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On larnite (calcium orthosilicate, a new mineral) and its associated minerals from the limestone contact-zone of Scawt Hill, Co. Antrim.

By C. E. Tilley, B.Sc., Ph.D., F.G.S.
Department of Geology, University of Cambridge.

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THE contact-zone of Chalk and Tertiary dolerite at Scawt Hill, near Larne, Co. Antrim, consists of an assemblage of comparatively rare minerals, including a mineral of the composition Ca_2SiO_4 not previously recognized as a naturally occurring compound. In the assemblages of the contact-zone the chief minerals, apart from calcite, are spurrite, calcium orthosilicate (larnite), melilite (gehlenite), merwinite, spinel, perovskite, and wollastonite. Outside this contact-zone, the chalk consists almost wholly of calcium carbonate; nearer the contact it is recrystallized to a granular mosaic of calcite of coarse texture, while at the immediate contact the chalk is completely transformed into an aggregate of new-formed silicates in varying proportions. A hybrid zone between the dolerite and the exogenous contact-rock is composed of a coarsely crystalline rock built up essentially of titanaugite, melilite (humboldtilite), nepheline, wollastonite, perovskite, and various zeolites. An account of the melilite of this hybrid zone has already been given.[1] The present note deals particularly with the assemblages forming the exogenous contact-zone that have resulted by metamorphism and metasomatism

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[1] C. E. Tilley, Geol. Mag., 1929, vol. 66.

of the chalk. A preliminary notice on the constitution of this zone was given in 1927.[1]

The rocks of the contact-zone of Scawt Hill were described as long ago as 1907 by G. C. Gough,[2] but this account is unfortunately largely erroneous. The figures accompanying his paper are sufficiently clear to allow of their reinterpretation, e. g. plate v, fig. 3 is a photomicrograph showing in addition to calcite idiomorphic crystals of spurrite. Larnite is also probably represented.

The chief assemblages of the contact-zone are the following:

(*a*) Spurrite
(*b*) Spurrite-larnite
(*c*) Spurrite-larnite-melilite (gehlenite)
(*d*) Spurrite-melilite (gehlenite)-merwinite-spinel-larnite
} calcite.

There is thus a considerable range of rock type, from assemblages rich in spurrite and larnite respectively to those rich in spinel with minor spurrite. Some rock types are also rich in merwinite.

(1) *Spurrite* ($2\,Ca_2SiO_4.CaCO_3$) is the most prominent mineral of the contact-zone, where it forms the essential component of the rock. It occurs usually as a finely crystalline mass of white colour with a vitreous, inclining to resinous, lustre. On fractured surfaces larger crystals reaching up to half an inch in length may occur. They are then elongated and show a well-marked cleavage. Spurrite is most commonly associated with more finely crystallized larnite (fig. 4). The mineral is readily attacked by hydrochloric acid with evolution of carbon dioxide and leaves a gelatinous residue of silica.

Under the microscope, spurrite is distinguished by its imperfect cleavage, high birefringence, and polysynthetic twinning. The optical properties are as follows: α 1·640, γ 1·680, double refraction negative, and small optic axial angle (2V 40°). The twinning is parallel to the dominant cleavage, a poor second cleavage at angles of 79–80° being also observed. Sections perpendicular to the acute bisectrix show symmetrical extinction of adjacent lamellae, and the crystals are frequently elongated in the direction of the twin-lines and the cleavage. As has been shown by Wright[3] the properties of spurrite agree with those of a monoclinic mineral in which $a = b$, the cleavages being parallel to the axis of symmetry. The orientation of the Scawt Hill spurrite is such that in the plane (010)

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[1] C. E. Tilley, Min. Mag., 1928, vol. 21, p. xlviii, 1929, vol. 22, p. xxviii; and Geol. Mag., 1927, vol. 64, p. 285.

[2] G. C. Gough, Geol. Mag., 1907, dec. 5, vol. 4, p. 145.

[3] F. E. Wright, Amer. Journ. Sci., 1908, ser. 4, vol. 26, p. 547.

the optic axial plane is inclined 57° to the twin-lines and the cleavage, the vibration-direction β making an angle of 33° with the twinning, with symmetrical extinction of adjacent lamellae. Much less common is a simple twinning on a plane practically parallel to the optic axial plane. These features are in agreement with the figured orientation given by Wright (loc. cit., p. 548), but not with the text description, where it is stated that the orientation is $\gamma = a$, the cleavage being taken parallel to (001).

