An X-ray Examination of decomposition products of chrysotile (asbestos) and serpentine.

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I. INTRODUCTION.

MANY of the experiments described in this paper were made in the course of an examination of problems arising in connexion with technical uses of fibrous asbestos, undertaken about three years ago at the request of Dr. W. Francis, at that time Director of Research for Messrs. Turner Brothers Asbestos Company Limited, Rochdale. We have recently been able to investigate in a little more detail certain points which seemed likely to be of fairly general interest, and we now present our results in the hope that they may be of use to other researchers in this field. We are indebted to Dr. Francis and his colleagues for valuable discussions on questions arising in the course of the work, and to the Directors of Messrs. Turner Brothers for financial assistance in connexion with the earlier experiments, and for permission to publish this paper.

In this paper the term 'chrysotile' is used for fibrous material (asbestos), 'serpentine' is used for the massive rock within which the veins of fibrous chrysotile are found, and 'antigorite' refers to the platy mineral of similar chemical composition. We have examined chrysotiles and serpentines from three different localities, and also the products obtained from them by prolonged extraction with water, and by heating for periods of a few hours at temperatures around 600° C. For this purpose we have used X-ray fibre photographs and powder photographs. Some of these are reproduced, but in view of the faintness of much of the significant detail in the X-ray patterns, it is necessary to give, in the text, full descriptions of observations made on the original X-ray films.

Our data, though inadequate at present to provide definite guidance in attacking specific problems of asbestos structure, are likely to have some bearing on three aspects of this fascinating subject—the atomic structure of chrysotiles and serpentines, the structural classification of chrysotiles and serpentines from different sources, and the relation between a fibrous chrysotile and the rocky serpentine in which it occurs. The following are the principal studies which have contributed, in recent years, to our understanding of these problems.

The first attempt to determine the atomic arrangement in fibrous chrysotile was published by Warren and Bragg (1930) in a paper showing that a structure based on Si_4O_{11} chains, but with some degree of randomness, might account for the peculiar physical properties, and for some features of the X-ray fibre photograph characteristic of the mineral. Gruner (1937) reported unsuccessful attempts to carry out a detailed analysis of the structure, and concluded that some fundamental modification of the structure of Warren and Bragg was required. More recently, Warren (1941, 1942) and Aruja (1943) independently have re-examined the problem and have advanced new suggestions as to the chrysotile structure; we are indebted to Professor Warren and to Dr. Aruja for detailed information

on the progress of their own work, most generously provided for our benefit in advance of publication.

The structural classification of chrysotiles and serpentines initiated in a survey (of a very general nature) by Anderson and Clark (1929), was discussed in detail by Caillère (1936), Selfridge (1936), and Gruner (1937). The products formed on heating chrysotiles and serpentines were examined by Haraldsen (1928) and Gruner (1939) and by Hey and Bannister (1941) and Aruja (1943). The importance of this structural classification in relation to physical (especially electrical) properties of chrysotile asbestos was discussed by Francis and Grayson (1941). We shall refer to all these researches later in the present paper.

For accounts of various hypotheses as to the mode of formation of the relatively small amount of fibrous chrysotile in the massive serpentine rock, reference may be made to comprehensive reviews by Lodochnikov (1936) and Cooke (1937).

II. Experiments on extraction, in water, of chrysotile and serpentine.

If fibrous chrysotile is treated with dilute acid the magnesia may be completely removed, and the hydrated silica remaining, though fibrous in form, has completely lost the elasticity characteristic of the original chrysotile fibre and gives an X-ray pattern of one or perhaps two diffuse broad bands indicating that the structure is 'amorphous' or 'glassy' in type.

In researches carried out in the laboratories at Rochdale prior to our X-ray work, Mr. J. Grayson (at that time Research Chemist with Messrs. Turner Brothers) made a detailed chemical examination of the products obtained by prolonged extraction of chrysotile fibre in water, amplifying the scanty data previously available. Extraction in a Sohxlet for 100–150 hours resulted in the separation of a small amount of solid material, of weight approximately 1 % of that of the original fibre and containing 45 % (by weight) SiO_2, 25 % MgO, 3–4 % R_2O_3, the remainder water. Continued extraction resulted in further separation of solid, but in diminishing amount until after 1800 hours no further appreciable separation occurred, the total amount of extract being approximately 6 % (by weight) of the original fibre. We have examined extraction products obtained from chrysotile fibre and the associated serpentine rock, using specimens from the Bell mines, Thetford, Canada, from the Shabani mine, Rhodesia, and from the New Amianthus mine, Transvaal—henceforward termed Canadian, Rhodesian, Transvaal materials. It should be noted that specimens for X-ray examination contain, in addition to the solid material extracted from the chrysotile or serpentine, small amounts of material extracted from the glass vessel and of water-soluble impurities which may be associated with the fibre or rock; in particular, the presence of sodium chloride and iron salts may be anticipated. In view of the difficulty of applying purely chemical methods to this problem, and in anticipation of the results of our X-ray examination of these materials, it is most interesting to note that Mr. Grayson suggested in a private communication that the chemical evidence indicated that the extracts might prove to consist of α-sepiolite, i.e. magnesium trisilicate, prepared as a commercial product by the Washington Chemical Company, ideal formula $2MgO.3SiO_2.2H_2O$.

