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## *The thermal decomposition of amosite*

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*Summary.* When amosite (fibrous grunerite,  $\text{Fe}_{5.5}\text{Mg}_{1.5}\text{Si}_8\text{O}_{22}(\text{OH})_2$ ), is heated in argon or nitrogen, physically combined water is lost up to 500–700° C. Above 500° C (static) or 700° C (dynamic), dehydroxylation occurs endothermically, giving a pyroxene as the main product. Under dynamic heating conditions, part of the hydroxyl water is lost as hydrogen, with concurrent oxidation of the iron. At about 1000° C the pyroxene is decomposed to olivine and cristobalite; at about 1100° C melting begins. In oxygen or air, physically combined water is again lost below 500–700° C. At 350–1200° C a sequence of overlapping dehydrogenation, oxygen absorption, and dehydroxylation reactions occurs, which gives rise to a broad exotherm on the d.t.a. curve. The main products (for static heating conditions) are an oxyamphibole at 350–800° C, and a spinel, hematite, a pyroxene, and X-ray amorphous material at 800–1100° C. Silica crystallizes as cristobalite at 1100–1350° C, and as tridymite at 1450° C. Most of the products in either neutral or oxidizing atmospheres are formed topotactically. The mechanisms and rates of the reactions are discussed, and the problem of determining the chemically combined water in amosite and other minerals of similar composition is considered.

**A**MOSITE is the fibrous variety of the monoclinic amphibole, grunerite. It is known to occur only in the eastern Transvaal, South Africa, in metamorphosed banded ironstones of the Transvaal System. It is mined on a large scale, current annual production being around 70 000 tons. Its composition approximates to  $\text{Fe}_{5.5}^{2+}\text{Mg}_{1.5}\text{Si}_8\text{O}_{22}(\text{OH})_2$ . Its thermal decomposition in air was first studied by Vermaas (1952), who used d.t.a. and X-ray powder patterns. He reported a broad exothermic effect at 580–830° C, which he attributed to oxidation and decomposition, and showed the products of decomposition at 1200° C to be magnetite and cristobalite. Heystek and Schmidt (1953) also reported d.t.a. data, which agree broadly with those of Vermaas.

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No detailed X-ray study of amosite has been reported, but Ghose and Hellner (1959) determined the crystal structure of a non-fibrous grunerite similar in composition to amosite. They found that iron was almost exclusively preferred in the  $M_4$  sites, that is, at the edges of the octahedral bands, and that iron and magnesium were distributed at random in the other cation sites.

Vermaas showed that non-fibrous grunerite, when heated in air, behaved like amosite but that decomposition and oxidation occurred more slowly and at higher temperatures. In contrast, a finely fibrous variety of amosite, called montasite, reacted more rapidly than typical amosites and at lower temperatures.

The aim of the present work was to study the thermal decomposition of amosite in greater detail, in both oxidizing and neutral atmospheres.

#### *Material and experimental methods*

Several specimens from the asbestos mines at or near Penge, in the Steelpoort-Lydenburg area of eastern Transvaal, were used (specimens PRS 3, 4, 5, and 6, H 7, 9, 10, 12, 16, and 18, WRS 2 and 3, and KRS 1 from the collection at the Cape Asbestos Fibre Laboratory). Despite the fact that extensive mining operations have been carried out for many years, the geology of the area is not known in detail; studies are now in progress and will be reported elsewhere. The specimens consisted of cross-fibre seams, often about 10 cm thick, in a coarse-grained grey rock. The fibres, which were white, were often contaminated with magnetite grains, and sometimes also with other minerals. These included a carbonate, which appeared to be a magnesian siderite of approximate composition  $\text{Fe}_{0.8}\text{Mg}_{0.2}\text{CO}_3$ . X-ray photographs showed that the fibres were composed of very thin crystallites rotated at random around the fibre axis, so that only powder and fibre rotation photographs could usefully be obtained. However, occasional amphibole crystals were found among the fibres that were large enough to give true single-crystal patterns. All the fibre specimens had closely similar optical properties: parallel extinction, positive elongation, refractive indices 1.689 and 1.668 for light vibrating respectively parallel and perpendicular to the fibre direction. They also had virtually identical cell parameters, which agreed substantially with those reported by Ghose and Hellner (1959) for a grunerite of roughly similar composition, viz.,  $a$  9.56<sub>4</sub>,  $b$  18.30<sub>2</sub>,  $c$  5.34<sub>8</sub> Å,  $\beta$  101° 50' ( $a \sin \beta$  9.36 Å), space group  $C2/m$ . X-ray powder patterns agreed closely with that reported by

Flood (1957) for a grunerite from Collobrières, and less closely with that reported by Vermaas (1952) for amosite from Penge. Chemical analyses showed some variation between specimens, but all corresponded approximately to the formula  $\text{Fe}_{5.5}^{2+}\text{Mg}_{1.5}\text{Si}_8\text{O}_{22}(\text{OH})_2$  (table I).

The thermal behaviour was studied in argon and in air or oxygen mainly by differential thermal analysis (d.t.a.), thermogravimetric

TABLE I. Chemical analysis and atomic ratios for amosite from the Penge area.

