A further investigation of tobermorite from Loch Eynort, Scotland.

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Summary. The specimen described by Claringbull and Hey (1952) has been re-examined using electron-microscope, electron-diffraction, X-ray, and dehydration isobar methods. It differs from other specimens in several respects. The basal spacing does not shrink appreciably on dehydration. The principal cleavage is (100) and not (001). The body-centred pseudo-cell is of normal dimensions, but the distribution of the weak reflections differs from that found for other specimens. The mechanism of conversion into wollastonite has also been examined.

THE specimen of tobermorite ($Ca_5Si_6O_{18}H_2 . 4H_2O$; McConnell, 1954) to which this paper relates was discovered by Heddle (1893). It has since been examined by Claringbull and Hey (1952) and by McConnell (1954). The present examination, which was carried out on a portion of analysed material (BM. 1937,1490) kindly provided by Dr. G. F. Claringbull and Dr. M. H. Hey, shows that this specimen differs in several respects from tobermorite specimens from some other localities, or made in the laboratory.

Electron-microscope investigation.

Each of the specimens described in this section was prepared by crushing a small quantity of the material in water, and allowing a drop of the diluted suspension to dry on a specimen grid coated with formvar film. Electron micrographs (fig. 1), obtained using a Metropolitan-Vickers type EM3 electron microscope, show that the material splits into fibrous or acicular crystals. The ones examined were mostly about 5μ long and 2μ broad, and their thickness was found by shadow-casting (Williams and Wyckoff, 1944) to be somewhat less than their breadth. Electron-diffraction patterns were obtained from about one hundred individual crystals. In all but three cases substantially identical patterns were obtained (fig. 2). Measurement of these patterns, and comparison of the resulting data with the known unit-cell parameters of tobermorite (McConnell, 1954), showed that the crystals yielding them were lying on (100) and that they were elongated parallel to *b*. Some of the crystals

(fig. 1, inset) lying on (100) exhibited multiple dark fringes similar to those observed in graphite by Mitsuishi, Nagasaki, and Uyeda (1951)
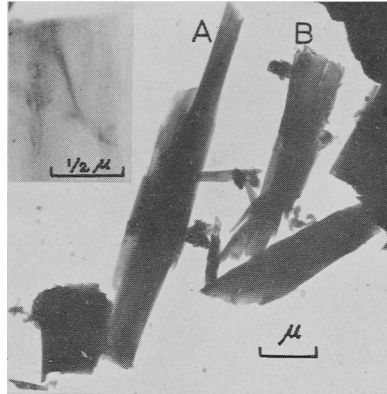

FIG. 1. Electron micrograph of tobermorite from Loch Eynort, showing crystals lying on (100) (A) and on (001) (B). *Inset*: crystal lying on (100) showing multiple dark fringes (see text).
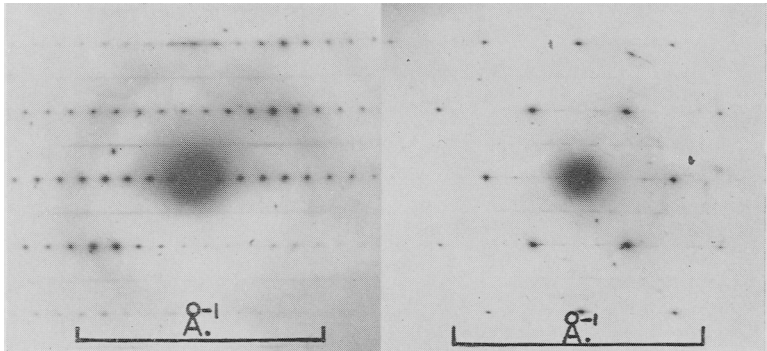

FIG. 2. FIG. 3.

FIG. 2. Electron-diffraction pattern of tobermorite from Loch Eynort; (100) normal to the electron beam. b^* vertical.

