*The occurrence of an orthorhombic high-temperature form
of Ca_2SiO_4 (bredigite) in the Scawt Hill contact-zone and
as a constituent of slags.*

(With Plates XV and XVI.)

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INTRODUCTION.

R ECENT research on the polymorphism of calcium orthosilicate has
broadened and to some extent modified the picture of the phase
relations of this substance as presented in the pioneer studies of Day and
Shepherd (1906) and Rankin and Wright (1915). These investigators
recognized three distinct forms, α, β, and γ, related by transformation as
follows: $\alpha \rightleftarrows \beta$ at 1420° C. and $\beta \rightleftarrows \gamma$ at 675° C. The high-temperature
α form was described as monoclinic or triclinic and intimately twinned,
the β form orthorhombic, and the low-temperature γ form as probably
monoclinic. The optical properties of these α and β forms as reported
are so closely similar that were it not for the twinning, regarded as
diagnostic, the two forms would be distinguishable only with difficulty.
This optical similarity was later found to be paralleled by a close agree-
ment of the X-ray powder diffraction patterns of the two phases early
noted by Hansen (1928) and confirmed among others by Insley (1936).
These similarities led both these workers to the conclusion that the α
form actually may never have been observed, the intimate twinning of
the supposed α form appearing as a consequence of rapid inversion of
a high-temperature form to the β form. The leucite analogy thus inferred
appeared a logical interpretation of the evidence when critically
examined.

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Such was the position reached in studies up to 1941. At that time Bredig (1941, 1942), who had been investigating the structures of calcium phosphates and had under study a group of compounds of the general formula A_2XO_4, reviewed the evidence for the existence of the 'ternary compounds' in the system $CaO-SiO_2-P_2O_5$ and indicated the probability that the substance $7CaO.P_2O_5.2SiO_2$ possessed the simple crystal lattice of a group of simple compounds of the type A_2XO_4, e.g. K_2SO_4, $CaKPO_4$, the high-temperature α (hexagonal) modifications of which form extensive solid solutions with other compounds. He was led to infer, partly on evidence of X-ray powder photographs, that the 'compound' referred to was in fact a solid solution of an α-Ca_2SiO_4 (hexagonal) phase analogous to α hexagonal K_2SO_4 or glaserite $(K,Na)_2SO_4$. Similarly, Bredig (1942, 1943) claimed another 'compound' in this system $27CaO.P_2O_5.12SiO_2$, described by Schleede (1940) with a β-K_2SO_4 structure, to be in fact an orthorhombic Ca_2SiO_4 (desig-nated as α'-Ca_2SiO_4) solid solution to which also the 'K' phase of Trömel (1943) in the same silicophosphate system and the 'compound' $K_2O.23CaO.12SiO_2$ prepared by Taylor (1941) in Portland cement studies belonged. Bredig concluded that pure Ca_2SiO_4 would be expected to possess in its various forms an α hexagonal and a β (but now designated, as noted above, α') orthorhombic structure, in addition to the usual β and γ (olivine type[1]) structures of the forms described by Day and Shepherd, and that the α' form would be expected to be stable in the temperature region between an α (high, hexagonal) field of stability and the tempera-ture of 1420° C. when the β-Ca_2SiO_4 stability region is entered.

In 1944 Greene published his study of dicalcium silicate solid solu-tions, obtaining an optically positive uniaxial form of the orthosilicate (containing Na_2O and Al_2O_3 in solid solution) and showing in its X-ray powder pattern the structure of the α hexagonal A_2XO_4 group.

Still more recently Van Valkenburg and McMurdie (1947) have pre-pared and examined pure Ca_2SiO_4 in a high-temperature X-ray powder diffraction furnace at 1500° C. obtaining a characteristic hexagonal pattern. Bredig's prediction in this connexion has thus been amply justified.

It was in the light of these conclusions that a restudy was begun of a number of larnite assemblages of the Scawt Hill contact-zone. It had already become clear from the earlier work reported that the mineral

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[1] The γ phase formerly referred to as monoclinic was shown by O'Daniel and Tscheischwili (Zeits. Krist., 1942, vol. 104, pp. 124–141) to be orthorhombic with the olivine structure. [M.A. 8–290.]

larnite with its characteristic twinning was to be referred to β-Ca_2SiO_4, which phase in view of the optical data available should be regarded as monoclinic in character. In some of the Scawt Hill assemblages rare isolated grains of a pseudo-hexagonal mineral with a low optic axial angle had long been observed but its composition had remained un-determined, though its paragenesis suggested that it was a calcium silicate. At the time of this later study a group of spiegeleisen slags containing an obvious Ca_2SiO_4 phase was under examination. This orthosilicate phase of the slag was characterized by an optic axial angle much smaller than that usually found in larnite and, though twinned, it had not the normal twin pattern of that mineral. There was reason to believe that the rare Scawt Hill mineral and the mineral of the slag were probably identical and accordingly a more detailed examination of the suite of Scawt Hill rocks was made to ascertain if more of the material could be made available for identification. Fortunately this has proved successful and a parallel examination of the natural and the slag mineral has been made. Both have proved to be orthorhombic, pseudo-hexagonal in character, the abundance of the slag phase allowing its isolation for chemical analysis. The results now set down indicate that the two minerals are in fact the predicted orthorhombic silicate structure designated as α'-Ca_2SiO_4 by Bredig, but that in the case of the slag phase a considerable amount of material in solid solution is present. It is in recognition of Bredig's important contribution to the solution of the problem of calcium orthosilicate polymorphism that it is proposed to designate the new mineral phase *bredigite*.[1]

THE SCAWT HILL MINERAL.

