

A note on the thermal decomposition of chrysotile.

(With Plate XIX.)

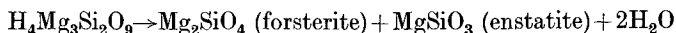
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DURING the course of a detailed X-ray study of chrysotile, antigorite, and gümbelite by E. Aruja¹ we were asked to confirm some interesting results he had obtained on heating chrysotile to various temperatures. This we were able to do and also to provide additional data which were recently referred to in a paper by A. Hargreaves and W. H. Taylor.² Although we have not succeeded in providing a completely satisfactory explanation of the optical changes observed on heating chrysotile our observations for a limited range of temperatures in the neighbourhood of 1000° C. are here recorded.

Aruja has found that the X-ray pattern for chrysotile begins to disappear after heating to 600–620° C. and that simultaneously a partially oriented pattern of forsterite appears comprising sharp reflections linked by powder lines. X-ray photographs of chrysotile heated to higher temperatures show an enhanced oriented spot-pattern of forsterite and a weakening of the forsterite powder lines. We obtained the same results on heating a specimen of chrysotile fibre (pl. XIX, figs. 1, 2) and were able to confirm Aruja's statement that after heating at 1000° C. the predominant pattern is due to forsterite and that enstatite is not formed in sufficient quantity to be recorded by X-rays. Chrysotile does not, therefore, break down on heating according to the reaction



as suggested by Mlle Caillère.³

Chrysotile when heated loses its flexibility and becomes brittle, changing in colour from green to gold or straw-yellow. We have obtained optical data on three heat-treated samples from the same

¹ E. Aruja. Dissertation for Ph.D. degree, University of Cambridge, 1943; *Min. Mag.*, 1945, vol. 27, pp. 11 and 65.

² A. Hargreaves and W. H. Taylor, *Min. Mag.*, 1945, vol. 27, p. 204.

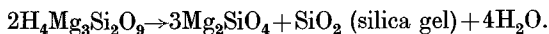
³ S. Caillère, *Bull. Soc. Franç. Min.*, 1936, vol. 59, p. 163. [*M.A.* 6-475.]

specimen¹ which agree with those measured by Professor C. E. Tilley and recorded by Aruja for chrysotile from Thetford, Quebec.

No.	Temperature. ° C.	Duration of heat-treatment.	Refractive indices.	Sign of elongation.
1	900	5 hours	1.56-1.57	positive
2	1000	5 hours	1.59	positive
3	1000	12 hours	1.61-1.62	negative

All three samples yield an oriented photograph of forsterite (pl. XIX, fig. 2), the powder lines giving place to distinct spots and the perfection but not the nature of the orientation improving from nos. 1 to 3. There is no further increase of refractive index or change in the sign of elongation when chrysotile is heated for longer periods at 1000° C.

After an examination of chrysotile heated by Aruja, Professor Tilley suggested that the low refractive index of the product compared with that of forsterite (β 1.65) might be due to the liberation of free silica (n 1.46) and that decomposition proceeds according to the reaction:



Our X-ray photographs of heated chrysotile show low-angle back-ground scattering, some of which may be due to the presence of amorphous material. It has not been possible, however, to detect the broad haloes characteristic of silica gel. We therefore attempted a physical separation of free silica from the heated chrysotile. A small quantity of no. 3 was ground in a mortar and centrifuged for an hour in bromoform. No separation of a component with specific gravity <2.85 could be detected, however finely the sample was ground before centrifuging.

As this preliminary attempt at a physical separation of silica failed we turned to a chemical method. Samples of olivine, unheated chrysotile, and two of the heated samples nos. 1 and 3 were finely ground and then boiled gently for 15 mins. with 50 c.c. of 10 % caustic soda. The mixture was filtered and silica determined in the filtrate. The following data were obtained by Miss Hilda Bennett:

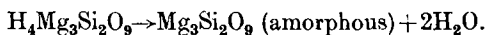
Silica extractions from:

Pale green olivine	3.2 %
Unheated chrysotile	3
Chrysotile heated to 900° C. for 5 hours (no. 1) ...	18.8
Chrysotile heated to 1000° C. for 12 hours (no. 3) ...	6.3

These results encouraged us to attempt a physical separation of the components of chrysotile heated to 900° C. for 5 hours (no. 1). This

¹ B.M. 83118. Chrysotile; Johnson mine, Thetford, Megantic Co., Quebec. Compact, oil-green, yielding fibres $8\frac{1}{2}$ cm. long, α 1.535, γ 1.550, positive elongation.

