real *c* direction, in the original nekoite and the manner in which the  $c^*$ , or real *a*, direction is changing. The other cell is only geometrically orthorhombic and shows symmetry no higher than monoclinic in the intensities of its reflexions. It is also a compound cell, with doubled  $a_0$  and  $c_0$  parameters in terms of the apparent true repeat distances, and has been chosen because of its relationship to the other high temperature phases. Rotation photographs about the common *b* axis again show moderately strong pseudo-halving, similar to nekoite.

The relative orientations of nekoite and phase *A* 1 have been derived, particularly, from crystals N7 and N11, in which both phases coexist and hence reflexions from both appear on the same Weissenberg films. Despite the marked Debye-Scherrer streaking in the phase *A* 1 reflexions, the reported orientations are considered to be correct to within  $\pm 5^\circ$ .

#### Phase *A* 2

Phase *A* 2 appears in nekoite crystals heated to temperatures above 450°C, *i.e.* under conditions where, according to the weight-loss curve, the material is completely anhydrous. Its X-ray diffraction pattern is very similar to that of phase *A* 1, showing, again, marked streaking along Debye-Scherrer directions only and much evidence of increased mosaic randomness, as is to be expected. The pattern differs from that of phase *A* 1 in that rotation photographs about the *b* axis show virtually complete pseudo-halving, with reflexions having *k* odd being almost entirely absent. Moreover, the pattern is almost identical to that of the calcium silicate mineral xonotlite



and all the reflexions can be indexed in terms of the xonotlite unit cell, as shown in Fig. 3 and Table 2. This cell is again a monoclinic cell with orthogonal axes, *i.e.*  $I_{hki} \neq I_{hk\bar{i}}$ . The intensities of corresponding

reflexions in the two patterns correlate well, with the exception of the 040 reflexion in phase *A* 2 which is anomalously strong, suggesting that the structures are closely similar. Furthermore, Weissenberg photographs show that the intensity of the 401 reflexion is much greater than that of the  $40\bar{1}$ , so the phase must be present in a unique orientation and not as a twin. Comparison of other strong-weak reflexion pairs confirms the unique orientation, given in Fig. 3.

The chemical composition of phase *A* 2 cannot, of course, be identical with that of xonotlite, since the former phase is anhydrous while the mineral is hydrated. Nevertheless, the compositions are probably very similar and, in particular, it is likely that the Ca:Si ratio is the same in the two compounds. The very strong pseudo-halving of the xonotlite *b* axis is caused by the stacking of the calcium atoms, the strongest scattering centres in the structure, in pairs at heights  $y=0$  and  $\frac{1}{2}$  or  $y=\frac{1}{4}$  and  $\frac{3}{4}$ . The marked change in the degree of pseudo-halving of *b* with the appearance of phase *A* 2 implies an important change in the calcium packing during the formation of this phase, and it is reasonable to suppose that this is connected with the Ca:Si ratio reaching 6:6 in the product phase.

Nekoite and phase *A* 2 coexist in crystal N11 and composite Weissenberg photographs, containing reflexions from both phases, show that the  $a^*$  axis of phase *A* 2 is at 31° to the original nekoite  $a^*$  direction, and parallel to  $a^*$  of phase *A* 1. The orientations are again estimated to be correct to within 5°.

#### Wollastonite

The product of heating to temperatures above 750°C is well-oriented wollastonite, in agreement with the results of Gard & Taylor (1956). The appearance of this compound confirms that the chemical composition of at least parts of the crystal must have changed from  $3\text{CaO} \cdot 6\text{SiO}_2 \cdot 8\text{H}_2\text{O}$  to  $6\text{CaO} \cdot 6\text{SiO}_2$  during the dehydration.

Weissenberg photographs obtained from crystal N11 again provided the principal data on the relative orientations of nekoite and wollastonite, and so the relative orientations of phase *A* 2 and wollastonite could be found directly. Fig. 3 shows that this latter orientation is identical with that found by Dent & Taylor (1965) for the dehydration of xonotlite to wollastonite at 775–800°C. This result can be taken as further proof of the close similarity between the structures of phase *A* 2 and xonotlite.