The new phase occurs together with spurrite, larnite, and gehlenite. Though never abundant, it is rather widely distributed in a group of rocks composed of these minerals in the form of squat orthorhombic grains showing in cross-section hexagonal outline and in vertical section barrel- or boat-shaped forms. The appearance of these crystals is indicated in pl. XV, figs. 1, 2, and 4. In the cross-sections twin structure is commonly apparent, the twinning being simple, multiple, or even cyclic. Such cross-sections show the normal emergence of an acute bisectrix and exhibit traces of cleavages, obviously prismatic, forming angles of approximately 60°. The vertical sections show parallel extinction with reference to the cleavage trace, this being slow parallel

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[1] The mineral has, more recently, been observed in the limestone contact-zone of the Camas Mòr gabbro of the island of Muck, Inverness-shire.

to the acute bisectrix (γ). A good example of a cross-section showing simple twinning is seen in pl. XV, figs. 2 and 4.

The relation of the optical features to the twinning and cleavages is reproduced in the simple and cyclic twins of text-fig. 1. The optic axial plane forms an angle of approximately 60° with the trace of the composition (twin) plane and bisects the acute angle between the two cleavages of each part of the twin. The extinction in these basal sections is β:twin-plane = 30°. These optical properties are those characteristic
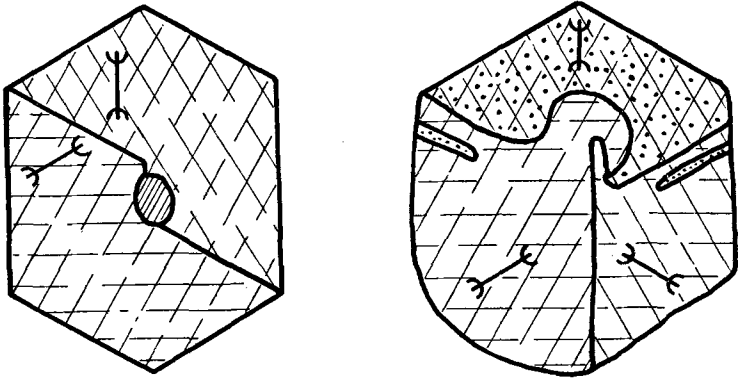

FIG. 1. Basal sections of bredigite in spurrite-larnite-rocks, showing simple and cyclic twinning. If by analogy with β-K_2SO_4 the optic axial plane is taken as (100), the prismatic cleavages at approximately 60° become (110), and the twin-plane (130). In the left-hand crystal the central inclusion is larnite cut perpendicular to the acute bisectrix (γ) with the twin striae indicated.

of an orthorhombic pseudo-hexagonal structure, reproducing in essence the features encountered in the sulphates of the alkali metals. If by analogy with β-K_2SO_4 we arbitrarily define the optic axial plane as (100), the prismatic cleavages become (110) and the twin-plane (130) (text-figs. 1 and 2).

The optical properties of the mineral may be summarized as follows: $\gamma = c$, $\alpha = b$, $\beta = a$; 2V 30°, but variable, lower values being also recorded; α 1·712, β 1·716, γ 1·725.

Grains isolated from their matrix dissolve readily in the weakest acids leaving a silica pseudomorph, give no effervescence, and yield abundant evidence of calcium. They behave in these respects like larnite itself.

In many of the sections the grains stand out from enclosing larnite or spurrite because they exhibit in patches a fibrous structure reducing their translucency under low power. Their refraction is not greatly different from larnite, and where this fibrous character is absent they

differ in section by the presence of better developed cleavage lines. The basal sections are of course distinctive. Examination of this fibrous development shows that the optical properties of the fibrous element are noticeably different from those of the normal non-fibrous part of the mineral. The fibres have in fact the optical characters of the low γ form of Ca_2SiO_4, lower refraction, negative sign, and the optic axial plane across the length of the fibre (elongation $\pm$). It is clear that such composite grains are the new phase associated with its inversion product. Occasionally the transformation may be seen complete. Normally the fibres of the γ form run parallel to the cleavage of the parent phase as seen in the vertical sections. In basal section the fibres appear as sheets or bunches for the most part oriented in the 60° prismatic cleavage directions and extinguishing with the main mineral. At first sight these sheets have the appearance of foreign material developed by exsolution, but closer examination reveals that they have the properties of γ-Ca_2SiO_4, being viewed along the direction β and so exhibiting the maximum birefringence. None of this sheet development appears in the basal sections of grains which show in vertical section no sign of the fibrous development already noted. There is clearly evidence that the inversion product is regularly oriented, for the most part, in relation to the unchanged phase. In itself this inversion provides the confirmatory evidence that the new phase now described has essentially the composition Ca_2SiO_4.