	1		2	3		
$\text{SiO}_2$	49.76	Si	7.92	7.92	} 8.00	Z
$\text{Al}_2\text{O}_3$	0.24	Al	0.05	0.05		
$\text{Fe}_2\text{O}_3$	0.49	Fe <sup>III</sup>	0.06	{ 0.03		
FeO	40.09			{ 0.03	} 5.00	$(M_1 + M_2 + M_3)$
MgO	6.15	Mg	1.45	1.45		
MnO	0.53	Fe <sup>II</sup>	5.30	{ 3.52		
CaO	0.91			{ 1.78	} 2.00	$M_4$
$\text{Na}_2\text{O}$	0.10	Mn	0.07	0.07		
$\text{K}_2\text{O}$	0.13	Ca	0.15	0.15		
$\text{CO}_2$	0.18	Na	0.03	0.03	} 0.06	A
$\text{H}_2\text{O}^{+600}$	1.87	K	0.03	0.03		
$\text{H}_2\text{O}^{-600}$	0.27	H	1.99	1.99		

100.72

1. Chemical analysis; mean for 10 specimens (see text).  $\text{H}_2\text{O}^{+600}$  and  $\text{H}_2\text{O}^{-600}$  from dynamic dehydration curves. Analyst, W. Bennis.
2. Atomic ratios calculated from col. 1, referred to  $(\text{O} + \text{OH}) = 24$ .  $\text{CO}_2$  in col. 1 was assumed to occur as a magnesian siderite of composition  $\text{Fe}_{0.8}\text{Mg}_{0.2}\text{CO}_3$ .
3. Suggested allocation of atoms to sites.

analysis (t.g.a.), dynamic dehydration, static weight change curves, and X-ray fibre rotation photographs and  $\text{Fe}^{2+}$  analyses of heated specimens. The techniques were the same as those used with crocidolite (Hodgson, Freeman, and Taylor, 1965). The heating rates were  $10^\circ \text{C}/\text{min}$  for d.t.a. and  $2.5^\circ \text{C}/\text{min}$  for t.g.a. and dynamic dehydration. With each of these three methods, 5 to 13 specimens were studied and gave results in broad agreement with each other.

Samples were prepared for examination by breaking up selected portions of the fibre seams with a hammer followed by cutting into short lengths with scissors and sieving or shaking to remove grains of magnetite and other impurities. Samples used for d.t.a., dynamic dehydration, and t.g.a. determinations were dried at  $100^\circ \text{C}$  in air before use; those used for static weight-change curves,  $\text{Fe}^{2+}$  determinations, and X-ray studies were not thus dried.

*Thermal decomposition in inert atmospheres*

*Visual examination.* When amosite is heated in argon or nitrogen, the tensile strength falls markedly at 200–400° C. The colour darkens progressively above about 700° C, especially when dynamic heating conditions are used. Samples heated dynamically to 1000° C contain nearly black fibres that have largely retained their original form, together with fluffy, white material. Melting begins at about 1100° C.

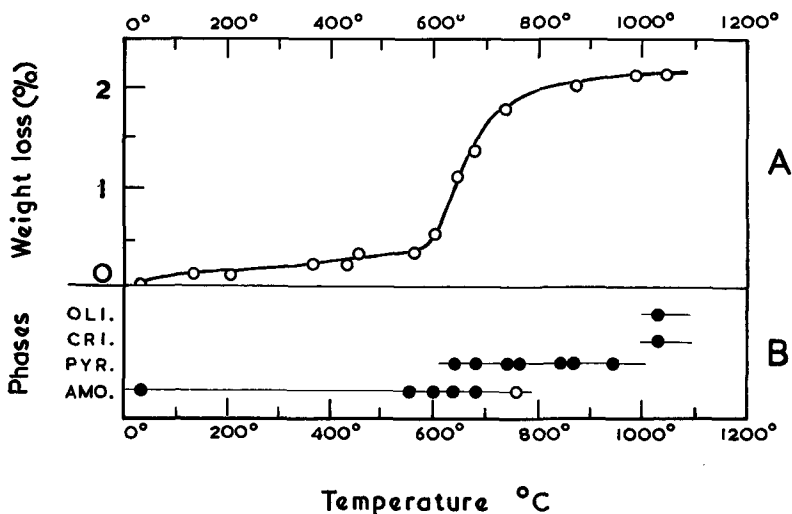


FIG. 1. Static heating in nitrogen (specimen PRS 5). (a) Weight-loss curve. (b) Phases detected by X-rays (amo. = amosite, pyr. = pyroxene, cri. = cristobalite, oli. = olivine; full and open circles denote major and minor constituents respectively).

*Static heating.* Fig. 1a shows the static weight-change curve for a typical specimen, and fig. 1b shows the phases detected from X-ray fibre rotation photographs on heated samples. There is a gradual loss in weight up to about 550° C. No change is detectable with X-rays, and it was concluded that, as with crocidolite (Hodgson, Freeman, and Taylor, 1965), the loss was of physically combined water. At 550–950° C there is a sharp loss of 1.85%, and the X-ray results show that decomposition occurs concurrently. The only product detectable with X-rays up to 950° C is a pyroxene. It showed strong preferred orientation; the orientation relationship was determined fully by employing a single crystal of grunerite picked out from one of the fibre specimens and was



standard deviation 0.17. The difference between the two means is highly significant ( $p = 0.005$ ) and can perhaps be attributed to differences in the preliminary treatment of the samples.

