

*The thermal decomposition of crocidolite from  
Koegas, South Africa*

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*Summary.* When crocidolite (fibrous riebeckite,  $\text{Na}_2\text{Fe}_2^{3+}\text{Fe}_{0.6}^{2+}\text{Mg}_{0.4}\text{Si}_8\text{O}_{22}(\text{OH})_2$  approx.) is heated in argon or nitrogen at 50–400° C, uncombined water is lost. The tensile strength drops sharply at 300–400° C. At 500–600° under static, or 570–700° C under dynamic conditions, an endothermic dehydroxylation yields an anhydride with a structure close to that of the initial material. At about 800° C, the anhydride decomposes endothermically, giving acmite, cristobalite, a spinel, and liquid. At 950–1000° C the acmite decomposes. Melting is extensive by 1050° C.

On heating crocidolite in oxygen or air, uncombined water is again lost below 400° C. At 300–450° C (static), or 400–600° C (dynamic), hydrogen ions and electrons are lost, to give an oxyamphibole,  $\text{Na}_2\text{Fe}_4^{3+}\text{Fe}_{0.6}^{2+}\text{Mg}_{0.4}\text{Si}_8\text{O}_{24}$ . The process is exothermic and probably occurs by proton and electron migration, as suggested by Addison *et al.* (1962). At 600–950° C the oxyamphibole decomposes endothermically, and most of the remaining  $\text{Fe}^{2+}$  is oxidized, giving acmite, hematite, cristobalite, and a spinel. The spinel has largely disappeared by about 950° C, while at 975–1000° C the acmite also decomposes and melting begins.

When crocidolite is heated in hydrogen, no change is detectable by X-rays below 530° C, when the amphibole decomposes to give mainly a pyroxene, metallic iron, cristobalite, and liquid. The same products are detectable up to at least 850° C; the proportion of metallic iron increases with temperature.

With the exception of metallic iron, all the crystalline products formed, whether under neutral, oxidizing, or reducing conditions, show varying degrees of preferred orientation. This could be explained if the reactions occur mainly by the migration of cations through relatively undisturbed oxygen frameworks.

VERY large deposits of crocidolite, which is the fibrous variety of the alkali amphibole, riebeckite ( $\text{Na}_2\text{Fe}_2^{3+}(\text{Fe}^{2+}, \text{Mg})_3\text{Si}_8\text{O}_{22}(\text{OH})_2$ ), occur in reefs in Precambrian strata in South Africa and Australia. In South Africa it occurs widely over a 600-mile (1000 km) arc in the Banded

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Ironstone horizons of the Transvaal System, extending from the Orange River in Cape Province to the eastern edge of the Bushveld Complex in the Transvaal. The deposits are sedimentary in origin; formation of the crocidolite is attributed to dynamic forces and diagenetic processes. Other known deposits include those in Bolivia and Southern Rhodesia, both of which are of metasomatic origin and distinctly magnesian in composition. Crocidolite, which is also called blue asbestos, is of considerable economic importance, the combined annual output of the South African and Australian mines being over 100 000 tons.

Vermaas (1952) made the first important study of the thermal decomposition of crocidolite, using X-ray powder patterns and differential thermal analysis (d.t.a.). He concluded that, in an oxidizing atmosphere,  $\text{Fe}^{2+}$  was partly oxidized at 400–500° C and decomposition to acmite, cristobalite, hematite, and water occurred above 890° C. D.t.a. curves for crocidolite in oxidizing atmospheres were also reported by Heystek and Schmidt (1953), Ivanova (1961), and Cilliers *et al.* (1961).

Ernst (1957, 1958, 1959) studied the stability relations of riebeckite and magnesioriebeckite under hydrothermal conditions, using buffer mixtures to control the oxygen pressure. Various products from the range pyroxene, magnetite, quartz, olivine, and vapour were formed according to the conditions. Riebeckite was found to decompose at lower temperatures than magnesioriebeckite.

Addison, Addison, *et al.* (1962) examined the oxidation and reduction of crocidolite and also the effects of outgassing *in vacuo* at 450° and 615°. They used gas-absorptiometric and other techniques, and their specimens were the same as those used in the present work. They showed that outgassing *in vacuo* at 450° C caused loss of uncombined water, but not of hydroxyl; at 615° C, the hydroxyl water was also lost. On heating in oxygen at 450° C, partial oxidation occurred, giving  $\text{Na}_2\text{Fe}_4^{3+}(\text{Fe}^{2+}, \text{Mg})\text{Si}_3\text{O}_{24}$ ; the mechanism was considered to depend on migration of protons and electrons through the crystal. On heating in hydrogen at 450° or 615° C, reduction occurred. It was concluded from X-ray and infra-red evidence that material reduced at 450° C was still basically an amphibole, although some of the iron had been reduced to the zero oxidation state. Further reduction occurred at 615° C, and the product obtained at this temperature was described as amorphous.

The object of the present work was to study more fully the mechanism and products of decomposition in neutral, oxidizing, and reducing atmospheres at atmospheric pressure. No attempt was made to study equilibria.

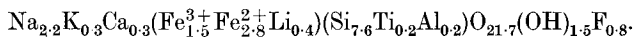
### *Material*

*Crocidolite.* Except where otherwise stated, specimens of fresh crocidolite from the Koegas–Westerberg area, South Africa, were used. The mine workings in this area penetrate one of the largest known deposits of crocidolite. They lie on either side of the Orange River in Cape Province, and asbestos fibre has been extracted without interruption in the area for seventy years. These specimens have been described by Cilliers *et al.* (1961), whose system of reference numbers for individual specimens will be used here. The term ‘fresh crocidolite’ indicates that the specimens came from the unweathered strata below the general water table. Of sixteen specimens completely examined by thermal analysis methods, thirteen from the Koegas–Westerberg mine and two from the adjacent Hounslow mine had been taken from depths of 50–100 m below the ground surface, while one was a core sample from 400 m below the surface at Koegas. The primary rock samples each weighed up to 5 kg and contained seams of cross-fibre crocidolite, 3–40 mm thick and deep blue in colour with a distinct sheen. The massive rock adjacent to the fibre seams was a matte, dark blue colour, with some banding in lighter and darker shades.

These crocidolite specimens differed only slightly from each other in composition, which approximated to  $\text{Na}_2\text{Fe}_2^3+\text{Fe}_{2.6}^2+\text{Mg}_{0.4}\text{Si}_8\text{O}_{22}(\text{OH})_2$ . The unit-cell parameters, which were the same for all the specimens, were  $a$  9.80,  $b$  17.85,  $c$  5.30 Å,  $\beta$  103° 50',  $a \sin \beta$  9.52 Å (referred to  $C$ -face centred axes, space group  $C2/m$ ). Attempts to obtain true, single crystal X-ray patterns were unsuccessful, even the thinnest usable fibres (about 5  $\mu$  thick) proving to be bundles of crystallites with random orientation around the fibre direction. The  $c$ -axes of the crystallites were well aligned with this direction. In preparing samples for d.t.a., thermogravimetric, or other chemical investigations, care was taken to avoid undue grinding or crushing of the material, as this was found to cause oxidation and sorption of moisture. For most purposes, part of a fibre seam was first placed on a steel plate and tapped with a hammer. The disintegrated fibre was then cut into short, coarse lengths with scissors and shaken on an 18-mesh sieve to remove traces of non-fibrous material.

*Single crystal material.* For some of the crystallographic work, true single crystals were needed. Three specimens were used: specimen A6, from the Sara–Fier complex, Nigeria, described by Borley (1963); a specimen from the Jos Plateau, Nigeria (Aberdeen University Geology Department Collection No. AU 9418); and a specimen from Kenya

(Building Research Station Collection No. N 180). The first of these was analysed by Borley (1963), who showed the composition to be approximately



It is thus perhaps better described as an arfvedsonite than as a riebeckite. The other two specimens were not analysed. All three gave X-ray rotation photographs that closely resembled those of the crocidolite specimens, apart from small differences in cell parameters.