A variety of bredigite exhibiting distinctive features is met with in two or three specimens of the melilite-rocks which have originated by soaking of the chalk by the igneous magma already made alkaline by assimilation (Tilley, 1931). These rocks, as described, carry large plates of honey-coloured melilite, and in the few examples now referred to, the chief additional primary minerals in close association with the bredigite are coarse-grained braided larnite, perovskite, and magnetite. The distinctive feature of the bredigite is its colour and pleochroism. In thicker sections a common pleochroism scheme is as follows: α pale violet, β and γ colourless to palest green. Absorption $\alpha > \gamma > \beta$. The refractive indices measured on a coloured grain gave the values:

$$\alpha\ 1\!\cdot\!725,\ \beta\ 1\!\cdot\!728,\ \gamma\ 1\!\cdot\!740,\ \text{and}\ 2V_\gamma = 33°.$$

Twinning, both multiple and cyclic, on the same law as described is characteristic (pl. XVI, fig. 2). Occasionally twinning on (110) may be associated with the prevalent (130) type. Cleavage is poorly developed, but when present is of the prismatic type (60°). Between crossed nicols

the mineral may show anomalous interference tints, these being par-
ticularly evident in sections cut nearly normal to the acute bisectrix.
Such sections may exhibit a greenish to purplish tint in place of the
normal grey of the first order. Dispersion of the optic axis, $r < v$, is
noticeable. The optic axial angle shows considerable variation, values
as low as 10° being recorded though these are very exceptional. The
mineral behaves like normal bredigite in dissolving readily in weak acid
without effervescence and in leaving a silica residue. Besides a micro-
chemical reaction for calcium (very abundant), it yields a strong ferro-
cyanide test for iron. The distinctive optical properties noted above are
doubtless to be ascribed to solid solution, and the unusual paragenesis
suggests that, in addition to iron, titanium probably enters in small
amount in its composition.

<div align="center">BRAIDED LARNITE OF THE MELILITE-ROCKS.</div>

The braided larnite of the melilite-rocks differs from normal larnite
by its coarse structure—a complex set of lamellae in place of, or in
addition to, the very fine parallel system of twin lamellae seen in sections
of the latter cut perpendicular to the acute bisectrix (pl. XVI, figs.
1 and 4). The broader lamellae of the former (0·004–0·01 mm. in
breadth) are best seen in sections cut normal to the axis β. At least three
sets can be distinguished, a double set intersecting at angles close to 60°
and a third set bisecting the acute angle between the former. In the
cutting position noted the three sets extinguish at very small angles to
one another and they stand inclined at high angles to the section; the
acute bisectrix (γ) of the group lies in, and almost bisects, the obtuse
angle between the double set of lamellae. In ordinary light the lamellae
are outlined by thin transparent films and minute opaque granules
which define their boundaries and emphasize the structure. Like
bredigite the complex may show a pale violet colour and pleochroism,
but these features are not constant and both may be confined to par-
ticular sets of lamellae within the complex. The structural features noted
above present much similarity to those described by Sundius (1933) for
one variety of calcium orthosilicate of cement clinker, and they recall the
illustrations of clinker orthosilicate quenched from 1450° C. which are
provided by Insley (1936, fig. 9, type I Ca_2SiO_4; also 1938, p. 360, fig. 1,
type Ia) in his study of the constituent phases of Portland cement.

Sections of braided larnite cut effectively normal to the acute bisectrix
show characteristically a low interference tint, and, in accordance with
the orientation noted in section normal to β, yield in part a set of sub-

parallel lamellae with positive elongation and the optic axial plane across the length of the lamellae. Individual lamellae may be traced out by rims of opaque granules as seen in the sections normal to β. There are, however, other sections showing a similar low interference tint which exhibit a seemingly confused extinction seen, however, under high power to result from the presence of irregular bands and patches with differing extinction but having in common the γ direction emerging normally from their sections. These show the exceedingly fine twin lamellae (often a double set at right angles) distinctive of larnite. Three group orientations of these units of the aggregate can be distinguished and recognized by the traces of the optic axial planes and the courses of the twin striae. The three groupings make angles of approximately 60° with each other, the relationship being illustrated in text-fig. 2.

The lamellar structure of braided larnite is clearly one of considerable complexity and not yet completely resolved. It has all the characteristics of an inversion product occurring in the form of grains within melilite or intimately associated with bredigite. The two minerals may show in part a common extinction. The braided areas appear in places to eat into the boundaries of the bredigite or the latter may appear like isolated residuals in a base of this structure. Such residuals may be distinguished under high power in sections like text-fig. 2,

0·2mm.

FIG. 2. Inversion intergrowth of braided larnite in a melilite-rock, showing the grouping of the parts into three sets, each with the acute bisectrix normal to the section, but with the mean optic axial plane directions of the sets inclined at 60° to one another. Only one of the triple sets is shown in full development.

