New data on the slag-minerals nagelschmidtite and steadite.

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NAGELSCHMIDTITE.

IN 1937 G. Nagelschmidt described a new silicophosphate mineral obtained from basic slag. It resembled the earlier described silico-carnotite (A. Carnot and A. Richard, 1883; D. P. Riley and E. R. Segnit, 1949) in its solubility in citric acid. Nagelschmidt gave optical, chemical, and X-ray data which indicated that the material had a composition of approximately $7CaO.P_2O_5.2SiO_2$, and agreed closely with a phase reported by G. Trömel (1943) in his investigation of the system $CaO-P_2O_5-SiO_2$. The material was further considered by M. A. Bredig (1941), who published cell dimensions worked out from powder photographs, assuming that nagelschmidtite was a solid solution of tricalcium phosphate in a predicted high-temperature hexagonal form of dicalcium silicate. R. L. Barrett and W. J. McCaughey (1942) gave further data, chiefly connected with phase relationships in the binary system $Ca_2SiO_4-Ca_3P_2O_8$. Finally, S. O. Agrell (1946) published further data on the slag mineral, giving the chemical analyses and optical properties of two samples, together with a discussion of the phase relationships of the material in slags, and hence in the binary system mentioned above. The name 'nagelschmidtite' is due to Barrett and McCaughey.

Description of samples.

During this examination at least two varieties of colourless silicophosphate were encountered. One of these is dull and cloudy, sometimes almost opaque; the second is quite clear and transparent. These will be

referred to generally as the 'cloudy phase' and the 'clear phase' respectively. In one case (slag C, below) the clear phase itself is often divided into an inner and outer zone of crystallographically dissimilar material.

A. A fine-grained slag (specimen 47715, Dept. Min. Petr.), composed of the clear phase and iron oxide, with minute needles of apatite in occasional vugs. The silicophosphate makes up about 70 % of the slag. It has a good cleavage, and shows no more than a slight tendency to elongation parallel to this cleavage, which is basal. A small amount of the cloudy phase occurs around the edge of some crystals. It is generally associated with the oxide phase. The latter is a wüstite, which, with some calcium ferrite, makes up the rest of the slag.

B. A slightly coarser slag (54216) with a lower percentage of phosphorus. Small vugs contain needles of apatite or steadite, and minute colourless hexagonal plates of tricalcium silicate. This slag together with the following analysis, was supplied by Mr. J. H. Whitely of the Consett Iron Co. Ltd., Durham: SiO_2 15·60, Fe 10·00, MnO 5·58, CaO 46·60, MgO 9·02, S 0·33, P_2O_5 6·24. It contains considerable free iron. The chief constituent is the cloudy phase; the clear phase is entirely absent. This material shows irregular extinction between crossed nicols. The grain-size is of the order of 0·2 mm. Orange coloured magnesiowüstite and occasional crystals of apatite make up the remainder of the slag.

C. This slag (57554) contains both the cloudy and the clear phases of the silicophosphate material. The former always occurs as a rim or outer zone around the latter. The rimming is rather indistinct in ordinary light but quite sharp when seen between crossed nicols (figs. 1–3). The cloudy material stands out by virtue of its higher birefringence. The inner clear zone of this slag shows phenomena which are not seen, at least as clearly, in any of the other slags of the group examined. It appears quite homogeneous in ordinary light, but between crossed nicols two zones with a sharply defined border between them can be seen. The inner of these two clear zones has a lower birefringence, and extinguishes homogeneously. The outer zone shows variable extinction possibly due to composition zoning of the crystals. Apart from the birefringence and the extinction there is no sensible difference in the optical properties. The oxide phase is dark-red magnesiowüstite. It is interstitial and evidently a late crystallization. A little calcium ferrite is also present.

D (57555). Composed almost entirely of the cloudy phase with interstitial wüstite. The material causing the cloudiness is much coarser in this sample and can be resolved into tiny droplets arranged in parallel fashion.

E. Sections cut from this slag (57556, from Messrs. Stewart and Lloyd of Corby) show considerable variation. One side of the hand-specimen

FIG. 1. Crystal of the phosphate phase in a basic open-hearth slag. Plane polarized light.

FIG. 2. As fig. 1, showing zoning between crossed nicols.

is rather porous and was more quickly cooled than the other side, except for a glazed edge where the still molten slag had flowed away. Sections of the porous part consist chiefly of rounded grains of the clear phase which are entirely free from the cloudy phase and are sensibly uniaxial. Sporadically distributed are small patches of cloudy material which increase in size and number as one approaches the other side of the specimen. Rimming is not characteristic; rather, a grain is completely or only half cloudy. The dividing line between crossed nicols is still quite sharp. The cloudy phase nearly always occurs associated
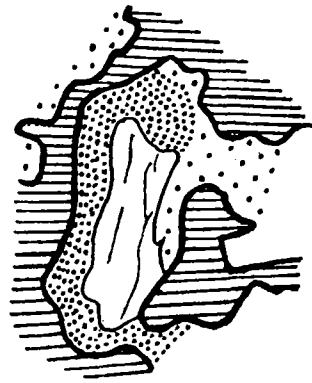

FIG. 3. Sketch of fig. 1. Clear zone, nagelschmidtite; dark stippling, larnite at extinction; light stippling, larnite; shaded area, chiefly wüstite.

with the oxide phase, which is interstitial and present in only small amount.

