

*An optical and X-ray examination of the basic-slag mineral silicocarnotite.*

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BLUE pleochroic crystals obtained from basic slag were first described by Carnot and Richard.<sup>1</sup> They published a chemical analysis, some of the optical properties, and a brief description of the forms they observed. The crystals were stated to be orthorhombic, with a composition of  $5\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{SiO}_2$ . Several authors<sup>2</sup> later described similar crystals. None, however, gave a thorough account of the optical properties. These various papers were summarized and discussed by Kroll,<sup>3</sup> who accepted Carnot's formula, but concluded, from Bücking and Linck's examination, that the material was monoclinic. Kroll applied the rather unfortunate term 'silico-carnotite' to these crystals.

The present work shows that silicocarnotite occurs in only one modification—orthorhombic. The crystals drawn by Bücking and Linck and described as monoclinic are, in fact, identical with our orthorhombic crystals.

Silicocarnotite is found in basic slags rich in phosphorus. If the slag is not too fine-grained the mineral can be seen as clear blue grains with lens or naked eye. In thin section large areas of grains commonly show preferred orientation. Crystals are rare and are usually very small and show few forms. A number of different samples were examined in the course of the present work and are listed below according to their source and habit.

*Source and general description of samples.*

A. Granular material showing no definite faces. This was separated by the usual methods from a slag. (Specimen 50068, Dept. Min. Pet.)

<sup>1</sup> A. Carnot and A. Richard, *Bull. Soc. Min. France*, 1883, vol. 6, p. 237.

<sup>2</sup> J. E. Stead, C. H. Ridsdale, and H. A. Miers, *Journ. Chem. Soc.*, 1887, vol. 51, p. 601. H. Bücking and G. Linck, *Stahl und Eisen*, 1887, vol. 4, p. 245. G. Hilgenstock, *Stahl und Eisen*, 1883, vol. 3, p. 498.

<sup>3</sup> V. A. Kroll, *Journ. Iron and Steel Inst.*, 1911, vol. 84, p. 126. [*Min. Mag.* 19-349.]

- B. Occasional small blue crystals from vugs in a fine-grained slag.
- C. Idiomorphic crystals embedded in monticellite. This was the only colourless sample examined. (Slide 48749, Dept. Min. Pet.) These three samples (A–C) were kindly supplied by Dr. S. O. Agrell, Department of Geology, University of Manchester.
- D. Slag powder containing small blue grains and occasional crystals of silicocarnotite. This was Miers's original material (B.M. 1919,64). Later we received three small crystals picked out from this same British Museum sample.
- E. Blue plates and blades (B.M. 1919,67). Short pseudo-hexagonal prisms and elongated prisms (B.M. 1919,70). These two specimens were kindly sent us from the British Museum collection by Dr. F. A. Bannister.
- F. Blue blade-like crystals on slag (P 157–9, Rothamsted). These were kindly provided by Dr. E. M. Crowther of the Rothamsted Experimental Station.
- G. Synthetic silicocarnotite powder from the Building Research Station, Garston, through the courtesy of Mr. R. W. Nurse.

*Habits observed, or nature of material.*

1. Prismatic (fig. 3).
2. Plates (001) (fig. 4).
3. Blades (101) elongated along [010], often showing existence of skeletal growth (fig. 5).
4. Small grains or powder showing no crystal shape.
5. Short pseudo-hexagonal prisms and prisms with lozenge-shaped cross-section. Only examined when mounted in slides.
6. Long colourless pseudo-hexagonal prisms.

*Chemical composition.*

A sample was separated from a slag (sample A) of sufficient coarseness for the blue grains to be seen in the hand-specimen. In section large areas of grains have a similar orientation, and are associated with considerable amounts of black magnetic iron oxide and minor amounts of pale-brownish steadite, a silica-containing apatite.

The results of the chemical analysis are given in table I, column 2, together with the analyses of other authors, and the ideal composition for  $5\text{CaO}\cdot\text{P}_2\text{O}_5\cdot\text{SiO}_2$ .

TABLE I. Chemical analyses of silicocarnotite.