then appearing as rounded or wedge areas of very low birefringence between the larnite sets noted, and cut normal to the acute bisectrix. On the other hand, though the feature is not common, very thin lamellae of larnite with the characteristic fine twin striae may be seen developing and coursing through grains of twinned bredigite. A striking example is depicted in text-fig. 3, where the orientation of the lamellae and their twin striae (nearly parallel to α) are shown in relation to the twinned parts of a basal section of bredigite. The mutual relations give indeed strong grounds for the interpretation of much at least of this complex as an inversion product of bredigite itself, the films and opaque granules delineating the lamellae of the complex representing material exsolved

on inversion (pl. XVI, figs. 1, 3, 4). Another possibility must be kept in mind. An apparently similar structure is known to result from inversion of an α hexagonal modification of Ca_2SiO_4, as shown in the experiments of Greene (1944) on the inversion of an artificial α-Ca_2SiO_4 solid solution (1944, p. 5, and figs. 4A, 4B) and it remains uncertain whether some of the braided larnite of these rocks has not inverted from an α hexagonal phase now completely transformed.
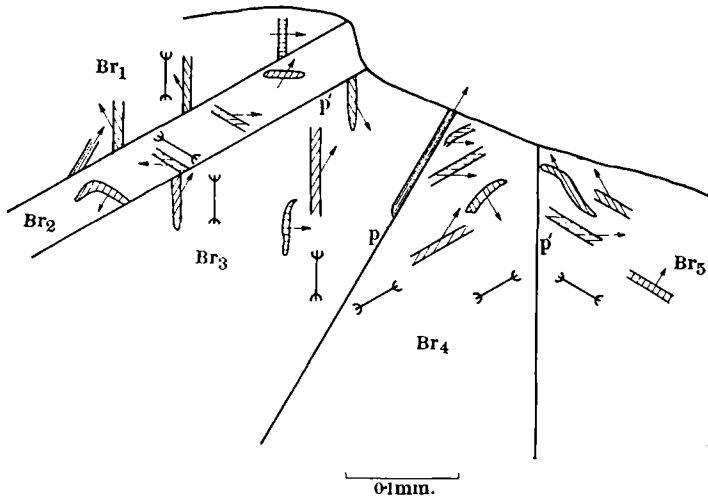

FIG. 3. Inversion lamellae of larnite in a twinned crystal of bredigite. The basal section of bredigite shows repeated and cyclic twinning on p' (130) and is also twinned on p (110) (Br₁–Br₅).

The larnite lamellae likewise have the acute bisectrices perpendicular to the section and are resolved in the bredigite twin into three groups at 60° as indicated by the fine striae and arrow lines—twin edge directions in the several lamellae.

At the right edge of sector Br₅ (but not shown in the sketch) a γ-Ca_2SiO_4 inversion of bredigite is seen superimposed on the larnite type of inversion. The bunched γ-Ca_2SiO_4 fibres stand perpendicular to the section, their orientation relative to bredigite being such that the γβ plane of γ-Ca_2SiO_4 is very nearly parallel to the optic axial plane of bredigite in this sector, and therefore nearly parallel to a βγ plane of one of the lamellar sets of larnite.

Bredigite, whether in the normal contact-rock or in the melilite types, gives no indication that it itself has inverted from an α hexagonal phase. The broad and often simple twin structure is that characteristic of a primary orthorhombic form: it does not resemble, for instance, the complex fine twinning seen in β-K_2SO_4 inverted from the α hexagonal K_2SO_4 phase crystallized from the melt.

Braided larnite is not seen in the normal contact-rocks, and there the

only inversion of bredigite recognized is to the γ phase. The origin of the fine multiple twinning of normal larnite is not clearly established. Though suggestive of inversion twinning it should be remarked that this structure can be reproduced in the laboratory with material that has never been subjected to a temperature of 1420° C. The type II Ca_2SiO_4 (of Insley) produced by quenching from 1375° C. appears to correspond to normal larnite (Insley, 1936, fig. 10), and the structure may occur in orthosilicate synthesized at even lower temperatures.

In the original description of larnite it was shown that different specimens of this phase showed great differences in tendency to invert. Some examples were so susceptible to inversion that transformation could be accomplished by the blow of a hammer; others, on the contrary, could be subjected to severe thermal or mechanical treatment without sign of inversion. Laboratory investigations on the capacity of β-Ca_2SiO_4 to invert have shown that the presence of material in solid solution in the phase may have a marked effect on its inversion tendency, some material increasing that tendency, other material stabilizing the phase. It is remarkable that the larnite associated with the bredigite in the normal larnite-rock may show less tendency to inversion than bredigite itself. This is clear from the descriptions already given and from the illustrations of pl. XV. Not infrequently twinned grains of uninverted larnite may be enclosed in the larger grains of the new phase already exhibiting partial inversion to the γ phase.

The γ inversion product of larnite itself may show, as in the case of the bredigite inversion, a regular orientation with the uninverted parent. In such case the fibre direction of the γ phase stands approximately parallel to the acute bisectrix of the larnite.

The orientation relations of the phases produced by inversion in these Scawt Hill rocks may now be summarized:

α'-Ca_2SiO_4 (bredigite)->β-Ca_2SiO_4 (larnite). $\gamma \parallel \gamma$.

α'-Ca_2SiO_4 (bredigite)->γ-Ca_2SiO_4. $\gamma \parallel \beta$, $\alpha \parallel \gamma$ nearly.

β-Ca_2SiO_4 (larnite) ->γ-Ca_2SiO_4. $\gamma \parallel \beta$, $\alpha \parallel \alpha$ nearly.

It is hoped that further study of the intimate growth relations of the three phases (α', β, and γ) will, in the light of X-ray data yet to be obtained on single crystals of the bredigite phase, add materially to the evidence now available.

THE SLAG MINERAL.

