On tilleyite and its associated minerals from Carlingford, Ireland.

(With Plates XI and XII.)

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THE mineral tilleyite was first discovered by Larsen and Dunham in thermally metamorphosed limestones from the contact zone at Crestmore, California.[1] It is associated there with merwinite, wollastonite, spurrite, and gehlenite, and the rock is traversed by streaks of idocrase with grossular. The amount of tilleyite in these rocks was apparently small, but in certain thermally metamorphosed limestones from Carlingford it is abundant and some specimens are practically pure tilleyite-rocks. It has been possible, therefore, to make a more detailed optical and chemical examination of this mineral. The tilleyite occurs as subidioblastic crystals when abundant, or as rounded grains in calcite-rich rocks, or as irregular plates.

(a) *Optical properties of tilleyite.*

According to Larsen and Dunham tilleyite is monoclinic with one perfect cleavage, assumed to be parallel to (100), and with traces of another ill-defined cleavage which makes an angle of about 42° with the perfect cleavage. The β index direction was found to be in the plane of the perfect cleavage, i.e. $\beta = b$. The α index direction was said to make an angle of 18° with the trace of the perfect cleavage in a section parallel to (010). The refractive indices were determined as α 1·617, β 1·635, γ 1·652, while 2V was found to be large, approaching 90°, and probably positive. Twinning was not detected.

These results are confirmed in part by an examination of the Carlingford tilleyite, but several cleavages have been found in addition to the

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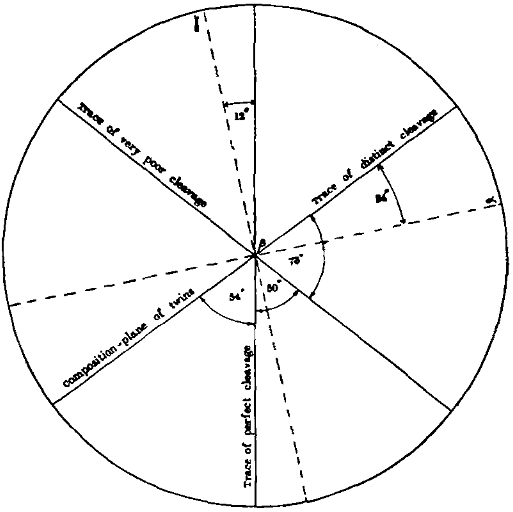
[1] E. S. Larsen and K. C. Dunham, Tilleyite, a new mineral from the contact zone at Crestmore, California. Amer. Min., 1933, vol. 18, pp. 469–473. [M.A. 5–387.]

perfect one. Simple or, more rarely, lamellar twinning is common (pl. XI, figs. 1 and 2), and the optical orientation is different. The refractive indices of the Carlingford material were determined by means of the immersion method; and the optical orientation, optical axial angle, position of the cleavages and of the composition-plane of the twin-lamellae, by means of the Fedorov universal stage. The results may be summarized as follows:



Text-fig. 1. Stereographic projection of tilleyite on a plane normal to $\beta = b$, showing the relations between the cleavages and the optical orientation.

α 1·612, β 1·632, γ 1·653 (all ±0·003), positive, 2V ranges 85–89° with an average value of 87°.

The optical orientation is shown in text-fig. 1, where the plane of projection is normal to $\beta = b$, that is, the (010) plane if we accept Larsen and Dunham's orientation. In addition to the perfect cleavage parallel to (100), there is a distinct cleavage at right angles to (010) and making an angle of 54° with the perfect cleavage, a poor cleavage parallel to (010), and a very poor cleavage at right angles to (010) making an angle of 50° with the perfect cleavage and of 75° with the distinct cleavage. The composition-plane of the twins coincides with the plane of the distinct cleavage and, in sections normal to β and to the composition-plane, the symmetrical extinction angle (α to trace of composition-plane) is 24°. It will be noticed that the optical orientation is not the same as that given by Larsen and Dunham. It is the *slow* vibration direction γ which lies near the trace of the perfect cleavage and the angle it makes with the latter is 12° and not 18°. This has been confirmed by an examination of such Crestmore material as is available in the Department of Mineralogy and Petrology, Cambridge.[1]