#### *Experimental Methods*

*Differential thermal analysis.* D.t.a. curves were determined in two different laboratories: at the Cape Asbestos Fibre Laboratory (CA) and the Macaulay Institute for Soil Research (MI). The apparatus used in each case has been described elsewhere (Hodgson, 1963a; Mitchell and Mackenzie, 1959). In both instances, the furnace atmosphere was controlled and the heating rate was 10° C/min. In the technique used at the MI laboratory, the samples were prepared as previously described. In that used at the CA laboratory, they were further subdivided by brief crushing in a micro hammer mill.

*Thermogravimetric analysis (t.g.a.).* In this method, the temperature is increased at a steady rate and the sample weight continuously recorded. A controlled atmosphere thermobalance was used (Hodgson, 1963a). The heating rate was 2.5° C/min. The samples were partially dried at 100° C in air before being placed in the apparatus.

*Dynamic dehydration.* Samples were heated in a tube furnace in a stream of either argon or oxygen, and the evolved water determined gravimetrically by absorption in magnesium perchlorate. The heating rate was 2.5° C/min, and all conditions were as far as possible the same as those used in the t.g.a. determinations. The argon was purified over activated charcoal and magnesium perchlorate before entering the furnace, and the flow rate was 75 ml/min. Blank corrections (under 2 mg in 12 hr) were applied. The samples were partially dried at 100° C in air before being placed in the apparatus.

*Static weight-loss curves.* The sample was heated to successively higher temperatures, each of which was maintained until constant weight had been reached; it was contained in a boat or crucible, which was removed from the furnace for weighing. For work in air, a 5 g sample was heated in an open crucible. For work in nitrogen, smaller samples were placed in a boat within a tube furnace through which a current of the gas was passed. Traces of oxygen were removed from the nitrogen by first passing it over a separate sample of crocidolite maintained at 500° C. Each complete run took several weeks. The samples were cut up before use as previously described, but no preliminary drying at 100° C was carried out.

*X-ray diffraction and infra-red absorption.* X-ray fibre rotation photographs were taken using a 6 cm diameter camera with filtered copper or (preferably) cobalt radiation. With the single crystal specimens, oscillation and Weissenberg methods were also used. Infra-red techniques are described later.

#### *Neutral atmospheres (argon or nitrogen)*

*Visual examination of products.* At about 200° C, the fibres lose their lustre and the tensile strength begins to fall; it drops markedly at 300–400° C. By about 500° C the colour has faded to a greyish blue. The

presence of glass, caused by partial fusion, is apparent by 830–850° C; above 850° C, the proportion of glass steadily increases. Fibres cooled from 1050° C retained their shapes but contained much glass, individual crystallites being no longer distinguishable. They were blue-black.

*D.t.a., weight loss, and dehydration data.* Fig. 1 *a-d* and fig. 2*a* show typical curves obtained by the d.t.a., dynamic dehydration, t.g.a., and static weight loss methods. With each of the first three methods, 10–16 specimens were studied; table I gives mean results and variation between specimens. The data obtained at the CA laboratory are described more fully by Hodgson (1963*b*). The d.t.a. curves obtained in the two different laboratories are in broad agreement, though the ranges of temperature found for the 610–700° C endotherm are somewhat different. This can perhaps be attributed to the fact that the CA samples were more finely ground. Beyond the sharp endotherm at 800–830° C the curves varied considerably, both for different specimens studied in the same laboratory and for the same specimen studied in different laboratories. The sharp endotherm was usually followed immediately by an exotherm, which in turn was sometimes followed by an indefinite endotherm at 850–900° C. The poor reproducibility above 830° C can probably be attributed to the partial melting of the material. Fig. 3 shows the effect on the t.g.a. curves of differing mechanical treatments of the sample. Mechanical disintegration causes the loss below 600° C to increase, but the loss above 600° C decreases. Addison, Addison, Neal, and Sharp (1962) observed similar effects. The Fe<sup>2+</sup> content, if expressed as a percentage on the dry weight, does not change significantly below 890° C (table II). No loss of either H<sub>2</sub> or O<sub>2</sub> therefore occurs.

*X-ray investigation.* Samples were heated in argon or nitrogen under various conditions and were then cooled and examined by X-ray fibre rotation photographs. In some cases, ignition losses in nitrogen and Fe<sup>2+</sup> contents were also determined. Table II lists the heating conditions used, and gives the phases detected by X-rays, together with other data.

Two kinds of heating conditions, which are described in table II as static and dynamic, were used. Static heating denotes that the sample was heated at a steady temperature for a time sufficient for constant weight to be attained, as in the determination of the static weight loss curve. Dynamic heating denotes that an otherwise normal d.t.a. run was stopped at the temperature stated, and the sample then removed as quickly as possible from the furnace. The points on the d.t.a. curve to which these samples correspond are shown in Fig. 2*a*. The specimen

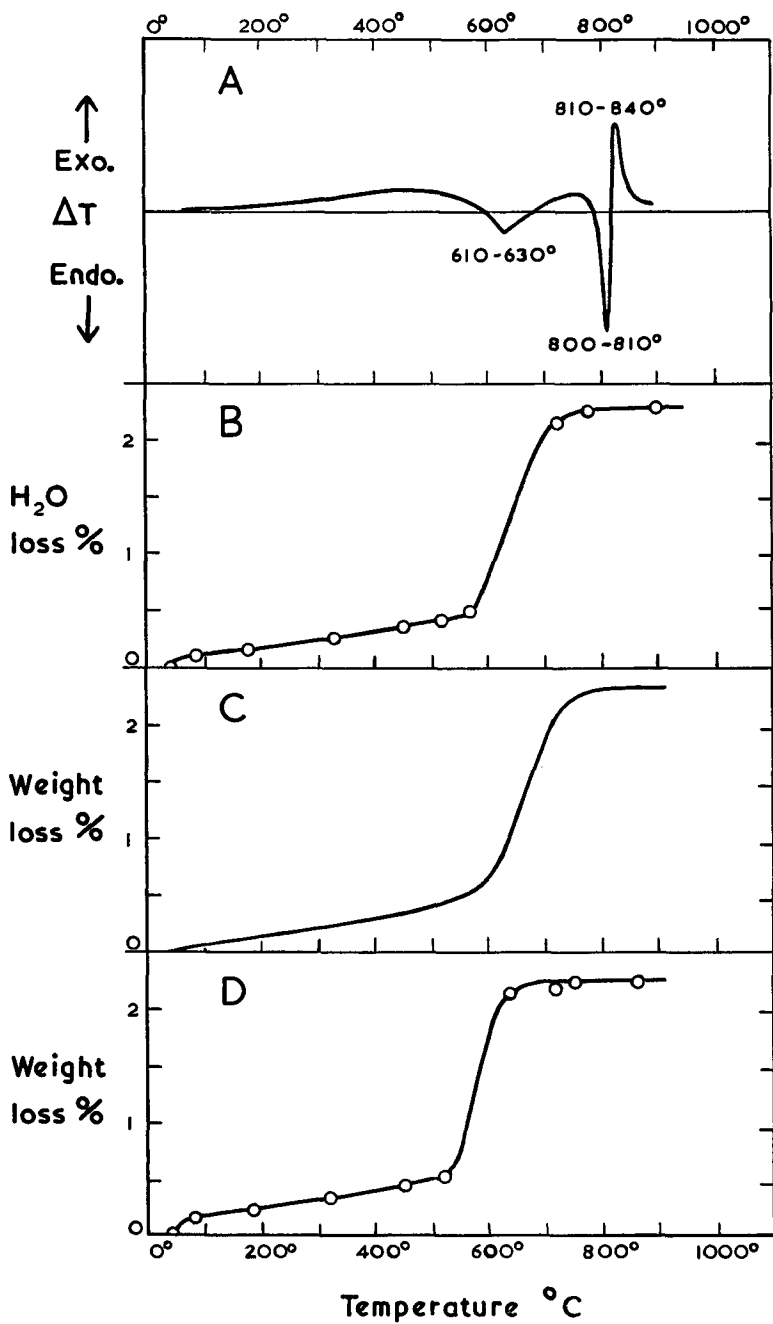


FIG. 1. Thermal behaviour of crocidolite in neutral atmospheres. (a) D.t.a.; typical curve obtained with CA apparatus. (b) Dynamic dehydration (specimen RS7). (c) T.g.a. (specimen RS7). (d) Static weight loss (specimen RS23).