	1.	2.	3.	4.	5.	6.
$\text{SiO}_2$ ... ..	12.46	13.64	12.42	10.79	9.47	9.42
$\text{P}_2\text{O}_5$ ... ..	29.44	27.96	29.65	29.15	31.19	30.85
$\text{CaO}$ ... ..	58.10	56.78	53.20	56.58	57.42	57.60
$\text{MgO}$ ... ..	—	trace	trace	0.74	trace	—
$\text{FeO}$ ... ..	—	—	1.80	—	0.95	2.94
$\text{MnO}$ ... ..	—	0.03	trace	0.21	trace	—
$\text{Al}_2\text{O}_3$ ... ..	—	0.41	2.76	—	1.13	—
$\text{Fe}_2\text{O}_3$ ... ..	—	1.66*	—	1.00	—	—
$\text{S}$ ... ..	—	—	—	0.05	—	—
$\text{V}$ ... ..	—	—	—	1.64	—	—
$\text{NiO}$ ... ..	—	—	—	0.04	—	—
	100.00	100.48	99.83	100.20	100.16	100.81
Sp. gr. ... ..	—	3.06	3.042	—	3.06	—

\* Total iron as  $\text{Fe}_2\text{O}_3$  (chiefly impurity).

1, Theoretical for  $5\text{CaO}\cdot\text{P}_2\text{O}_5\cdot\text{SiO}_2$ . 2, Riley and Segnit (this paper). 3, Carnot and Richard (1883). 4, Stead and Ridsdale (1887). 5, Bücking and Linck (1887). 6, Hilgenstock (1883).

The composition  $5\text{CaO}\cdot\text{P}_2\text{O}_5\cdot\text{SiO}_2$  lies on the binary system  $\text{Ca}_2\text{SiO}_4$ – $\text{Ca}_3\text{P}_2\text{O}_8$ . Several phase diagrams have been proposed for this system.<sup>1</sup> The synthetic work indicates that silicocarnotite has a rather limited range of stability and over this range forms solid solutions. Further evidence of this is to be seen in the zoning of our analysed material. This accounts for the differences in composition shown in table I.

In our analysis the iron oxide is chiefly contained as impurity; a small amount of it remained as inclusions in the silicocarnotite grains. Omitting minor constituents (the alumina can be grouped with silica, and manganese with lime) the analysis can be calculated to  $5.2\text{CaO}\cdot\text{P}_2\text{O}_5\cdot 1.15\text{SiO}_2$ , or, recalculating on the basis of 12 oxygen atoms, we get  $\text{Ca}_{4.96}\text{P}_{1.93}\text{Si}_{1.11}\text{O}_{12}$ , which is close to the theoretical  $\text{Ca}_5(\text{P},\text{Si})_3\text{O}_{12}$ . An interesting property of the mineral is its solubility in organic acids. This property of basic-slag phosphates was known before any examination of the constituent minerals took place. Ground slag has consequently been used directly as a plant fertilizer since the latter half of the nineteenth cen-

<sup>1</sup> R. L. Barrett and W. J. McCaughey, *Amer. Min.*, 1942, vol. 27, p. 680. [M.A. 8-312.] G. Trömel, *Stahl und Eisen*, 1943, vol. 63, p. 21. M. A. Bredig, *Amer. Min.*, 1943, vol. 28, p. 594. [M.A. 9-92.]

ture. The specific gravity was determined by suspension in methylene iodide.

*X-ray examination.*

In view of the strikingly different habits exhibited by the crystals, it was thought desirable to examine a number of specimens in order to

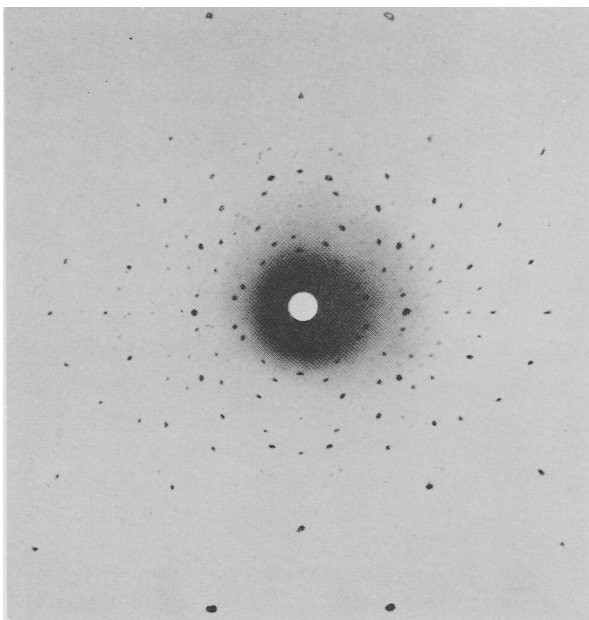


FIG. 1. Laue photograph of single crystal of silicocarnotite, showing orthorhombic symmetry.

ascertain whether they were crystallographically identical. The habit, in a number of cases, made it difficult to establish the symmetry and, at first sight, the possibility of dimorphism could not be excluded.