The spiegeleisen slags containing the calcium orthosilicate phase came from Middlesbrough and have been for many years in the slag collection

at Cambridge. As a group these slags range from comparatively coarsely crystallized varieties to others largely glassy. The glassy examples are greenish in colour and a greenish hue is imparted even to the crystalline types. This colour is due to the disperse distribution of a calcium sulphide phase coloured green through the presence of manganese.

Apart from glass in variable amount the constituent phases are melilite, the Ca_2SiO_4 phase, a monticellite solid solution, and the ubiquitous calcium sulphide. While melilite is constantly present in bulk, the proportions of the Ca_2SiO_4 phase and monticellite vary greatly. In some, monticellite is almost wholly absent, in others it is the dominant phase, and the Ca_2SiO_4 phase may be present in very subordinate amount.

In those slags rich in the new phase, the mineral appears as elongated hexagonal prismatic crystals, showing prominent development in the interspaces between the melilite tables. It has, however, begun to crystallize early appearing as a fine dendritic growth in the cores of the melilite crystals, or as skeletal crystals in parallel position in the same environment. The periphery of the melilites may be wholly free from inclusions, but idiomorphic prisms of the new phase may occur in this position as well as in the melilite interspaces. When monticellite is present it occupies a similar position as sheaves of crystals, though shreds of it may appear in the core and at the periphery of the Ca_2SiO_4 phase.

The sulphide phase, usually green in colour, forms arborescent growths in the chief phases and as independent grains in the interstitial ground.

A typical spiegeleisen slag, rich in the new orthosilicate phase is figured on pl. XV, fig. 3.

Monticellite has the usual habit of this mineral in slags, elongated parallel to the a-axis and showing edges of the forms k (021) and b (010) in cross-section. It has the high birefringence of a monticellite solid solution containing either iron or manganese or both and the cross-sections show the emergence of γ the obtuse bisectrix.

For the isolation of the new orthosilicate phase a slag containing only traces of monticellite was chosen in order to facilitate a clean separation devoid of another orthosilicate phase. The slag selected was rich in the new phase and showed a sulphide phase, light brown in colour and believed to contain but little manganese. In addition to melilite, the remaining phase was a brown glass present only in small amount. This slag itself was subjected to analysis and the results are set down in table I,

column 1. It shows a comparatively low content of MnO, negligible iron oxide, and a significant content of BaO. The origin of the barium in this slag must be traced to the manganese ore used in smelting, possibly minerals of the psilomelane group in which barium is often an essential constituent.[1] The presence of barium has necessitated consideration of its partition between the sulphide and silicate phases as noted below.

The preponderant mineral of the slag is the orthosilicate phase, melilite being subordinate. The mineral was isolated from melilite by repeated fractionation in the centrifuge, but owing to the fine state of dispersion of the sulphide, this could not be completely eliminated from the final product, which contained in addition a little brown glass. The analysis of the mineral thus far purified is given in table I, column 4.

The final product of separation obtained from centrifuging had a specific gravity of 3·40±0·02. Some of the grains contained minute drops of sulphide and there was in addition a little glass. Microchemical tests showed that the orthosilicate and the small amount of sulphide dissolved in the weakest acids, though the glass remained unattacked in this treatment. The analysis was therefore made of a dilute acetic acid extract representing the orthosilicate and included sulphide. Separate determinations were made of sulphur and the ratio of CaS:BaS in the sulphide enabling the barium content of the orthosilicate to be determined after deducting Ca and Ba in the sulphide of the analysis. A few minutes' extraction in cold 5 % acetic acid followed by treatment with dilute Na_2CO_3 to dissolve the separated silica served to isolate the pure orthosilicate and sulphide from the glass impurity. The last was weighed and represented 4·55 % of the total mineral analysed. In the acetic acid extract all the constituents except water and sulphur were determined.

To derive the figure of barium in the orthosilicate it was necessary to determine its distribution relative to calcium in the sulphide phase. It had been noted early in the centrifuge separation that the sulphide

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[1] This analysis is probably exceptional among the group available for study (from the former firm of Messrs. Bolckow and Vaughan, Ltd., Middlesbrough) in its low content of MnO and high figure for BaO. A comparison of available analyses of ferromanganese and spiegeleisen slags shows that they vary considerably in bulk composition. Manganese, however, is consistently higher and BaO much less, though figures of 2 % and over for the latter constituent are on record. The variation in chemical and mineral composition of these types of slags is clearly dependent not only on the character of the primary manganese ore but also on the flux, whether limestone or dolomitic limestone.

TABLE I. Chemical analyses of slag and isolated bredigite.

	1.	2.	3.	4.	5.	6.	
SiO_2	27·04	30·34	32·39	29·96	33·08	5513	1
Al_2O_3	8·56	9·60	—	nil	nil	—	
TiO_2	0·23	0·26	0·36	0·31	0·34	—	
Fe_2O_3	0·29	0·32	0·44	0·11	0·12	—	
MnO	3·02	3·39	4·67	3·06	3·38	476	0·086 ⎫
CaO	45·71	44·65	46·94	47·53	49·23	8791	1·594 ⎪
BaO	6·09	5·22	7·19	7·12	6·91	450	0·081 ⎬ 2·068
MgO	5·19	5·82	8·01	6·14	6·78	1695	0·307 ⎭
Na_2O	0·36	0·40	—	—	—		
K_2O	nil	—	—	—	—		
H_2O+	0·70	—	—	0·29	—		
CO_2	0·22	—	—	—	—		
F	0·31	—	—	0·14	0·16		
SO_3	0·32	—	—	. .	—		
S	3·13	—	—	1·86	—		
Insol.	nil	—	—	4·55	—		
	101·17	100·00	100·00	101·07	100·00		
Less O ᵜ S,F	1·69			0·99			
	99·48			100·08			