TABLE I. Thermal behaviour of crocidolite in argon

Method Laboratory No. of specimens studied	T.g.a. CA 16		Dynamic dehydration CA 12	
	1st loss	2nd loss	1st loss	2nd loss
Mean	0.38 %	1.90 %	0.38 %	1.90 %
Standard deviation	$\pm 0.087$	$\pm 0.07$	$\pm 0.093$	$\pm 0.057$
Mean temp. limits ( $^{\circ}\text{C}$ )	100-580 $^{\circ}$	580-700 $^{\circ}$	100-570 $^{\circ}$	570-700 $^{\circ}$
Range of upper limit ( $^{\circ}\text{C}$ )	560-630 $^{\circ}$	680-730 $^{\circ}$	550-580 $^{\circ}$	670-720 $^{\circ}$

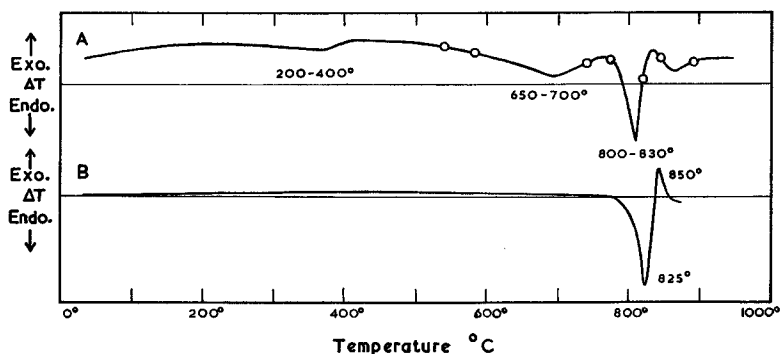


FIG. 2.

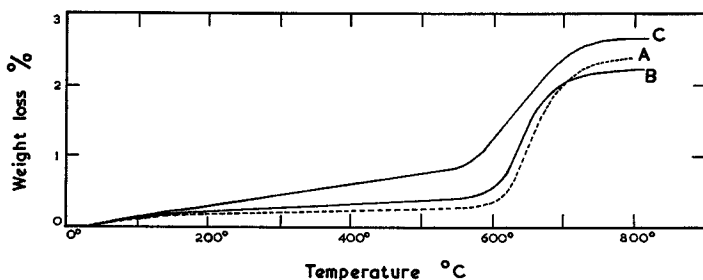


FIG. 3.

FIGS. 2 and 3. FIG. 2 (top): D.t.a. curves in argon. (A) Typical curve obtained with MI apparatus, showing points at which samples were removed for X-ray examination. (B) Specimen RS7 after previous heating in argon for three hours at 730 $^{\circ}\text{C}$  to remove the chemically bound water. FIG. 3 (bottom): Effect of differing mechanical treatments on the t.g.a. curve in argon for specimen RS7. (A) Unbroken pieces. (B) Sample cut and partly disintegrated. (C) Sample finely ground in micro hammer mill.

(RS1) used for this work was from the oxidized zone of the Koegas locality, but did not differ greatly in composition from the other specimens used in this investigation.

All three of the crystalline products (pyroxene, spinel, and cristobalite) showed varying degrees of preferred orientation. The pyroxene was always well oriented; the spinel was usually less well oriented, and

TABLE II. X-ray and other data for samples of crocidolite examined after heating in neutral atmospheres (Ar or N<sub>2</sub>)

Temp. (°C)	Phases detected by X-rays*				Ignition loss at 1000° C in N <sub>2</sub>	Temp. (°C)	Phases detected by X-rays*				Ignition loss at 1000° C in N <sub>2</sub>	Fe <sup>2+</sup> †
	R	P	S	C			R	P	S	C		
<i>Static conditions, specimen RS7</i>						<i>Dynamic conditions, specimen RS7</i>						
20°	+				2.4 %	20°	+				2.4	
680°	+				0.3	710°	+				0.9‡	
720°	+	w	w		0.2	740°	+				0.4§	
750°	+	w	w		0.1							
770°	+	w	w	w	0.1	<i>Dynamic conditions, specimen RS1</i>						
780°	+	w	w	w	0.1	20° C	+				3.0	15.71 %
790°	+	w	w	w	0.1	540°	+				n.d.	15.82
800°	+	+	+		0.04	572°	+				n.d.	15.82
850°	+	+	+		n.d.	740°	+				n.d.	15.75
900°	+	+	+		n.d.	772°	+	w	w		n.d.	15.75
950°		w	+	+	n.d.	820°		+	+	+	n.d.	15.78
1000°		w	+	+	0.0	840°		+	+	+	n.d.	15.79
1050°			+		n.d.	890°		+	+	+	n.d.	15.79

\* R = riebeckite; P = pyroxene; S = spinel; C = cristobalite.

† expressed as % on dry weight.

‡ includes 0.5 % lost at 600° C.

§ includes 0.3 % lost at 600° C.

the cristobalite showed only slight orientation or none at all. With the crocidolite fibres, only rotation photographs about the fibre axis could usefully be obtained. The studies on these specimens were therefore supplemented by ones on those for which single crystals were available. The same phases were formed on heating these specimens as with the crocidolite, although the temperatures of corresponding reactions and the cell parameters of the pyroxene were somewhat different.

The cell parameters of the pyroxene and the relative intensities of its reflections were near to those of acmite ( $a$  9.658,  $b$  8.795,  $c$  5.294 Å,  $\beta$  107.42°;  $a \sin \beta$  9.214 Å, space group  $C2/c$ , Nolan and Edgar, 1963). If the crocidolite was referred to the body-centred cell ( $a$  9.97,  $b$  17.85,



$c$  5.30 Å,  $\beta$  107.5°; Cilliers *et al.*, 1961) and the pyroxene to the normal  $C$ -centred cell, the orientation relationship is that, to within a degree or so, the  $a$ -,  $b$ -, and  $c$ - axes of the pyroxene are formed parallel to the corresponding axes of the amphibole. A similar relationship was observed in the decomposition of tremolite (Freeman and Taylor, 1960).

The spinel had an  $a$ - axis of 8.40 Å; this corresponds approximately to the value for magnetite (8.3963 Å; Basta, 1957), although partial replacement of  $\text{Fe}^{2+}$  by  $\text{Mg}^{2+}$  cannot be ruled out. The orientation relationship was that spinel ( $\bar{1}10$ ) is formed parallel to amphibole (010) and spinel (111) parallel to amphibole (100). This is similar to the principal orientation relationship found by Bown and Gay (1959) for magnetite inclusions in pyroxene crystals.

The cristobalite crystallized poorly: it gave only a single group of X-ray reflections with a  $d$ -spacing of 4.07 Å. This is the 101 reflection of low-cristobalite (tetragonal;  $a$  4.97,  $c$  6.92 Å approx.). Indefinite maxima in the angular distribution of this reflection suggested that several different orientations can occur. The most important of these was such that the cristobalite  $a$ -axis is formed parallel to the amphibole  $c$ -axis, and cristobalite (011) parallel to amphibole (100).