(b) *Chemical composition of tilleyite.*

Larsen and Dunham managed to separate a small quantity of tilleyite for chemical analysis, but the analysed powder contained a little wollastonite and spurrite. After correcting for the estimated amount of impurity and recalculating the principal constituents to 100 %, they obtained molecular ratios suggesting an empirical formula $3CaO.SiO_2.CO_2$, though not agreeing very closely with the theoretical molecular proportions derived from the latter. They conclude, 'Examination of other possible formulae showed that only a very complex one would fit the analysis better than the one assigned, and we have decided, pending the availability of purer material for analytical purposes, to present the formula in its simple form' (loc. cit., p. 472).

There is thus some element of doubt as to the true composition of tilleyite and, in an effort to resolve the problem, two samples of tilleyite were separated from their parent rocks and chemically analysed by Mr. H. G. C. Vincent with the following results:

	1.	2.	1a.	2a.	3a.	1b.	2b.	3b.
SiO_2	24·48	23·72	24·96	24·16	24·66	0·414	0·401	0·409
Al_2O_3, &c. ...	0·42	0·64	—	—	—	—	—	—
Fe_2O_3... ...	0·40		—	—	—	—	—	—
MgO	—	0·03	—	—	—	—	—	—
CaO	55·51	55·79	56·61	56·82	57·34	1·010	1·013	1·023
CO_2	18·07	18·68	18·43	19·02	18·00	0·419	0·432	0·409
$H_2O+110°$ ...	1·26	1·16	—	—	—	—	—	—
$H_2O-110°$ ...	0·30		—	—	—	—	—	—
	100·44	100·02	100·00	100·00	100·00			

1. Tilleyite, tilleyite-rock with accessory wollastonite and idocrase, locality 1, Barnavave, Carlingford. (Weight of sample 0·8 gm.)

2. Tilleyite, tilleyite-calcite-rock with minor idocrase, locality 1, Barnavave, Carlingford. (Weight of sample 0·3 gm.)

1a. Analysis 1 recalculated to 100 % ignoring Al_2O_3, &c., and H_2O.

2a. Analysis 2 recalculated to 100 % ignoring Al_2O_3, &c., and H_2O.

3a. Theoretical percentage weights for an empirical formula $3CaO.2SiO_2.2CaCO_3$.

1b–3b. Molecular ratios for 1a–3a.

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[1] Prof. Tilley has also found this orientation in tilleyite occurring in metamorphosed limestones from the Island of Muck. C. E. Tilley, The gabbro-limestone contact zone of Camas Mòr, Muck, Inverness-shire. Bull. Comm. Géol. Finlande (Eskola volume), 1947 (in press).

Unfortunately tilleyite is a mineral that alters very readily and although separated in a pure state it was not free from traces of alteration. The first sample showed slight alteration to calcite and hillebrandite along the cleavage planes of the grains, while in the second sample a number of the grains were turbid, probably through the development of minute granules of secondary carbonate. If these facts are taken into account, the agreement of both the analyses with the theoretical percentage weights for an empirical formula $3CaO.2SiO_2.2CaCO_3$ must be considered as good, and there can be little doubt that perfectly fresh tilleyite has this empirical composition. Tilleyite is thus related to rankinite in much the same way as spurrite is to larnite:

larnite ...	... Ca_2SiO_4	spurrite ...	$2Ca_2SiO_4.CaCO_3$
rankinite ...	... $Ca_3Si_2O_7$	tilleyite ...	$Ca_3Si_2O_7.2CaCO_3$

(c) *Paragenesis of tilleyite in the thermally metamorphosed limestones of the Carlingford district.*

The following assemblages containing tilleyite have been found:

1. Tilleyite (with minor idocrase and wollastonite).
2. Tilleyite—calcite (with minor idocrase, wollastonite, melilite).
3. Tilleyite—calcite—idocrase.
4. Tilleyite—idocrase (with minor spurrite).
5. Tilleyite—idocrase—wollastonite.
6. Tilleyite—idocrase—spurrite.
7. Tilleyite—spurrite (with minor idocrase).
8. Tilleyite—spurrite—calcite (with minor idocrase and melilite).
9. Tilleyite—melilite—calcite.

