

*Tricalcium disilicate (rankinite), a new mineral from  
Scawt Hill, Co. Antrim.*

(With Plate V.)

By C. E. TILLEY, B.Sc., Ph.D., F.R.S.

Department of Mineralogy and Petrology, University of Cambridge.

[Read November 6, 1941.]

**T**RICALCIUM disilicate, first described by Shepherd, Rankin, and Wright<sup>1</sup> in their investigations on the lime-silica and lime-alumina-silica systems has since been reported as a constituent of technical slags.<sup>2</sup> An account has also been given of its occurrence as a reaction product in a glass furnace.<sup>3</sup>

In the ternary system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  the compound forms with pseudowollastonite-gehlenite and larnite-gehlenite two three-phase equilibrium assemblages, associations which are in part recorded in the technical products.

G. V. Wilson recorded the disilicate together with wollastonite and melilite in reconstituted limestone fragments enclosed in glass, while S. G. Gordon has described and presented an analysis of a slag composed of pseudowollastonite and the 3:2-compound approaching in composition that of the binary eutectic in the synthetic system. As minerals, the immediate associates of the disilicate in the ternary system are represented by larnite, melilite, and wollastonite at the locality of Scawt Hill, but hitherto the compound itself has not been recorded.

Recent examination of further material among the larnite-rocks of Scawt Hill has now revealed its presence in several specimens of these assemblages and it thus takes its place as a new mineral.

The identification has been facilitated by a parallel study of the compound in a number of slags. In these the relatively good form development of the crystals has permitted additional data to be obtained, and account of the mineral at Scawt Hill will therefore be prefaced by a note on the slag occurrence.

<sup>1</sup> E. S. Shepherd and G. A. Rankin, *Journ. Indust. Eng. Chem.*, 1911, vol. 3, p. 211. G. A. Rankin and F. E. Wright, *Amer. Journ. Sci.*, 1915, ser. 4, vol. 39, p. 1. [M.A. 1-320.]

<sup>2</sup> S. G. Gordon, *Amer. Min.*, 1923, vol. 8, p. 110.

<sup>3</sup> G. V. Wilson, *Trans. Soc. Glass Techn.*, 1918, vol. 2, pp. 181, 196.

The slags come from the old Carnforth (Lancashire) ironworks and were originally collected by Professor W. G. Fearnside to whom I am indebted for information on their history.<sup>1</sup> They are well-crystallized types built up of pseudowollastonite, melilite, and  $3\text{CaO}\cdot 2\text{SiO}_2$ . A small amount of interstitial glass is present together with accessory calcium sulphide and some grains of metallic iron. The 3:2-compound crystallized early and forms colourless subhedral crystals partly enveloped by melilite.

Hitherto optical data on the compound have been incomplete. From synthetic melts it is described as crystallizing as rounded grains with no cleavage: probably orthorhombic,  $\alpha$  1.641,  $\gamma$  1.650,  $2V_\gamma$  large. Gordon in his description of crystals from a slag referred to them as monoclinic, optically positive,  $\alpha$  1.641,  $\beta$  1.643,  $\gamma$  1.650. He noted a perfect cleavage (100) and an extinction-angle  $\alpha:c = 15^\circ$  in the plane of symmetry. With the exception that the Carnforth slag crystals exhibit no cleavage these data are in agreement with my own observations. The habit is usually in the form of subhedral flattened or tabular grains from the broad four- to six-sided sections of which emerges  $\gamma$  the acute bisectrix. The optic axial plane lies in the plane of symmetry. Elongated cross-sections showing the normal emergence of the obtuse bisectrix ( $\alpha$ ) have straight extinction,  $\beta$  parallel to elongation, those perpendicular to  $\beta$  showing an extinction-angle  $\alpha$  to the elongation taken as the trace of (001) =  $15^\circ$ . Besides the basal plane, prism and clinodome are frequently developed. Elongation is consistently negative. The optical properties may be summarized as follows:

Monoclinic,  $b = \beta$ ,  $\alpha$  : edge of (001) =  $15^\circ$ ;  
 $\alpha$  1.641,  $\beta$  1.644,  $\gamma$  1.650,  $2V_\gamma$   $64^\circ$ , positive.