FIG. 3. Electron-diffraction pattern of tobermorite from Loch Eynort; (001) normal to the electron beam. b^* vertical.

and in mica by Rang (1953). They are commonly observed in electron micrographs of layer-lattice specimens, and are believed to be due to interference of electron waves reflected successively from lattice planes of two lamellae that are in slightly different orientations. Their occur-

rence in the tobermorite crystals confirms the good (100) cleavage. Three crystals only were found that were lying on (001). In appearance (fig. 1) they do not differ significantly from those lying on (100); the diffraction pattern given by one of them is shown in fig. 3.

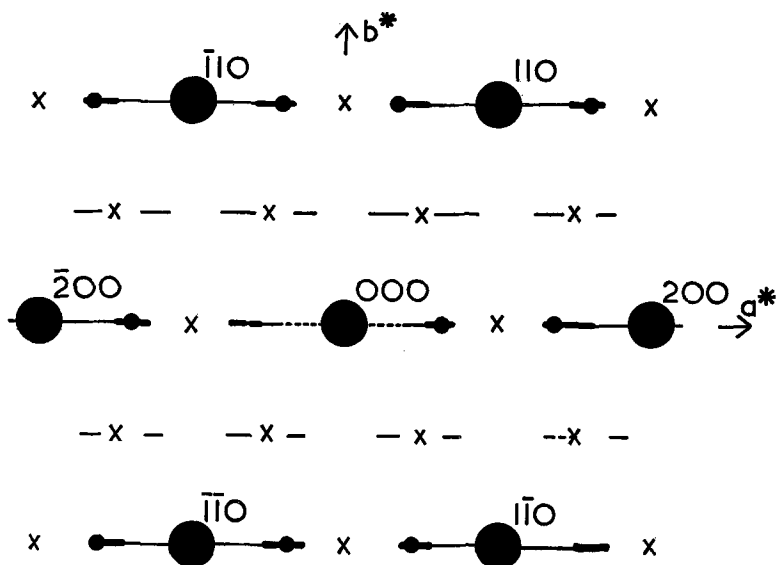The diffraction patterns for both orientations contain systematically

FIG. 4. Superimposed electron-diffraction patterns of tobermorite from Loch Eynort and made in the laboratory; drawing traced from enlargements of patterns given by crystals having (001) normal to the electron beam. Large full circles: strong reflections, given by both specimens, with indices in terms of the pseudo-cell (a 5·6, b 3·66 Å.). Small full circles and lines: weak reflections given by the specimen from Loch Eynort. Crosses: weak reflections given by the synthetic specimen.

strong and systematically weak groups of reflections. From measurements of the strong reflections the pseudo-cell was found to be body-centred with a 5·48±0·12, b 3·66±0·07, c 22·5±0·1 Å., $\alpha = \gamma = 90°$. The value of a was derived from the patterns given by the three crystals lying on (001). β could not be determined from the electron-diffraction patterns. Rather large variations were observed between individual crystals, and were probably outside experimental error.

The patterns given both by crystals lying on (100) and by those lying on (001) show strong pseudo-halving of b, so that the true value of b is twice that for the pseudo-cell. The true value of a is uncertain. The pattern given by crystals lying on (001) is shown in more detail in fig. 4,

with the strong reflections indexed in terms of the pseudo-cell. The weak reflections fall into two groups, characterized by odd and even true values of k. The reflections of both groups appear to have non-integral h-indices. All are elongated to some extent along a^*, and where true k is even, each of the strong reflections has two associated weaker spots joined to it by streaks. In order to obtain information concerning weak reflections not in the $0a^*b^*$ section of the reciprocal lattice shown in figs. 3 and 4, patterns were obtained from crystals tilted a few degrees from the position with (100) normal to the beam. In these patterns (fig. 5), Laue zones can be distinguished that correspond to different sections of the reciprocal lattice normal to a^*. The zones with h equal to 1, 0, and $\bar{1}$ (in terms of the pseudo-cell) are indicated in fig. 5. Between them lie various zones of weak reflections.
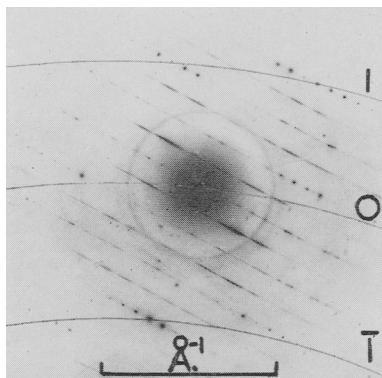

FIG. 5. Electron-diffraction pattern of tobermorite from Loch Eynort; (100) tilted a few degrees from the plane normal to the electron beam. Approximate positions of Laue zones corresponding to $h = 1$, $h = 0$, and $h = \bar{1}$ are indicated.