These are found interbanded with other assemblages at localities 1 and 2 (see sketch-map, text-fig. 2). Both of these are small patches of limestone resting on the eucrite of the district. Before describing the characters of the minerals associated with tilleyite, it will be convenient to deal with the other high-temperature assemblages.

(d) *Other high-temperature assemblages from the thermally metamorphosed limestones of the Carlingford district.*

A number of other high-temperature assemblages are found interbanded with the tilleyite-bearing rocks at localities 1 and 2:

1. Spurrite—calcite.
2. Spurrite—calcite—idocrase.
3. Spurrite—calcite—wollastonite.
4. Spurrite—wollastonite—idocrase.

5. Spurrite—idocrase (with minor tilleyite and melilite).
6. Wollastonite—idocrase.
7. Wollastonite—idocrase—melilite.
8. Wollastonite—melilite.
9. Melilite—calcite (minor idocrase and wollastonite).
10. Melilite—calcite—idocrase.
11. Melilite (with minor calcite).

The metamorphosed limestones from localities 3 to 7 inclusive (see sketch-map, text-fig. 2) do not contain either tilleyite or spurrite, but a number are rich in melilite. Certain new assemblages are found there, in addition to those already recorded:

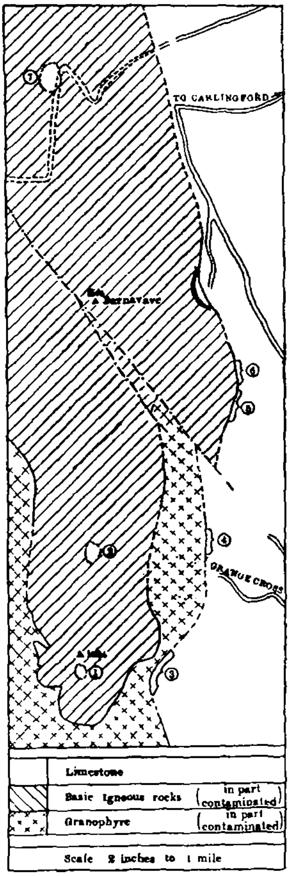
1. Melilite—wollastonite—calcite.
2. Melilite—wollastonite—calcite—augite.
3. Melilite—augite.
4. Melilite—wollastonite—augite.
5. Melilite—wollastonite—garnet (±calcite).
6. Melilite—wollastonite.
7. Wollastonite—augite.
8. Wollastonite (accessory augite).
9. Augite—calcite (±melilite).
10. Monticellite—calcite (phlogopite).
11. Forsterite—calcite (spinel).
12. Forsterite—brucite (after periclase) (spinel).

(e) *Description of the minerals.*

Spurrite is very common in a number of the specimens from localities 1 and 2, and, like tilleyite, is colourless in thin sections. It may be distinguished from the latter by its higher refractive indices and by its small negative optic axial angle. The optical data obtained from the spurrite in these Carlingford rocks are: α 1·641, β 1·676, γ 1·681 (all ±0·003), negative, 2V 38°.

It occurs as subidioblastic or rounded grains, also as irregular plates. When found with tilleyite, the latter is normally less idioblastic and may enclose the spurrite grains, while in one or two cases these minerals were intimately intergrown. This may indicate that tilleyite is replacing spurrite in rocks where they occur together, but no conclusive evidence of this was found.

Wollastonite usually forms subidioblastic crystals but may be more or less granoblastic in fine-grained rocks where it is abundant, or may form semi-poikiloblastic plates as, for instance, in some of the rocks rich in melilite. In certain bands composed almost exclusively of wollastonite, this mineral may appear as crystals half an inch or more long. It is a variety practically free from iron with α 1·620, β 1·631, γ 1·635 (all ±0·003), negative, 2V 38·5°.