F (57557). A thin section only, from a group of slags containing only 1–2 % P_2O_5. This section is of interest because it contains almost

identical rimming phenomena as in sample C, and yet it contains little phosphorus.

Numerous other samples were also examined, but did not differ appreciably from one or other of those described above.

Chemical composition.

Samples of the clear and the cloudy phases were separated from specimens A and B respectively by the usual methods of centrifuging in heavy liquids. The powders eventually obtained for analysis still contained a small amount of magnesiowüstite as inclusions too small to separate. The results of the chemical analyses are given in table I, columns 2 and 3, together with analyses published by other authors, and the theoretical composition for $7CaO.P_2O_5.2SiO_2$.

The low summation of all but one of the analyses seems to have been due to the absorption of iodoform (from the decomposition of the methylene iodide used in their separation) by the very fine powders used. Nagelschmidt's powders were rather fine, as were also those of Agrell. The latter states that (private communication) his powders on heating gave off iodine vapours. The powder used for analysis 2 also gave off iodine vapours when heated in a closed tube, and a yellow sublimate, evidently iodoform, condensed on the cool part of the tube. The same powder had a loss on ignition of about 3·5 %. The powder of analysis 3 was coarser.

TABLE I. Chemical analyses of nagelschmidtite.

	1.	2.	3.	4.	5.	6.	7.
SiO_2	18·35	19·51	18·85	20·92	19·96	17·7	17·9
P_2O_5	21·69	16·80	5·60	12·28	13·10	20·0	19·9
CaO	59·96	55·62	62·88	57·64	58·70	58·4	58·3
MgO	—	0·04	1·21	0·92	0·87	0·6	—
FeO	—	—	2·77	—	—	—	—
MnO	—	1·24	—	0·41	0·67	—	—
Al_2O_3	—	—	5·00	1·52	0·80 ⎫	0·4	—
Fe_2O_3	—	2·73	3·73	1·61	2·03 ⎭		—
TiO_2	—	—	—	0·43	1·00	—	—
CO_2	—	—	—	0·48	nil	—	—
H_2O	—	—	—	0·87	nil	—	—
	100·00	95·94	100·04	97·08	97·13	97·1	96·1

1, Theoretical composition for $7CaO.P_2O_5.2SiO_2$. 2, Sample A (clear phase), also loss on ignition 3·5 %, this paper. 3, Sample B (cloudy phase), this paper. 4 and 5, Agrell, 1946. 6 and 7, Nagelschmidt, 1937; two analyses of the same material.

The six analyses show considerable variation, which is to be expected from any of the published diagrams representing the phase relations of

the system Ca_2SiO_4–$Ca_3P_2O_8$. All show extensive solid solution around this composition.

Barrett and McCaughey give a useful general formula for compositions lying in this system—$Ca_{(2Si + \frac{3}{2}P)}(P,Si)_{12}O_{48}$. In table II the analyses have been worked out on this basis. The final column gives the figure for calcium (worked out from the ratio $2Si+\frac{3}{2}P$) which would be needed in each case to bring the analysis exactly into the system. In the new analyses the iron and magnesia are known to be present as impurities.

These compounds, as was pointed out by Nagelschmidt, are quite readily soluble in organic acids. Their phosphorus content is therefore directly available to plants when the ground slag is used as a fertilizer.

TABLE II. Formulae on the basis of 48 oxygen atoms.

Analysis no.					Theoretical Ca.
2.	$(Ca,Mn)_{21.4}$	$P_{5.0}$	$Si_{6.9}$	O_{48}	$Ca_{21.4}$
3.	$Ca_{24.2}$	$P_{1.7}$	$(Si,Al)_{9.9}$	O_{48}	$Ca_{22.4}$
4.	$(Ca,Mg,Mn,Fe)_{22.7}$	$P_{3.6}$	$(Si,Ti,Al)_{8.2}$	O_{48}	$Ca_{21.8}$
5.	$(Ca,Mg,Mn,Fe)_{23.4}$	$P_{3.8}$	$(Si,Ti,Al)_{7.5}$	O_{48}	$Ca_{21.8}$
6 and 7.	$Ca_{18.4}$	$P_{5.0}$	$Si_{5.2}$	O_{48}	$Ca_{17.9}$

From table II it can be seen that in each case the composition falls close to the Ca_2SiO_4–$Ca_3P_2O_8$ system.