Laue and oscillation photographs were taken of single crystals of the following sources and habits; B1, D1, E2, E3, F3, following the nomenclature given above. All these crystals were shown to be identical crystallographically and to have orthorhombic symmetry, *mmm*. In addition, powder photographs in both 9-cm. and 19-cm. diameter cameras were taken of the following specimens, A4, D1, D4, E2, G4. These photographs were identical apart from very minor differences not to be ascribed to differences in crystal-structure. The X-ray examination

therefore showed that the synthetic material was identical with that found in slags of different sources, and that the marked difference in habit observed had no structural significance. The dimensions of the orthorhombic unit cell are:

$$a \ 10.1, \ b \ 6.7, \ c \ 15.4 \text{ \AA.}; \ a:b:c = 1.51:1:2.30.$$

The space-group is probably *Pnnn*. The unit-cell molecular weight corresponding to the measured density of 3.06 is 1930, in good agreement with the molecular weight 1925 of four ideal formula units  $5\text{CaO} \cdot \text{SiO}_2 \cdot \text{P}_2\text{O}_5$ .

The X-ray photographs were taken with nickel-filtered Cu- $K\alpha$  radiation. One of the Laue photographs was particularly good and is reproduced in fig. 1, as is the best of the powder photographs (fig. 2). In table II are listed the spacings of the lines observed on the powder photograph of specimen A4 taken in a 19-cm. diameter camera with filtered Cu- $K\alpha$  radiation,  $\lambda \ 1.54 \text{ \AA.}$

#### Morphology.

1. *Prismatic*.—The crystals from samples B and D were essentially similar. They are minute, stout, orthorhombic crystals less than 0.5 mm. in length, and are evidently closely similar to those which Miers examined. They are also similar to those illustrated by Bücking and Linck, and Carnot's crystals were probably of this type. Our crystal from B is depicted in fig. 3. The crystal examined from D did not show the (100) face.

We have chosen the same orientation of axes as Miers, and the axial ratios as determined by X-ray methods,  $a:b:c = 1.51:1:2.30$ , agree well with his values derived from goniometrical measurements, 1.5023:1:2.2943. The X-ray and morphological unit-cells are thus identical. Approximate values of the interfacial angles are given below, together with the corresponding measurements by other authors.

			Riley and Segnit.	Miers.	Bücking and Linck.	Carnot.
(100):(101)	...	...	57°	56° 47'	56° 46'	—
(101):(001)	...	...	33	—	—	—
(101):(10 $\bar{1}$ )	...	...	66	66 26	—	66° 50'
(110):(1 $\bar{1}$ 0)	...	...	64	67 11	63 3	64 —

FIG. 2.

TABLE II. X-ray diffraction lines of silicocarnotite;  $d$  in Å.

8-516	2-030	1-403	1-133	0-974	0-851
7-763	2-003	1-393	1-123	0-968	0-849
5-610	1-955	1-381	1-117	0-961	0-847
5-272	1-893	1-364	1-107	0-956	0-845
4-542	1-881*	1-355	1-100	0-953	0-841
4-047	1-865	1-341	1-097	0-950	0-839
3-912	1-846	1-330	1-092	0-941	0-834
3-782	1-851	1-319	1-089	0-939	0-832
3-581	1-781	1-311	1-086	0-934	0-830
3-289*	1-747*	1-305	1-079	0-933	0-828
3-181*	1-733	1-292	1-072	0-930	0-825
3-080*	1-692	1-278	1-064	0-928	0-822
3-010*	1-672	1-261	1-059	0-924	0-816
2-953*	1-643	1-247	1-056	0-924	0-814
2-819†	1-623	1-240	1-052	0-921	0-808
2-706	1-602	1-234	1-043	0-908	0-807
2-603*	1-581	1-228	1-036	0-905	0-805
2-574*	1-558	1-216	1-030	0-903	0-803
2-534	1-544	1-211	1-027	0-899	0-801
2-459	1-532	1-201	1-024	0-897	0-798
2-340	1-515	1-195	1-013	0-876	0-796
2-335	1-505	1-192	1-001	0-874	0-794
2-295	1-501	1-184	0-996	0-871	0-792
2-269	1-494	1-172	0-994	0-870	0-785
2-219	1-478	1-160	0-991	0-865	0-783
2-170	1-464	1-156	0-987	0-863	
2-106	1-447	1-140	0-983	0-855	
2-077	1-411	1-136	0-979	0-853	