Text-fig. 2. Sketch-map of Barnavave and its surroundings, showing the positions of localities mentioned in the text.

Some of the metamorphosed limestones containing tilleyite, spurrite, and wollastonite have been much affected by later retrograde changes. Associated minerals such as idocrase and grossular remain unchanged, but these three are replaced by calcite and varying amounts of a mineral which has all the properties of *hillebrandite* (pl. XII, fig. 2). This occurs as colourless fibrous aggregates and has α 1·607, γ 1·614 (both ±0·003), positive elongation, straight extinction, negative, 2V 51°. Certain sections show anomalous ultra-blue interference colours between crossed nicols. It compares closely with the type material from Velardeña, Durango, Mexico.[1]

Idocrase is present as a subordinate constituent in many of the assemblages and is sometimes important. It usually builds well-formed idioblastic crystals (pl. XI, fig. 3), though it may be present as more irregular fine-grained aggregates intergrown with wollastonite or melilite. In every example tested it was optically negative with ω 1·726 and ε 1·723 (both ±0·003).

Melilite is found as a subordinate constituent in rocks carrying spurrite and tilleyite where it forms small, rather rounded grains. In certain bands interbedded with these rocks and throughout considerable thicknesses of rock at other localities, it becomes abundant and quite a large number of specimens are practically pure melilite-rocks. Under these conditions, the melilite is almost idioblastic and some of the rocks are coarse grained.

This melilite varies somewhat in composition from band to band as is

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[1] F. E. Wright, Amer. Journ. Sci., 1908, ser. 4, vol. 26, p. 545.

shown by its optical properties. Some is optically negative with ω 1·650, ϵ 1·648, and shows abnormal ultra-blue colours between crossed nicols; some is isotropic with $\omega = \epsilon$ 1·647; and some is optically positive with ω 1·641, ϵ 1·645, and shows abnormal ultra-brown colours between crossed nicols. In one rock, the melilite was zoned with negative cores and positive margins. It is clear that these melilites contain a considerable amount of the åkermanite molecule, but some of the melilite associated with spurrite and tilleyite in the more calcitic rocks is negative with normal interference colours and must show a closer approach to gehlenite.

Melilite may suffer later alteration and is then converted to a turbid brownish aggregate which is practically isotropic and whose nature could not be further resolved.

The *augite* present in a number of the assemblages from localities 3 to 7 varies from a pale green or colourless diopsidic variety to a pink, somewhat pleochroic titanaugite. The latter is confined to assemblages carrying melilite and is not normally an abundant constituent.

Monticellite, *forsterite*, and *brucite* (forming pseudomorphs after periclase) are confined to rocks occurring at locality 3. These have been described in detail by Osborne (p. 217)[1] together with the phlogopite, pleonaste, apatite, and custerite which accompany the monticellite and also occur in the melilite rocks. The 'vesuvianite' mentioned in Osborne's account of the rocks at this locality is melilite.

Although *custerite*[2] is most abundant in these rocks from locality 3, it is not confined to them. It has been found in small amounts in a spurrite-calcite-rock from locality 1 and more abundantly in some of the melilite-bearing rocks from localities 4, 6, and 7.

The most important accessory constituents are *garnet*, *iron-ore*, and *spinel*, all of which appear in practically every rock examined. The garnet is usually grossular, yellow-green in thin sections, forming small irregular grains enclosed in the main constituents. Occasionally, as in certain melilite-bearing assemblages at locality 6, the garnet is brown in thin sections and must contain an appreciable amount of the andradite molecule. In a melilite-rock at this locality the garnet is poikiloblastic and wrapped round the melilite crystals (pl. XII, fig. 1). Iron-ore is never very abundant, but rarely absent; most of it appears to be

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[1] G. D. Osborne, The metamorphic limestones and associated contaminated igneous rocks of the Carlingford district, Co. Louth. Geol. Mag., 1932, vol. 69, pp. 209–233. [M.A. 5–134.]