Optical properties.

The clear phase.—The material of sample A is characteristic. It is quite colourless and biaxial positive with a very small optic axial angle. The maximum and minimum refractive indices observed in sodium-light were 1·668 and 1·660 (± 0.002). A good cleavage is frequently seen; it is parallel to the fast vibration direction in the grains, and is evidently basal. A second possible cleavage is sometimes seen at right angles to the first. Crystal edges are not often seen, but occasional nearly isotropic basal sections giving a centred almost uniaxial interference figure have hexagonal outlines. The evidence here seems to confirm Bredig's work on the hexagonal nature of nagelschmidtite.

Of considerable interest is the zoning of the clear phase in sample C. As mentioned above, there is very little difference between the optical properties of the two parts, but the division between the two zones is very distinct when seen between crossed nicols. Little positive proof of the relative natures of these two zones can be obtained; it is thought, however, that the difference is purely structural. The part with the irregular extinction is probably a lower-temperature form. This is discussed in more detail below.

The cloudy phase.—Sample B is characteristic of this type. It is colourless, but always turbid. It is biaxial positive, with a moderate to low optic axial angle. The maximum and minimum refractive indices observed in sodium-light were 1·675 and 1·661. The birefringence is much higher than that of the clear phase. The grains show no crystal form, and rarely cleavage. Extinction is irregular.

The optical properties of these phases are set out in table III, together with the optics of the other analysed samples of table I. Agrell (1946) and K. Balajiva and co-authors (1946) have also given a number of refractive index determinations which show a continuous increase as silicon replaces phosphorus.

TABLE III. Optical data of nagelschmidtite.

Analysis no.	Refractive indices. Max.	Min.	Bire-fringence.	2V(+).	Variety.
2.	1·668	1·660	0·008	Very small	Clear
3.	1·675	1·661	0·014	Moderate to small	Cloudy
4.	1·690	1·680	0·010	10°	Clear
5.	1·693	1·682	0·011	10°	Clear
6 and 7.	1·661	1·652	0·009	Small	Clear

The nature of the two phases.

The clear phase.—The X-ray powder diagram proves this to be similar to the mineral examined by Nagelschmidt. Table IV gives the spacings and relative intensities of the strongest lines of the material extracted from sample A, and the corresponding lines of Nagelschmidt's material from his paper.

TABLE IV. X-ray spacings and intensities of nagelschmidtite.

1. d.	I.	2. d.	I.
3·80	m	3·93	w
3·42	m	3·54	w
2·80	s	2·85	s
2·66	vs	2·70	s
2·20	m	2·22	vw
1·94	s	1·960	s
1·54	w	1·562	w
1·48	w	1·485	m
1·34	m	1·346	m

1, Sample A, this paper. 2, Nagelschmidt, 1937.

The small differences between the two samples are always in the same direction, and are to be ascribed to the difference in com-

position (analyses 2 and 6, table I). This, then, is the phase which Bredig (1943) correlates with a high-temperature hexagonal form of dicalcium silicate solid solution, and which has been termed 'nagelschmidtite'.

The cloudy phase.—An X-ray powder photograph of the material separated from slag sample B is reproduced in fig. 4 together with photographs of larnite from Scawt Hill, Co. Antrim, and nagelschmidtite from
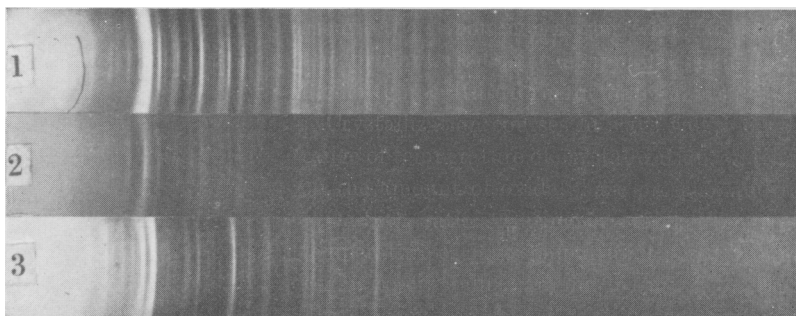

FIG. 4. X-ray powder photographs of: (1) larnite from Scawt Hill, Co. Antrim; (2) larnite solid solution from slag B; (3) nagelschmidtite from slag A.

sample A. By a comparison of the photographs it can be seen that the cloudy phase is not the same as nagelschmidtite, but in fact, is related to larnite, the β-form of dicalcium silicate. The cloudiness is due to the fact that it cannot take as much material into solid solution as the higher-temperature form. In slag sample D the material causing the cloudiness is much coarser than usual. A regular arrangement of small globules is seen under the high power. This is very reminiscent of the exsolved material obtained by the writer on the slow cooling of artificial melts of silicate compounds beyond their solid solution limits.

