The thermal disintegration of crocidolite in air and in vacuum

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Summary. The thermal disintegration of crocidolite has been investigated with X-ray powder and rotation photographs. Initial disintegration products include monoclinic pyroxene, iron oxide phases, and cristobalite as a pseudomorph of the original fibre bundles but at about 1000° C fusion occurs due to incongruent melting of the pyroxene. The products are strongly oriented along the fibre axis and full orientation relationships have been deduced with the aid of structural models. From these relationships it is suggested that regions of the amphibole structure on (100) are retained in the product phases without change in orientation.

CROCIDOLITE is a monoclinic amphibole and is the fibrous form of the mineral riebeckite. At about 900° C it breaks down to pyroxene (acmite), hematite, and cristobalite (Vermaas, 1952). For tremolite the crystallographic axes of the amphibole are retained in the conversion to pyroxene (Freeman and Taylor, 1960) and the thermal distintegration of crocidolite appeared of particular crystallographic interest because of the occurrence of hematite and cristobalite among the reaction products. After the completion of this work the author has become aware of recent work on the thermal disintegration of crocidolite from South Africa (Freeman, 1962, and Hodgson *et al.*, this number).

Experimental. Samples of crocidolite were obtained from Wittenoom Gorge, in the Hammersley Ranges of Western Australia. The asbestos veins occur in banded ironstones and quartzites of Proterozoic Age (Trueman, 1963) and chemically the asbestos can be closely represented by the formula $Na_{1.5}Ca_{0.1}Mg_{1.0}Fe^{++}_{1.9}Fe^{+++}_{2.5}Si_8O_{22}(OH)_2$.

Fibre bundles cut from the centre of crocidolite veins were heated both in air and in vacuum. The vacuum-heated samples were used in kinetic studies of the dehydration of crocidolite (O'Connor, to be published). X-ray powder and rotation photographs were recorded with filtered chromium radiation.

Thermal disintegration of crocidolite in air. The crystalline phases detected at various temperatures are listed in table I.

The amphibole structure was stable until 850° C in spite of the loss of

hydroxyl groups and the partial oxidation of ferrous iron from 300°–500° C (Addison *et al.*, 1962); a 1 % contraction in both *b* and $a \sin \beta$ was observed over this temperature range. At 1000° C the products were pyroxene (acmite), α-hematite, and cristobalite, but between 850° and 950° C a spinel phase very similar to magnetite was also observed. After the thermal disintegration a pseudomorph of the original fibre bundles was produced but fusion began at about 1000° C.

TABLE I. Products of the thermal disintegration of crocidolite, where A = amphibole, P = pyroxene, Q = quartz, T = tridymite, H = hematite, C = cristobalite, and S = spinel (magnetite)

In air			In vacuo		
Temperature (°C)	Time (hours)	Products	Temperature (°C)	Time (hours)	Products
800°	1	A	600°	196	A
850°	1	A, H	700°	152	P, C
	24	A, H, P, C, S	750°	190	P, C
900°	1	A, H, P, C, S	800°	2	P, Q
	24	A, H, P, C, S		143	P, Q
950°	1	H, P, C, S	850°	364	P
	24	H, P, C	950°	195	P, T, S
1000°	1	H, P, C	1000°	314	P, T, S
	24	H, P, C	1100°	224	P, T, S

Thermal disintegration of crocidolite in vacuum. Initial breakdown of the amphibole structure was observed at 700° C when pyroxene and cristobalite were obtained as reaction products (table I).

At 800° C pyroxene and quartz were observed while above 950° C pyroxene, tridymite, and increasing amounts of randomly oriented spinel were detected as fusion proceeded. The distribution of quartz was not uniform within fibre bundles and it may therefore have been a spurious formation.

Orientation of the product phases. Under oxidizing conditions the phases are all preferentially oriented along the fibre axis but in vacuum only the pyroxene and cristobalite are similarly oriented.

The pyroxene phases formed in air and in vacuum are structurally similar to acmite and the unit-cell dimensions for the vacuum-heated sample were $a \sin \beta$ 9·30, b 8·95, c 5·26, all ±0·05 Å. The *c*-axis of the pyroxene was parallel to the original fibre axis.

X-ray powder data for the iron oxide phases was in good agreement with that of α-hematite and magnetite and preferred orientation was such that $c_A \parallel a_H \parallel [\bar{2}11]_S$, where the subscripts represent the phases so designated in table I. For a sample heated 24 hours at 900° C some

additional X-ray reflections not consistent with the spinel structure of magnetite were observed. These reflections can be associated with the formation of an intermediate phase in the conversion of spinel to hematite.