[2] 'Custerite' = cuspidine, C. E. Tilley, Min. Mag., 1947, vol. 28, p. 91.

pyrrhotine. Spinel is present in varying amounts and tends to be most abundant in the melilite-rich assemblages. It is usually brown in thin sections except in the forsterite-bearing rocks of locality 3 where it is practically colourless.

(f) *The position of tilleyite in the decarbonation series of N. L. Bowen.*

Bowen has dealt recently with the progressive metamorphism of siliceous limestone[1] and has suggested that, after the formation of wollastonite, the next step (at a higher temperature) is the formation of spurrite according to the following equation:

$$3CaCO_3 + 2CaSiO_3 \rightleftharpoons 2Ca_2SiO_4.CaCO_3 + 2CO_2.$$

In view of the new data on the chemical composition and occurrence of tilleyite, it seems likely that the formation of this mineral represents an intermediate step between the formation of wollastonite and spurrite:

$$3CaCO_3 + 2CaSiO_3 \rightleftharpoons Ca_3Si_2O_7.2CaCO_3 + CO_2,$$

followed by the reaction:

$$Ca_3Si_2O_7.2CaCO_3 \rightleftharpoons 2Ca_2SiO_4.CaCO_3 + CO_2.$$

EXPLANATION OF THE PLATES XI AND XII.

PLATE XI.

FIG. 1. Tilleyite with simple twinning, tilleyite-rock, locality 1, Barnavave. Crossed nicols. × 25.

FIG. 2. Tilleyite with repeated twinning, spurrite-tilleyite-calcite-rock, locality 2, Barnavave. Crossed nicols. × 25.

FIG. 3. Idioblastic idocrase in spurrite-wollastonite-idocrase-rock, locality 2, Barnavave. Ordinary light. × 25.

PLATE XII.

FIG. 1. Poikiloblastic grossular in melilite-rock, locality 6, Barnavave. Ordinary light. × 25.

FIG. 2. Tufted aggregates of hillebrandite with calcite; altered tilleyite-spurrite-calcite-rock, locality 1, Barnavave. Ordinary light. × 32.

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[1] N. L. Bowen, Progressive metamorphism of siliceous limestone and dolomite. Journ. Geol. Chicago, 1940, vol. 48, pp. 225–274. [M.A. 8–243.]

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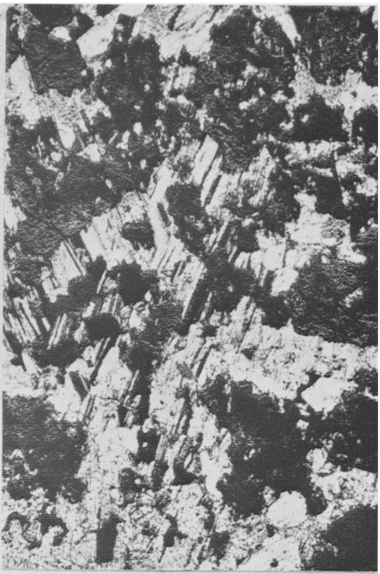