The development of abundant  $3\text{CaO}\cdot 2\text{SiO}_2$  in these slags is associated with a high lime content, indicated in the analysis that has been made of one of them. The results are set down in table I, no. 1. This slag contains approximately equal proportions of pseudowollastonite,  $3\text{CaO}\cdot 2\text{SiO}_2$ , and melilite. If we compare the analysis with that of the normal type of melilite slag, the chief points of difference are high lime and silica and low alumina (cf. table I, no. 4), features which account for the content of pseudowollastonite as well as that of the 3:2-compound.

The analysis may be compared with the composition of the ternary

<sup>1</sup> The former Carnforth ironworks manufactured pig iron from Furness haematite (chief gangue mineral, quartz), and Durham coke and local limestone were used in smelting.

eutectic, pseudowollastonite- $3\text{CaO}\cdot 2\text{SiO}_2$ -gehlenite in the lime-alumina-silica system (table I, no. 3).

The identification of the 3:2-compound in slags has not frequently been recorded. In a discussion on the composition of iron blast-furnace slags, McCaffery, Oesterle, and Schapiro<sup>1</sup> have attempted to calculate the mineral composition of slags from the analysis of the four chief component oxides, and they recognize a series of high-lime slags in which this compound is calculated to enter in large amounts. No optical examination of such slags is reported and it is doubtful whether any reliance can be placed on such calculations in view of the incompleteness of the analysis and the known variable composition of the melilite phase. Nevertheless, it seems probable that the 3:2-compound may be a not uncommon constituent of blast-furnace slags high in lime.

TABLE I.

	1.	2.	3.	4.
$\text{SiO}_2$ ... ..	39.47	39.22	41.0	36.25
$\text{TiO}_2$ ... ..	0.27	—	—	—
$\text{Al}_2\text{O}_3$ ... ..	7.96	5.86	11.8	13.04
$\text{Fe}_2\text{O}_3$ ... ..	nil	1.83	—	—
$\text{FeO}$ ... ..	1.18	—	—	0.91
$\text{MnO}$ ... ..	—	—	—	0.79
$\text{MgO}$ ... ..	1.46	trace	—	6.37
$\text{CaO}$ ... ..	46.39	44.56	47.2	40.60
$\text{Na}_2\text{O}$ ... ..	0.11	—	—	—
$\text{K}_2\text{O}$ ... ..	1.13	—	—	—
$\text{H}_2\text{O}$ — ... ..	0.28	0.55	—	—
S ... ..	0.86	—	—	1.53 (sulphide)
Insol. ... ..	—	2.24	—	—
Total ... ..	99.11			
Less O for S ... ..	0.43			
	98.68			

1. Slag, Carnforth, Lancashire; with  $\alpha\text{-CaSiO}_3$ ,  $3\text{CaO}\cdot 2\text{SiO}_2$ , and melilite. (Analysis, Geochemical Laboratories.)

2. Limestone xenolith in glass, Kinghorn bottle works, Fife; with wollastonite,  $3\text{CaO}\cdot 2\text{SiO}_2$ , and melilite. (G. V. Wilson, loc. cit., p. 196.)

3. Ternary eutectic;  $\alpha\text{-CaSiO}_3$ ,  $3\text{CaO}\cdot 2\text{SiO}_2$ , and gehlenite. (G. A. Rankin and F. E. Wright, loc. cit., p. 78.)

4. Mean composition of blast-furnace slags. (National Slag Association, Symposium, Cleveland, Ohio, 1928, no. 11.)

At Scawt Hill the disilicate is found in association with the minerals wollastonite, larnite, and melilite (*a*) in melilite-rocks, (*b*) at the contact of flint nodules in the metasomatized chalk.

The melilite-rocks have arisen as the result of intense but localized soaking of solutions from the dolerite into the chalk (Min. Mag., 1931,

<sup>1</sup> Amer. Inst. Min. Met. Eng. Technical Pub., 1927, no. 19.

vol. 22, p. 457) and occur as small patches in the larnite-spurrite-rocks. Normally they consist of coarse aggregates of melilite and wollastonite together with iron-ores and have often undergone late-stage alteration with the development of afwillite, ettringite, and other hydrated alteration products in vugs and venules.

It is in the primary association that the disilicate is met with in several specimens as colourless rounded or irregular grains devoid of cleavage. Its common associate is melilite, but it occurs in immediate proximity either with larnite or with wollastonite.