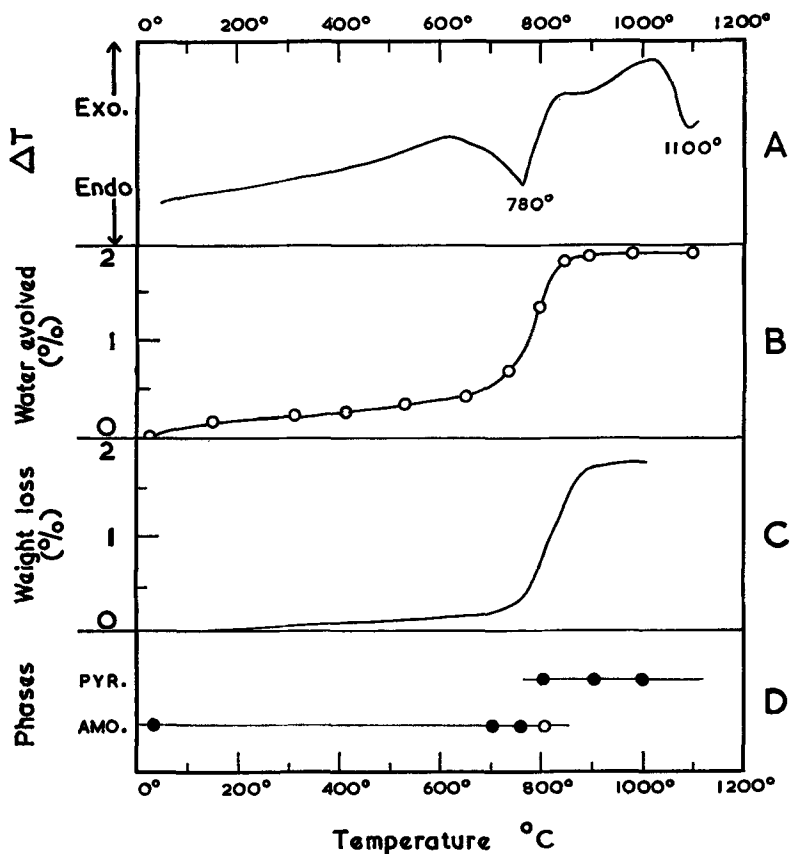


FIG. 2. Dynamic heating in argon (specimen PRS 5). (a) D.t.a. curve. (b) Dynamic dehydration curve. (c) T.g.a. curve. (d) Phases detected by X-rays (same notation as in fig. 1).

The course of the t.g.a. curves above 500–600° C differs from that of the static weight-change curve (fig. 1a) in two important respects. Firstly, as would be expected, the sharp loss corresponding to dehydroxylation occurs at a higher temperature; the amphibole is half decomposed at about 650° C under static conditions, but under dynamic conditions a temperature of about 800° C is needed to reach this degree

of reaction. Secondly, the step in the curve is lower than when static conditions are used. For twelve specimens of amosite from Penge and neighbouring localities examined by t.g.a. in argon, the mean loss above about 700° C was 1.51% with a range of 1.42–1.59% and a standard deviation of 0.04. The dynamic dehydration curve (fig. 2*b*) broadly resembles the t.g.a. curve; for the same twelve specimens, the mean percentage of water evolved above about 650° C was 1.47% with a range of 1.34–1.61% and a standard deviation of 0.07. The standard error of the difference between the two means is 0.02, and the difference between the t.g.a. and dynamic dehydration curves is therefore barely significant ( $p = 0.10$ , or 0.05 if a one-tailed test is used). It can nevertheless be explained quantitatively, as is shown below.

The water loss of about 1.5% found by either method is considerably below the theoretical value of 1.89%. The difference is not caused by a failure to complete the reaction under dynamic conditions. Several specimens that had been heated dynamically to 1000° C in argon were cooled (in argon) and then heated in oxygen for 7 hours at 1000° C. As shown later, this would remove as water any hydrogen ions remaining in the sample. In fact, no water was evolved during the heating in oxygen, although, as would be expected, there was a gain in weight due to absorption of oxygen.

The low weight losses found on dynamic heating in argon can be attributed to the loss of some of the hydrogen ions in the mineral, not as water, but as hydrogen gas, with simultaneous oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ :  $2\text{H}^+ + 2\text{Fe}^{2+} = \text{H}_2 + 2\text{Fe}^{3+}$ . Several lines of evidence support this hypothesis. Firstly, five different specimens were analysed for  $\text{Fe}^{2+}$  before and after heating to 1000° C in argon. The  $\text{Fe}^{2+}$  contents, expressed in all cases as percentages on the dry weight of material, fell by a mean of 2.5%, with a range of 1.4–3.3% and a standard deviation of 0.65. The fall in  $\text{Fe}^{2+}$  content may also be calculated on the basis of the above equation from the difference between the amounts of water evolved on heating in oxygen and in argon. The mean value thus calculated for the same five samples was 2.5%, with a range of 1.8–3.4% and a standard deviation of 0.81. Secondly, the amount of hydrogen evolved may also be calculated from the difference between the amounts of water evolved in oxygen and in argon. The mean value for this difference for eleven different specimens was 0.40%, which corresponds to a hydrogen evolution of 0.04%. This agrees exactly with the difference between the weight loss in argon, determined by t.g.a., and the amount of water evolved in the same atmosphere. Thirdly, five

specimens were studied by dynamic dehydration in argon, but the evolved gases were passed over oxidants to convert any  $H_2$  to  $H_2O$  before the latter was absorbed and weighed. For this purpose either crocidolite at a temperature  $100^\circ C$  below that of the sample, or cupric oxide at the sample temperature was used. The mean amount of water produced was thereby raised from 1.47 % to 1.85 %, which approaches the theoretical value of 1.89 %.

It was not found possible to detect any products of this internal oxidation reaction by X-rays. Perhaps the most likely product is a spinel; if it is assumed that all of the  $Fe^{3+}$  formed, together with that present in the initial mineral ( $Fe_2O_3$  content about 0.5 %) was present as magnetite, some 6 % of the latter would be formed. The darkening of the fibres is consistent with this hypothesis; 6 % of magnetite, if finely dispersed, would probably not be detectable with X-rays. Part of the  $Fe^{3+}$  could also be present in the pyroxene or in the amorphous parts of the product.

Hodgson (1963) has given fuller details of the dynamic studies reported here, both in argon and in oxygen.