The orientation of elongated sections perpendicular to the acute bisectrix for polysynthetic twins of spurrite is shown in fig. 1. Sections perpendicular to (010) show high interference-tints and possess straight extinction with reference to the dominant cleavage. If the principal cleavage be taken as (100), the orientation is $a = b$, $\beta : c = 33°$.

At the original locality, Velardeña, Mexico, spurrite occurs in association with gehlenite, idocrase, and grossular (also merwinite).[1] It has also been recorded from Riverside, California, here again in association with gehlenite, grossular, merwinite, and monticellite.[2]

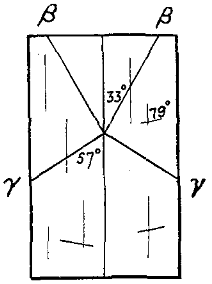

FIG. 1. Optical orientation of spurrite on the plane of symmetry (010).

(2) *Larnite* (Ca_2SiO_4).—Next in importance to spurrite comes a mineral consisting of calcium orthosilicate. As this is the first recorded natural occurrence[3] of this compound it is proposed to designate it as larnite, from Larne, in the vicinity of which these contact minerals occur.

The texture of the rocks composed essentially of larnite is much finer grained than that of the spurrite rocks. In hand-specimens the larnite-rich rocks are greyish and frequently so close-textured that individual grains cannot be made out by the unaided eye. Even in

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[1] C. E. Tilley, Geol. Mag., 1928, vol. 65, p. 372. [Min. Abstr., vol. 4, p. 84.]

[2] W. F. Foshag, Amer. Min., 1920, vol. 5, p. 80; E. S. Larsen and W. F. Foshag, ibid., 1921, vol. 6, p. 143.

[3] The Tasmanian mineral recorded as calcium orthosilicate by F. P. Paul (Tschermaks Min. Petr. Mitt., 1906, vol. 25, p. 309), and named shannonite (C. E. Tilley, Geol. Mag., 1927, vol. 64, p. 144) on the basis of Paul's data, has since been shown to be monticellite (C. E. Tilley, Geol. Mag., 1928, vol. 65, p. 29). Rather than transfer the name 'shannonite' to the mineral now described, any further confusion will be avoided by adopting a new name. [See Min. Mag., 1928, vol. 21, p. 576.]

its purest occurrence, some spurrite is usually found associated with it. Typically, however, the spurrite forms much larger crystals scattered sporadically through the rock; and these contain numerous enclosures of small drop-like grains of larnite (fig. 2).

Optically, the larnite is distinguished from the spurrite by its higher refringence and noticeably lower birefringence. Typically, the larnite forms grains showing one good cleavage and an imperfect cleavage 90° thereto. The most characteristic feature of this mineral is exceedingly fine polysynthetic twinning parallel to the prominent cleavage. Much less commonly a second set of twin-lamellae is developed at right angles to the first set. The twinning is usually not made out except under high-power objectives.

The optical properties are as follows: optically positive with a moderately large optic axial angle; α 1·707, β 1·715, γ 1·730, $\gamma-\alpha$ 0·023. Sections cut perpendicular to the acute bisectrix (γ) show a symmetrical extinction of the adjacent lamellae of the very fine polysynthetic twins, the orientation being α: twin-line $=13-14°$. In sections cut perpendicular to the obtuse bisectrix the mineral has straight extinction with reference to the cleavage, and no twin structure is visible. These properties are those of a monoclinic mineral where $\gamma=b$. If the prominent cleavage and twinning are taken as parallel to (100) the orientation is then $\alpha : c=13-14°$.

When the mineral gives indication of crystal habit the grains appear flattened parallel to (010) with prominent clinodome and pyramid faces, but crystal outline is not very well marked.

The larnite is attacked slowly by water with production of $Ca(OH)_2$, the solution turning red litmus blue. It is destroyed readily by the weakest acid (HCl) without effervescence, but with gelatinization. An analysis of material separated from the rock and still containing very small amounts of spurrite, is given below under I.

		Calculated for	
	I.	Ca_2SiO_4.	$Ca_3Si_2O_7$.
SiO_2 ...	31·00	34·9	41·7
Al_2O_3 ...	1·12	—	—
Fe_2O_3 ...	trace	—	—
FeO ...	0·64	—	—
MgO ...	0·69	—	—
CaO ...	64·98	65·1	58·3
CO_2 ...	0·82	—	—
$H_2O+105°$ ...	0·61	—	—
	99·86		

The carbon dioxide in the analysis is that contained in the small amount of admixed spurrite, while the Al_2O_3, FeO, and MgO are probably represented in finely divided spinel. The analysis without further treatment is sufficient to show that the material here described is calcium orthosilicate.