\* lines of approximately equal intensity.

† strongest line, probably 220.

All spacings were calculated using  $\lambda \text{Cu-K}\alpha = 1.5418 \text{ \AA}$ . (weighted mean of  $\alpha_1$  and  $\alpha_2$ ). Each line in an  $\alpha$ -doublet was recorded separately and appears in the table under its own apparent spacing. The first four highest spacing lines are 101, 002, 110, and 200.

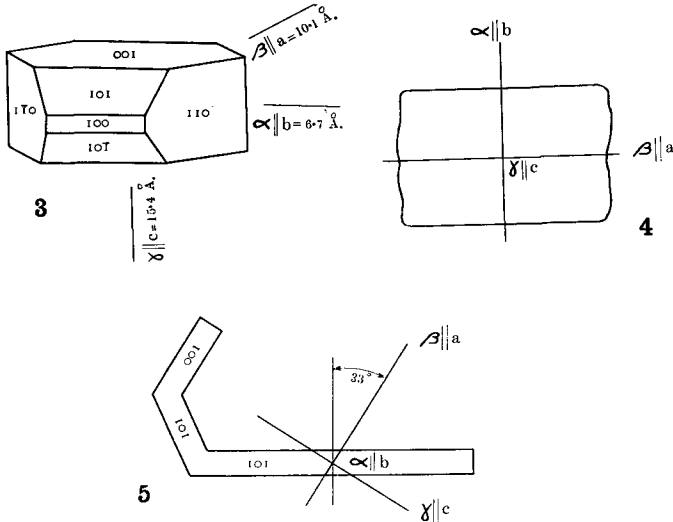
2. *Plates*.—These thin but large (up to 2 mm. square) plates of habit (001) were predominant in sample E. They show a perfect (010) and a poor (100) cleavage. The obtuse bisectrix  $\gamma$  is normal to the principal face (001) of the plates. The perfect (010) cleavage gives two parallel straight edges to the plates (fig. 4), while the poor (100) cleavage is sometimes seen at right angles to the other. Occasional fragments are rectangular.

3. *Blades*.—These thin blades of habit (101) are elongated parallel to the  $b$ -axis, and often show evidence of skeletal growth. The perfect (010)

FIG. 2. X-ray powder photographs of silicocarnotite, taken in a 19-cm. diameter camera with filtered Cu-K $\alpha$  radiation. One-half of the film only is shown.

cleavage is once more exhibited. A cross-section of a typical crystal is drawn in fig. 5, which also shows the orientation of the optical indicatrix. These blades were the main constituent of sample F, and they were also observed in sample E.

4. The separated grains showed no recognizable crystallographic faces and no significant observations were possible.



FIGS. 3-5. Crystals of silicocarnotite, showing optical orientation. (In fig. 3 the indices refer to faces intersected by the plane of section.)

5. A few crystals from E were examined only when mounted in microscope slides. In one case they appeared to be short pseudo-hexagonal prisms as viewed down the  $b$ -axis and were almost certainly orthorhombic. In the other case, they were long needles of lozenge-shaped cross-section elongated along the  $b$ -axis.

6. The long colourless pseudo-hexagonal prisms were observed in a slide of sample C. The crystals are elongated along the  $b$ -axis.

#### *Optical properties.*

The best measurements were obtained from the (001) plates (fig. 4) to which the obtuse bisectrix  $\gamma$  is normal. The relation of the optical scheme to the crystallographic axes is:

$$\alpha \parallel b, \beta \parallel a, \gamma \parallel c.$$

The optic orientations of the plates and blades are given in figs. 3-5.