It is convenient to discuss in turn extracts from fibres, extracts from rocks, and the condition of the fibres after prolonged extraction treatment.
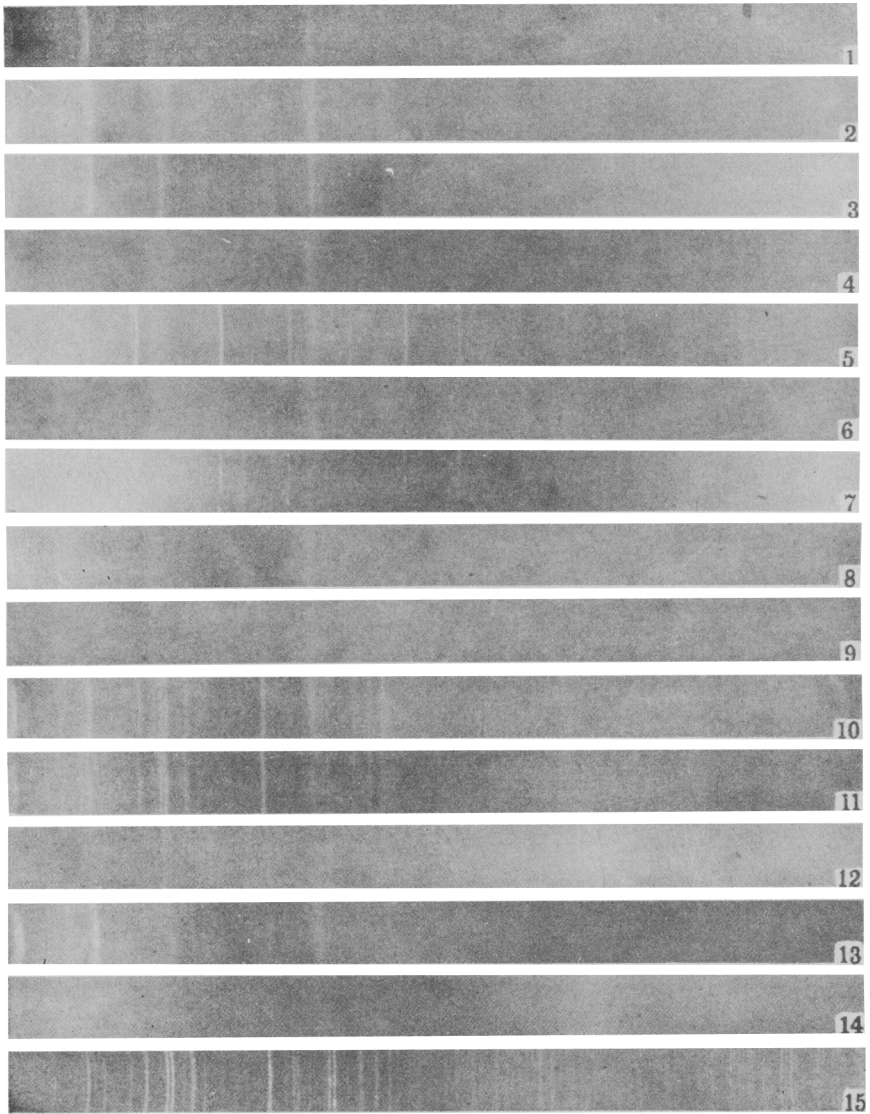
FIGS. 1–8. X-ray powder photographs of materials examined in the experiments on extraction, in water, of chrysotile and serpentine. 1, Chrysotile fibre (powder photographs of chrysotiles from Canada, Rhodesia, and the Transvaal, are identical on visual examination). 2, Serpentine rock (Transvaal). 3, Serpentine rock (Rhodesian). 4, Extract from Rhodesian fibre. 5, Extract from Transvaal fibre. 6, Extract from Canadian fibre. 7, Extract from Transvaal rock. 8, Extract from Rhodesian rock.

FIG. 9. Synthetic α-sepiolite.