A noteworthy feature of the larnite solid solution in these occurrences is the lack of the fine multiple twinning which is usually associated with this phase of dicalcium silicate. The usual interpretation of the twinning is that it has been formed during inversion from a higher-temperature form. The optical data of a typical larnite are α 1·707, β 1·715, γ 1·730, 2V positive, moderate to small (C. E. Tilley, 1929). Lower refractive indices of the slag material are caused by phosphorus in solid solution. It is thought that probably all the cloudy phase in these slags is larnite solid solution. Only the extra zone in slag C can be tentatively classed as the α'-form, bredigite.

The system dicalcium silicate–tricalcium phosphate with special reference to slags.

All of the colourless silicophosphate phases in these slags are considered to be forms of dicalcium silicate. For convenience, the names of the slag and natural mineral forms will be used. The clear phase will be called nagelschmidtite (hexagonal α-Ca_2SiO_4) and the cloudy phase larnite (β-Ca_2SiO_4) with, here, some $Ca_3P_2O_8$ in solid solution). Bredigite (orthorhombic α'-Ca_2SiO_4) (C. E. Tilley and H. C. G. Vincent, 1948) may occur in slag C. The various forms of pure Ca_2SiO_4 are summarized in table V.

TABLE V. Properties of the four forms of dicalcium silicate, Ca_2SiO_4.

| Form. | Name. | Crystal system. | Inversion to higher form. | Optical data. | | | |
				α.	β.	γ.	2V(+).
α	—	Hexagonal	—	—	—	—	—
α'	Bredigite	Orthorhombic	1450° C.	1·712	1·716	1·725	30°
β	Larnite	Monoclinic	675° C.	1·707	1·715	1·730	—
γ	—	Orthorhombic	850° C.	1·642	1·645	1·654	60°

The order of inversion of the forms on cooling is $\alpha \rightarrow \alpha' \rightarrow \beta \rightarrow \gamma$, and on heating $\gamma \rightarrow \alpha' \rightarrow \alpha$. If the β-form is stabilized, the order of inversion on heating is $\beta \rightarrow \alpha' \rightarrow \alpha$ (G. Trömel, 1949). J. H. Welch and R. W. Nurse (private communication) have confirmed these inversion temperatures by means of thermal analysis.

The phase relationships of silicocarnotite.—This compound undergoes a change in the solid state. In order to gain some idea of the temperature of this change, a number of samples of silicocarnotite were heated to various temperatures up to 1450° C. These results indicated that a reversible change took place between 1400° C. and 1450° C. (D. P. Riley and E. R. Segnit, 1949). A synthetic product of this composition prepared at 1500° C. gave, however, a nagelschmidtite powder photograph (R. Klement and F. Steckenreiter, 1940). Silicocarnotite evidently exists in a high-temperature hexagonal form analogous to nagelschmidtite, and, under certain conditions, metastable (see also K. Balajiva and co-authors, 1946). The silicocarnotite of slags crystallizes below the inversion temperature.

In the simple binary system as suggested by M. A. Bredig in 1943 (see fig. 5), a nagelschmidtite would crystallize from a melt of the composition $5CaO.P_2O_5.SiO_2$ and would invert at a lower temperature to silicocarnotite. When, say, 20 % of iron oxide is present as in a slag, the liquidus temperatures will be lowered to below the inversion tempera-
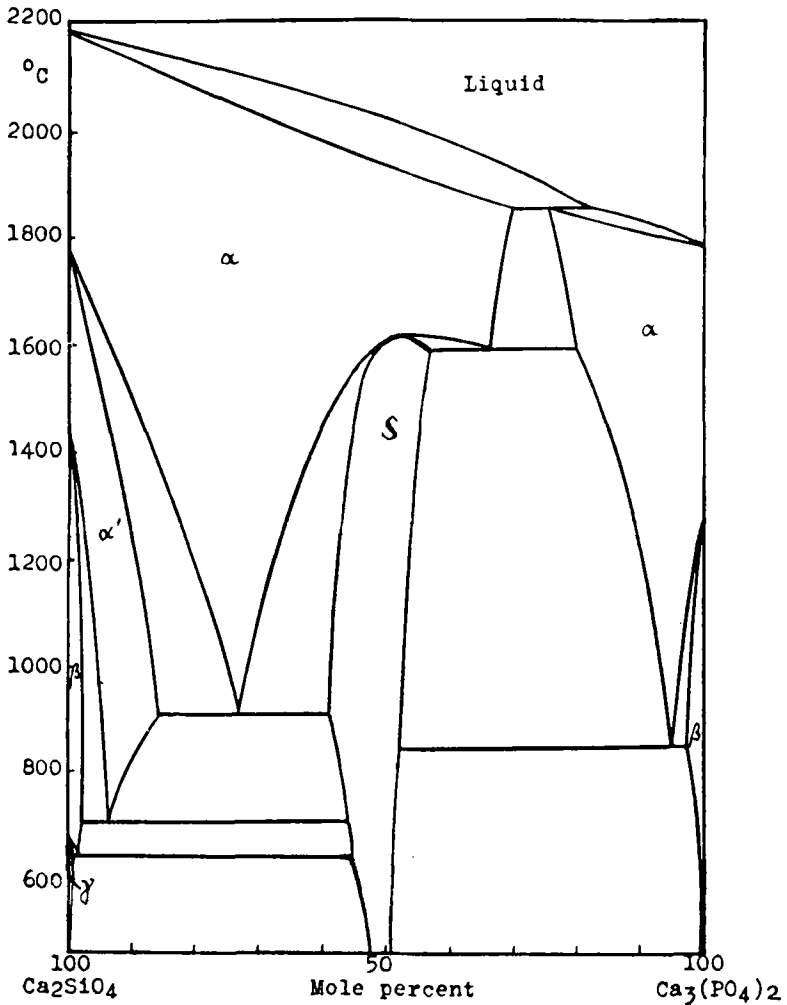
FIG. 5. Phase diagram of the system Ca_2SiO_4–$Ca_3P_2O_8$ (after Bredig, 1943).