1. Spiegeleisen slag, Middlesbrough. P_2O_5 trace, Cr_2O_3 nil.
2. Spiegeleisen slag, recalculated after removal of water, SO_3 and CO_2 as $CaSO_4$ and $CaCO_3$, F as CaF_2, and S allotted to Ca and Ba as CaS 6·37, BaS 1·59.
3. Spiegeleisen slag with gehlenitic fraction of melilite removed as $Ca_2Al_2SiO_7$ and Na in $CaNaAlSi_2O_7$.
4. Bredigite, isolated from slag.
5. Bredigite, recalculated after allotting sulphur to Ca and Ba as CaS 3·78, BaS 0·95, and removal of insoluble.
6. Molecular ratios of bredigite ($Ca_{1·59}$, $Ba_{0·08}$, $Mg_{0·31}$, $Mn_{0·09}$) $[SiO_4]$.

phase had a noticeably greater specific gravity than that recorded for pure CaS (2·6), and it became clear when barium was recorded in the analysis that the higher values obtaining for the specific gravity of the sulphide were to be traced to BaS in solid solution. Microchemical tests established barium in both silicate and sulphide phases. Single grains of the silicate when treated with dilute acetic acid and potassium chromate yielded the characteristic crystals of $BaCrO_4$ which covered the dissolving mineral and became entangled in the silica pseudomorph left by dissolution. Isolated grains of sulphide showed a similar $BaCrO_4$ precipitate but less abundantly. As the use of acids to separate sulphide was excluded, the method adopted was extraction of the sulphide by water in the absence of air and carbon dioxide. Both calcium and barium sulphides react with water to form soluble hydrosulphides, the latter very readily. The finely ground impure orthosilicate was leached

with water over a period of three days, this extraction removing up to 3 % by weight of the material. Microscopic examination of the residue indicated that free sulphide had gone into solution. The virtual absence of silica in the aqueous extract and the character of the silicate grains indicated that no appreciable attack of the silicate phase had taken place under this treatment. From several estimates the average figure of CaS:BaS = 4:1, determined from the content of Ca and Ba in the extract, was obtained. No great accuracy can be claimed for this estimate, but it is to be noted that the correction to any error in the determination, owing to the greater solubility of BaS in water, would result in more Ba being allotted to the silicate phase than has been done using the determined ratios. It is believed, however, that the allocation of BaO to the silicate phase is not in error by more than one-half of one per cent. The molecular ratio $(CaO + BaO):SiO_2$ is of course unaffected by any inaccuracy in the determination of the partition of Ba and Ca between the two phases. With distribution of barium, determined in the sulphide as indicated, the composition of the silicate phase was recalculated to the figures given in column 5 of table I.

It is to be noted that a small content of F $(0 \cdot 14 \%)$ is recorded in the analysis. This small amount of fluorine may of course be replacing oxygen in the mineral, but as its amount is relatively insignificant it has not been considered in the calculation of molecular proportions given in column 6 of table I.

The resultant figures, considering the analytical complexity, reveal reasonably good accord with an orthosilicate ratio. The mineral is thus clearly a calcium orthosilicate with Ca partly replaced by Mg, Mn, and Ba.

The analysis presented in column 5 (table I) may be compared with that of the recalculated slag (column 3). The figures in this column have been derived from the slag analysis by removal of CaS and BaS (in the ratio 4:1) and after removal of all alumina as gehlenite $(Ca_2Al_2SiO_7)$ and the hypothetical melilite $(CaNaAlSi_2O_7)$—thus removing also the soda. The close approximation of the two sets of figures (columns 3 and 5) shows that the melilite phase is essentially a gehlenite though probably containing a small percentage of MgO to which also the glass and the rare monticellite would contribute to the total of the slag. Further, that the great bulk of the BaO in the silicate fraction of the slag is contained in the calcium orthosilicate phase. Calculated in terms of phases the slag has approximately 60 % orthosilicate phase, 25 % melilite, 8 % sulphide, and minor glass and monticellite traces.

In text-fig. 4 the composition of the orthosilicate solid solution is plotted in the triangle $(Ca,Ba)O-(Mg,Mn)O-SiO_2$ to show its position in relation to other phases recognized in slags or dry melts. The extended solid solution it exhibits brings it closest in composition to merwinite, a phase which is not recorded in any of these spiegeleisen slags and which is readily differentiated from the new phase by its distinctive optical properties.

FIG. 4. Composition of the bredigite phase in the slag in relation to the composition of other phases in the system $CaO-MgO-SiO_2$ (here $(Ca,Ba)O-(Mg,Mn)O-SiO_2$).
Br bredigite solid solution, La Ca_2SiO_4, Mw merwinite, Ak åkermanite, Ra rankinite, Wo (pseudo)wollastonite.