Only one powder line (d 4·06 Å) consistent with the strongest line of tetragonal α-cristobalite was detected. The main orientation was such that $c_A \parallel a_C$ but weaker orientations $c_A \parallel [102]_C$ or $[531]_C$ were also detected. Both $[102]_C$ and $[531]_C$ would be [411] directions in the closely similar cubic β-cristobalite.

Discussion. The structural changes of crocidolite can be considered in the following stages with increasing temperature: dehydroxylation and oxidation, disintegration of the amphibole structure, structural transformations, and melting of the pyroxene.

The dehydroxylation of the amphibole is an essential part of the mechanism for the oxidation of crocidolite proposed by Addison *et al.* (1962). In vacuum when oxidation was suppressed the loss of hydroxyl groups occurred at about 600° C. Although it is not the object of this paper to discuss these processes in any detail it is necessary to point out that the amphibole structure is essentially maintained after the completion of these changes and only a small decrease in lattice dimensions was observed.

In air the initial disintegration of the amphibole to pyroxene (acmite), α-hematite, spinel and cristobalite occurred at 850°–900° C while in vacuum the breakdown to pyroxene and cristobalite was observed at 700° C. At this stage all of the product phases were oriented along the fibre axis as a pseudomorph of the original fibre bundles. After the initial disintegration further increase in temperature caused transformation of the spinel to hematite in air and transformation of cristobalite to tridymite in vacuum. In the transformation of the spinel phase an intermediate iron oxide phase possibly similar to the spinel phases of γ-Fe$_2$O$_3$ (Bernal *et al.*, 1959) was also detected.

Close to 1000° C incongruent melting of the pyroxene caused fusion of the pseudomorphs. In air acmite melts incongruently to hematite and glass at 990° C (Bowen and Schairer, 1929). The randomly oriented spinel phase observed in increasing amounts as fusion occurred in vacuum can be considered as resulting from the breakdown of the pyroxene to spinel and glass when oxidation of ferrous iron is suppressed.

In the above sequence of reactions the fusion of crocidolite has been associated not with the disintegration of the amphibole but with subsequent breakdown of the pyroxene. It is likely that other amphibole

disintegrations can be considered in similar manner, the occurrence of fusion depending upon the thermal stability of the pyroxene product. Although tridymite has not previously been reported as a product of amphibole disintegrations, in this instance the fusion of crocidolite might be expected to favour the recrystallization of tridymite due to the incorporation of sodium ion impurity (Flörke, 1963). However, although fusion also occurs in oxidizing conditions the formation of tridymite was not observed.

After the initial breakdown of the amphibole the products are pre-ferentially oriented along the fibre (c-axis) of crocidolite such that $c_A \parallel c_P \parallel a_H \parallel [\bar{2}11]_S \parallel a_C$ where the subscripts refer to those phases so designated in Table I. The consideration of structural models revealed strikings tructural similarities between the amphibole and all of the product phases (fig. 1). On the basis of these structural similarities and the preferred orientation along the fibre axis the following orientation relationships were deduced: $(100)_A \parallel (100)_P \parallel (0001)_H \parallel (111)_S \parallel (011)_C$ and $c_A \parallel c_P \parallel a_H \parallel [\bar{2}11]_S \parallel a_C$.

These relationships have also been found for the thermal disintegra-tion of crocidolite from Koegas in South Africa (Hodgson et al., this number) and the orientation relationship between the spinel and hema-tite is consistent with that reported for this transformation by Bernal et al. (1957).

In the conversion of the amphibole to pyroxene some chains of silicon tetrahedra are retained while others are changed by the migration of silicon into adjacent approximately tetrahedral oxygen sites and a consequent rearrangement of the oxygen framework. Most of the cation positions are also closely retained. This transformation would appear therefore to be accomplished by cation migration within an oxygen framework that is in the main retained (Freeman and Taylor, 1960).