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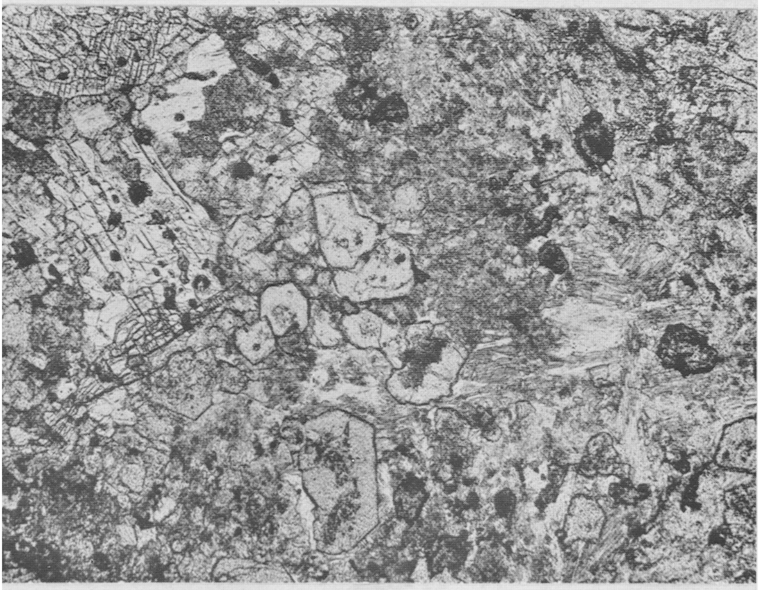

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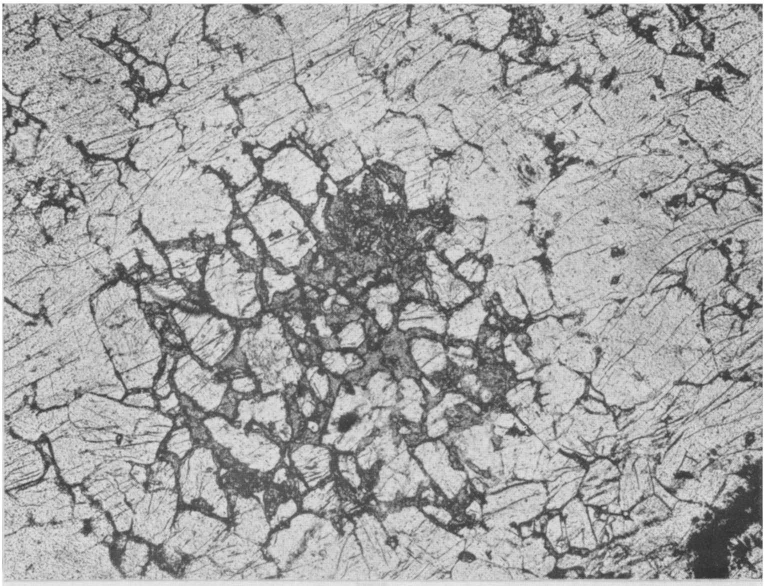
S. R. NOCKOLDS: TILLEYITE, ETC., IRELAND.



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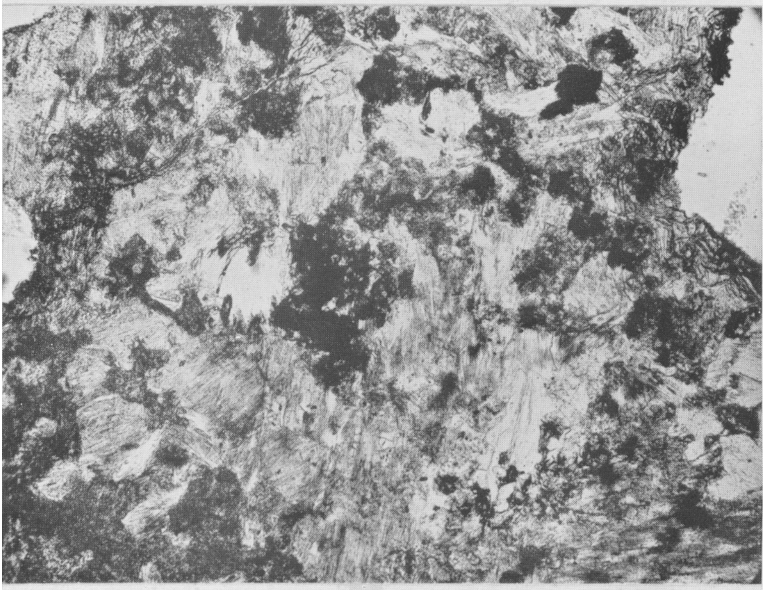

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S. R. Nockolds: Tilleyite, etc., Ireland.