Examination of these intermediate zones showed that the weak reflections with true k odd are elongated into streaks, parallel to c^*, with only diffuse maxima. The weak reflections with true k even are only slightly elongated parallel to c^*. Their positions along c^* are not very clear, but suggest that their distribution relative to the strong spots is the same within each layer of the reciprocal lattice normal to c^* as that shown for the zero layer in fig. 4. An impression of the reciprocal lattice thus obtained is given in fig. 6a.

For comparison, electron micrographs and diffraction patterns were obtained of a typical synthetic tobermorite which had been prepared hydrothermally at 140° C. The specimen,[1] which had the approximate composition $CaO.SiO_2.H_2O$, was closely similar to the one for which X-ray powder data were quoted by Claringbull and Hey (1952). The electron micrographs (fig. 7) showed it to consist of thin foils with no marked elongation in any direction. Electron-diffraction patterns (fig. 8) given by these showed that the sheets were in all cases parallel to

[1] Specimen 67 of Heller and Taylor (1951).

(001). The strong reflections were identical with those given by the Loch Eynort specimen in the same orientation, but the weak reflections differed, and their positions are shown in fig. 4. An impression of the reciprocal lattice for the synthetic material is given in fig. 6b.
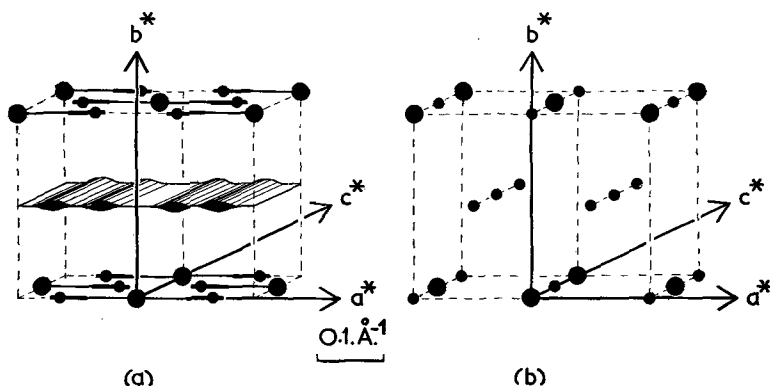

FIG. 6. Three-dimensional impression of the reciprocal lattices for tobermorite, (a) from Loch Eynort, and (b) made synthetically, illustrating the more complex distribution of the superlattice reflections in (a) and their elongations in the a^* and c^* directions. The discontinuous lines merely indicate the outlines of the reciprocal pseudo-cells. Space-group absences are omitted.
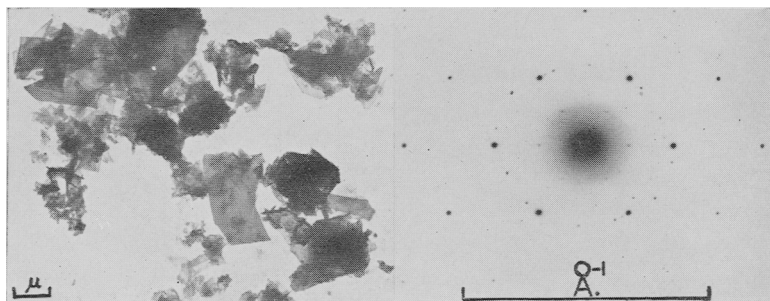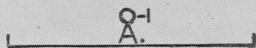

FIG. 7.   FIG. 8.

FIG. 7. Electron micrograph of synthetic tobermorite made hydrothermally at 140° C.
FIG. 8. Electron-diffraction pattern of synthetic tobermorite; (001) normal to the electron beam, b^* of the principal crystal vertical.

X-ray investigation.