FIGS. 10–14. X-ray powder photographs of products obtained by heating chrysotile fibre and serpentine rock; after 4 hours heating at 600° C. 10, Canadian chrysotile. 11, Rhodesian chrysotile. 12, Rhodesian serpentine. 13, Transvaal chrysotile. 14, Transvaal serpentine.

FIG. 15. Natural forsterite (olivine).

(i) *Extracts from chrysotile fibres.*

The products obtained by extraction of Canadian, Rhodesian, and Transvaal chrysotile fibres (figs. 4–6) give X-ray powder photographs in which there appears a pattern of four diffuse wide lines, common to all three photographs, together with other lines and wide bands which differ for the three extracts.

The photograph of Rhodesian extract (fig. 4) contains, in addition to the common pattern of four diffuse lines, a set of six or perhaps seven fairly sharp but very weak lines. We have not been able to identify the structure or structures responsible for this sharp pattern, but consider it probable that it is due to an impurity, or impurities— perhaps iron salts—present in the original fibre.

The Transvaal extract (fig. 5) gives a prominent set of sharp lines due to sodium chloride, and one sharp but extremely weak line different from all the weak sharp lines of the Rhodesian extract pattern, as well as the common pattern of diffuse lines. Again it seems reasonable to suppose that only the diffuse lines of the common pattern are characteristic of the extract, the other lines representing impurities.

Canadian extract (fig. 6) gives a pattern consisting of the four diffuse lines of the Rhodesian and Transvaal patterns, together with three very weak and diffuse lines which, as we shall see below, may probably arise from the same structure which gives the four lines common to all three extracts.[1]

A powder photograph of synthetic α-sepiolite (fig. 9) contains three diffuse 'lines' or bands, and probably a fourth, which coincide in position with the lines of the diffuse pattern common to all three extracts. The relative intensities of the 'lines' are also the same, so far as may be judged by visual examination, and the separate 'lines' show identical intensity-variations across their widths, e.g. the second line (from the low-angle end of the film) shows a sharp edge on the low-angle side with a gradual fall of intensity on the high-angle side. The powder patterns thus appear to confirm that the extracts consist largely of α-sepiolite, as suggested by Mr. Grayson; this point is discussed at length in section IV.

Photographs of 'powdered' chrysotiles (fig. 1) (prepared for us at Rochdale by sectioning in a microtome) from Canada, Rhodesia, and the Transvaal, are identical on visual examination and show a pattern containing broad bands and sharp lines: the broad bands correspond to the four bands common to the extracts and α-sepiolite, together with the three additional broad bands seen only in the Canadian extract; the sharp lines in the chrysotile pattern are, of course, absent from the extract patterns. This correspondence between the extract pattern and

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[1] It is perhaps worth while to remark that the photograph of the Canadian extract also shows the diffuse broad bands seen in a photograph of hydrated silica obtained by acid extraction of chrysotile fibre as described above (Section II, first paragraph). These bands cannot be seen in photographs of the Rhodesian and Transvaal extracts, a fact which may possibly be significant in view of a statement by Caillère (1936, table on p. 202) that after prolonged water extraction Thetford chrysotile loses silica and magnesia in the molecular ratio SiO_2/MgO $\sim$1·3, while for five other materials tested (*not*, as it happens, including specimens from Rhodesia or the Transvaal) the ratio is SiO_2/MgO $\sim$0·5 under identical treatment. Too much importance should not be attached to this observation; first, because in our Rhodesian extract, the only one fully analysed, the molecular ratio SiO_2/MgO is $\sim$1·2; secondly, because we are not completely satisfied that these wide bands, so diffuse as to be recognizable only with extreme difficulty, are really characteristic of the experimental samples under examination.

the diffuse reflections of the chrysotile pattern is clearly of great interest, but we postpone discussion of its structural significance for the present. We may, however, note that there are differences in detail in the intensity-distribution within the bands: thus the second band from the low-angle end of an extract pattern (with characteristic fall of intensity across the band, as described above) is replaced in the chrysotile pattern by a pair of lines with a band of general scattering stretching between—the first line corresponding in position with the sharp (low-angle) edge of the extract band, the second lying approximately half-way across the apparent width of the extract band. We may also remark that in view of the correspondence between the bands of chrysotile and the seven bands of Canadian extract, it seems reasonable to assume that this pattern may be characteristic of the extracts, and that only four of the seven bands are seen in Rhodesian and Transvaal extracts as a consequence of less perfect crystallinity in these materials.