#### *Static heating in air*

*Visual examination.* When amosite is heated in air, the tensile strength falls at  $200\text{--}400^\circ C$ . The fibres turn grey at  $350^\circ C$ ; with further rise in temperature they become increasingly soft and much fluffy material is formed. The colour changes gradually, to a deep brown at  $500^\circ C$  and a reddish-brown at  $800^\circ C$ . At  $1000\text{--}1200^\circ C$  the material is dark brown when hot and red-brown when cold; at  $1350\text{--}1450^\circ C$  it is almost black when hot and deep purple when cold. No liquid was observed up to  $1450^\circ C$ , the highest temperature studied. To a considerable extent the fibres retain their shapes even at  $1450^\circ C$ , but they are very fragile and much dust is present.

*Reactions below  $800^\circ C$ .* Figs. 3 *a*, *b*, and *d* show the weight-change curve, the results of  $Fe^{2+}$  analyses on heated samples (expressed as molar ratios,  $Fe^{2+}/8Si$ ), and the phases detected by X-ray fibre rotation photographs on heated samples. The reactions at  $500\text{--}800^\circ C$  were slow, about a week being needed at each successive temperature in order to attain constant weight. The total time needed to obtain the weight-change curve was about three months. The weight-change curve,  $Fe^{2+}/8Si$  ratios, and X-ray results relate to samples heated under identical conditions.

The gradual loss in weight up to  $350^\circ C$  (fig. 3*a*) can be attributed to



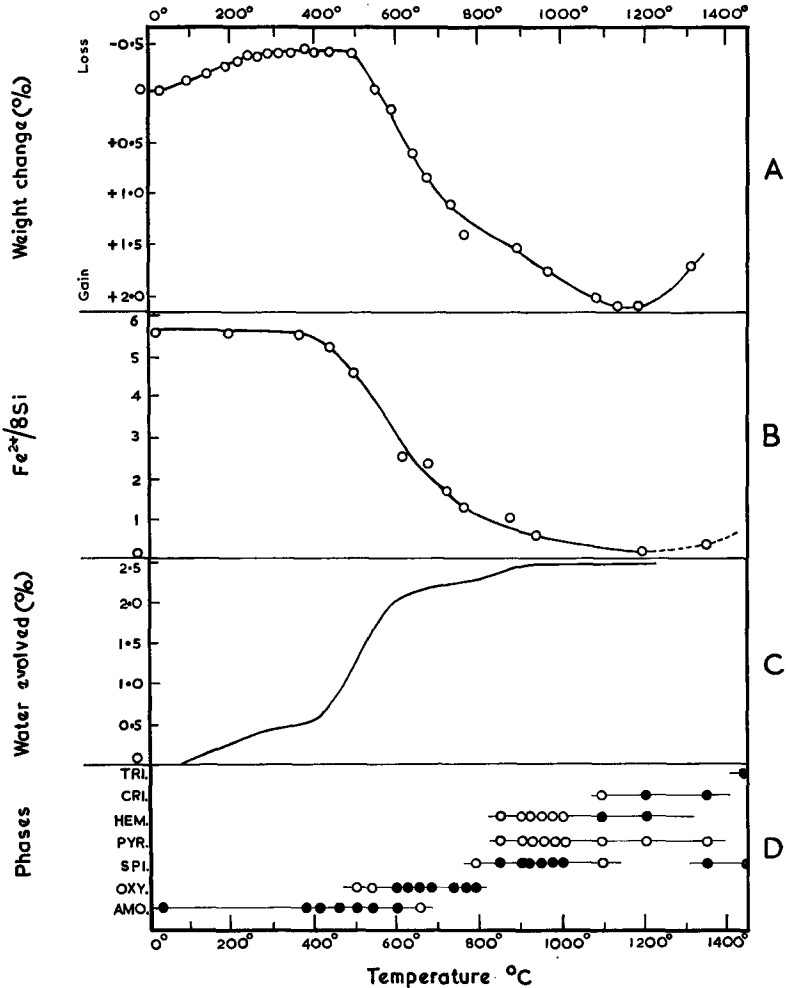


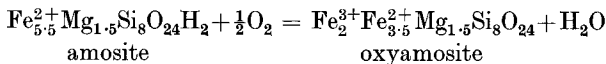
FIG. 3. Static heating in air (specimen PRS 5). (a) Weight-change curve. (b) Fe<sup>2+</sup>/8Si ratios. (c) Water loss, calculated from (a) and (b). (d) Phases detected by X-rays (amo. = amosite, oxy. = oxyamosite, spi. = spinel, pyr. = pyroxene, hem. = hematite, cri. = cristobalite, tri. = tridymite; full and open circles denote major and minor constituents respectively).

expulsion of physically combined water, as in neutral atmospheres. The weight is virtually steady at 350–450° C. This is probably due to a balancing of opposed effects, including loss of the last traces of physically

combined water together with a gain of oxygen and a loss of hydrogen resulting from reactions described in the following paragraphs.

The  $\text{Fe}^{2+}/8\text{Si}$  ratio begins to fall at about  $350^\circ\text{C}$  (fig. 2*b*); the change results in a darkening of the colour. The only product detectable by X-rays below  $780^\circ\text{C}$  is an oxyamphibole, to which the name oxyamosite will be given (fig. 3*d*). This gave X-ray fibre rotation and powder patterns resembling those of the original amosite, but with smaller cell parameters. Most of the powder reflections decreased in spacing by 1.0 to 2.0 %, and there were some noticeable changes in relative intensities. The four strong amosite reflections at 3.08, 2.77, 2.63, and 2.52 Å were shifted to 3.03, 2.73, 2.59, and 2.48 Å respectively. In samples heated at 500 to  $650^\circ\text{C}$  both amosite and oxyamosite reflections were observed, the relative intensities of the two patterns gradually changing as the temperature was raised. There is therefore no detectable solid solution between amosite and oxyamosite.