The plates give a good interference figure, and the optic axial angle about  $\gamma$  was measured on the universal stage using filtered mercury light owing to the rather strong dispersion. The average of a large number of measurements gave:

$$2V \ 94\frac{1}{2}^\circ \text{ (yellow), } 94^\circ \text{ (green), } 92\frac{1}{2}^\circ \text{ (blue).}$$

Hence the optic sign is negative with dispersion  $r < v$  marked. The refractive indices, as determined in sodium-light ( $\alpha$  and  $\beta$  from the plates directly,  $\gamma$  as a maximum on crushed grains), are:

$$\alpha \ 1.641, \beta \ 1.653, \gamma \ 1.663 \pm 0.002.$$

The pleochroism is very striking. The crystals are a clear blue colour, and the change from blue to colourless is readily seen by the naked eye by rotation in polarized light. The pleochroism scheme is  $\alpha$  bright blue,  $\beta$  pale greyish-blue or colourless,  $\gamma$  light blue or colourless, absorption  $\alpha > \beta > \gamma$ .

The pleochroism and colour of the analysed material are weak in sections of normal thickness, but are sufficient to show the colour zoning of the grains; inner zones are colourless, outer pale blue. Marked dispersion is shown near the extinction positions in sections cut nearly normal to an optic axis, as well as in the interference figure. The optic axial angle measured in sodium-light varied in individual sections from  $76^\circ$  about  $\gamma$  to  $84^\circ$  about  $\alpha$ . Of zoned crystals, the inner parts have the lower  $2V$  about  $\gamma$ .

Table III summarizes the optical properties of a selection of specimens. The minimum and maximum refractive indices are  $\alpha \ 1.639$ ,  $\gamma \ 1.677 \pm 0.002$ . The birefringence is somewhat less than indicated by this owing to variation in composition of grains.

TABLE III. Optical properties of silicocarnotite.

Sample and habit.	Refractive Indices			Axial angle and sign.	Dispersion.
	$\alpha$ .	$\beta$ .	$\gamma$ .		
A4 ...	1.639	—	1.657	$+75^\circ$ to $-84^\circ$	$r > v$ marked
E2 ...	1.641	1.655	1.663	$-85^\circ$ (Na-light)	" "
D1 ...	1.648	—	1.669	$-80^\circ$ to $-85^\circ$	$r < v$ rather weak
B1 ...	1.642	—	1.661	$+80^\circ$ to $+85^\circ$	$r < v$ weak
C6 ...	1.640	—	1.658	$+77^\circ$	very weak
F3 ...	1.660	—	1.677	$-80^\circ$	—

All refractive index measurements  $\pm 0.002$ .

#### *Effect of heat.*

In an endeavour to gain some idea of the temperature of a possible phase transition, a number of samples were heated and then examined



optically and by X-ray powder photographs. Experiments with their results are as follows:

1. Silicocarnotite powder (sample A) heated to 1330° C. The only change was the disappearance of the blue colour. This was a characteristic change of the material and occurred in all the following cases. The X-ray powder photographs of the heated and unheated material were identical in all respects.

2. Further sample of A heated to 1450°. The product was a fine grey powder. Under the microscope a phase change was evident—grains were broken and showed fan extinction and fine multiple twinning. A careful comparison of the powder photograph given by this specimen with that of the unheated material showed slight but probably significant differences. The new structure must therefore be very closely related to the old.

3. A slab of the original slag from which A was separated was heated to 1400° C. A thin section showed a breaking up of the grains into smaller units, and undulose extinction over the larger original grain areas. Zoning was no longer evident, and 2V was determined as 83° positive. The small broken grains, however, appear homogeneous and do not show any change.

4. A clear blue plate, E2, about a millimetre square was first heated to 1330°. Apart from decolorization there was no change. The plate was further heated to 1450°. At this temperature it had broken down to a fine powder, and the grains showed broad twinning bands and irregular extinction.

5. Blades, F3, showed a similar reaction to the plate mentioned above.

These experiments indicate that a change certainly takes place below 1450° C., and probably above 1400° C.

*Acknowledgements.*—We desire to record our thanks to Professor C. E. Tilley for bringing the problem to our notice, and for his constant help; and also to Mr. K. Rickson for his assistance in the X-ray work.