#### Infrared spectra

Comparison of the spectra of untreated nekoite and samples heated to various temperatures showed that, up to about 300°C, water is being progressively lost but the slight changes in absorption in the region between 9 and 11 $\mu$  show that there are no major alterations in the silicon-oxygen portion of the structure up to this

temperature. All the water appears to have been lost by about 400°C, in reasonable accord with the dehydration curve, and there appears to be an appreciable change in the silicon–oxygen bands at about 500°C, suggesting that a repacking of the structure has occurred by this temperature. Beyond confirming the information obtained from the dehydration studies, little further can be obtained from the infrared absorption data.

### Discussion

A detailed discussion of the dehydration of nekoite must await the determination of the crystal structure. Certain conclusions of a more or less tentative nature can, however, be drawn from the data presented above.

The thermal weight loss curve indicates clearly that the composition of nekoite is  $3\text{CaO} \cdot 6\text{SiO}_2 \cdot 8\text{H}_2\text{O}$  and not  $3\text{CaO} \cdot 6\text{SiO}_2 \cdot 6\text{H}_2\text{O}$  as reported by Eakle (1917). Moreover, the fact that the first five molecules of water, per formula unit, are initially lost reversibly at relatively low temperatures, whereas the last three are only lost irreversibly, suggests that the form in which the water is incorporated into the crystal structure is different for the two groups. Taylor (1959) has discussed the correlation between the form in which water is found in the crystal structure and the temperature at which it is lost and he has shown that water lost below 250°C is usually present as discrete water molecules and is lost as such. Water lost at temperatures up to about 400°C may be present as molecules or as hydroxyl groups bound to silicon, but free hydroxyl ions are not lost below about 550°C.

The single-crystal studies show that the products formed on loss of the first and the second pairs of water molecules are well oriented and are still good single crystals, indicating that the mechanism of loss at each stage does not involve processes tending to disrupt the crystal structure. It is possible that the water may be lost in much the same way as water is lost from a zeolite. This loss of water molecules is accompanied by a shrinkage along the *c* direction together, probably, with a minor repacking of the rest of the framework.

The higher temperature dehydration occurs at temperatures similar to those at which afwillite loses its water. Taylor (1955) has studied the topotactic dehydration of afwillite ( $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ) to dicalcium silicate at about 300°C. He and Dent (1959) have shown that the mechanism probably involves initial loss of the water molecules at above 285°C followed by migration of  $\text{Ca}^{2+}$  ions from parts of the crystal to replace  $\text{H}^+$  ions from the Si–OH groups in other parts. The regions into which the calcium ions have migrated recrystallize to dicalcium silicate while the remaining regions lose water but do not recrystallize to a recognizable phase. McIver (1962) has further shown that limited reversible loss of the water molecules may occur below the dehydration temperature. Note that the Ca:Si ratio has changed from 3:2 in

afwillite to 2:1 in dicalcium silicate. Since it is very unlikely that  $\text{SiO}_2$  would be lost from the crystal at 300°C, there must exist regions of lower Ca:Si ratio in the final product but no crystalline phases corresponding to such regions can be detected by X-ray diffraction. Taylor (1955) considered that these areas contained amorphous silica, but subsequent work by Nicol (1962) has indicated that they contain material of Ca:Si ratio close to unity which has not recrystallized.

It is reasonable to suppose that nekoite will dehydrate by a mechanism similar to that of afwillite at temperatures above 250°C, and that the processes involved may be in evidence as low as 200°C. Ideally, we may suppose that nekoite dehydrates to the dehydrated nekoite 2 stage, *i.e.* to  $3\text{CaO} \cdot 6\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ , by simple loss of water molecules. The fifth molecule is lost by a mechanism similar to that obtaining at lower temperatures and represents the last of the molecular water in the structure. Loss of the remaining water involves Si–OH groups in the structure as calcium ions migrate from ‘donor’ to ‘acceptor’ regions in the crystal (Ball & Taylor, 1961) to displace the hydrogen atoms and change local Ca:Si ratios. This ratio increases in the ‘acceptor’ regions (and these recrystallize to the products observed by X-ray diffraction) and decreases in the ‘donor’ regions, which break down to form the water which is eventually lost, but which are not identifiable by X-ray techniques. On this theory, the composition of phase *A* 1 will be  $4\text{CaO} \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  and phase *A* 2 will be



as required by its similarity to xonotlite. Concurrently with the movement of calcium ions there must be a repacking in the rest of the structure, which means principally the silicon–oxygen framework.