Various calcium orthosilicates have been prepared experimentally in the laboratory. According to F. E. Wright[1] there are three distinct forms:

	Crystal-system.	Cleavage.	α.	β.	γ.	$\gamma - \alpha$.	Optic sign.
α-Ca_2SiO_4...	Monoclinic or triclinic	‖ prism axis	1·715	1·720	1·737	0·023	+
$\downarrow$ 1420°							
β-Ca_2SiO_4...	Orthorhombic	‖ prism axis	1·717	—	1·735	0·018	+
$\downarrow$ 675°							
γ-Ca_2SiO_4...	Monoclinic	‖ prism axis	1·642	1·645	1·654	0·015	−

α-Ca_2SiO_4 is much twinned, 2V is large, and the optic axial plane is nearly parallel to the prism axis, $\alpha' : c = 18°$.

β-Ca_2SiO_4 has 2V large and optic axial plane parallel to the prism axis.

γ-Ca_2SiO_4 has 2V 60°, optic axial plane perpendicular to the *c*-axis, extinction practically parallel to the cleavages.

The optical characters of γ-Ca_2SiO_4 are sufficiently distinctive, and if our larnite is to be correlated with any of these forms it must be with either the β or α form. The resemblance is closer to the α form, though the refraction of the β form is close to that of larnite. Referring to β-Ca_2SiO_4, Wright[2] says it 'appears in irregular rounded grains, often prismatic in shape with cleavage parallel to the prism axis. The crystal system is apparently orthorhombic, though the presence of twinning lamellæ with low extinction angles up to $c : \alpha' = 10°$ in certain of the grains which may be of the α form would indicate a still lower symmetry'. If β-Ca_2SiO_4 is truly orthorhombic, then the properties of our larnite are such as to suggest that it is α-Ca_2SiO_4.

The artificial α- and β-calcium orthosilicates are unstable minerals tending to pass over into the γ form at ordinary temperatures, and the inversion of β-Ca_2SiO_4, accompanied as it is by a large increase in volume (10% approximately), is known to be the cause of the dusting of cement. It is of interest, therefore, to determine whether any such signs of instability are indicated in the mineral larnite. It was noticed early in the examination of these rocks that certain of them

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[1] A. L. Day, E. S. Shepherd, and F. E. Wright, Amer. Journ. Sci., 1906, ser. 4, vol. 22, p. 294.

[2] G. A. Rankin and F. E. Wright, Amer. Journ. Sci., 1915, ser. 4, vol. 39, p. 7.

were very difficult to prepare in thin section, the thin slice of rock breaking away suddenly into powder before the completion of the grinding. This was noted especially in rocks composed of the assemblage larnite-spurrite-spinel. That this powdering has nothing to do with the decomposition of the mineral in the presence of water is clearly indicated by the fact that dry specimens of the rock may be caused to powder or dust by the simple expedient of heating in a platinum dish to dull redness or even at lower temperatures. The powdering takes place when the rock fragment is allowed to cool, beginning at numerous points and gradually affecting the whole rock. Powdering may also be produced by shock. If a fragment be struck with a hammer and the surface then examined, it is seen that at the point of impact a thin skin of the rock after a short interval begins to swell and falls to powder. Shock then as well as heat may bring about dusting. The powder thus produced, when examined under the microscope, is seen to be constituted of the unchanged minerals spurrite and spinel, some unchanged larnite, and fibres of a mineral

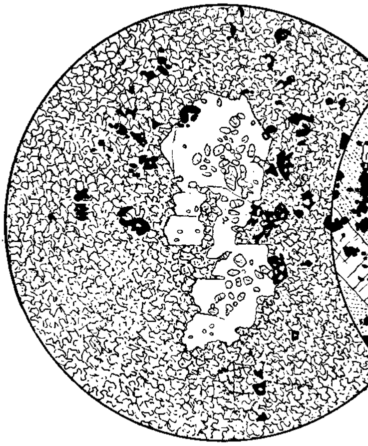

FIG. 2.

FIG. 3.

FIG. 2. Larnite-spurrite-rock, showing a large porphyroblast of clear spurrite enclosing grains of larnite in a ground of granular larnite. ×21. (Sedgwick Museum Collection, Slice no. 26253.)