(ii) *Extracts from serpentine rocks.*

No specimen is available of the rock associated with the Canadian fibre, but we have examined the natural rock and the extraction product (obtained by the same treatment as for the preparation of fibre extracts) for Rhodesian and Transvaal materials.

The powder photographs of the natural rocks are similar one to the other, and to those of 'powdered' chrysotile fibres, as was to be expected in view of the data published by previous workers. Careful examination reveals the following features, which appear to be significant. First, photographs of samples of rock (Transvaal) very close to a fibre band, and in the centre of the rocky mass, are identical on visual examination. Secondly, photographs of rock (Transvaal) (fig. 2) and of the associated fibre show small but definite differences in intensities of certain lines, but we have confirmed that these are explicable on the assumption that the 'powdered' chrysotile fibre fails to take up a completely random orientation; partial preferred orientation would be expected with fibrous material of this kind. And in the third place, the photograph of Rhodesian rock (fig. 3) is quite definitely different from the photographs of Transvaal rock and of chrysotile fibres, in showing fairly sharp lines in place of bands, and differences of relative intensity. These differences, if confirmed and systematized, might provide a basis for a structural classification similar to those of Caillère (1936), Selfridge (1936), and Gruner (1937), to which reference has been made in the introduction to this paper, but we have not been able to pursue this line of inquiry.

The photograph of Transvaal rock extract (fig. 7) is very similar to that of the Transvaal fibre extract (fig. 5), showing the α-sepiolite bands, the prominent sharp lines due to sodium chloride and also a few weak lines and one of moderate intensity not seen in the patterns of Transvaal rock, fibre, or fibre extract, which we have been able to identify as probably due to products originating from the Sohxlet used in the extraction process.

Rhodesian rock extract (fig. 8) gives a pattern identical with that of Rhodesian fibre extract (fig. 4) so far as the broad (α-sepiolite) bands are concerned, but the pattern of very weak, sharp, lines seen in the fibre extract and attributed to impurities is no longer visible, while another single sharp line presumably indicates the presence of a different impurity (unidentified) in the rock.

Thus, although the natural rocks give patterns which differ in detail, the

Transvaal and Rhodesian rock extracts are apparently identical with the fibre extracts.

(iii) *Chrysotile fibres after prolonged extraction.*

The powder photograph is not sensitive to very small changes in a sample, such as might be expected to take place during prolonged extraction with water, unless there is a dimensional change which may be revealed by displacement of high-angle lines. As rock specimens must be examined by the powder method, and as the patterns of the natural materials before treatment contain few sharp lines, there is no hope of obtaining information on possible slight changes in constitution for the serpentine rocks.

For the chrysotiles fibre photographs may be used, but although this is a more sensitive method (*except* for small dimensional changes) nothing of interest can be found unless the most refined technique is applied. Thus fibre patterns taken with filtered $CuK\alpha$ radiation are identical, on visual inspection, for natural Canadian, Rhodesian, and Transvaal fibres, confirming the evidence of photographs of 'powdered' chrysotiles (see section (i) above), for the same fibres after extraction for periods of 100 hours, and for samples taken from different parts of a given fibre—although the ends of the fibre are darkened by the extraction process.

Fibre photographs obtained with monochromatized radiation were described by Aruja (1943). He used chrysotile fibres from Quebec, Canada, and detected, in addition to the intense pattern of sharp spots and 'streaky' or 'tailed' reflections lying on the principal layer-lines, faint traces of reflections on subsidiary layer-lines lying between these layer-lines, and in positions corresponding to some of the most intense reflections of the chrysotile pattern, but for an oriented structure with axis [010] or [013] parallel to the length of the chrysotile fibre, instead of [001] for the main chrysotile pattern. Aruja estimated that approximately 3 % of the chrysotile must be in one or other of the two possible (abnormal) orientations, to account for the observed intensities of reflection of the small number of extra spots observed. It should be noted that according to this interpretation, other relatively strong reflections of the chrysotile pattern, for the abnormal orientation(s), are superposed on reflections for the normal orientation and so are not directly observed.

Our own fibre photographs, with monochromatized radiation, show interesting differences according to the place of origin: Canadian and Transvaal fibres show the extra reflections, with approximately the same intensities relative to the principal reflections so far as can be estimated on visual inspection, but in Rhodesian fibre the extra spots, though probably present, are so feeble that their detection is a matter of extreme difficulty. So far as we are aware, this is the first structural test to reveal any difference between fibres (in the natural state) from different sources.