It must be stressed that the above analysis of the reaction is necessarily idealized, since it is based on the ideal crystal structure of the mineral and it suggests that the calcium ions are immobile at low temperatures. In fact the course of the reaction will be strongly affected by the non-equilibrium defect concentration in the crystal and it is probable that calcium ions will show a tendency to move as soon as water is lost from the crystal. The interaction of these two factors makes it not surprising that phase *A* 1 appears at anomalously low temperatures in certain crystals.

Mamedov & Belov (1958) have proposed a model for the silicon–oxygen structure in nekoite. They postulate a sheet of empirical composition  $\text{Si}_6\text{O}_{15}^{4-}$  which is constructed from double dreierketten, as in xonotlite, condensed to form a two-dimensional structure comprising rings of five and eight tetrahedra with adjacent double chains displaced by  $b/2$ . They have shown that this configuration is energetically favoured over any other, but give no analysis based on intensity measurements. The sheets are oriented parallel to (001) and are associated with  $\text{Ca}^{2+}$  ions and water molecules. The structure appears reasonable in terms of the

cell dimensions and the distribution of lattice points on (001), but it does not appear to explain the dehydration reactions. Two-dimensional sheets parallel to (001) would be likely to move in directions either perpendicular to, or parallel to, the (001) plane, during the low temperature dehydration of nekoite, but it is difficult to see how they could tilt out of this plane without setting up unacceptable strains in the crystal. The observed behaviour of nekoite on dehydration, namely the retention of the *c* direction and the shift of the *a* axis, requires just such a tilt. Moreover, the structure proposed by Mamedov & Belov does not permit of the existence of Si-OH groups, which appear to be required to explain the dehydration reactions.

It is possible, however, that the structure of Mamedov & Belov requires only modification. The repeat distance of 7.32 Å along the fibre axis suggests the presence of dreierketten chains in the structure, and the pattern of lattice points suggests that these chains are stacked so as to be displaced by *b*/2 along the *a* axis and by *b*/4 along the *c* direction. The proposed sheet may be 'de-condensed' to give either single or double dreierketten chains, of empirical compositions  $\text{Si}_3\text{O}_9\text{H}_3^{3-}$  or  $\text{Si}_6\text{O}_{17}\text{H}_4^{6-}$ , which are hydrogen bonded into a pseudo-sheet very similar to the original in projection on (001). Such a structure will have similar dimensions to the condensed sheet but will be more flexible and will be able to undergo the required low-temperature re-arrangements without needing to tilt a rigid structure. Also, there will be Si-OH groups on the dreierketten chains, as required.

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## The Molecular and Crystal Structure of Trifluoromethylarsenic Tetramer ( $\text{AsCF}_3$ )<sub>4</sub>

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Crystals of trifluoromethylarsenic tetramer,  $(\text{AsCF}_3)_4$ , are tetragonal, with 2 molecules in a unit cell with symmetry  $P4_2/nmc$  and lattice constants  $a = 10.483$  (2),  $c = 6.381$  (1) Å. The required molecular symmetry is  $\bar{4}2m$ . Three-dimensional data were collected at 25°C with an automated diffractometer. The heavy atoms were located by Patterson synthesis, and Fourier and least-squares refinement were used to obtain optimum values for the nine positional and eighteen thermal parameters. The value of *R* is 6%. The bond distances found are: As-As  $2.454 \pm 0.001$ , As-C  $2.012 \pm 0.015$ , average C-F  $1.296 \pm 0.022$  Å. The four-membered arsenic ring is not planar, having bond angles of 83.6° and torsion angles of 36.8°. These and other molecular quantities are compared with the isostructural  $(\text{PCF}_3)_4$ , and with other arsenic compounds.

#### Introduction

Cowley & Burg (1966) reported for the first time the synthesis of a compound which contained a four-mem-

bered arsenic ring. Compounds having five- and six-membered arsenic rings have been previously characterized (Burns & Waser, 1957; Hedberg, Hughes & Waser, 1961). The synthesis of a molecule with a four-