time the specimen was ground for $\frac{1}{2}$ hour before centrifuging. A separation into two fractions, *A* with specific gravity just <2.85 and the darker fraction *B* specific gravity >2.85 was achieved. Both fractions consist of pale yellow fragments of low birefringence (grey) with refractive index 1.56–1.57. The darker fraction *B* of higher specific gravity contains some opaque fragments confirmed as haematite by an X-ray photograph. Powder photographs of fraction *A* taken with copper radiation and repeated with cobalt radiation reveal only forsterite lines (pl. XIX, fig. 3). Spots due to haematite as well as forsterite lines were observed on the photographs of fraction *B*, but no haloes or lines due to any other substance were detected for *A* or *B*. So far then our tests show that although alkali-soluble silica is present in heated chrysotile centrifuging results only in the separation of free haematite, but does not succeed in separating a low refractive index component from the forsterite. These results suggest that Professor Tilley's equation is on the right lines, but do not exclude the possibility of the formation of an intermediate amorphous magnesium silicate particularly in chrysotile heated for shorter periods at temperatures below 1000° C. The following reaction may also play a part in the thermal decomposition of the mineral:



The X-ray pattern of sample no. 3 (pl. XIX, fig. 1) is so well oriented that an attempt was made to describe the orientation. From comparison with a rotation photograph of an olivine crystal about the *b*-axis [010] it was obvious that a proportion of the forsterite crystallites must be oriented in that direction and also obvious that the larger layer-line spacing of 20.8 Å. demands one or more additional orientations. The axial ratios of forsterite and olivine are sufficiently close to permit the use of the unit-cell dimensions of olivine for calculating the orientation of forsterite from the layer-lines on our photographs. The unit cell of olivine has the dimensions *a* 4.755, *b* 10.21, *c* 5.985 Å., and the layer-line spacing of 20.8 Å. corresponds closely to the axis [013]. It seems probable that the breakdown of chrysotile fibre at comparatively low temperatures would involve restricted atomic rearrangement, in particular small rotations and shifts of the silica tetrahedra. In the accepted crystal-structure of forsterite the silica tetrahedra are pointing with a tetrahedron face-diagonal along the *b*-axis [010]. If the SiO_4 groups of the chrysotile during heating build up into forsterite crystallites there are seven possible orientations of the forsterite crystallites which have their SiO_4 groups pointing with their face-diagonals along the original

fibre axis of the chrysotile. The seven possible directions are [010], [013], [323], [653], [12.1.3], [610], [619]. Of these Aruja has already determined the first two from his photographs. The remaining axes would give layer-line spacings 19.6, 61.2, 60.7, 30.3, and 61.8 Å. We have not been able to detect spots close to the equator corresponding to a layer-line spacing larger than 20.8 Å. Thus no evidence has been found for the orientations [653], [12.1.3], [610], or [619]. The axis [323] has a layer-line spacing 19.6 Å, so close to that for [013] that any mis-setting of the fibre axis would invalidate any attempt to deduce too much detail from layer-line measurements. The shape of the elongated spots resulting from a fibre photograph also limits the accuracy of such measurements.

The changes in refractive index of heated chrysotile and the low birefringence can possibly be explained by the mixture of minute forsterite crystallites embedded in seven different directions in amorphous silica or magnesium silicate. If chrysotile decomposes into forsterite, free silica, and water then the calculated refractive index of the mixture is 1.61 and the percentage of free silica formed should be 12.5. Our figures for chrysotile heated to 900° C. for 5 hours yield a lower refractive index and a higher quantity of alkali-soluble silica. This is evidence for the intermediate reaction involving the formation of amorphous magnesium silicate. There are still too many unknown factors to account quantitatively for the observed refractive indices and the sign of elongation of the heated fibres. It should not be overlooked, however, that the phenomenon of form-birefringence successfully applied to the anomalous optical properties of, for example, chalcedony and vaterite by J. D. H. Donnay¹ may also be involved. In particular, the change from positive to negative elongation on more prolonged heating of the fibres at 1000° C. which accompanies the increase in forsterite without change in orientation may be due essentially to form-birefringence.

Since the above account was written Dr. Aruja has brought to our notice the recent work of W. Epprecht and E. Brandenberger.² They have made careful dehydration and X-ray studies which do not differ significantly from our results. We are, however, unable to agree with their orientation of the forsterite crystallites. It is difficult to see what X-ray evidence is available for the orientation of the *a* and *c* axes of forsterite relative to the original axes of chrysotile. Both Aruja's X-ray photographs and ours are convincing evidence of a 20.8 Å. spacing lying

¹ J. D. H. Donnay, Ann. (Bull.) Soc. Géol. Belgique, 1936, vol. 59, pp. 215, 289. [M.A. 6-460.]

² W. Epprecht and E. Brandenberger, Schweiz. Min. Petr. Mitt., 1946, vol. 26, p. 229. [M.A. 10-298.]

along the fibre axis. Neither Epprecht and Brandenberger nor ourselves have been able to determine the exact nature of the amorphous phase or phases which may be formed during the transformation.