A photograph of Canadian fibre after extraction has been carried on for 200 hours cannot be distinguished from the photograph of the original fibre, but after prolonged extraction (approximately 1700 hours, when according to Mr. Grayson's observations no further action may be expected) the extra spots have almost, or perhaps completely, disappeared from the pattern, which is otherwise unchanged to visual inspection except for some falling-off in the perfection of the

fibre-orientation of the main pattern. We have not yet been able to make similar tests on the Transvaal fibre because of the excessive demands which they make on apparatus needed for other work. These results are discussed later.

III. THERMAL DECOMPOSITION OF CHRYSOTILE AND SERPENTINE.

Before describing our own experiments it is convenient to review, as briefly as possible, published data on the products obtained by heating chrysotile and serpentine.

Haraldsen (1928) applied X-ray methods to identify the products of thermal decomposition of a serpentine from Snarum, Modum, Norway, selected for its purity, and of greenish-yellow colour. On heating, most of the water was driven off between 500° and 700° C. X-ray powder photographs showed that the chrysotile pattern, unchanged after heating at 500° C., disappeared completely after heating at 600° C., to be replaced by a single broad diffuse line at glancing-angle 41° (for $FeK\alpha$ radiation), but that after heating at 700° C. the olivine (forsterite) pattern began to appear and increased in sharpness and detail after heating at temperatures up to 1000° C.; at still higher temperatures, up to 1300° C., some of the most prominent lines of the enstatite pattern also appeared. Chemical tests confirmed these observations on the high-temperature formation of enstatite.

Caillère (1936) used X-ray powder photographs along with chemical, optical, and thermal methods, in establishing her classification of serpentine minerals— fibrous chrysotiles, platy antigorites, and serpentine rocks—into two groups, which she called α and β. On heating materials of group α, dehydration begins at approximately 550° C. and is completed at approximately 720° C., and an endothermic effect around 650° C. is followed by an exothermic change between 750° and 825° C., the latter accompanied by incandescence interpreted as indicating a recrystallization process. The X-ray powder pattern gradually becomes less distinct during dehydration, and has disappeared completely when dehydration is complete; a new pattern appears on heating to approximately 850° C. (i.e. after the completion of the exothermic change) which indicates the formation of well-crystallized olivine and enstatite. In contrast with this behaviour, materials of group β show only the endothermic change at 650° C. (small exothermic changes observed at higher temperatures in some cases are not comparable with those observed in α materials, nor is there any incandescence), and the appearance of the X-ray powder pattern also changes in quite a different way: for now as the chrysotile pattern begins to fade at approximately 620° C. (as dehydration proceeds) the olivine and enstatite patterns begin to appear—there is in this case no gap between the disappearance of one and the appearance of the other. Caillère showed that massive rock (serpentine) and included fibre (chrysotile) always belong to the same group, α or β. She was unable to detect any differences between X-ray powder photographs of specimens of chrysotiles of the two groups, and only very minor differences in a photograph of a massive rock of group β; no rock of group α was examined. Of all the materials examined, only two asbestiform varieties were found to belong to group α, one from the Amianthus mine, Barberton, Transvaal, the other from Nerchinsk, Siberia, and of other α materials one was antigorite from Snarum (specimen no. 69.207),[1] facts of great interest in

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[1] We have not been able to decide, with certainty, whether all Caillère's material from

relation to the work of Haraldsen (1928), reviewed above, and our own observations. The much more numerous β group was found to include many asbestiform varieties, including specimens from Shabani in Rhodesia and Thetford in Quebec, which may well be expected to correspond to our Rhodesian and Canadian materials.

Selfridge (1936) and independently Gruner (1937) examined by optical and X-ray methods large numbers of minerals of this family, and established the existence of two main structural types named 'chrysotiles' and 'antigorites' which give characteristic X-ray powder photographs. A supplementary note by Gruner (1939) pointed out that this classification does not conform with Caillère's —either an 'antigorite' or a 'chrysotile' may be either 'α' or 'β' type--and reported (briefly) the results of heating materials of both types in air at temperatures around 600° C. Gruner found that a 'chrysotile' changes to olivine (and probably colloidal silica) on heating at 560° C. for periods of 4 to 19 days, but that an 'antigorite' changes more slowly unless the temperature is raised to 650° C. He found no trace of the enstatite pattern after treatment at either of these temperatures.

Aruja (1943) found that after heating to 600°-620° C. the fibre-pattern characteristic of chrysotile (from Thetford, Quebec) begins to disappear, but simultaneously a partially oriented olivine pattern appears, comprising sharp reflections, Debye arcs linking the reflections, and some general background. After heating to 735° C. a further orientation in the olivine (forsterite) pattern takes place, the Debye arcs and general background tending to break up into sharp reflections. After heating to 1000° C., a powder photograph shows the olivine pattern and a very weak, broad, line corresponding in position with the strongest line of the enstatite pattern. Optical examination and chemical analysis (Hey and Bannister, 1941) suggested that silica is probably formed as the chrysotile breaks down to olivine. Aruja, and Hey and Bannister, discussed in detail the nature of the preferred orientation of the olivine formed.