*Infra-red examination* (by V. C. Farmer). Infra-red absorption spectra were recorded in the 5000–630  $\text{cm}^{-1}$  (2–16  $\mu$ ) region on a Grubb Parsons Double Beam Infrared Spectrometer equipped with NaCl prism, at sample concentrations of 2 mg and 0.33 mg in 12.7 mm diameter KBr disks. Hydroxyl absorption near 3640  $\text{cm}^{-1}$  (2.75  $\mu$ ) was recorded at the higher resolution given by a 2500 lines/inch grating fitted in the spectrometer, using 4 mg of sample per disk. The three crocidolites examined (RS1, RS7, RS21) gave identical spectra, of which the principal features are three sharp bands around 3640  $\text{cm}^{-1}$  (fig. 4) arising from ionic hydroxyl groups, a pattern of strong bands at 1200–900  $\text{cm}^{-1}$  due to Si–O stretching vibrations, and a series of medium or weak bands at 900–630  $\text{cm}^{-1}$ , which probably arise from Si–O–Si vibrations of mixed stretching and bending character (fig. 5). The spectra are almost identical with that of an asbestiform amphibole given by Moenke (1962), covering the 1800–400  $\text{cm}^{-1}$  region. A sample of amosite studied by us gave a similar pattern, with some displacements of absorption bands. The published spectra of other amphiboles differ more widely from these (Moenke, 1962; Lyon, 1962). In addition to ionic hydroxyl and silicate absorption bands, the crocidolite spectra showed weak absorption near 3300 and 1625  $\text{cm}^{-1}$  due to adsorbed water; some of this was retained after heating the disks to 200° C. The absorption of this water

was distinguished from that of liquid water in having stronger absorption at  $1625\text{ cm}^{-1}$  than at  $3300\text{ cm}^{-1}$ ; the reverse is true for liquid water. There is evidence from studies of montmorillonites that this intensity pattern is associated with water molecules adsorbed through their oxygen atoms at positive sites, rather than by hydrogen bonding to

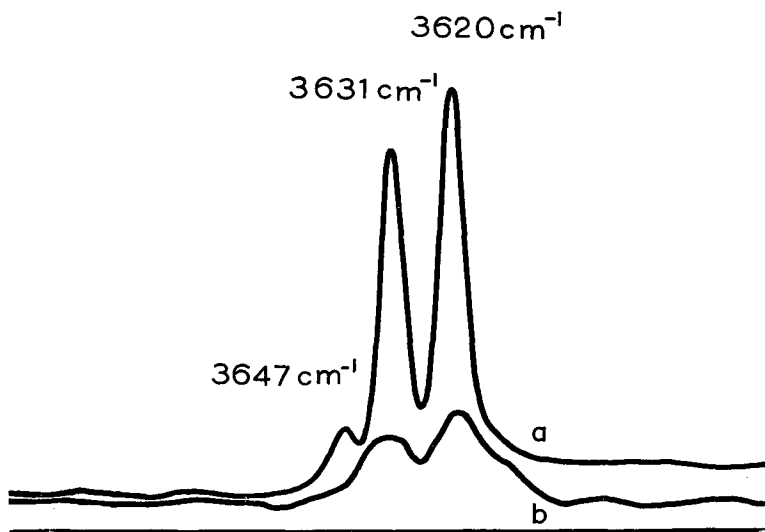


FIG. 4. Infra-red absorption of ionic hydroxyl groups in crocidolite. (a) unheated, and (b) after heating to  $750^{\circ}\text{C}$  in nitrogen. Concentration 4 mg in 12 mm diameter KBr disks.

negative sites (Russell, 1964). Adsorbed water was significantly higher in samples ground before preparing the KBr disks.

The spectra of samples heated in nitrogen to the temperatures indicated are also shown in fig. 5. These samples were harder than unheated material, and required 2 min pregrinding with isopropyl alcohol in a ball mill to give satisfactory spectra. Heating to  $500^{\circ}\text{C}$  caused little change in the spectrum apart from a reduction in intensity of the pair of bands at  $881$  and  $895\text{ cm}^{-1}$ . The increased absorption of the heated sample near  $640\text{ cm}^{-1}$  was a result of pregrinding; unheated material, however, was not affected by the grinding conditions used. Heating to  $750^{\circ}\text{C}$  left little ionic hydroxyl absorption (fig. 4) and caused marked changes in the pattern of absorption due to Si-O vibrations. The more diffuse absorption in the  $1200\text{--}900\text{ cm}^{-1}$  region suggests a less well

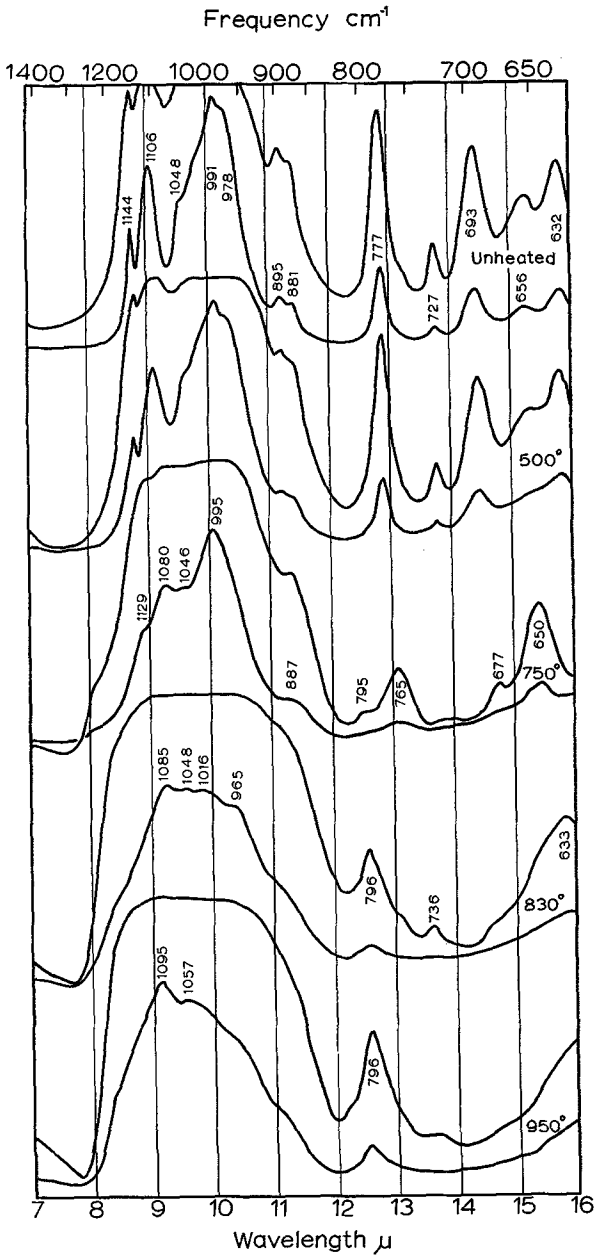


FIG. 5. Infra-red absorption due to silicon-oxygen vibrations in crocidolite, unheated and after heating to the temperatures indicated. Each sample was studied at 2 mg and 0.33 mg in 12 mm diameter KBr disks. Peak positions are given in wave numbers ( $\text{cm}^{-1}$ ).

ordered structure, and the change in absorption pattern in the 900–630  $\text{cm}^{-1}$  region probably reflects either changes in the configuration or environment of the amphibole chain. The overall pattern is similar to that given for riebeckite by Lyon (1962), indicating that the amphibole chain is essentially unaltered. The absorption pattern is, however, fundamentally altered on heating to 830° or 950° C. Bands at 1095  $\text{cm}^{-1}$  and 796  $\text{cm}^{-1}$ , which are stronger in the sample heated to 950° C, can be ascribed to cristobalite. Bands at 1016, 965, 736, and 633  $\text{cm}^{-1}$ , which weaken considerably between 830° and 950° C, can be ascribed to a pyroxene phase; an acmite spectrum given by Lyon (1962) has comparable bands at 1012, 954, 730, and 642  $\text{cm}^{-1}$ .

The samples heated to 830° and 950° were intensely black, and this high, continuous absorption continued into the infra-red region, but fell off rapidly between 3000 and 1300  $\text{cm}^{-1}$ . The high absorption implies closely spaced electronic energy levels in the samples, similar to those occurring in semiconductors.

*Sequence of thermal changes.* The dynamic dehydration, t.g.a., and static weight loss curves (fig. 1) agree in showing a gradual evolution of water, which begins little above room temperature and continues until the main loss begins; this happens at about 500° C under static conditions or at about 570° C under dynamic conditions. The mean value for the percentage loss in weight at 100–570° C under dynamic conditions is 0.38% (table I), and the X-ray and infra-red evidence show that it is due to loss of physically combined water. Part of this water is probably adsorbed (Addison, Neal, and Sharp, 1962), but the tenacity with which much is retained, and the fall in tensile strength that accompanies its loss, suggest that part may occur as liquid inclusions between the crystallites. These would probably not persist in the finely ground material used for the infra-red examination. The loss of the physically combined water may account for the broad endotherm at 200–400° C present on the d.t.a. curve shown in fig. 2*a*.