Though insufficient material is available for quantitative analysis, microchemical tests on sections isolated from slides provide confirmatory evidence of its composition. It gelatinizes readily in weak HCl-H<sub>2</sub>SO<sub>4</sub> solutions, precipitating abundant gypsum. It contains no magnesium nor aluminium and is unaffected by prolonged heating at 1100° C. Like the accompanying melilite, it has suffered the effects of late solutions and shows an interesting development of afwillite (3CaO. 2SiO<sub>2</sub>. 3H<sub>2</sub>O) in veins which ramify and isolate cores of the more highly refracting disilicate.

This ready production of afwillite at the expense of tricalcium disilicate in nature is of interest in view of laboratory studies on the hydrothermal alteration of this compound. Flint, McMurdie, and Wells<sup>1</sup> treated the anhydrous silicate with water under pressure at elevated temperatures but failed to produce afwillite. The X-ray pattern of the alteration products so obtained could not be identified, but at the highest temperatures (500° C., 380 atmospheres) they obtained a new phase, which they identify as a low-temperature form of the tricalcium disilicate which on ignition is converted back to the usual form.

The second development of tricalcium disilicate is associated with certain flint nodules found in the metasomatized chalk. An account of these interesting assemblages has been detailed in earlier papers (Min. Mag., 1931, vol. 22, p. 443; 1934, vol. 23, p. 513; 1937, vol. 24, p. 569). The flint nodules pass by metasomatism into quartz-wollastonite aggregates encased by larnite-spurrite assemblages and the borders of the nodules are frequently rimmed by wollastonite crystals. The border of the nodule against the larnite-rock has frequently been the seat of later solutions which have attacked preferentially the less stable larnite, so that the immediate contact with wollastonite is represented by a narrow zone of alteration products. This zone affected by altera-

<sup>1</sup> Journ. Research Nat. Bur. Standards (Washington), 1938, vol. 21, pp. 628-629 [M.A. 7-283.]

tion may amount to less than a tenth of a millimetre in width and had previously been taken as representing altered larnite. Since that time a large number of sections across the critical border has revealed a number with perfectly fresh contacts and the photograph of pl. V, fig. 3, presents the relations then obtaining. The wollastonite crystals studding the border of the flint nodule are separated from the larnite aggregate by a very narrow zone of colourless crystals of lower refraction, birefringence, and the properties of which agree with those of  $3\text{CaO}\cdot 2\text{SiO}_2$ .

In one example these crystals extend in a small pocket into the larnite-rock forming a nest composed of wollastonite and  $3\text{CaO}\cdot 2\text{SiO}_2$ . The optical data on these crystals are as follows: optically positive,  $2V$   $63^\circ$ ,  $\alpha$  1.640,  $\beta$  1.644,  $\gamma$  1.650, and these crystals exhibit the same feature of the slag compound in the absence of cleavage. Here, as in the border zone, wollastonite is always armoured from larnite by an intervening zone of the disilicate (pl. V, fig. 2).

The relations now described show a remarkable similarity to those developed in limestone fragments recrystallized in glass from the Kinghorn bottle works, Fife. In these G. V. Wilson noted the occurrence of  $3\text{CaO}\cdot 2\text{SiO}_2$  together with wollastonite and melilite. An analysis of such material is quoted in table I, no. 2, and shows a close accordance with the Carnforth slag, composed essentially of the same minerals (pseudowollastonite in place of wollastonite).

Sections through some of these limestone xenoliths, cut from material presented by Mr. Wilson, have revealed that larnite is also developed among the other constituents noted above. Within the xenolith the phases  $3\text{CaO}\cdot 2\text{SiO}_2$ , melilite, and wollastonite occur as immediate associates, but where larnite is developed it is shielded from wollastonite by a zone of the disilicate. This feature is well shown in the photograph of pl. V, fig. 4, where a narrow rim to the larnite aggregate is built up of crystals of  $3\text{CaO}\cdot 2\text{SiO}_2$ , which in turn make contact with wollastonite concentrated at the edge of the enclosing glass.

For the new mineral the name rankinite is now proposed in honour of Mr. G. A. Rankin who has contributed so much to our knowledge of the binary and ternary systems in which it was first discovered as a constituent phase. Rankinite has closely similar refractive indices to the magnesium end-member of the monticellite series from which it may be distinguished by its moderate optic axial angle and lack of cleavage: from the iron-bearing monticellites it differs by its lower refraction and positive sign. In slags, monticellite is commonly elongated



## EXPLANATION OF PLATE V.

(All figures  $\times 20$  diameters.)