In our experiments we have taken care to ensure that the recorded temperature is as nearly as possible that of the heated specimens, and for each temperature specimens of all five materials have been treated at the same time in the same large-capacity furnace. The furnace was heated in approximately 3 hours to the selected temperature, and was then maintained at that temperature for 4 hours in each case. After treatment, a portion of each specimen was used for powder photographs, and a portion of each of the chrysotile samples for fibre photographs; the results of a careful examination of the X-ray patterns are summarized below; a discussion of the significance of our data, especially in relation to earlier published work, is given in the next section (IV).

(i) *Canadian chrysotile.*

After heating at 550° C., the fibre photograph (filtered Cu$K\alpha$ radiation) is identical with that of untreated material; after treatment at 600° C. (fig. 10) the

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Snarum was of group α, for she refers to this locality in four places in the text: p. 218, 'pseudomorphs of olivine from Snarum (no. 69.207)' are included in group α; p. 224, (pseudomorphous) 'antigorite from Snarum' is included in group β; p. 234, 'antigorite from Snarum (no. 69.207)' is included in group α; p. 260, 'antigorite from Snarum' is quoted as an example of α. It seems probable that the second reference (p. 224) is in error.

powder-pattern corresponds to a mixture of chrysotile and olivine (forsterite) (fig. 15), and the fibre pattern confirms this; heating at 650° or 700° C. results in complete disappearance of the chrysotile pattern, its place being taken by the forsterite pattern. In view of Aruja's discussion (1943) of the nature of the orientation of the forsterite crystals, we need only remark that our fibre patterns are similar to his, though of course our experiments are confined to a smaller temperature-range.

(ii) *Rhodesian chrysotile and serpentine.*

Rhodesian chrysotile behaves exactly as Canadian chrysotile, except that after heating at 600° C. (fig. 11) it seems that a rather higher proportion of the Rhodesian chrysotile has been converted to forsterite.

Rhodesian serpentine (rock) is unchanged after heating at 550° C. for 4 hours. It is, however, partly converted into forsterite at 600° C. (fig. 12); the lack of sharpness in some of the high-angle lines of forsterite, and the relatively low intensity of this pattern, in comparison with the photograph of Rhodesian fibre after identical heat-treatment, show that a much smaller proportion of the serpentine has been converted into forsterite, and that the forsterite produced is less perfectly crystalline. In addition, one or two extra lines can be seen which we have not been able to identify, and which probably correspond to some impurity present in the rocky serpentine but absent from the associated fibrous chrysotile. Treatment at 650° or 700° C. converts the serpentine completely into forsterite which is, however, less perfectly crystalline than that obtained from the chrysotile; the same 'impurity' lines can also be seen.

(iii) *Transvaal chrysotile and serpentine.*

The behaviour of Transvaal chrysotile is similar to that of Canadian and Rhodesian chrysotiles, except that after treatment at 600° C. (fig. 13) the proportion of chrysotile converted into forsterite is smaller than for Canadian, and much smaller than for Rhodesian material. Too much importance should not be attached to these quantitative differences, however, since it is possible that they may arise from differences in the state of subdivision of the specimens during the heating treatment.

After heating at 550° C. the Transvaal rock is unchanged, but after treatment at 600° C. (fig. 14) the serpentine pattern has almost disappeared—only three, or possibly four, of the diffuse bands remain, and those are of very low intensity—while there is no trace at all of the lines characteristic of forsterite. After heating at 650° C. the pattern of bands is again visible, unaltered, but in addition there are extremely faint traces of the three strongest lines of the forsterite pattern— so weak that they can be detected only with the greatest difficulty. Treatment at 700° C. results in the disappearance of the band pattern, and the appearance of the forsterite pattern though with relatively low intensity and some lack of perfection of crystalline development. Thus the stages in the thermal decomposition of Transvaal serpentine rock are quite different in detail from those for the Rhodesian serpentine, and the chrysotiles, examined in the course of this investigation; in all three, the forsterite pattern is quite strongly developed before the chrysotile (serpentine) pattern disappears. These results are discussed below.

IV. Discussion of Results.

Our experiments have not been confined to detailed examination of one sample of chrysotile, nor can they provide a comprehensive survey of chrysotiles and serpentines from the large number of sources available; they do, however, open up a number of interesting problems in connexion with structures of the 'asbestos' type, more particularly when they are considered in relation to previous investigations. We consider first the experiments on thermal decomposition of chrysotile and serpentine, and afterwards the products of water extraction of these materials.