ture, and silicocarnotite will crystallize directly. With a slightly greater silica content, nagelschmidtite and silicocarnotite should occur together. One slag actually showed this association. The dominant phase is nagelschmidtite rimmed by larnite, with silicocarnotite as a subordinate interstitial phase.

The phase relationships of nagelschmidtite.—If all the colourless phases in slags were not dicalcium silicate solid solutions, the latter compound

should be frequently seen rimmed by or associated with nagelschmidtite as a second, ternary, phase. Such an association has not been seen, and is not believed to exist.

Both the nagelschmidtite and larnite phases have been seen in slags ranging in P_2O_5 content from less than 2 % to about 14 %. This represents a range of about 3 % to 20 % P_2O_5 in the silicophosphate material. The rimming is always present to a slight extent in the dominantly nagelschmidtite slags, although pronounced examples of this effect do not seem to be as common as the two extremes. The presence of more than one form of Ca_2SiO_4 in the same slag is due to the stabilizing effect on the higher-temperature forms of material in solid solution (K. T. Greene, 1944).

Crystallization courses in slags will depend to a large extent on the range of temperature of crystallization, which will in turn depend chiefly on the amount of oxide phase present, and to a smaller extent on the P_2O_5–SiO_2 ratio. During crystallization in these slags, the inversion temperature of nagelschmidtite is passed, and a lower-temperature form begins to crystallize around it (figs. 1–3). In most cases this is larnite. This does not agree well with the latest determinations of the stability range of larnite, which should appear at about 700° C. Unfortunately, there is nothing known about the effect of the phosphorus in solid solution on this inversion temperature. In some slags, however, a third zone between nagelschmidtite and larnite appears (C, p. 174). It is very closely related to the centre zone of nagelschmidtite, but is sharply separated when seen between crossed nicols, has a slightly higher birefringence, and uneven extinction. If the stability order of the four forms of dicalcium silicate is accepted (table V) then it seems sound to assume that we have here a zone of bredigite. The optical properties as far as can be determined agree with those for a bredigite with material in solid solution. Such material should have similar properties to nagelschmidtite. This zone may be more common than has been noticed, but too narrow to be easily seen.

Slags containing only nagelschmidtite will have crystallized above the temperature of phase transition of this form. It is 1450° C. for pure Ca_2SiO_4; to what extent this is altered by solid solution is not known, but it is probably lowered somewhat. Below this temperature larnite will crystallize. Nagelschmidtite might therefore be expected in the higher melting-point, and larnite in the lower melting-point slags. In the slags examined, this seemed to be the case, as larnite became commoner with increase in the iron oxide content of the slag.

G. Trömel (1943) showed that the rate of cooling can have a marked

effect on the final mineral composition of the slag. Some of the effects of varying rates of cooling were given by a slag specimen with a glazed surface formed by still liquid slag flowing away from a partially crystallized slag ball. A section cut through the glazed surface was chiefly opaque material with rounded crystals of nagelschmidtite, while the interior, more slowly cooled part of the specimen, was chiefly larnite. The other side of the specimen had undergone fairly rapid cooling, leaving the two phases together. Rimming was not characteristic. The larnite usually started from a grain of wüstite, and worked outwards through perfectly clear nagelschmidtite grains, large areas of which are quite unchanged. The border between the two phases is again sharply defined. The change in this slag seems to be due to inversion which seems to have started mainly from the neighbourhood of wüstite grains in the late crystallizing part of the slag.