Oxyamphibole formation results in loss of hydrogen, which combines with oxygen molecules to form water (Barnes, 1930). If it is assumed that the oxyamosite is anhydrous, the reaction can be represented by the equation



If this were the sole reaction at  $350\text{--}800^\circ\text{C}$ , the weight would decrease by 0.2 % and  $\text{Fe}^{2+}/8\text{Si}$  would decrease by 2.0. In reality (figs. 3 *a* and *b*) the weight increases by 1.8 % and  $\text{Fe}^{2+}/8\text{Si}$  decreases by 4.4. Oxyamosite formation is therefore supplemented by a second oxidation reaction, which occurs by absorption of oxygen. It will be convenient to refer to the reaction yielding oxyamosite as a dehydrogenation and to this second oxidation reaction as an oxygenation. The starting material of the oxygenation could be amosite, or oxyamosite, or both; oxyamosite is perhaps the more likely. The products of the oxygenation reaction below  $800^\circ\text{C}$  are amorphous to X-rays.

The  $\text{Fe}^{2+}/8\text{Si}$  ratios given in fig. 2*b* are bulk values for the entire samples to which the weight changes in fig. 3*a* correspond.  $\text{Fe}^{2+}$  analyses for selected portions of heated samples showed the latter to be heterogeneous, the residual fibres being richer in  $\text{Fe}^{2+}$  than the fluff. Thus a sample consisting predominantly of fluffy material, picked out from a larger sample heated at  $500^\circ\text{C}$ , had  $\text{Fe}^{2+}/8\text{Si} = 4.04$ , while a sample consisting predominantly of harder fibres from the same larger sample had  $\text{Fe}^{2+}/8\text{Si} = 4.96$ . X-ray examination showed no significant differ-

ences between fibres and fluff, apart from the degree of preferred orientation. It seems likely that the fluff is produced largely in the oxygenation reaction described above, since this must involve destruction of the amphibole structure, but that it also contains amosite and oxyamosite in proportions sufficient for detection by X-rays.

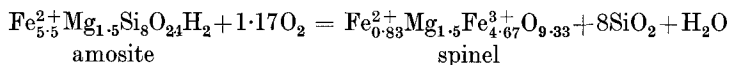
From the weight change and  $\text{Fe}^{2+}/8\text{Si}$  ratios for any given heated sample the total amount of water expelled and produced in oxyamosite formation can be calculated. The resulting curve (fig. 3c) shows three steps of 0.4 % at 20–350° C, 1.8 % at 350–800° C, and finally 0.3 % at 800–1000° C. These results are perhaps best explained by assuming that all the water evolved below 350° C, as well as 0.2 % from that evolved at 350–800° C is physically combined initially, the remaining 1.9 % evolved above 350° C being chemically combined. The small amount of water (0.3 %) retained in the 800° C product probably occurs as hydroxyl groups in the amorphous material.

*Reactions at 800–1450° C.* At about 800° C the oxyamosite reflections disappear from the X-ray pattern and new products begin to crystallize. These comprise a spinel, a pyroxene, and hematite. The spinel reflections were much stronger than those of the pyroxene or the hematite. At 1100° C and above, cristobalite also begins to crystallize. These results are consistent with Vermaas' (1952) conclusion that magnetite and cristobalite are formed. He used X-ray powder photographs, and the small amounts of hematite and pyroxene would have been difficult to detect by this method. His times of heating at 1200° C were too short for conversion of spinel to hematite to occur.

The present results were consistent with Vermaas' conclusion that the spinel had  $a = 8.390 \text{ \AA}$ . This is slightly below the value for magnetite (8.3963 Å; Basta, 1957). Vermaas pointed out that this could be due to substitutions of  $\text{Mg}^{2+}$  for  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$  for  $\text{Fe}^{3+}$ ,  $2\text{Fe}^{3+}$  for  $3\text{Fe}^{2+}$ , or to a combination of these. In view of the relatively high  $\text{Mg}^{2+}:\text{Fe}^{2+}$  ratio at 800° C and above, the first of these substitutions is perhaps likely to be the most important. The pyroxene appeared identical with that formed in neutral atmospheres. All the crystalline products were formed topotactically; the orientation relations were not fully determined, but so far as could be established from fibre rotation photographs, they were the same as those observed when the corresponding phases are formed from crocidolite (Hodgson, Freeman and, Taylor, 1965).

The  $\text{Fe}^{2+}/8\text{Si}$  ratio of 1.0 at 850° C (fig. 3b) corresponds to a  $(\text{Mg}^{2+} + \text{Fe}^{2+}):\text{Fe}^{3+}$  ratio of 0.55. This agrees with the X-ray evidence that a spinel is the main crystalline product at this temperature. To a first

approximation the net result of the reactions up to this temperature can be expressed by the equation



it being assumed that amorphous silica is also present. Better agreement with the analytical data could easily be obtained by taking into account the fact that pyroxene and hematite are also formed, since the pyroxene contains ferrous iron and the hematite ferric.

At 900–1150° C the oxidation continues; the X-ray results show that the proportion of hematite increases at the expense of the spinel. At 1150–1200° C the Fe<sup>2+</sup>/8Si ratio is at a minimum value of 0.2, and spinel was no longer detected by X-rays. Above 1200° C oxygen is expelled and the Fe<sup>2+</sup>/8Si ratio again rises. The colour deepens, and the X-ray evidence shows that spinel is again formed at the expense of hematite. Above 1350° C the pyroxene disappears, and cristobalite is replaced by tridymite.

#### *Dynamic heating in oxygen*

*Results.* Fibres heated dynamically in oxygen at temperatures up to 1000° C are broadly similar in appearance to fibres heated statically in air at corresponding temperatures, but they tend to be less reddish in colour and smaller proportions of fluffy material are produced.