A. Thermal decomposition.

We find no trace, in any of our powder photographs of heat-treated materials, of the sharp line pattern characteristic of enstatite. Our experiments thus confirm the observations of Haraldsen (1928), Gruner (1939), and Aruja (1943) in that low-temperature treatment does not result in the formation of enstatite; they are not in agreement with Caillère's assertion (1936) that the pattern which replaces that of chrysotile indicates the presence of crystalline enstatite as well as olivine. We have no new evidence on the possibility of high-temperature formation of enstatite, except that the powder photograph of Canadian chrysotile, after (accidental) heating to a temperature probably considerably exceeding 750° C., shows an extremely faint wide band in a position corresponding to the strongest line of the enstatite pattern; the presence of this band may indicate the beginning of the formation of enstatite.

Our experiments give partial support to Caillère's classification into groups α and β. Thus our Canadian fibre, and Rhodesian fibre and rock, give X-ray patterns (after heat-treatment) corresponding to group β, in that the new (forsterite) pattern appears strongly before the chrysotile (serpentine) pattern has disappeared; this would be expected since Caillère found that specimens from Thetford in Quebec and Shabani in Rhodesia were of type β. Again, our Transvaal serpentine (rock) behaves as would be expected for a material of type α, in agreement with Caillère, whose classification is also supported by Haraldsen's examination (1928) of Snarum material, α type. But chrysotile fibre from this same rock is found to correspond to type β, thus contradicting Caillère's assertions that asbestiform material from this locality proved to be of type α, and that rock and associated fibre are always of the same type, α or β.[1] As only two asbestiform varieties, of the many examined, were found by Caillère to be of type α, and as our data are in disagreement with hers on one of these, we suggest that it is quite possible that all asbestiform varieties are actually type β.

No direct clue is provided by our heating experiments as to the fundamental structural significance of the α-β classification, which, indeed, clearly requires reinvestigation for a more representative selection of samples than have been available for our work. We consider it very probable that some such classification

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[1] In this connexion it is interesting to note that Caillère did not apply X-ray tests to the asbestiform varieties which she classified as α on the basis of thermal observations during dehydration; that while our 'Transvaal' material is from the *New* Amianthus mine, hers is described as from the Amianthus mine; and that since she found another sample of asbestiform material from the same neighbourhood (Kaapsche Hoop, Barberton, Transvaal) to belong to the β group, there is obviously some uncertainty as to the association of a definite type, α or β, with this region.

of chrysotiles and serpentines can be established, but it seems unlikely that any one of the previous attempts (Caillère, 1936; Selfridge, 1936; Gruner, 1937) has taken all the relevant factors into account. Any such classification must obviously include the antigorite structure-type as described by Aruja (1943, 1945).

It is interesting to note that the pattern of three (or four) diffuse bands given by Transvaal serpentine (rock) after heat-treatment at 600° C., which presumably represents the semi-crystalline portion of the products of thermal decomposition, is identical with the patterns of synthetic α-sepiolite and of the chrysotile and serpentine water-extraction products, described in section II. This fact is considered below. It is also interesting to note that the most prominent of these bands corresponds in angular position with that reported by Haraldsen (1928) for Snarum serpentine heated at 600° C.

B. *Water extraction.*

The experimental evidence summarized in section II suggests strongly that prolonged extraction of any of these materials, fibrous or rocky, results in the removal of small amounts of material, of semi-crystalline structure corresponding to the simple pattern of diffuse bands also characteristic of synthetic α-sepiolite. In the first place, therefore, the presence of this material in the original sample does not, apparently, directly determine whether the material assumes the fibrous form or not. On the other hand, it is interesting to find, in the case of the Canadian fibre examined with the necessary refinements of technique, that the 'extra spots' (representing abnormally oriented material) disappear in the course of prolonged extraction. This observation suggests that perhaps this part of the chrysotile fibre is more readily removed than the major part with the normal orientation: we have not yet been able to test this by the preparation of monochromatic photographs of Transvaal fibre after extraction, and by quantitative comparison of the total amounts of extract yielded by Canadian and Transvaal fibres on the one hand, and Rhodesian fibre (which shows no extra spots, or relatively very weak ones) on the other.