The various relationships exhibited by these dicalcium silicate solid solutions in slags cannot be summarized easily. However, those most commonly seen may be stated as follows. If crystallization takes place:

1. Above the α inversion temperature—nagelschmidtite.
2. Below the α inversion temperature—larnite.
3. Passing through the α inversion temperature—nagelschmidtite rimmed by larnite.

The final mineral composition of the slag will therefore depend on its crystallization range, which will in turn depend on the amount of iron oxide present, and on the content of P_2O_5.

In Bredig's phase diagram (fig. 5) all the boundaries between the Ca_2SiO_4 phases are below the solidus. Some of the inversion temperatures are too high; nevertheless, in slags, the liquidus-solidus boundaries cut across some of the phase boundaries so that nagelschmidtite may frequently crystallize first, to be followed by a lower-temperature form when the requisite temperature is reached. In low-phosphate slags primary crystallization of a lower-temperature form is to be expected.

Finally, it may be emphasized that these investigations were carried out on slags essentially free from fluorine. In the presence of fluorine the crystallization of apatite will shift the equilibrium towards the lime–silica side of the $CaO-SiO_2-P_2O_5$ system.

Note on the occurrence of tricalcium silicate.

In the larnite slag (sample B, p. 174) are occasional vugs into which are growing small crystals. The bulk of these are hexagonal needles of

apatite, but a few minute flat plates with an hexagonal outline some-
times occur. These are sometimes quite transparent, sometimes filled
with inclusions. Microchemical tests showed the presence of silica, lime,
and phosphorus, and the crystals were decomposed by dilute acetic acid.
A Laue photograph showed trigonal symmetry, and the spacings of the
main lines of a powder photograph agreed with those given for tricalcium
silicate by L. T. Brownmiller and R. H. Bogue (1930).

The interest of this occurrence lies in the fact that the crystals contain
considerable phosphorus in solid solution, and that they only occur in the
vugs of the slag. No tricalcium silicate was seen in the thin section of
the slag.

STEADITE.

V. A. Kroll (1911) applied the term 'steadite' to the small yellowish
hexagonal needle-shaped crystals from slag described by J. E. Stead and
C. H. Ridsdale (1887). Similar material was also described by G. Hilgen-
stock (1883) who, like the other authors, assumed that the crystals were
a form of tetracalcium phosphate. H. Bücking and G. Linck (1887) also
described these crystals, but recognized their similarity to the natural
mineral apatite, as did Kroll (1911) later.

Steadite occurs more or less commonly in basic slags. No strict divid-
ing line can be drawn between it and apatite and they both occur under
very similar circumstances. It was noticed by earlier workers that
steadite was very commonly associated with silicocarnotite. This may
be a reflection of the siliceous environment. Steadite is frequently a late
constituent to crystallize; its crystals are the commonest in the vugs of
basic slags.

Source and description of the samples.

There is little difference in the appearance of steadite from different
slags or places. The only outward difference is in colour.

Sample A. Small colourless crystals in vugs in a slag from Irlam,
Lancashire (Dept. Min. Petr. no. 57558). The main part of the slag is
composed of a dicalcium silicate solid solution, probably larnite, together
with wüstite and about 10–15 % of idiomorphic steadite.

Sample B. Abundant, some quite large brownish crystals obtained
from the interior of a slag ball from Corby, Northamptonshire (57559).
The majority of the crystals are packed with fine inclusions of iron oxide,
although the smallest of the crystals are often quite clear.

Sample C. Crystals and grains in silicocarnotite slags from various
sources. These are all very similar, and were only examined in thin

section or as minute grains of no crystal shape. They are pale brown in thin section.

Chemical composition.

Two small samples were separated from A and B. Neither sample was perfectly satisfactory owing to the small amounts available and the difficulty of separating the material in the pure state. The results of the analyses are in table VI, together with analyses taken from earlier papers. The new analyses are not perfectly satisfactory, but they do show the essential composition and the presence of considerable amounts of fluorine and silica.

The separation of sample A caused some difficulty because of the presence of large amounts of dicalcium silicate solid solution. When crushed, few grains were entirely free of iron oxide, so that it was not possible to effect a direct gravity separation of the light phases. A separation was eventually made by digesting the powdered slag for some time in dilute acetic acid. This treatment decomposed the dicalcium silicate to a large extent; any remaining grains had a skin of silica which lowered the density enough for a gravity separation to be effective. Any gelatinous silica remaining on the steadite grains was removed by digesting in sodium carbonate solution. Microscopic examination now showed that the grains were quite free from adhering silica, although they still contained inclusions of iron oxide.

TABLE VI. Chemical analyses of steadite.