The main weight loss occurs at 500–600° C under static conditions, or at 570–700° C under dynamic conditions. Except with a few specimens that contained traces of carbonate impurity, the dynamic dehydration curve agreed closely with the t.g.a. curve, showing that the loss was of water. The mean loss was 1.92 %, which is close to the theoretical value for the hydroxyl water in the mineral.

Comparison of the d.t.a. curve (fig. 1*a*) with the dynamic dehydration and t.g.a. curves (figs. 1*b* and 1*c*) shows that the 610–700° C endotherm on the d.t.a. curve can be associated with dehydroxylation. To test this

further, a sample was heated at 730° C until all the combined water had been lost, and a d.t.a. curve then determined. It was identical with that of the unheated material except that the 610–700° C endotherm was absent (fig. 2*b*). The latter is therefore associated with dehydroxylation. The sharp endotherm at about 800° C was unaffected and thus cannot be associated with dehydroxylation.

The X-ray evidence (table II and fig. 2*a*) shows that the immediate product of dehydroxylation gives an X-ray pattern identical with that of the original material. The product is therefore an anhydride with a structure close to that of the original amphibole. This conclusion is supported by the infra-red evidence, and agrees with that of Addison and Sharp (1962).

The X-ray evidence shows that the amphibole anhydride begins to decompose at 720–740° C to yield a pyroxene and a spinel. Above 770° C, cristobalite also begins to form. The reflections of these products are very weak below about 800° C, when the rate of decomposition suddenly increases. The reflections of the amphibole anhydride disappear, and those of the products become much stronger. Partial melting occurs either simultaneously with the decomposition, or soon afterwards. The infra-red evidence is consistent with these conclusions. The rapid phase of the reaction is associated with the sharp endotherm on the d.t.a. curve at 800–830° C, and with the sharp exotherm that usually follows it.

Considerations of stoichiometry also indicate that the decomposition products of the anhydride must include liquid or amorphous material. The anhydride has the approximate composition  $\text{Na}_2\text{Fe}_2^{3+}\text{Fe}_{2+6}^{2+}\text{Mg}_{0.4}\text{Si}_8\text{O}_{23}$ , and the crystalline products have the approximate compositions  $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ ,  $(\text{Fe}^{2+}, \text{Mg})\text{Fe}_2^{3+}\text{O}_4$ , and  $\text{SiO}_2$ . It is not possible for all the  $\text{Na}^+$  to go into the pyroxene, because if it did, no  $\text{Fe}^{3+}$  would be left over to go into the spinel. Hence some  $\text{Na}^+$  must go into a liquid or amorphous solid. There is no evidence regarding the composition of this phase, but it almost certainly contains also some of the  $\text{SiO}_2$  and probably contains some of the  $\text{FeO}$ ; mixtures in the  $\text{Na}_2\text{O}$ – $\text{FeO}$ – $\text{SiO}_2$  system melt below 800° C over a wide range of composition (Carter and Ibrahim, 1952). It is not possible from the present evidence to estimate the relative proportions of the pyroxene, spinel, cristobalite, and amorphous material formed.

The X-ray and infra-red results show that the pyroxene decomposes at 950–1000° C; the cristobalite also decomposes by 1050° C. The proportion of liquid gradually rises above 850° C. It was not found possible to correlate these changes with the d.t.a. curve.

The problem of the structure of the amphibole anhydride, and the significance of the preferred orientation shown by the decomposition products, are discussed later.

*Oxidizing atmospheres (oxygen or air)*

*Visual examination of products.* Below 300° C the colour and tensile strength undergo changes similar to those observed in neutral atmospheres. At 330–550° C the colour changes to a deep brown. This

TABLE III. Thermal behaviour of crocidolite in oxygen (CA laboratory)

Method No. of specimens studied	T.g.a. 16				Dynamic dehydration 12	
	Total loss	Step loss	Total gain	Step gain	1st loss	2nd loss
Mean	0.48 %	0.16 %	0.34 %	0.26 %	0.36 %	1.90 %
Standard deviation	±0.06	±0.03	±0.10	±0.085	±0.085	±0.047
Mean temp. limits (°C)	100–600°	450–600°	600–950°	850–900°	100–450°	450–550°
Range of upper limit (°C)	—	*450–510°	—	870–910°	420–480°	520–580°

\* Range of lower limit (°C)

change is slow at 330° C, but is rapid at 450° C or above. At 650–950° C the colour changes gradually to brick red. The change is slow at 650° C, reddish areas becoming visible only after a few days' heating in air, but at 900–950° C it is completed within a few hours. The fibres remain soft up to 950° C, with no obvious sign of glass formation. Fibres heated at 975° C are dull brown when hot; on cooling they become reddish brown and somewhat brittle, suggesting that melting has begun. Fibres heated at 1000–1100° C are blue-black when hot. After cooling, they are chocolate brown and brittle, and have a markedly fused appearance.

*D.t.a., dynamic dehydration, t.g.a., static weight loss curves, and Fe<sup>2+</sup> analyses.* Fig. 6 *a–e* shows typical results obtained by these methods. With each of the first three methods, 12–16 specimens were studied. Table III shows mean results and the variation between specimens. Hodgson (1963*b*) has described these results in more detail.

*X-ray investigation.* Samples were heated in air under static conditions and then examined by X-ray fibre rotation photographs. Table IV shows the phases detected. The phase described there as oxyriebeckite gave a pattern closely similar to that of the original material, but with smaller cell parameters. The variation was continuous; in no case were two forms of the amphibole with different cell parameters found in the

same sample. The maximum decreases in  $b$  and in  $a \sin \beta$  were each about 1 %. The data did not show whether there were significant changes in  $c$  or in  $\beta$ . The crystalline decomposition products detected at 840° C and above were a pyroxene, a spinel, cristobalite, and hematite. As

TABLE IV. X-ray data for samples of crocidolite examined after heating in air

Temp. (°C)	Specimen	Phases detected by X-rays*					
		<i>R</i>	<i>OR</i>	<i>P</i>	<i>S</i>	<i>C</i>	<i>H</i>
150°	RS21	+					
310°	„	+					
350°	„	†	†				
400°	„		+				
512°	„		+				
670°	„		+				
730°	RS7		+				
760°	RS21		+				
770°	RS7		+				
790°	RS21		+		?	?	
840°	RS7		wk	+	wk	+	?
865°	RS7		wk	+	wk	+	?
883°	RS21		wk	+	+	+	?
920°	RS7			+	?	+	+
940°	RS21		wk	+	+	+	+
950°	RS21			+		+	+
950°	RS7			+	?	+	+
975°	„			+	?	+	+
1010°	„			wk		wk	+
1025°	„			wk		+	+
1040°	„			wk		wk	+
1050°	„			wk	?	+	+
1060°	„					?	+
1100°	„					wk	+

\* *R* = riebeckite, *OR* = oxyriebeckite, *P* = pyroxene, *S* = spinel, *C* = cristobalite, *H* = hematite

† Cell parameters between those of riebeckite and oxyriebeckite.

with the products of decomposition formed in neutral atmospheres, all showed varying degrees of preferred orientation. In general, the pyroxene and the hematite showed the highest degree of orientation, and the cristobalite the lowest; the cristobalite was, however, usually more highly oriented than when formed in neutral atmospheres.

The pyroxene, the spinel, and the cristobalite all resembled the corresponding phases formed in neutral atmospheres in cell parameters, relative intensities, and orientation relations. The hematite, referred to hexagonal axes, had  $a$  5.03,  $c$  13.7 Å, and was formed with an  $a$ -axis

parallel to the fibre direction (amphibole *c*). Experiments using single crystal material showed that the hematite *c* axis was formed parallel to the (100) plane of the amphibole.