Fig. 4 shows d.t.a., dynamic dehydration, and t.g.a. curves for specimens heated in oxygen, together with the phases detected from X-ray fibre rotation photographs of samples heated to various points on the dynamic dehydration curve. The d.t.a. curve (fig. 4a) shows a broad exotherm at 400–900° C. The peak temperature varied between 630° and 670° C for different specimens. The broad exotherm can be attributed to the dehydrogenation and oxygenation reactions described in the previous section; its breadth is accounted for by the slowness of these reactions. Some specimens gave subsidiary exotherms at 180–200° C or 310–350° C or both. The 310–350° C exotherm can, as Vermaas (1952) noted, be attributed to magnetite. The origin of the 180–200° C exotherm was not established. Because of the diffuseness of the effects, d.t.a. in oxygen is not a reliable way of identifying amosite; d.t.a. in an inert atmosphere is much more satisfactory.

The dynamic dehydration curve (fig. 4b) begins with a gradual rise up to about 600° C. For eleven specimens studied, the mean loss over this part of the curve (excluding water lost below 100° C) was 0.27 %, with a range of 0.15–0.45 % and a standard deviation of 0.08. The bulk of the

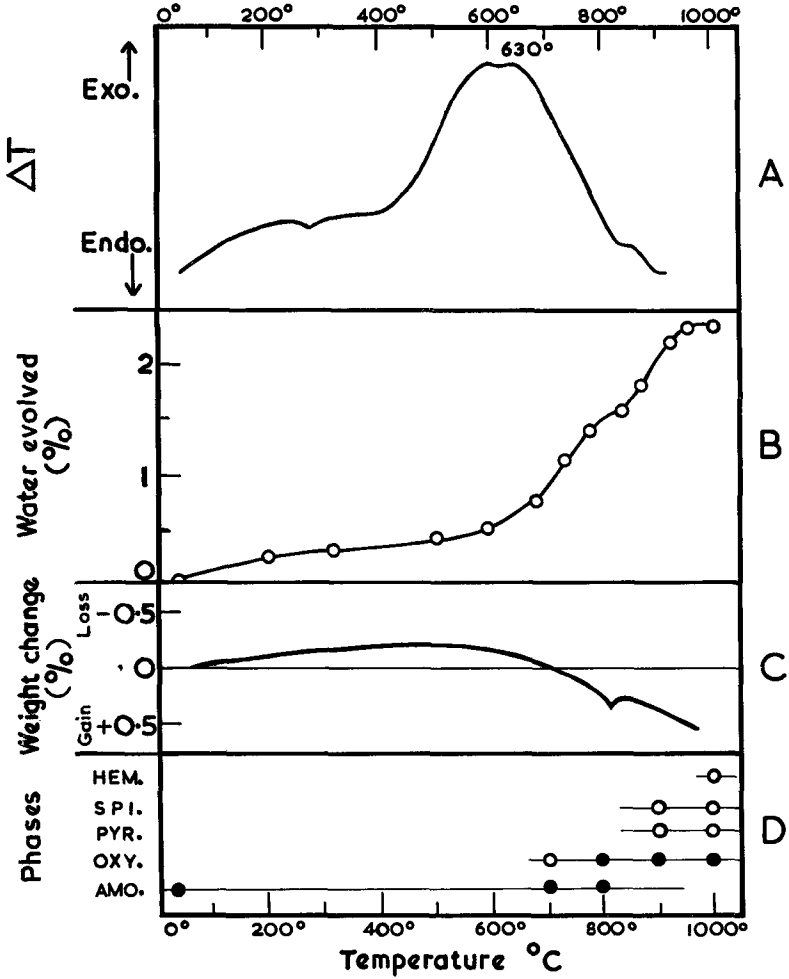


FIG. 4. Dynamic heating in oxygen (specimen PRS 5). (a) D.t.a. curve. (b) Dynamic dehydration curve. (c) T.g.a. curve. (d) Phases detected by X-rays (same notation as in fig. 3).

water is lost at 600–950°C; the mean total amount of water produced in this range was 1.87% with a range of 1.69–2.18% and a standard deviation of 0.15. This agrees well with the theoretical content of chemically combined water (1.89%). With most of the specimens studied the steep rise at 600–1000°C in the dynamic dehydration curve

showed a distinct break at about 800° C, which divided it into two roughly equal sections. The significance of this is discussed later.

The t.g.a. curve (fig. 4c) shows a gradual loss in weight up to about 550° C. The mean loss between 100° C and about 550° C for thirteen specimens was 0.15 %, with a range of 0.06–0.29 % and a standard deviation of 0.06. This is followed by a gradual gain, which is temporarily arrested by a further loss of 0.01–0.24 % between 800° and 900° C. At 900–1000° C the weight, relative to that at 100° C, varied from 0.50 % net gain to 0.06 % net loss.

The X-ray results (fig. 4d) show that oxyamosite formation begins by 700° C and that it is more advanced by 800° C. At 900–1000° C, the main crystalline phase present is oxyamosite, with smaller proportions of pyroxene, spinel, and hematite. Unchanged amosite was no longer detected. A difference was detected between the fluffy material present in the 1000° C sample and the larger fibres that remained. The fibres consisted mainly of oxyamosite with a little pyroxene and spinel, while the fluff consisted mainly of spinel and hematite with only traces of the other phases.