The Loch Eynort specimen contained no crystals of sufficient size for single-crystal X-ray work. A powder photograph was obtained using a

6-cm. diameter camera with filtered copper radiation. The results (fig. 9, line 1) agreed closely with those of Claringbull and Hey (1952). The
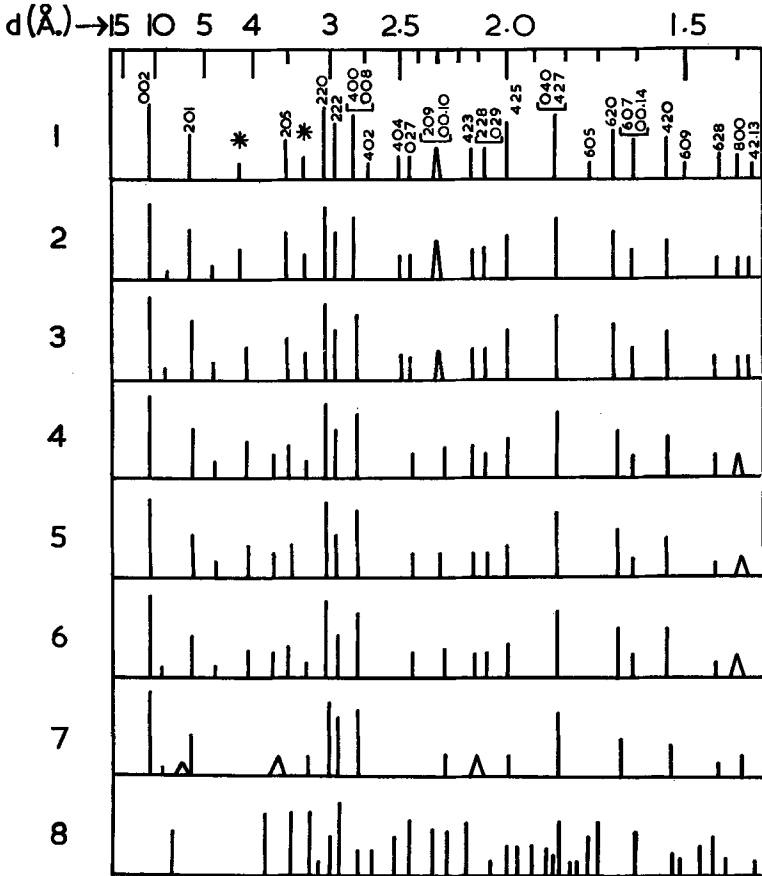

FIG. 9. X-ray powder data for tobermorite from Loch Eynort, in its natural state and after heating. (1) Unheated; also after 24 hours at 110° C., 24 hours at 200° C., or 24 hours at 290° C. (patterns virtually identical); for basis of indexing, see text. (2) 24 hours at 295° C. (3) 24 hours at 390° C. (4) 56 hours at 525° C. (5) 14 days at 550° C. (6) 24 hours at 625° C. (7) 24 hours at 750° C. (8) 96 hours at 900° C.

reflections were indexed by direct comparison of the powder photograph with single-crystal photographs of a specimen of tobermorite from Ballycraigy, kindly provided by Dr. J. D. C. McConnell. The pseudo-cell dimensions for the Loch Eynort specimen were thus found to be a 5·60, b 3·67, c 22·6 Å., $\alpha = \beta = \gamma = 90°$, in agreement with the