- FIG. 1. Pseudowollastonite-melilite-rankinite slag, Carnforth, Lancashire.  
Rankinite (equidimensional and elongated sections), pseudowollastonite (turbid feathery laths), with melilite partly enclosing the former.
- FIG. 2. Rankinite-wollastonite-rock, Scawt Hill, Co. Antrim.  
Rankinite forms the clear rounded grains and is intergrown with wollastonite, the latter especially prominent at the bottom and right of the photograph.  
In the upper part, darker grains of larnite surrounded by rankinite.
- FIG. 3. Border of metasomatized flint nodule and larnite-rock, Scawt Hill, Co. Antrim.  
The border of the flint nodule divides the photograph. The inner border is studded with wollastonite crystals which are separated from the encasing larnite-rock by a zone of rankinite crystals.
- FIG. 4. Reconstituted limestone 'xenolith' in wollastonite-bearing glass, Kinghorn bottle works, Fife.  
Wollastonite crystals in glass (above) are separated from the larnite (dark) by a rim of rankinite crystals. Left, aggregates of rankinite intergrown with melilite.

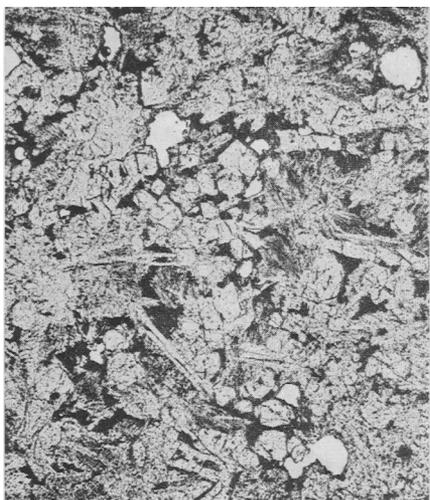


Fig. 1

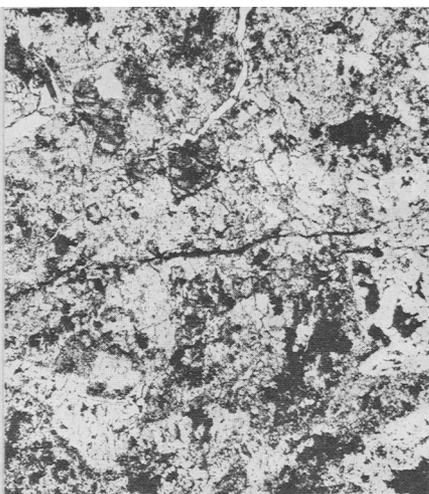


Fig. 2

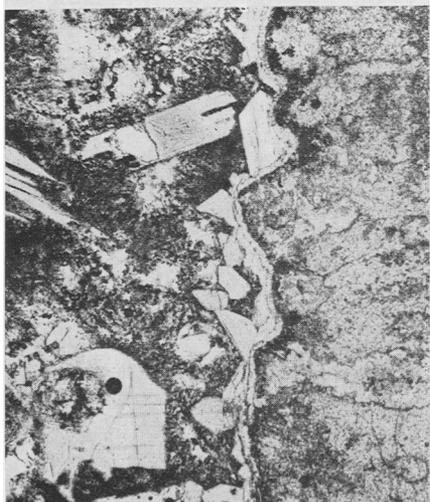


Fig. 3

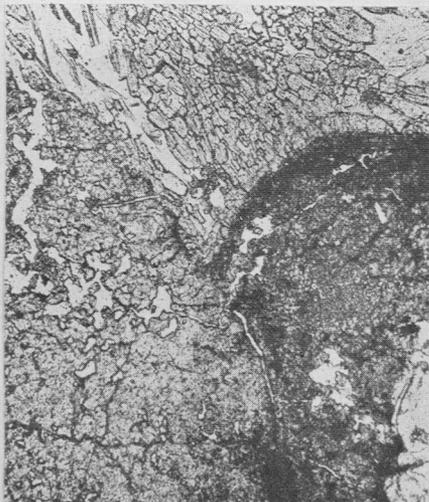


Fig. 4