*Sequence of thermal changes.* Below 300° C under dynamic conditions, physically combined water is lost, as in neutral atmospheres. The first stage of oxidation occurs at 300–450° C (static) or 400–600° C (dynamic). In this process, the hydroxyl water is completely lost (fig. 6*b*), but the corresponding weight loss is only about 0.2 % (figs. 6*c* and *d*). The process is marked by an exotherm at about 415° C on the d.t.a. curve (fig. 6*a*), and by a colour change from grey-blue to deep brown. About three-quarters of the Fe<sup>2+</sup> is oxidized (fig. 6*e*). These results support the conclusion of Addison, Addison, Neal, and Sharp (1962) that the main process at this stage is the formation of an oxyamphibole of approximate composition  $\text{Na}_2\text{Fe}_4^{3+}\text{Fe}_{0.6}^{2+}\text{Mg}_{0.4}\text{Si}_8\text{O}_{24}$ . As they pointed out, such a process could very well occur through the migration of protons and electrons to the surfaces of the crystallites, where they would combine with oxygen molecules to form water. Similar mechanisms for the oxidation of amphibole and other minerals containing hydroxyl groups have been suggested by Barnes (1930), and, more clearly, by Brindley and Youell (1953) and others. The loss in weight (about 0.2 %) agrees with that expected (0.21 %) for such a mechanism. The proportion of the Fe<sup>2+</sup> oxidized in this first stage is limited by the hydroxyl content of the mineral, since one atom of hydrogen must be lost for each Fe<sup>2+</sup> atom oxidized.

The X-ray results show that the oxyamphibole has slightly smaller cell parameters than the unoxidized material. This can be attributed to replacement of Fe<sup>2+</sup> ions by the smaller Fe<sup>3+</sup> ions. Comparable reductions in cell parameters have been found in the other oxidation reactions for which mechanisms of the same type have been suggested.

Decomposition of the oxyamphibole and the second stage of oxidation occur at 600–950° C. These processes are slow below 870–910° C, when they become much more rapid. They are together associated with a colour change to brick red, and the rapid phase of the process is also marked by the endotherm on the d.t.a. curve at about 900° C and the immediately succeeding exotherm. It is difficult to see how the oxyamphibole could undergo further oxidation without decomposition taking place. Probably decomposition precedes or accompanies the second stage of oxidation, although the latter process can be detected at lower temperatures than the former on account of the relatively greater sensitivity of the methods employed.



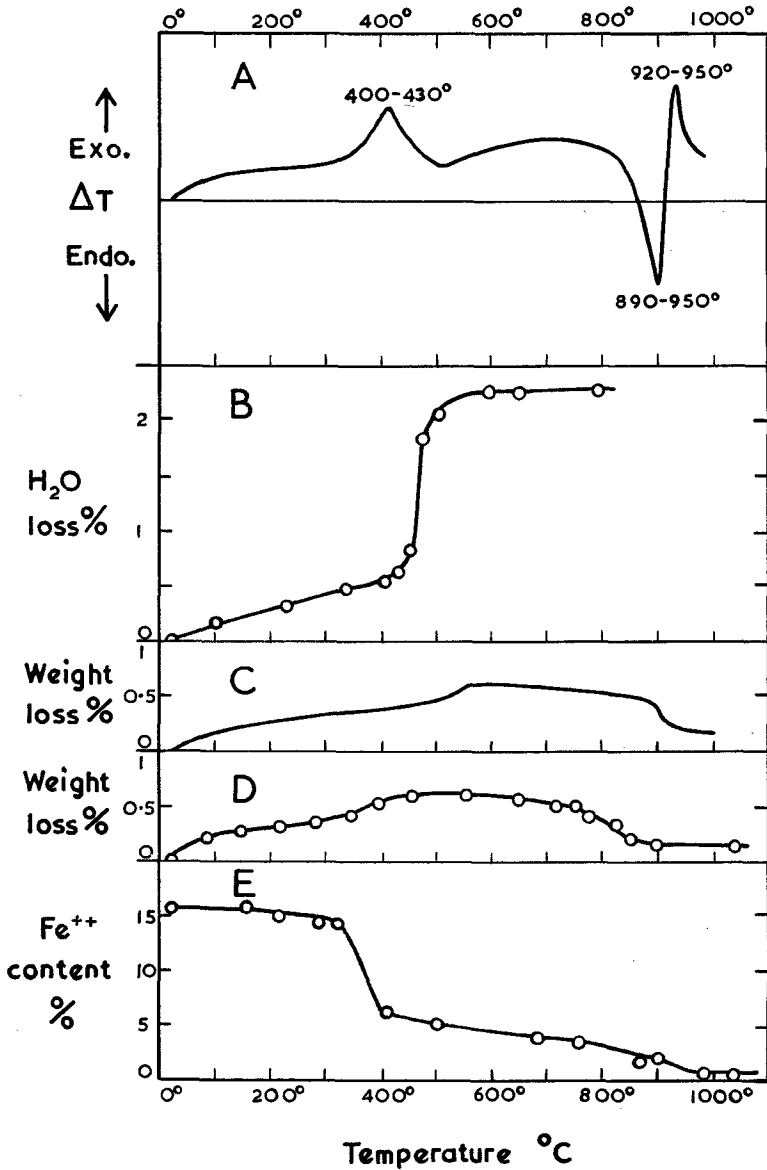
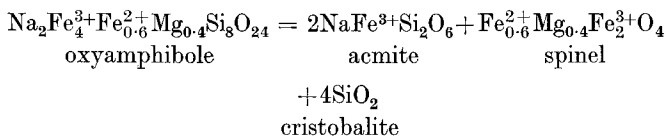


FIG. 6. Thermal behaviour of crocidolite in oxidizing atmospheres. (a) D.t.a.; typical curve obtained with CA apparatus. (b) Dynamic dehydration (specimen RS7). (c) T.g.a. (specimen RS7). (d) Static weight loss (specimen RS7). (e) Fe<sup>++</sup> contents of heated samples (specimen RS21).

The d.t.a. effects at about 900° C in oxidizing atmospheres (fig. 6*a*) resemble those at about 800° C in neutral atmospheres (fig. 1*a*), showing that there is some similarity between the decomposition of the oxyamphibole and that of the amphibole anhydride. The decomposition of the oxyamphibole occurs more gradually than that of the anhydride; this is shown both by the X-ray results and by the relative breadths of the d.t.a. endotherms.

The data given in fig. 6*e* show that 0.4 % of Fe<sup>2+</sup> remains after heating to constant weight in air at 950–1000° C. This amount is probably controlled by equilibrium and not kinetic considerations. Since the oxyamphibole is anhydrous, the oxidation cannot occur through loss of hydrogen, but only by gain of oxygen. It is represented by weight gains at 600–950° C on the t.g.a. and static weight loss curves (figs. 6*c* and *d*). The theoretical gain in weight, corresponding to the observed change in Fe<sup>2+</sup> content, is 0.51 %. The static curve (fig. 6*d*) showed a gain of 0.44 %, which is in fair agreement with this. The t.g.a. curves (fig. 6*c*) showed a mean gain of 0.34 % (mean for 16 specimens; table III). This discrepancy is almost certainly significant, and can perhaps be attributed to incompleteness of reaction under dynamic conditions.

The products of the decomposition and second stage oxidation are a pyroxene, cristobalite, hematite, and a spinel (table IV). There is no evidence of melting below 975° C. The facts are consistent with the hypothesis that decomposition proceeds approximately according to the equation:



the spinel being afterwards largely oxidized to hematite. The role of the Mg<sup>2+</sup> and residual Fe<sup>2+</sup> (about 0.07 ions per formula unit of crocidolite) in the final product is uncertain. Perhaps the most likely assumption is that they remain in a spinel, the amount of which is too small for detection by X-rays.

Above about 950° C the pyroxene reflections become weaker and finally disappear. The hematite reflections become stronger, and at 975° C and above, the presence of liquid is apparent. In some fibres that had been heated at 950–1000° C, the hematite was more highly oriented than any other of the decomposition products except the pyroxene. These facts suggest that the pyroxene is melting incongruently to give

additional hematite together with liquid. This agrees with the fact that pure acmite melts at 990° C to give hematite and liquid (Bowen and Schairer, 1929). At 1050–1100° C, the cristobalite reflections also become weaker or disappear, indicating that this phase is being dissolved by the liquid.