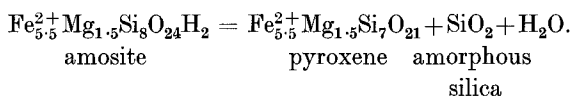
*Reactions below 800° C.* These results differ considerably from those obtained on static heating, because of the slowness of both the dehydrogenation and oxygenation reactions. Both these reactions occur below 800° C under the dynamic conditions used, but only to a limited extent. The course of the dehydrogenation reaction below 800° C can be followed from the dynamic dehydration curve (fig. 4b); the reaction begins relatively rapidly, but, despite the rise in temperature, becomes slower as it proceeds, so that by 800° C the curve is tending to flatten out. The course of the t.g.a. curve (fig. 4c) shows that oxygenation also begins below 800° C. By this temperature, about half the amosite has been converted into oxyamosite, and part of the latter, or of the remaining amosite, or both, has been converted into amorphous products.

*Reactions above 800° C.* At 800–1000° C, the remaining amosite is decomposed; the resulting evolution or formation of water can be followed from the dynamic dehydration curve (fig. 4b). The t.g.a. curve (fig. 4c) shows a generally downward trend, attributable to the continuance of oxygenation, but there is a temporary reversal of this trend at 800–900° C, which can only be explained by assuming that the gain due to absorption of oxygen is more than balanced by a loss. This loss could be of hydrogen, resulting from oxyamosite formation, or of water, produced by dehydroxylation of the remaining amosite. The following reasoning shows that the second of these processes must be wholly or partly responsible:

The magnitude of the loss is 0.01–0.24 %, and is superimposed on a gain due to absorption of oxygen, which is probably around 0.1–0.2 %. Correction for this effect gives a loss of 0.1–0.4 %.

The maximum loss attributable to oxyamosite formation is 0.2 %, corresponding to complete conversion of amosite to oxyamosite. But by 800° C, about one half of the amosite has already been changed to oxyamosite. Hence the maximum loss attributable to oxyamosite formation above 800° C is about 0.1 %.

The loss is thus too great to be attributable wholly to oxyamosite formation and dehydroxylation must therefore occur. The main reaction at 800–1000° C is probably dehydroxylation of the residual amosite, according to the equation:



This reaction is the same as that occurring in neutral atmospheres at comparable temperatures and is probably the main source of the water evolution represented by the step in the dynamic dehydration curve at 800–1000° C.

The oxygenation reactions at 800–1000° C could involve amosite, oxyamosite, pyroxene, or all of these phases as starting material. The absence of crystalline silica shows that, even at 1000° C, the products of these reactions are partly amorphous. Crystallization of spinel has, however, started by 900° C, and by 1000° C some hematite has also been formed. Some of the pyroxene may also be formed by crystallization of the amorphous material.

#### DISCUSSION

##### *Mechanisms of the decomposition reactions*

The mechanisms of the thermal reactions that have been described fall into three groups, each operative above a certain temperature.

*Loss of molecular water.* Loss of physically combined molecular water begins below 100° C and continues up to about 500° C for static heating conditions, or to about 700° C for dynamic heating conditions. Amosite resembles crocidolite (Hodgson, Freeman, and Taylor, 1965) in the amount of physically combined water it contains, and also in the conditions under which this is lost and the effect of the loss on the mechanical properties of the fibre. As with crocidolite, it is probable that part of the physically combined water is adsorbed, and that the rest occurs as intercrystalline inclusions.

*Migration of hydrogen ions and electrons.* The dehydrogenation reaction that occurs in oxidizing atmospheres can be assumed to occur by migration of hydrogen ions and electrons through the amphibole structure to the surface, where they react with molecular oxygen to form water,  $\text{Fe}^{2+}$  thus being changed into  $\text{Fe}^{3+}$  and  $\text{OH}^-$  into  $\text{O}^{2-}$  throughout the body of the material. Similar mechanisms have been postulated for the oxidation reactions of other hydroxyl-containing minerals (Barnes, 1930; Brindley and Youell, 1953; Addison, Addison, Neal, and Sharp, 1962). With amosite, this type of migration begins at about  $350^\circ\text{C}$ . Under static heating conditions, all the amosite has disappeared by  $700^\circ\text{C}$  from the combined action of this and oxygenation processes, but under dynamic heating conditions conversion of amosite to oxyamosite probably continues to beyond  $800^\circ\text{C}$ .

The dehydrogenation of amosite broadly resembles the corresponding reaction of crocidolite, but differs in two important respects. Firstly, with crocidolite there is probably a complete solid solution series between the amphibole and the oxyamphibole; this is not the case with amosite. Secondly, with crocidolite, the process is completed over a narrow temperature range; on static heating it begins at  $300^\circ\text{C}$  and is complete by  $450^\circ\text{C}$ . Oxygenation processes are inappreciable with crocidolite below about  $600^\circ\text{C}$ ,<sup>1</sup> and it is therefore possible to isolate the oxyamphibole free from other phases. With amosite, the dehydrogenation process begins rapidly, but becomes slower as it proceeds, especially after about half of the original mineral has been converted. Oxygenation processes occur simultaneously, and it does not seem possible to isolate pure oxyamosite.

Addison, Addison, Neal, and Sharp (1962) have suggested that dehydrogenation reactions in  $\text{Fe}^{2+}$ -containing amphiboles may be impeded through the substitution of  $\text{Mg}^{2+}$  for  $\text{Fe}^{2+}$ ; they postulated that electrons migrate along the bands of octahedra that lie parallel to the fibre direction, and that their movement can be blocked at points where a group of adjacent cation sites happens to be occupied by  $\text{Mg}^{2+}$ . This effect would clearly tend to increase with the  $\text{Mg}^{2+}:\text{Fe}^{2+}$  ratio in the mineral. Addison, Addison, Neal, and Sharp originally applied their hypothesis to the case of crocidolite. Our own results on South African crocidolite (Hodgson, Freeman, and Taylor, 1965) do not support the view that blocking by magnesium is an important effect with that

<sup>1</sup> According to the evidence of the present authors (Hodgson, Freeman, and Taylor, 1965). Addison, Addison, Neal, and Sharp (1962) reported that some oxygenation occurs at  $450^\circ\text{C}$ .



mineral. On the other hand, the hypothesis can perhaps account for the relative slowness of dehydrogenation in amosite, which has a higher content of  $Mg^{2+}$  than has crocidolite.