Arising from these attempts to obtain information as to the nature of the extraction process, we have demonstrated that the presence of 'extra spots' serves to differentiate our Canadian and Transvaal fibres from our Rhodesian fibre, and it is interesting to consider the possible significance of this differentiation. In the first place, whereas the examination of the process of thermal decomposition (discussed in 'A.' above) would suggest that all three fibres are similar (by contrast with Caillère's classification of Transvaal chrysotile as α, the others β), the examination of fibre patterns for 'extra spots' now indicates that Rhodesian fibre differs from Canadian and Transvaal, which are similar one to the other; it seems clear that only a fuller examination of a number of different materials can lead to the establishing of a reliable classification of structures of this type. Secondly, it is possible that the electrical properties of asbestos (resistance and break-down voltage) may be directly correlated with any classification of structure-types. Thus Francis and Grayson (1941) described experiments which demonstrate the superiority, in electrical properties, of Rhodesian fibre by comparison with Transvaal fibre, and also stated that Canadian (Quebec) fibre would have poor electrical properties even if it were possible to remove completely

the magnetite which is intimately associated with the chrysotile.[1] They concluded that the observed superiority in the electrical properties of Rhodesian fibre, by comparison with Transvaal (and Canadian) fibres, was another manifestation of the difference between β and α types of structure according to Caillère's classification. It seems, however, that Francis and Grayson were in error in thus making their correlation include Canadian as α, even if Caillère's classification were acceptable, since only Transvaal and a particular Siberian fibre were found by her to belong to the α group, Canadian fibre being of the β type. Further, our own experiments (discussed in 'A' above) have shown that this actual Transvaal fibre is of the Caillère β type, at least in respect of the process of thermal decomposition as shown by X-ray tests, so that the α-β differentiation does not serve to account for the difference in electrical properties. We have, however, found that whereas Rhodesian fibre gives no 'extra spots' (or extremely weak ones), both Transvaal and Canadian fibres show 'extra spots' which Aruja has interpreted as arising from material with abnormal orientation, which we suggest may possibly be responsible for a modification of the electrical properties of the fibre: it would obviously be of interest to examine further this possible correlation of properties with structure-type.

Finally, it is necessary to consider the significance of the diffraction-pattern characteristic of the extraction products. This has been found to include four diffuse lines, or bands, for the fibre extracts (and in synthetic α-sepiolite), (with three additional fainter bands for the Canadian extract), all of which correspond to diffuse reflections in the pattern of the chrysotile fibre itself. We do not consider that these experimental data demonstrate that the α-sepiolite structure exists, as such, within the untreated chrysotile fibre, and that this component is simply removed by water extraction, although this would be the straightforward interpretation where the original complex powder-pattern of a mixture contains a simpler pattern due to a 'soluble' constituent. In our case, however, the chrysotile pattern, containing some sharp lines and some diffuse lines, represents an imperfect structure; and the extract pattern contains no sharp lines at all, but only diffuse lines corresponding to some of those of the chrysotile pattern. From this we conclude that the extracts (and α-sepiolite) are imperfect structures, based on the same pattern-units as the chrysotile structure, but showing even less tendency to perfect arrangement in a three-dimensional lattice. In view of the recent work of Warren (1941, 1942) and Aruja (1943) it is reasonable to suggest that the 'imperfection' consists in irregularity in stacking of the mica-like sheets, and in the placing of magnesium ions. Consideration of the variation in intensity across the wide bands of the powder-pattern of the extracts gives rise to interesting speculations on the precise nature of these irregulatities—one 'line' is obviously of the type associated with a two-dimensional lattice—but a more refined experimental technique, and actual photometric measurements of intensity-variation, are required as a basis for more detailed analysis. One suggestion may perhaps be advanced, with due diffidence: the bands of the extract pattern correspond with the extremely faint 'extra spots' discovered by Aruja in the chrysotile

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[1] From the wording of the paragraph in the original paper, it is clear that this assertion is based, at least in part, on the authors' application and interpretation of Caillère's α-β classification. It is perhaps useful to remark that the authors' structural interpretation of the difference between α and β types appears to be over-simplified.

fibre-pattern; it is therefore permissible to interpret the 'extra spots' as arising not from a small proportion of chrysotile fibre structure (complete as such, with the degree of perfection proper to chrysotile) in an abnormal orientation, but rather from the presence of a small proportion of the material with an imperfection in stacking of successive sheets (similar to that of the extract, and of synthetic α-sepiolite) greater than that which produces the characteristic chrysotile fibre-pattern.

V. CONCLUSION.

It will be obvious that our experimental data require amplification if a serious theoretical study is to be made of some of the outstanding problems of the chrysotile-serpentine structures. We hope, however, that the investigations described will be of interest to others working in this field. We understand that Dr. A. Guinier has recently examined X-ray patterns of chrysotiles, but we have not yet obtained any detailed information as to the nature and aim of his researches.

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