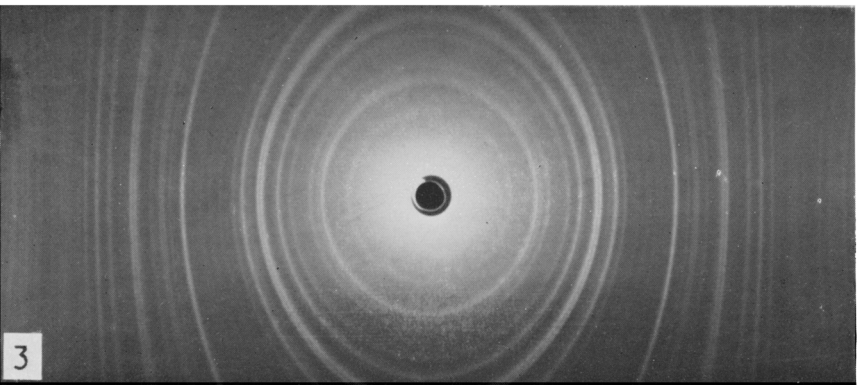
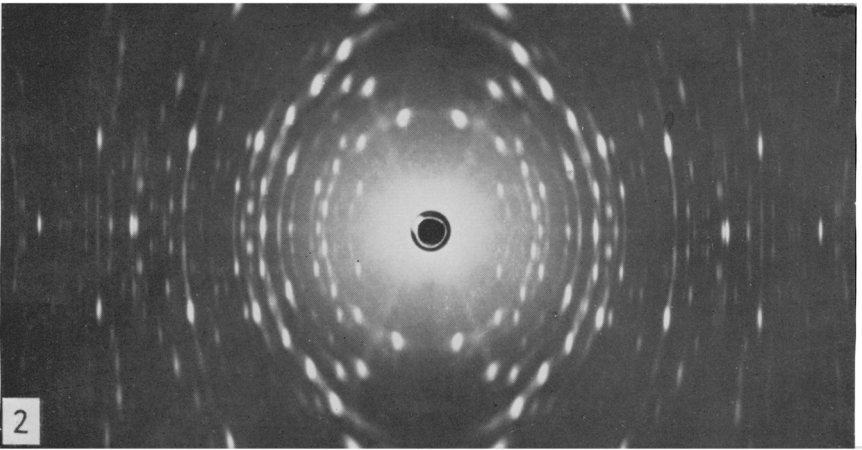
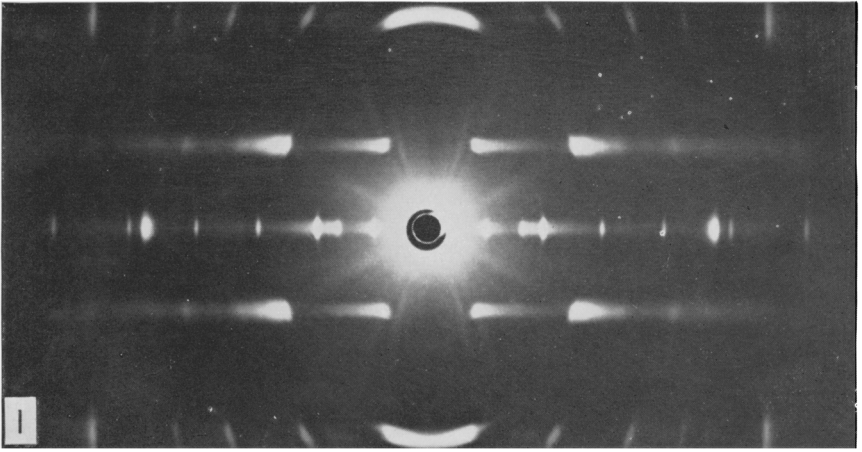
EXPLANATION OF PLATE XIX.

X-ray photographs with filtered cobalt radiation λ 1.7889 taken in a cylindrical camera (6 cm. diameter). Actual size.

FIG. 1. Rotating sheaf of oil-green fibres of chrysotile from Johnson mine, Thetford, Quebec (B.M. 83118).

FIG. 2. Stationary compact straw-yellow fibrous aggregate obtained by heating chrysotile to 1000° C. for 12 hours (sample 3, page 334). Only spots and lines due to forsterite can be detected on this photograph. Allowing for possible mis-setting all the spots can be explained by the axes [010] and [013] of forsterite lying along the fibre axis of the original chrysotile.

FIG. 3. Rotation photograph of the fraction of specific gravity < 2.85 obtained by powdering heated sample 1, page 334, which yielded the highest silica extraction 18.8 %, and after powdering centrifuging in bromoform. Only the powder lines of forsterite are present on this photograph.



M. H. HEY AND F. A. BANNISTER: X-RAY PHOTOGRAPHS OF CHRYSOTILE (UNHEATED AND HEATED).