FIG. 3. Melilite (gehlenite)-merwinite-spinel-calcite-rock, showing sections of large tabular crystals of gehlenite and merwinite in a ground of calcite. The dark crystals are spinel, while perovskite is also present. ×21. (Slice no. 26036.)

with distinctly lower refraction ($\alpha > 1{\cdot}640$, $\gamma < 1{\cdot}660$), the position of the optic axial plane being perpendicular to the fibres and the optic sign negative. These features correspond with those determined for γ-Ca_2SiO_4. (The values of the refractive indices for the artificial γ-Ca_2SiO_4 (p. 81) will require amendment if the determination of the optic sign as negative is correct, for then $\beta - \alpha$ should be greater than $\gamma - \beta$.)

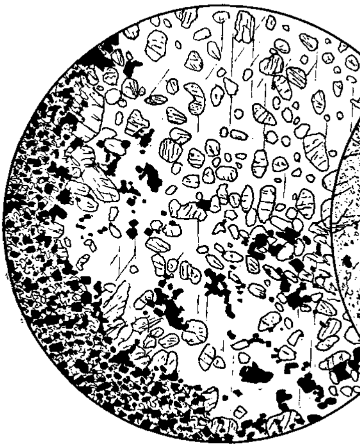

FIG. 4.

FIG. 5.

FIG. 4. Spurrite-larnite-rock, showing a large cleaved (and polysynthetically twinned) porphyroblast of spurrite enclosing grains of larnite and surrounded by a ground of larnite with dark spinel. ×21. (Slice no. 14888.)

FIG. 5. Spurrite-merwinite-rock, showing sections of large twinned and tabular crystals of merwinite in a ground of spurrite, both minerals enclosing numerous drop-like grains of larnite. ×21. (Slice no. 26262.)

It is noteworthy that the transformation is in some rocks remarkably sluggish. Even when powdering is produced by heat or shock, there may remain considerable amounts of unchanged larnite, the higher form being associated with the γ form, and residues of the former are sometimes found enclosed in a mantle of the latter. It is clear that a closer study of the transformation under controlled conditions is necessary, a study which may well go hand in hand with a closer examination of the artificial calcium orthosilicates.

(3) *Melilite-Gehlenite.*—A mineral of this group is sometimes an abundant constituent of these assemblages, especially those rich in spinel or merwinite. It occurs as idioblastic tabular (on 001) or

squarish crystals with a prominent basal cleavage and positive elongation (fig. 3). It is optically uniaxial and negative and never shows any anomalous birefringence. In these respects it resembles the much larger melilite crystals of the hybrid rock between the chalk and dolerite already described. Its refraction, however, is distinctly higher than that of the humboldtilite; ϵ is somewhat greater than 1·660, whereas ϵ of the humboldtilite is only 1·636. It is clear, therefore, that this melilite is richer in the gehlenite molecule, and the refraction is comparable with natural gehlenites, e. g. that of Velardeña, Mexico, which has ϵ 1·661. The natural gehlenites, however, still contain considerable percentages of the åkermanite molecule (Velardeña, 76% Ge, 18% Åk). We may therefore refer the melilite of the contact-zone of Scawt Hill to the gehlenite group.

(4) *Merwinite* ($3CaO.MgO.2SiO_2$).—This mineral, first described from the limestone contact-zone of Riverside, California,[1] in association with gehlenite, monticellite, and spurrite, is also a constituent of the Scawt Hill assemblages. Its association with spurrite is characteristic of the three occurrences from which it is now recorded. Its common associates at Scawt Hill are spurrite, melilite (gehlenite), and spinel. The optical properties agree closely with those determined for the mineral of the Riverside locality, and like larnite it stands out in relief from associated melilite or spurrite.

Its distinctive feature is its moderate double refraction and polysynthetic twinning. The mineral is optically positive, β 1·71, $\gamma-\alpha$ 0·012. The prominent cleavage is (010), γ standing perpendicular thereto. The polysynthetic twins are united along a prism plane (110) and twinning is on the c-axis. These lamellae form two sets at angles of 43° to one another, γ bisecting the obtuse angle between the lamellae. The orientation is $\gamma=b$, $\alpha:c=36°$. The crystals are tabular along (010), and they may reach in length up to 3 mm., though usually much smaller (fig. 5).