*Migration of ions other than  $H^+$ .* These processes occur in amosite to a small extent above 350–400° C, but only become rapid at 700–800° C. They are involved in the oxygenation and dehydroxylation reactions.

In neutral atmospheres, dehydroxylation begins at about 550° C and is complete by about 950° C. It is rapid above 700° C. The same process occurs on dynamic heating in oxygen, at 800–1000° C; its occurrence under these conditions is due to the slowness of the competing dehydroxylation and oxygenation reactions. This process, in which a pyroxene is formed together with amorphous material, necessarily involves migration of both  $H^+$  and other ions. Freeman and Taylor (1960) and Taylor (1962) suggested, for the analogous case of tremolite, that there is no loss of oxide ions from the parts of the structure that are changed into pyroxene. A system of donor and acceptor regions may be postulated, in which the acceptor regions are converted into pyroxene, while the donor regions are partly destroyed and partly changed into amorphous material. Hydrogen ions migrate from acceptor to donor regions, where they combine with oxide ions to form water; metal cations migrate in the opposite direction. The amorphous residues of the donor regions may have the composition  $SiO_2$  (Freeman and Taylor, 1960), though they could also retain some metal cations (Taylor, 1962).

The conversion of amosite to pyroxene occurs without the detectable formation of an amphibole anhydride. In this respect, amosite resembles tremolite and differs from crocidolite. The absence of a detectable intermediate stage can perhaps be attributed to the virtual absence of tripositive cations (Taylor, 1962).

The oxygenation reactions must also involve migrations of cations other than  $H^+$ . It is suggested that they occur by the deposition of oxygen atoms or molecules on the surfaces of the crystal, where they are changed into oxide ions, the charges being balanced by outward migration of cations and conversion of  $Fe^{2+}$  to  $Fe^{3+}$ . Similar mechanisms have long been accepted for the oxidation of magnetite and other minerals. When amosite is heated in air or oxygen, these processes begin at 350–400° C, but below about 800° C they are slow and yield products that are amorphous to X-rays. This indicates that migration of cations other than  $H^+$  is probably difficult in amosite below 800° C. The products of oxygenation below 800° C can perhaps be regarded as composed of nearly close packed oxide ions in a relatively well ordered arrangement,

together with an arrangement of cations that is largely or completely disordered.

Above about 800° C movements of cations take place more readily; the reactions are more rapid and the products begin to crystallize. Despite the poorly ordered nature of the product of oxygenation below 800° C, all of the products formed above 800° C show preferred orientation. Two factors probably account for this. Firstly, the material formed below 800° C, though amorphous to X-rays, is unlikely to be completely disordered; as already suggested, the oxide ions are probably nearly close packed. Secondly, the last traces of amosite or oxyamosite, and also the pyroxene formed directly from it by dehydroxylation, could serve as nuclei for crystallization. The mechanisms of the various reactions that occur above 800° C will not be discussed further, as they are probably closely similar to the corresponding reactions of crocidolite (Hodgson, Freeman, and Taylor, 1965; Patterson, 1965).

*Interpretation of chemical analyses.* Some of the sources of error that can occur in making chemical analyses of crocidolite were discussed by Hodgson, Freeman, and Taylor (1965), and the same considerations apply equally to amosite. Excessive disintegration of the sample before analysis causes the FeO and hydroxyl water contents to decrease and the Fe<sub>2</sub>O<sub>3</sub> and physically combined water contents to increase. The water determinations require particular attention; much of the physically combined water is retained above 110° C, and any attempt to use the value of H<sub>2</sub>O<sup>+110</sup> for the calculation of atomic ratios will lead to serious errors. In the case of amosite, the content of chemically combined water is most readily determined from the dynamic dehydration curve in oxygen (fig. 4b); water evolved over the range 600–1000° C may be considered combined. Dynamic dehydration or t.g.a. curves in inert atmospheres give low results, because some of the hydrogen in the mineral is lost, not as water, but as molecular hydrogen. This effect may be considered liable to occur with any mineral that contains Fe<sup>2+</sup> or other reducing cations, together with hydroxyl water that is retained up to a high enough temperature.

Table I, col. 1, gives the mean chemical analysis for ten of the specimens used in this investigation (PRS 3–6 and H 7, 9, 10, 12, 16, and 18). The water contents are derived from the dynamic dehydration curves in oxygen. Vermaas (1952) reported broadly similar results for specimens from the Penge area, but quoted higher Fe<sub>2</sub>O<sub>3</sub> contents and correspondingly lower FeO contents; his material was probably somewhat oxidized. Col. 2 gives the atomic ratios calculated from the data in col. 1, and in

col. 3 the atoms have been allocated to sites according to the principles established by Ghose and Hellner (1952). It is seen that a reasonable allocation can be made.

The mean density, determined by weighing in water for the same ten specimens, was 3.44 g/cc (range 3.42–3.46 g/cc, standard deviation  $\pm 0.007$  g/cc). Correction for physically held water and for the carbonate impurity brings this to 3.45 g/cc. Vermaas (1952) reported a value of  $3.48 \pm 0.01$  g/cc, as the mean obtained from 50 determinations. The X-ray density, calculated from the cell parameters and atomic ratios (assuming the cell to contain 48 oxygen atoms) is 3.47 g/cc.

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