Properties of bredigite from the slag:

The occurrence of the mineral as elongated hexagonal prisms in the slag has already been described. This characteristic habit is also indicated in pl. XV, fig. 3, where several cross-sections of these prisms, hexagonal in shape, are visible. The habit is thus somewhat contrasted to that of the mineral in the Scawt Hill rocks.

Cleavage is by no means characteristic, but is recorded in one slag. Here the typical 60° prismatic cleavages are met with as in the Scawt Hill mineral.

The basal hexagonal sections show the emergence of the acute bisectrix (γ).

Twinning is very characteristic both of multiple and sector type. An example of repeated twinning seen in a basal section is shown in the accompanying text-fig. 5 and the optical orientation of the twinned parts conforms to the data on the natural mineral.

The refractive indices determined on the material analysed are α 1·713; β 1·717; γ 1·732.

The optic axial angle shows some variation in the sections examined in the various slags. A common value is $2V_\gamma = 30° \pm 2°$, but lower values of $20°$ are recorded.

X-ray powder photographs of the slag mineral show a pattern distinctive from those of larnite and merwinite. The photographs are closely similar to those obtained from a synthetic Ca_2SiO_4 prepared by Rait and Goldschmidt (1945) by quenching in water from $1790°$ C., a specimen of which was kindly presented to us by Mr. H. J. Goldschmidt. Optically the synthetic material resembles the slag

FIG. 5. Basal section of bredigite from the slag showing the repeated twinning and the optical orientation in the twinned parts.

phase in being biaxial, optically positive with a similar small optic axial angle, but with slightly lower refractive indices. Further X-ray data will be available when single crystals isolated from one of the spiegeleisen slags have been subject to detailed analysis.

The reluctance of the slag bredigite to invert has already been noted, but there are clear indications in one of the slags that inversion phenomena do occur. These reproduce the features met with in the natural mineral in that fibres of a γ form appear in some of the bredigite grains and yield a characteristic pattern in the basal sections. In general, however, the slag mineral is unaltered and the slags show no macroscopic signs of dusting or falling. It will be clear from a survey of the collective studies made to date on the four modifications of Ca_2SiO_4 (α, α', β, γ) the complications that invest a study of their equilibrium relations. While the capacity they show for solid solution is in great measure responsible for this complexity, there, nevertheless, remain for pure Ca_2SiO_4 problems of phase relationship, particularly of higher forms, which only further experimental work can hope to solve.
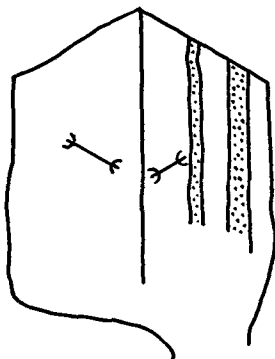
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EXPLANATION OF PLATES XV AND XVI.

PLATE XV.

Fig. 1. Spurrite-rock, Scawt Hill, Co. Antrim. ×15 diameters.

Showing a large plate of spurrite enclosing turbid boat-shaped grains of bredigite, some partially inverted (dark areas within the grains represent the fibrous development of γ-Ca_2SiO_4). Little cubes of magnetite and minute drops of larnite are present as inclusions in the spurrite.

Figs. 2 and 4. Spurrite-larnite-rock, Scawt Hill. ×22 diameters. Fig. 2 in ordinary light, fig. 4 crossed nicols.

In fig. 2: below, granular larnite with some bredigite; above, clear spurrite. The central crystal is a hexagonal twinned cross-section of bredigite. In the spurrite are other grains of bredigite and numerous drop-like grains of larnite.

Fig. 4 shows the twinning of the central grain of bredigite with a drop-like grain of twinned larnite showing at the centre (white).

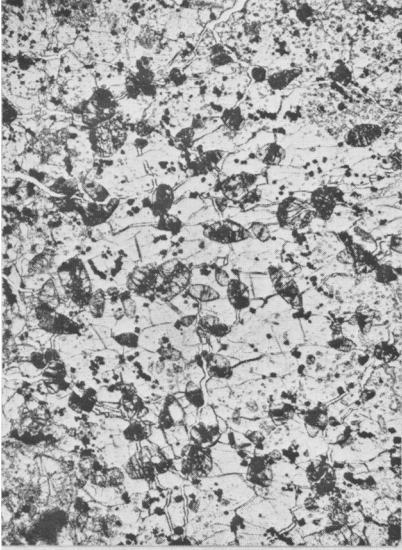Fig. 3. Spiegeleisen slag, Middlesbrough. ×15 diameters.

Melilite tables with turbid cores and clear peripheries. The cores of the melilites are filled with elongated drop-like grains of bredigite. Between the melilite crystals well-shaped pseudo-hexagonal prisms of bredigite. A cross-section is seen immediately to the left of the central vug and a prismatic section on the SE. edge of the vug. Numerous other prisms of bredigite are visible. Green calcium sulphide (dark) as arborescent growths and some associated bredigite.