(5) *Spinel.*—Some of the contact-rocks are black in colour due to the abundance of finely-divided spinel. In these spinel-rich rocks, calcite, spurrite, melilite (gehlenite), or merwinite are the common associated minerals. In thin sections they are seen to be rich in well-developed octahedra of spinel of a deep-brown or greenish-brown colour and optically isotropic.

Material in a pure condition is easily separated from the rock by treatment with hydrochloric acid, whereby calcite and the silicates

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[1] E. S. Larsen and W. F. Foshag, Amer. Min., 1921, vol. 6, p. 143.

are completely removed. The spinel thus purified has been analysed by W. H. Herdsman with the following result (I):

	I.	II.	Molecular ratios.		Molecular composition.	%
Al_2O_3	... 57·30	57·30	5617	6349	$FeO.Fe_2O_3$	... 17·0
Fe_2O_3	... 25·50	11·71	732		$FeO.Al_2O_3$	... 17·26
FeO	... —	12·41	1724	6349	$MgO.Al_2O_3$	... 65·67
MgO	... 18·50	18·50	4625			
	101·30	99·92				

In I all the iron is estimated as Fe_2O_3. A separate estimation of FeO gave a value of 10·40%, but owing to the great difficulty experienced in bringing the mineral into solution this estimate is low, as a small residue was left. In column II the analysis is restated with the 25·50% Fe_2O_3 adjusted in accordance with an $RO:R_2O_3$ formula. As thus computed the spinel is seen to be a pleonaste with significant percentages of the magnetite molecule.

Discussion.—Spurrite, larnite, melilite (gehlenite), merwinite, and spinel are thus the chief minerals of the Scawt Hill contact-zone. This enumeration does not exhaust the list of minerals found with these assemblages. There are secondary minerals produced by the decay of some of these primary constituents, but they have not yet been studied in any detail and any account of them must be deferred. Monticellite, though carefully sought for, has not been identified among the assemblages.

Wollastonite is not a normal constituent of the contact-zone, but it occurs rather plentifully in parts of the hybrid zone. There is, however, one type of occurrence of wollastonite which is of interest. It is developed at the immediate contact of flint nodules in the chalk. In the contact-zone small flint nodules have been observed occurring in a larnite-rich rock. At the immediate contact with the nodule the larnite gives place to wollastonite, which forms a sheath between the larnite and the microcrystalline quartz of the nodule, a clear indication that calcium orthosilicate is unstable in the presence of free silica at the temperature of metamorphism.

Among these minerals, merwinite is not recorded from dry melts, but is there represented by mixtures of monticellite and calcium orthosilicate. An orthorhombic spurrite (α-spurrite) has been produced by Shepherd[1] and by Eitel[2]; the former by heating $CaCO_3$ and Ca_2SiO_4 with 10% NaCl solutions at temperatures of 350–400°,

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[1] F. E. Wright, Amer. Journ. Sci., 1908, ser. 4, vol. 26, p. 551.

[2] W. Eitel, Neues Jahrb. Min., 1923, vol. 48, p. 63.

the latter from a melt at 120 atmospheres CO_2 pressure. According to Eitel, α-spurrite melts incongruently with separation of β-Ca_2SiO_4 at 1380°, while natural spurrite heated under pressure inverts to the orthorhombic synthetic form at 1200°. The reverse transformation has not been effected, and α-spurrite would appear to be the stable form of this compound.

It is clear that this contact-zone has suffered considerable metasomatic effects. The purity of the chalk outside the thermal zone clearly denotes that solutions from the dolerite magma enriched the contact-zone in silica, magnesia, iron oxides, and alumina, so enabling the formation not only of the calcium silicates, but also of merwinite, melilite (gehlenite), and spinel.

Many of these assemblages in normal aureoles would be represented by rocks composed of diopside-wollastonite-grossular-calcite. The unusual character of the Scawt Hill assemblages is probably connected with the high temperature prevailing during metamorphism. In this process, the solutions emanating from the magma played a necessary part, modifying the composition and effecting a rapid rise in temperature in the limestone apart from conduction. It seems not improbable that such unusual assemblages are likely to be preserved for observation where the rise and fall of temperature has been comparatively rapid, reactions among the minerals formed at high temperature being inhibited by rapid cooling. If this be so such assemblages are not unexpected in contact-zones of small intrusions.

Acknowledgements.—The writer is greatly indebted to Dr. Harker for his kindness in executing the drawings of fig. 2–5, which accompany the text, and to Mr. R. Bell, of Belfast, who has kindly forwarded specimens and conducted the writer to this interesting locality.