	1.	2.	3.	4.	5.	6.
P_2O_5 . .	34·19	32·96	33·71	36·77	34·94	42·28
SiO_2 . .	6·69	6·09	3·90	3·81	3·24	—
CaO . .	52·32	50·87	53·54	53·51	57·55	55·55
Fe_2O_3. .	—	—	4·86	1·78	—	—
Al_2O_3 . .	—	—	—	1·09	—	—
MnO . .	—	—	0·79	—	—	—
FeO . .	2·87*	8·74*	1·27	2·22	4·00	—
MgO . .	0·35	—	0·49	0·40	—	—
Cr_2O_3. .	—	—	trace	—	—	—
VO . .	—	—	1·34	—	—	—
S . .	—	—	0·46	trace	—	—
F . .	2·31	3·00	—	—	—	3·76
Less O for F	1·00	1·26	—	—	—	1·59
Total .	97·73	100·40	100·36	99·58	99·73	100·00

* Total iron as FeO.

1, Sample A, this paper. 2, Sample B, this paper. 3, Stead and Ridsdale, 1887. 4, Bücking and Linck, 1887. 5, Hilgenstock, 1883. 6, Theoretical for $3Ca_3P_2O_8.CaF_2$.

Sample B was obtained as individual crystals from the centre of a slag ball. They were almost free of contaminating silicophosphates of other kinds, but contained much included fine iron oxide. The large amount of iron oxide in the analysis can thus be taken as impurity, as qualitative tests on small crystals free from inclusions gave a negative result for iron. The small amount of silicocarnotite present was removed with acetic acid, and any remaining silica with sodium carbonate solution.

The actual silica figures obtained by the usual method of determination in analyses I and II were 4·87 % and 3·76 % respectively. The figures in the table were arrived at by adding the amount of silica theoretically lost with the fluorine during the evaporation with hydrochloric acid. The fluorine determinations are probably a little low, especially in the first case. Only a small amount of material was available, with the result that only a very small volume of thorium nitrate was used for titration. These two analyses have been recalculated on the basis of an apatite formula in table VII with silicon replacing part of the phosphorus. It appears from this table that the fluorine determinations are low, but, with this in mind, the relationship to the apatite structure is evident.

TABLE VII. Analyses I and II calculated to atomic ratios on the basis of the apatite formula $3Ca_3P_2O_8.CaF_2$.

I.

					Oxide %.	Mol. ratios.	Atomic ratios.
P_2O_5	.	.	.	.	34·19	0·241	1·64 ⎱ 2·02
SiO_2	.	.	.	.	6·69	0·111	0·38 ⎰
CaO	.	.	.	.	52·32 ⎰ 48·92 / 3·40*	0·874	2·98
FeO	.	.	.	.	2·87 ⎱ present as impurity		
MgO	.	.	.	.	0·35 ⎰		
F	.	.	.	.	2·31	CaF_2 4·74%	

Molecular ratio $Ca_3P_2O_8:CaF_2 = 4:1$.

II.

					Oxide %.	Mol. ratios.	Atomic ratios.
P_2O_5	.	.	.	.	32·96	0·234	1·70 ⎱ 2·06
SiO_2	.	.	.	.	6·09	0·101	0·36 ⎰
CaO	.	.	.	.	50·87 ⎰ 46·45 / 4·42*	0·830	3·02
FeO	.	.	.	.	8·74 present as impurity		
F	.	.	.	.	3·00	CaF_2 6·15 %	

Molecular ratio $Ca_3P_2O_8:CaF_2 = 3·4:1$.

* CaO required for fluorine.

D. McConnell (1937) has shown that there can occur a complete substitution of silica and/or sulphur for the phosphorus in the apatite

structure. He was able to show the relationships between ellestadite, which has an apatite structure although it contains very little phosphorus; wilkeite, in which there is a partial replacement of the phosphorus; and apatite. The structures were the same, and there was a continuous change in optical and physical properties. It is therefore evident that there is a very wide range of substitution possible in the apatite structure. Steadite, with a small amount of silicon (ionic radius 0·39 Å.) replacing phosphorus (ionic radius 0·35 Å.) is one of the less complex of these substitutions.

With the small amount of data available it is not easy to account for the older analyses which, on the surface, look satisfactory. But in no case was fluorine determined, either qualitatively or quantitatively. As the older analyses were done over sixty years ago, there is probably ground for suspicion, especially in view of the analytical difficulties involved in this combination of elements. If there was no fluorine present, the crystals dealt with by the earlier authors may have been related to something like an hydroxy-apatite, or even a carbonate- or a sulphate-apatite. But there are none of these extra constituents present in sufficient quantity to support this; and it is very doubtful if sufficient water, carbonate, or even sulphate could be present in the slags at their melting temperatures to allow of the formation of these compounds.