The d.t.a. curve (fig. 6*a*) agrees substantially with those obtained in air by Vermaas (1952) and others. Vermaas correctly attributed the exotherm at 415° C to partial oxidation, but he considered that the endotherm at about 900° C was due to dehydroxylation, and the succeeding exotherm to formation of the acmite and other products possibly accompanied by completion of oxidation. The present results show that his interpretation of the high temperature changes was incorrect.

### *Reducing atmospheres*

*Products of reduction.* Addison and Sharp (1962) have studied the reduction of crocidolite at 450° and 615° C in some detail, and only a few observations will be recorded here. They largely complement theirs.

TABLE V. Phases detected in crocidolite fibres after heating in hydrogen (specimen RS21)

Temp. (° C)	Period of heating (hr)	Phases detected by X-rays*					
		<i>R</i>	<i>P</i>	<i>C</i> (low)	<i>C</i> (high)	<i>F</i>	<i>Fe</i>
440°	48	+					
500°	24	+					
530°	24	wk	+	wk			wk
570°	24		+	wk		wk	wk
610°	48		wk	wk			+
840°	6		wk	+	wk	wk	+
850°	4		v. wk.	+	wk	wk	+

\* *R* = riebeckite, *P* = pyroxene, *C* = cristobalite, *F* = fayalite, *Fe* = iron.

When crocidolite is heated in hydrogen at 350–450° C the fibres lose their lustre and the colour changes to a greyish blue, as in other atmospheres. Fibres cooled from 530–850° are black and appear to contain much glass. Optical examination showed that the glass had a refractive index of about 1.51, and contained opaque particles up to 50  $\mu$  in diameter. Attempts to identify these by optical and electron microscopy were unsuccessful.

Table V shows the phases detected by X-ray fibre rotation photographs in fibres that had been heated under various conditions. The pyroxene showed strong preferred orientation, with its *c*-axis parallel

to that of the amphibole. Its cell parameters differed from those of the pyroxene formed in neutral or oxidizing atmospheres, and were near to those predicted for the hypothetical compound  $\text{FeSiO}_3$  ( $a \sin \beta$  9.33,  $b$  9.10 Å, Brown, 1960). The pyroxene is thus probably a member of the  $\text{FeSiO}_3$ - $\text{MgSiO}_3$  series, high in iron. The fayalite was well oriented when formed at 530–610° C; there were three orientations similar to those of the forsterite formed when fibres of clino-chrysotile are heated in air (Brindley and Zussman, 1957). When formed at 840–850° C, the fayalite was unoriented. Attempts to determine the orientations of the pyroxene and fayalite in the sense of rotation around the fibre axis were unsuccessful, because when single crystals of riebeckite or arfvedsonite were heated in hydrogen the products were unoriented.

The other crystalline products formed from crocidolite (low and high cristobalite and metallic iron) were unoriented. The persistence of high cristobalite at room temperature can perhaps be attributed to the presence of the glass, which is known to stabilize inclusions of high cristobalite (Greig, 1932).

*Sequence of reactions.* Addison and Sharp (1962) heated crocidolite samples in hydrogen at 450° and 615° C. In each case they determined the weight changes, volume of hydrogen sorbed, quantity of water produced, and content of  $\text{Fe}^{3+}$  remaining in the solid. They showed that, at both temperatures, reduction occurred by loss of oxygen, which combined with the hydrogen to form water. The product that had been reduced at 615° C was shown to be anhydrous. For each formula unit ( $\text{Na}_2\text{Fe}_2^{3+}\text{Fe}_{2.6}^{2+}\text{Mg}_{0.4}\text{Si}_8\text{O}_{24}\text{H}_2$ ) of crocidolite initially present, it contained approximately 1 atom of  $\text{Fe}(0)$ , 3.6 ions of  $\text{Fe}^{2+}$ , and no  $\text{Fe}^{3+}$ . From X-ray patterns, they concluded that the material was amorphous.

The present results are compatible with all but the last of these conclusions. Metallic iron is present, and could account for the presence of  $\text{Fe}(0)$ , while a pyroxene and cristobalite are also present in addition to glass. The formation of liquid at such a low temperature is explained by the fact that some compositions in the system  $\text{Na}_2\text{O}$ - $\text{FeO}$ - $\text{SiO}_2$  melt below 500° C (Carter and Ibrahim, 1952). The glass therefore almost certainly contains  $\text{FeO}$  as well as  $\text{Na}_2\text{O}$  and  $\text{SiO}_2$ .

Addison and Sharp (1962) found that partial reduction occurs at 450° C; calculation from their data shows that, for each formula unit of crocidolite taken, the product contains approximately 0.8 atoms of  $\text{Fe}(0)$ , 2.4 ions of  $\text{Fe}^{2+}$ , and 1.4 ions of  $\text{Fe}^{3+}$ . X-ray, infra-red, and weight loss evidence showed that the material was still basically an amphibole and that no hydroxyl water had been lost. They concluded that some

of the  $\text{Fe}^{3+}$  ions had been reduced to  $\text{Fe}(0)$  without moving from their positions in the structure, and that an equivalent number of oxide ions had been lost.

The present results confirm that no phases other than the amphibole can be detected by X-rays below  $530^\circ\text{C}$ . From a crystal chemical viewpoint, Addison and Sharp's hypothesis poses considerable difficulties, but no other explanation can be put forward on the basis of the present evidence.

### Discussion

*Interpretation of chemical analyses.* In the interpretation of chemical analyses of amphiboles, it has often been assumed that water lost above

TABLE VI. Mean chemical analysis and atomic ratios for crocidolite from the Koegas-Westerberg area

	1		2	3
$\text{SiO}_2$	51.04	Si	7.95	7.88
$\text{Al}_2\text{O}_3$	nil	Al	—	—
$\text{Fe}_2\text{O}_3$	17.15	$\text{Fe}^{3+}$	2.01	1.99
FeO	20.42	$\text{Fe}^{2+}$	2.66	2.64
MgO	1.60	Mg	0.37	0.37
MnO	0.06	Mn	0.01	0.01
CaO	0.69	Ca	0.11	0.11
$\text{Na}_2\text{O}$	6.24	Na	1.88	1.87
$\text{K}_2\text{O}$	0.10	K	0.02	0.02
$\text{H}_2\text{O}^{-105}$	0.21	H	1.97	2.35
$\text{H}_2\text{O}^{105-570}$	0.38	O	24.00	24.00
$\text{H}_2\text{O}^{+570}$	1.90			
	99.79			

1. Mean of analyses for specimens RS3, RS7, RS10, RS13, RS16, and RS23. Analyst: W. Bennis. Specimen RS23 had been treated with acetic acid before analysis to remove carbonates; the other analyses have been corrected for  $\text{CO}_2$  (mean 0.25 %), assumed present as calcite.  $\text{H}_2\text{O}$  values are taken from the dynamic dehydration curves described in the present paper.
2. Atomic ratios, referred to  $(\text{O} + \text{OH}) = 24$ , assuming that only the water lost above  $570^\circ\text{C}$  is combined.
3. As 2, but assuming that water lost above  $105^\circ\text{C}$  is also combined.

$105\text{--}110^\circ\text{C}$  is chemically combined. The present results show that this assumption is incorrect for crocidolite, as the loss above  $110^\circ\text{C}$  includes varying amounts of physically combined water. The true content of hydroxyl water in crocidolite can be found most conveniently from t.g.a. or dynamic dehydration curves in a neutral atmosphere. It is important to exclude air or oxygen from the sample before heating is started.

Table VI, column 1, gives the mean chemical analysis for six of the

specimens used in this study. In column 2, atomic ratios are calculated using  $\text{H}_2\text{O}^{+570}$  (determined under dynamic conditions) as the measure of combined water, and in column 3 they are calculated using  $\text{H}_2\text{O}^{+105}$  for this purpose. Table VII shows the corresponding allocations of atoms to sites, based in each case on the principles suggested by Whitaker (1961). It is seen that considerable errors arise if  $\text{H}_2\text{O}^{+105}$  is used. The  $M_2$  sites are shown as being incompletely occupied, and there is a surplus of hydrogen which can only be accounted for on the unlikely hypothesis that O is substituted by OH.