PLATE XVI. Melilite-bredigite-larnite assemblages of Scawt Hill, Co. Antrim. ×15 diameters.
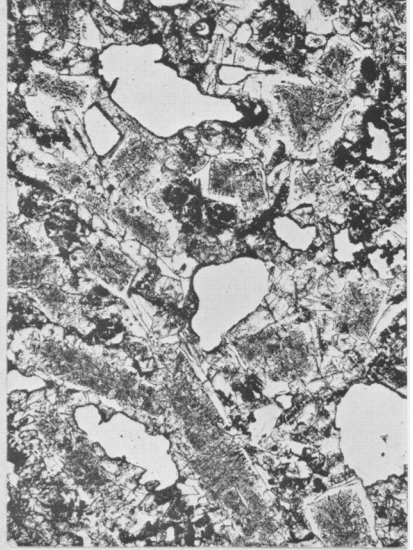
Fig. 1. The central crystal with straight edges is bredigite showing on its ragged SW. edge the development of braided larnite (as an inversion structure).

More braided larnite is seen above and to the left. Clear areas are mostly melilite. In the SW. corner a zone of normal larnite rock with magnetite and some spurrite. A hexagonal cross-section of bredigite is seen NNE. of the central bredigite crystal.
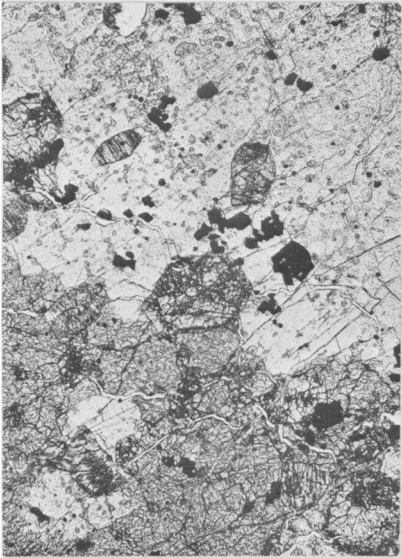
Fig. 2. Centre, a sector twin of bredigite cut nearly $\perp$ to Bx_a; cross-sections of melilite (laths); below, bredigite (white) partly enwrapping a lath section of melilite at extinction. Crossed nicols.

Fig. 3. Lower centre, a subidioblastic crystal of bredigite with prismatic cleavage (vertical section), enveloped by melilite; left above, an inverted grain (braided larnite); melilite (lath sections), dark areas include perovskite. Below, rounded grains in melilite now inverted to braided larnite.

Fig. 4. Above right, a large area of braided larnite showing the typical lamellae (3 sets visible). The remainder of the photograph shows chiefly bredigite and melilite with some perovskite.
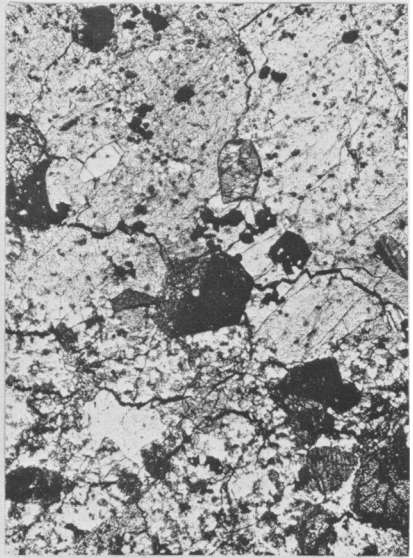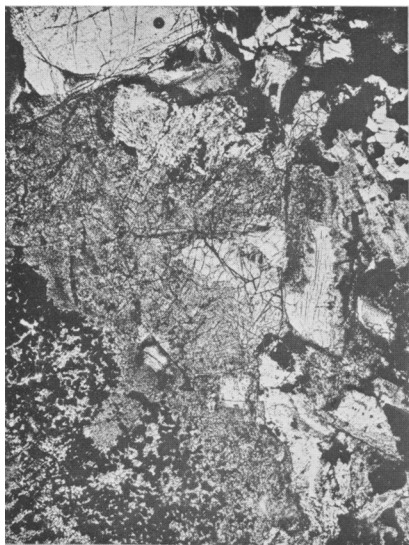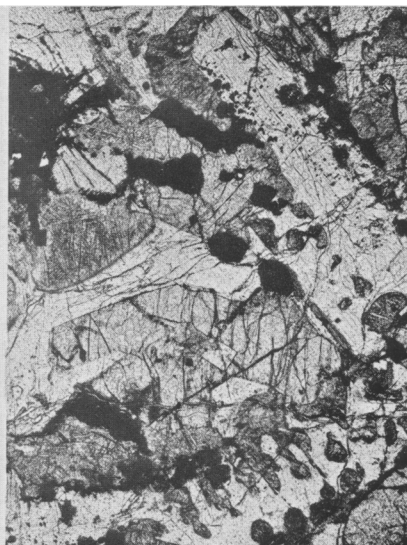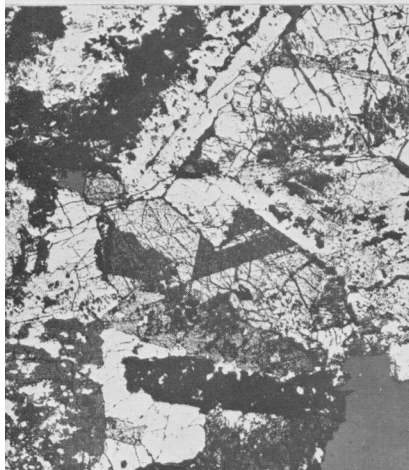
1

3

2

4

C. E. Tilley & H. C. G. Vincent: Bredigite.

C. E. Tilley & H. C. G. Vincent: Bredegite.