It is much more likely that fluorine was simply not determined, its weight being added to that of the other constituents. If the crystals were dissolved in acid, and the metallic elements determined by direct precipitation, calcium fluoride would be thrown out with the Group III metals, even if phosphorus was removed first. The fluorine would be weighed with the iron, &c., and would be hidden here in the analysis. The silica determination would be low as some would be lost during the evaporation with acid. In this connexion it is interesting to note that the old silica determinations are much the same as the figures quoted above for the new analyses before the loss with fluorine was allowed for. It suggests that there may be a definite limit to the simple substitution of silicon for phosphorus. S. O. Agrell (1946) gave partial analyses of some apatites from slags. These contain about 2½ % silica. There is clearly no dividing line between apatite and steadite; it is probable that most slag apatites contain some silica.

There remains little doubt that all of the samples of steadite which have been examined are fluorapatites with some of the phosphorus replaced by silica. There must also be some replacement of calcium by

elements of higher valency, probably Fe^{+++}, but this does not show up in the analyses owing to the amount of extraneous oxides.

Morphology.—The crystalline form is very constant. The mineral forms long needle-like crystals of hexagonal cross-section. The prism angle is exactly 60°, so there can remain little doubt that they belong to the hexagonal system. The crystals may be up to 2 cm. in length, and 1 mm. in diameter. They are commonly a pale-brown colour, but may be colourless. There are no terminal faces apart from the basal plane (0001), and a well-marked parting or cleavage is frequently seen parallel to this face. Confirmation of the crystal system and the identity of this mineral with the apatite group was provided by powder photographs.

Optical properties.—In thin section the colour is usually pale brown. Sample A is the one exception to this. The pleochroism of the coloured samples is very weak. The birefringence is very low, and it is very difficult to obtain optic figures. Basal sections are quite isotropic, and, as far as can be seen, give a uniaxial interference figure. The elongation of the crystals shows that they are negative in sign. The refractive indices are slightly higher than those for pure apatite. Some values for various samples are given in table VIII, as well as those for artificial fluorapatite. The higher figures for the steadite are evidently due to the replacement of the phosphorus by silicon. The same effect is seen in the nagelschmidtite series.

TABLE VIII. Optical data of steadite and apatite.

	1.	2.	3.	4.
ϵ	1·638	1·654	1·655	1·629
ω	1·642	1·657	1·657	1·632
$\omega-\epsilon$	0·004	0·003	0·002	0·003

1, Sample A. 2, Sample B. 3, Sample C. 4, Artificial fluorapatite (R. Nacken, 1912).

The most interesting phenomenon to be seen in thin section is the multiple twinning. When viewed between crossed nicols, two sets of twins are almost invariably seen in prismatic sections. One set is parallel to the basal plane, the other to the prism faces. A photograph of a single crystal showing the two sets of twins is shown in figure 6. The photograph was taken with the crystal nearly parallel to one of the cross-hairs, and clearly shows the two sets of twins at right angles. The twinning has previously been noted by Agrell (1946) and H. Schneiderhöhn (1931).

Apatite belongs to the crystal class 6/m. This class possesses one hexad axis normal to a plane of symmetry. As there are no diad axes or vertical

planes of symmetry, parallel and normal twins can be obtained simply by twinning on axes which coincide with the usual position of diad axes in the hexagonal system. Normal twins are obtained when the twin axis is normal to a composition plane which coincides with the prism faces. Continuous twinning of this form would result in multiple twinning parallel to the prism faces. Parallel twins are obtained when the basal plane is the composition face. Continuous twinning of this type will result in multiple twinning parallel to the basal plane. If both of these types of twinning were to occur, the result would be two sets of twins at right angles, one parallel to the basal plane and the other parallel to the prism faces.

The difficulty in applying this explanation to the present case lies in the fact that the twinning is most clearly seen when the crystals are parallel to the cross-hairs of the microscope, and are not visible at all in the 45° position. Simple twinning of either kind would not be visible at all in section between crossed nicols, as the effective orientation of the sectors will always be the same. It is difficult to see how such twinning is going to be visible under the microscope unless some more complex law enters. The steadite crystals show the two sets of twins best when they are parallel to the cross-hairs, so that certain parts of the crystal are showing apparent inclined extinction (fig. 6). It is possible that the twinning has been formed by inversion from a higher-temperature form.
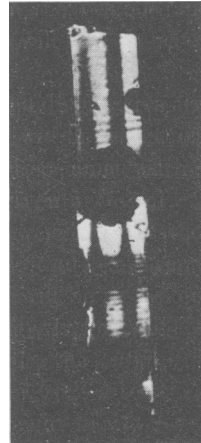

Fig. 6. Crystal of steadite showing the complex cross-hatched twinning. Crossed nicols, crystal length at about 5° to the vibration direction of one nicol.

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