electron-diffraction result. All the powder spacings, except two weak ones (marked * in fig. 9), can be attributed to the strong reflections indexable in terms of the pseudo-cell. The indices given in fig. 9 relate to a cell with $a\ 2 \times 5{\cdot}60$, $b\ 2 \times 3{\cdot}67$, $c\ 22{\cdot}6$ Å., $\alpha = \beta = \gamma = 90°$, which is similar to the true cell for the Ballycraigy specimen.
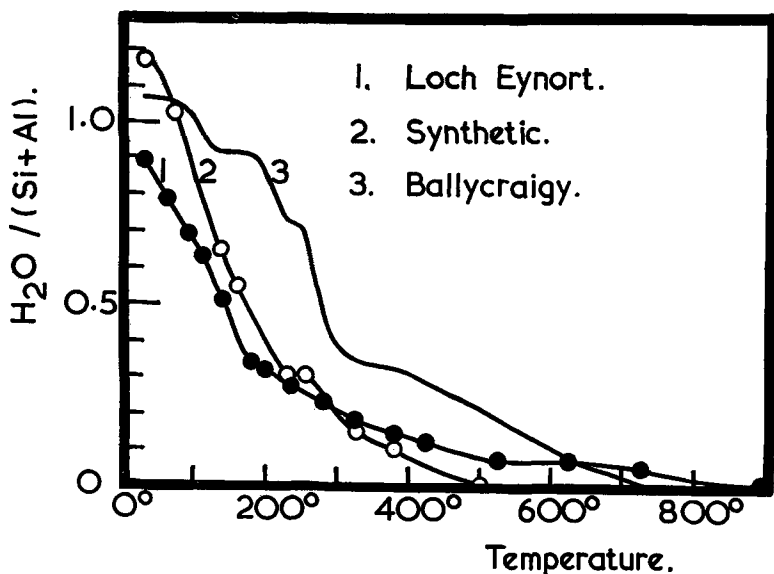

FIG. 10. Dehydration curves for tobermorite. (1) specimen from Loch Eynort; isobar determined at $p(H_2O) = 6$ mm. (2) synthetic preparation; isobar determined at $p(H_2O) = 6$ mm. (3) specimen from Ballycraigy; recalculated from data given by J. D. C. McConnell (1954).

Dehydration.

Dehydration isobars (fig. 10)[1] were determined at 6 mm. pressure of water vapour for the Loch Eynort specimen and for the synthetic preparation used in the electron-microscope investigation. The method has been described previously (Taylor, 1953). A dehydration curve for tobermorite from Ballycraigy (from McConnell, 1954) is also included in fig. 10.

Separate portions of the Loch Eynort specimen were heated to various temperatures and X-ray powder photographs then taken. The temperature, duration of heating, and results of each experiment are given in

[1] Plotted as $H_2O/(Si+Al)$ on the assumption that Al in the Loch Eynort specimen replaces Si; values of H_2O/Si would for this specimen be $10{\cdot}9$ % higher. Neither the Ballycraigy specimen nor the synthetic one contained appreciable alumina.

fig. 9. Except for the experiments at 550°, 750°, and 900° C., heating was done in an atmosphere containing 6 mm. partial pressure of water vapour and virtually free from carbon dioxide.

Specimens heated for 14 days at 550° C. or for a few hours at 1000° C. were examined using the electron microscope. The one heated at 550° C. showed no significant changes either in appearance or in the diffraction pattern given by crystals lying on (100). The one heated at 1000° C. consisted of pseudomorphs of the original material. These gave a diffraction pattern which resembled those of the original material in showing strong and weak layer-lines corresponding to a true repeat distance of about 7·3 Å. along the fibre direction. The even layers showed an irregular distribution of reflections, which could possibly have been caused by the presence of a number of crystallites rotated at random around the fibre direction. The odd layers were streaks.

Discussion.

The present results show that tobermorite from Loch Eynort has substantially the same pseudo-cell as that from Ballycraigy. The X-ray powder photographs are also closely similar (McConnell, 1954). The essential structure of the Loch Eynort material is therefore almost certainly the same as that established for the Ballycraigy specimen by Megaw and Kelsey (1956 a and b). At the same time, the Loch Eynort specimen differs from the Ballycraigy one, and also from synthetic and certain other natural specimens in three respects:

The principal cleavage for the Loch Eynort specimen is (100), and (001) is secondary; in tobermorite from Ballycraigy, and in synthetic preparations, (001) is a perfect cleavage and (100) is secondary.