The iron in crocidolite occupies octahedral oxygen sites (Whittaker, 1949) and this cation–oxygen coordination is retained in both the spinel and hematite. In the formation of iron oxides the migration of iron and silicon must be extensive but the initial nucleation could occur in these octahedral regions with a minimum rearrangement of the cation–oxygen framework. The oxygen array on (100) of the amphibole can in the main be retained during further growth and possible migration of oxygens within this plane are illustrated in fig. 1 f. Both the spinel and hematite can be constructed from these oxygen layers in the appro-priate stacking sequence, and the migration of iron to tetrahedral and octahedral sites. Movement of these layers by dislocation mechanisms
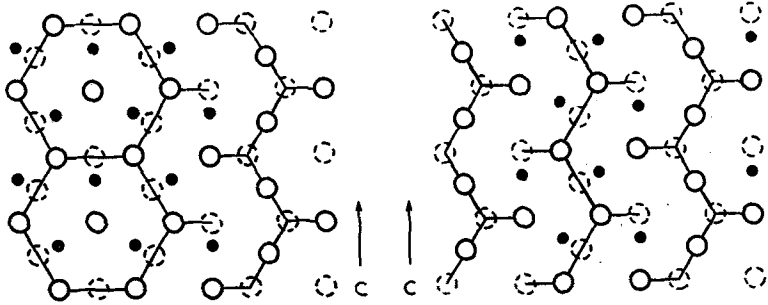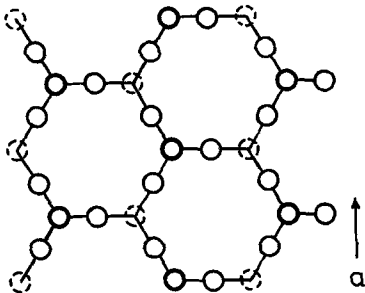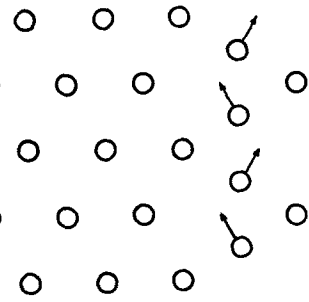
(a) (100) Amphibole

(b) (100) Pyroxene
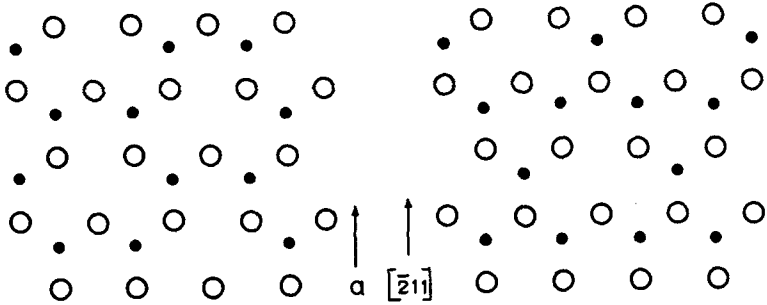
(c) (0001) Hematite

(d) (111) Spinel

(e) (011) Cristobalite

(f) Oxygen Shifts

FIG. 1. Idealized partial projections on: a, (100) amphibole; b, (100) pyroxene; c, (0001) hematite; d, (111) spinel; e, (011) cristobalite. Also f, possible oxygen migrations in the (100) plane of the amphibole in the conversion to iron oxides. Circles represent oxygen atoms, complete circles being above dashed circles, dots represent cations above the oxygen layers and lines join silicon atoms and emphasize the linking of silicon tetrahedra.

can be envisaged both in the initial formation and in the later conversion of spinel to hematite. Considered in this manner the spinel and hematite coexist in the same regions arising from different stacking sequences of these oxygen planes. This could account for the observation of only one orientation of hematite although it is partially derived from the spinel phase.

The formation of small regions of cristobalite does not involve great structural rearrangement of the amphibole but growth of these regions cannot proceed without extensive cation and anion migration. The displacement of amphibole chains relative to one another is such that a vacant roughly tetrahedral oxygen site shares the (100) face of silicon-oxygen tetrahedra. Migration of alternate silicon ions into this site followed by a consequent rearrangement of the oxygen framework forms a nucleus of cristobalite with the observed structural relationship to the amphibole. Growth of these nuclei is liable to be slow but the orientation can be retained. This picture of the formation of cristobalite does not of course account for the weaker preferred orientations also observed.

As in the case of tremolite the thermal disintegration of crocidolite occurs in an oriented manner and much of the amphibole structure on (100) is retained in the product phases (fig. 1). This appears to arise through the formation of product nuclei with a minimum rearrangement of the amphibole structure. With the exception of cristobalite further crystal growth also involves the retention of as much as possible of the original structure. Hence the pyroxene and iron oxide phases appear to be formed by cation migration through an oxygen array that undergoes a minimum of structural rearrangement.

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