TABLE VII. Occupancy of sites

Type and number of sites	Occupancy assuming $\text{H}_2\text{O}^{+570}$ combined	Occupancy assuming $\text{H}_2\text{O}^{+105}$ combined
(0-1) A	0.01 Ca	—
2 $M_4$	1.88 Na } 0.02 K } 2.00 0.10 Ca }	1.87 Na } 0.02 K } 2.00 0.11 Ca }
2 $M_2$	1.96 $\text{Fe}^{+++}$ } 0.04 Mg } 2.00	1.87 $\text{Fe}^{+++}$ } 0.02 Mg } 1.89
2 $M_1 + M_3$	2.66 $\text{Fe}^{++}$ } 0.33 Mg } 3.00 0.01 Mn }	2.64 $\text{Fe}^{++}$ } 0.35 Mg } 3.00 0.01 Mn }
8 Z	7.95 Si } 0.05 $\text{Fe}^{+++}$ } 8.00	7.88 Si } 0.12 $\text{Fe}^{+++}$ } 8.00
22 O	22.00 O 22.00	21.65 O } 0.35 OH } 24.00
2 OH	1.97 OH } 0.03 O } 2.00	2.00 OH 2.00

It has already been mentioned that mechanical disintegration causes the content of hydroxyl water to decrease, and that of physically combined water to increase (fig. 3). The  $\text{Fe}^{3+}:\text{Fe}^{2+}$  ratio also increases (Addison, Addison, Neal, and Sharp, 1962). These effects can be attributed to oxidation, resulting in loss of  $\text{H}^+$  and conversion of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , coupled with adsorption of water, including that formed in the oxidation. Some absorption of oxygen and decomposition of the oxy-amphibole may also occur on exposed surfaces. It is thus essential to avoid drastic mechanical treatment of the fibres, especially if these are to be used for water or  $\text{Fe}^{2+}$  determination. The results in tables VI and VII show that the hydroxyl contents tend to be slightly below theoretical. This can perhaps be attributed to oxidation during sample preparation, though weathering of crocidolite *in situ* can have the same effect (Hodgson, 1963b).

*The amphibole anhydride.* As has been shown, the immediate product of dehydroxylation in neutral atmospheres is an anhydride, which must have a structure very similar to that of the original mineral. When static heating conditions are used, the anhydride persists over a temperature range of about 200° C. This behaviour may be contrasted with that of tremolite, which appears to yield a pyroxene directly on dehydroxylation (Freeman and Taylor, 1960; Taylor, 1962). The difference in the behaviour of these two amphiboles is similar to that observed between di- and trioctahedral clay minerals; dioctahedral minerals, such as kaolinite and pyrophyllite, yield anhydrides that persist over substantial ranges of temperature, whereas trioctahedral ones, such as serpentine and talc, do not. The formation of an anhydride in the case of crocidolite, or its persistence over a wide temperature range, can therefore perhaps be attributed to the fact that tripositive ions are present.

It is possible only to speculate about the structure of the anhydride. The infra-red results show that the crystallinity is lower than that of the original material, that some distortional or other changes in the Si-O anions have taken place, and that not quite all of the hydroxyl water has been lost at 750° C. This last conclusion is supported by analytical results (table II). The main problem is to determine which of the oxygen atoms in the amphibole structure have been lost; at least three possibilities must be considered. First, approximately half of the hydroxyl groups originally present may be missing, most of the rest being replaced by oxide ions. Second, the same number of oxide ions could be missing as on the first hypothesis, but they might be lost at random from all the oxygen sites, and not exclusively from those initially forming parts of hydroxyl groups. The anhydride would thus have a structure with random anion defects. Third, an inhomogeneous mechanism (Taylor, 1962) may operate; parts of the structure may be destroyed completely, and thus provide all the oxygen for the water that is formed, while their cations migrate into the parts that remain to balance the charge of the hydrogen ions that are lost. On this hypothesis, the anhydride has a structure with interstitial cations. The three possibilities are perhaps not mutually exclusive. The main difference between them lies in whether the oxygen atoms are lost from specific sites, from random sites, or from distinct regions of greater than unit cell scale. The truth may lie somewhere between all three.

*The mechanisms of the decomposition reactions.* These reactions include the decomposition of the anhydride at about 800° C in neutral atmospheres of the oxyamphibole at about 900° C in oxidizing atmospheres,

and of crocidolite itself, or perhaps of a reduced form of it, at about 500° C in hydrogen. All these reactions occur topotactically; that is, the main crystalline products (except for metallic iron) are formed with definite preferred orientations relative to the starting material. These products include pyroxenes, a spinel, cristobalite, hematite, and fayalite.

(100)	(100)	(0001)
2Na 2Fe <sup>2+</sup> 3(Fe <sup>2+</sup> ,Mg)	4Na 4Fe <sup>2+</sup>	8Fe <sup>2+</sup>
8Si	8Si	8Fe <sup>2+</sup>
2Na 2Fe <sup>2+</sup> 3(Fe <sup>2+</sup> ,Mg)	4Na 4Fe <sup>2+</sup>	8Fe <sup>2+</sup>
8Si	8Si	8Fe <sup>2+</sup>
2Na 2Fe <sup>2+</sup> 3(Fe <sup>2+</sup> ,Mg)	4Na 4Fe <sup>2+</sup>	8Fe <sup>2+</sup>
<b>Crocidolite</b>	<b>Acmite</b>	<b>Hematite</b>
(100)	(111)	(011)
6Fe <sup>2+</sup> 3Si	9(Fe, Mg) Oct.	4Si 4O
3Si 6Fe <sup>2+</sup>	9(Fe, Mg) Tet.+ Oct.	4Si 4O
6Fe <sup>2+</sup> 3Si	9(Fe, Mg) Oct.	4Si 4O
3Si 6Fe <sup>2+</sup>	9(Fe, Mg) Tet.+ Oct.	4Si 4O
6Fe <sup>2+</sup> 3Si	9(Fe, Mg) Oct.	
<b>Fayalite</b>	<b>Spinel</b>	<b>Low Cristobalite</b>

FIG. 7. Schematic representations of some crystal structures in observed relative orientations. Each horizontal line represents 12 (O, OH).

To a first approximation, all these products, as well as the starting material, have structures based on sheets of nearly close-packed oxygen ions, with cations in interstices. These structures are shown diagrammatically in the observed relative orientations in fig. 7. The orientation relationships are such that the oxygen packing is preserved as far as possible. The decomposition reactions therefore probably occur by the migration of cations, including Si<sup>4+</sup>, through relatively stable oxygen frameworks. Similar mechanisms have been suggested for the formation of iddingsites from olivine (Gay and LeMaitre, 1961), periclase from brucite (Ball and Taylor, 1961), forsterite and MgSiO<sub>3</sub> from serpentine (Ball and Taylor, 1963), and in other cases. The reactions are perhaps best envisaged as involving migrations of cations so that, within a single



crystallite, regions corresponding in composition to each of the products are formed. Within each such region, the necessary changes in the type of oxygen packing then take place. Except in the formation of cristobalite, little or no bulk movement of oxygen ions is necessary. The smallest changes occur in the formation of the pyroxenes, which in consequence are almost always highly oriented. The types of ionic movements needed to convert an amphibole structure into a pyroxene have been discussed previously in relation to tremolite (Freeman and Taylor, 1960), and, with some qualifications, this discussion is probably applicable also to the present case.

In some of the reactions, the total extent of the framework of nearly close-packed oxygen atoms changes. It is extended in the oxidation reactions at 600–950° C, as a result of the absorption of oxygen molecules and their conversion into oxide ions, while parts of it are destroyed in the reduction reactions in hydrogen, and also when partial fusion occurs in any of the atmospheres employed. These fusion reactions appear to be the first cases in which incongruent melting has been observed to occur topotactically.

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