The basal or 002 spacing is virtually unaffected by heating, even after 14 days at 550° C. or 24 hours at 750° C. (fig. 9). A barely detectable spacing at 9·5 Å. sometimes occurs after heating at 295° C. or above, and may indicate a small degree of conversion into a state with a shorter c-axis, but the effect is very slight. This behaviour contrasts strongly with that of tobermorite occurring in intergrowths at Crestmore, California, or that made in the laboratory (Taylor, 1953), or that from Ballycraigy (McConnell, 1954), all of which show reduction of the basal spacing to 9·3–9·6 Å. after a few hours' heating at 300° C. The dehydration isobar for the Loch Eynort specimen, unlike the X-ray results, is not markedly anomalous (fig. 10), and the mineral must therefore be able to retain its original value of c when dehydrated to an extent which in other specimens causes a reduction. The X-ray pattern of the Loch

Eynort material is in general little affected by heating up to 750° C.; the principal effect is a relative weakening of reflections other than those with 002 and $hk0$ indices, indicating a certain disordering of the structure. This is most pronounced after heating at 750° C.

Thirdly, the spacial distribution of the reciprocal lattice points corresponding to the weak reflections is complex, and differs from that shown by the synthetic preparation (fig. 4). The electron-diffraction results obtained for the latter preparation are compatible with the view that it has the same true unit-cell (C-centred orthogonal with a 11·2, b 7·3, c 22·5 Å. approx.) as the specimen from Ballycraigy. The complex pattern of weak reflections given by the Loch Eynort specimen has not yet been interpreted. It may indicate that the true cell is different from and presumably larger than that of the Ballycraigy specimen. Alternatively, it may be more correct to regard the non-integral distribution of the weak reflections as a splitting caused by disorder, similar to that observed with plagioclase felspars (Cole, Sörum, and Taylor, 1951; Gay, 1956).[1] Disorder of a complex type undoubtedly exists in the Loch Eynort specimen, because the weak reflections are elongated in two ways, parallel to c^* and parallel to a^*. This may be correlated with the fact that (100) and (001) are both quite good planes of cleavage. Tobermorite specimens from Ballycraigy and from Scawt Hill (McConnell, 1954; Megaw and Kelsey, 1956 a and b) show streaking of weak reflections in only one direction, parallel to c^*, and have one predominant cleavage parallel to (001).

These peculiarities of the Loch Eynort specimen may be considered in the light of the structure determination by Megaw and Kelsey (1956 a and b), who confirmed that tobermorite from Ballycraigy has a layer structure, in some respects similar to those of clay minerals such as vermiculite; the layers are parallel to (001). The present results show that, in the Loch Eynort specimen, the cohesive forces between the layers are unusually strong, and that they are, in fact, stronger than those operating in the a-direction within the layers themselves.

The stability of the 11·3 Å. basal spacing in tobermorite from Loch Eynort has previously been noted by McConnell (1954). He found that the basal spacing of tobermorite from Loch Eynort was unaffected by grinding with water, whereas that of tobermorite from Ballycraigy readily increased to 14·6 Å. under similar conditions. He suggested that the stability of the basal spacing in the Loch Eynort specimen might be

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[1] Our thanks are due to Dr. H. D. Megaw for drawing our attention to this possibility.

caused by the presence of alkali ions in interlayer positions (Claringbull and Hey, 1952, found Na_2O 0·56 %, K_2O 0·25 %). McConnell also observed appreciable variations in the mean refractive index and opacity of individual crystals of the Loch Eynort specimen, and suggested that these variations might be caused by differences in water content. The present results show that the specimen is probably inhomogeneous also as regards unit-cell dimensions, though whether these variations are associated with differences in water content or with the degree of imperfection in the structure is not established.

The X-ray powder pattern obtained after heating at 900° C. (fig. 9, line 8) is that of α-$CaSiO_3$ (wollastonite or parawollastonite). The electron-diffraction pattern obtained after heating at 1000° C. shows that orientation is preserved in the fibre direction. This can be explained by the fact that tobermorite (Megaw and Kelsey, 1956 a and b) and wollastonite (Dornberger-Schiff, Liebau, and Thilo, 1954 and 1955; Buerger, 1956; Tolliday, 1956) both contain metasilicate chains of a similar type running in this direction. To what extent orientation is preserved in the sense of rotation around this axis is uncertain; the present results suggest that considerable disorientation probably occurs in the case of the Loch Eynort material; with tobermorite from Ballycraigy, on the other hand, experiments now in progress indicate that orientation is probably almost completely preserved during this transformation.

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