

Calcium sulphosilicate in lime-kiln wall coating

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SUMMARY. Green calcium sulphosilicate layers were formed in lime-larnite-calcite wall coating in a lime kiln at Rivervale, Western Australia. The compound formed in the kiln flame area by the combination of siliceous lime sand feed with sulphur trioxide from the sulphurous oil fuel.

The calcium sulphosilicate is orthorhombic with a 10.183, b 15.408, c 6.825 Å, space group *Pcmm*. Crystals are [100] tablets or prisms elongated along c , D 2.95, hardness 5, streak pale green, decomposed by organic acids. Optical properties α 1.632 = [001] blue, β 1.638 = [100] yellow-green γ 1.640 yellow-green, $2V\alpha = 60^\circ$, dispersion $r > v$, X-ray powder lines: 2.855 (10) 032,202; 2.838 (7) 330,321; 3.35 (6) 012; 2.622 (6) 331; 2.571 (6) 060; 3.20 (5) 231; 1.962 (5); 1.899 (5); 1.896 (5); 1.372 (5).

Chemical analysis by P. Hewson gave: SiO₂ 21.50, Al₂O₃ 1.83, Fe₂O₃ 0.50, CO₂ 0.49, P₂O₅ 0.23, CaO 57.19, MgO 0.35, Na₂O 0.22, K₂O 0.22, SrO 0.15, Li₂O 0.06, SO₃ 16.71, H₂O⁺ 0.28, H₂O⁻ 0.10, others 0.04, total 99.87. On a water-free basis the unit cell contains Ca_{19.66} Mg_{0.17} Na_{0.14} K_{0.08} Sr_{0.03} Li_{0.08} S_{4.02}⁻ Si_{6.90} Al_{0.78} Fe_{1.2}⁺ C_{0.21} P_{0.06}⁻ O_{47.71}, approximately 4[Ca₅(SiO₄)₂SO₄] and isostructural with silicocarnotite, 4[Ca₅(PO₄)₂SiO₄]. Type material is preserved at the Government Chemical Laboratories, Perth, Western Australia.

IN 1966 the W.A. Government Chemical Laboratories received some unusual samples from a troublesome coating forming in a lime kiln at Rivervale, Western Australia. The samples were mainly composed of lime, calcite, and larnite with a little coarse green material. A preliminary determination of the limited sample showed some of the green crystals to be orthorhombic, *Pnma*, with optical properties and unit cell constants similar to silicocarnotite Ca₅(PO₄)₂SiO₄ partially described by Riley and Segnit (1949).

In 1969 well-crystalized material was supplied to the author for a complete study mainly carried out in 1970. The full data showed substantial agreement with the X-ray powder data, and physical and optical properties reported for calcium sulphosilicate, Ca₅(SiO₄)₂SO₄, by Sundius and Petersen (1960) and by Gutt and Smith (1966, 1967, 1968). Further publications since, by Lea (1970), also Scholze and Hildebrandt (1970), who reviewed all published work on the compound and silicocarnotite, have added to the knowledge of the compound.

The work of Keppler (1968) and the crystal structure analysis of Dickens and Brown (1971) have fully described silicocarnotite and shown the isostructural relationship with calcium sulphosilicate.

The data of the present paper, from a complete study of typical kiln material, serves to complement the earlier studies mainly made on materials synthesized in the laboratory.

*Conditions of formation.*¹ The kiln feed at the Rivervale kiln is a natural lime sand with major components approximately 83 % CaCO₃ (as fine calcite) and 13 % SiO₂

¹ Described by P. J. Longley, Chemist, Swan Portland Cement Ltd., Riverdale, Western Australia.

(as quartz grains). The kiln is fired with a flame temperature of 1500 to 1600 °C using air-blast injected fuel-oil containing 3.8 % sulphur.

The green calcium sulphosilicate forms in the flame area between the refractory lining (30 % Al₂O₃ brick) and an outer layer of larnite. The kiln-wall coating in the flame area is maintained at approximately 1100 °C for as long as three weeks at a time.

At the cool end of the kiln a pink fine-grained CaSO₄ deposit builds up with deep exit-gas flow lineation. Kiln exit gas is mainly N₂ with approximately 20 % CO₂ and 5 % each of O₂ and SO₃.

TABLE I. *Chemical composition of calcium sulphosilicate and unit-cell contents calculated on a water-free basis, with specific gravity corrected for the water found*

	1	2	3			
SiO ₂	21.50	24.99	Si ⁴⁺	6.90	8.07	
Al ₂ O ₃	1.83	—	Al ³⁺	0.78		
Fe ₂ O ₃	0.50	—	Fe ³⁺	0.12		
CO ₂	0.49	—	C ⁴⁺	0.21		
P ₂ O ₅	0.23	—	P ⁵⁺	0.06		
CaO	57.19	58.35	Ca ²⁺	19.66	20.16	
MgO	0.35	—	Mg ²⁺	0.17		
Na ₂ O	0.22	—	Na ⁺	0.14		
K ₂ O	0.22	—	K ⁺	0.08		
SrO	0.15	—	Sr ²⁺	0.03		
Li ₂ O	0.06	—	Li ⁺	0.08	4.02	
SO ₃	16.71	16.66	S ⁶⁺	4.02		
H ₂ O ⁺	0.28	—	O ²⁻	47.71		47.71
H ₂ O ⁻	0.10	—				
Others*	0.04	—				
Total	99.87	100.00				

* FeO 100, Cr₂O₃ 150, TiO₂ 50, NiO 50, PbO 50, MnO 50, CuO 35, ZnO 5 p.p.m.

1. Analysis by P. Hewson on sample with D 2.95 ± 0.01.

2. Ca₅(SiO₄)₂SO₄; D calc. 2.957.

3. Unit-cell contents calculated on a water-free basis, with D 2.96 (corrected for 0.38 % H₂O) and V 1075 Å³.

Physical properties. Calcium sulphosilicate occurs in the kiln coating mainly as layers of granular nodules composed of radiating needles and blades with deeply etched surfaces and intergrown larnite. The largest crystals seen were thin [100] tablets elongated along *c*, 0.2 mm long, with minor development of prism and dome faces. The calcium sulphosilicate layers are Ridgway (1912) Deep Greenish Glauous 33^{'''}d to Dark Greenish Glauous 33^{'''}b with streak Greenish Glauous 33^{'''}f. H. 5, D 2.95 ± 0.01, lustre subvitreous, crystals are brittle and decomposed by organic acids.

Optical properties. α 1.632 || [001], Bremen Blue 43'b; β 1.638 || [100]; γ 1.640; β and γ Light Dull Green–Yellow 27'd, R.I.calc = 1.62, 2V_α = 60 ± 1°, simple twinning on *a* {100}, dispersion *r* > *v*.

Chemistry. A sample with $D = 2.95 \pm 0.01$, by sink-float centrifuge method, was prepared for analysis by repeated separations with bromoform–methylene iodide mixtures to better than 99.5% purity by optical examination. The slight impurity was adherent larnite, portlandite, and minute inclusions, most likely brownmillerite.

The analysis, Table I, was made by a combination of well known gravimetric, volumetric, and atomic absorption methods. The results indicate a composition close to $\text{Ca}_5(\text{SiO}_4)_2\text{SO}_4$ with some isomorphous replacements.

TABLE II. *X-ray powder data for calcium sulphosilicate; Guinier focusing camera, Cu-K α_1 radiation, ThO $_2$ internal standard, I visual*

<i>hkl</i>	<i>I</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i>	<i>d</i> _{obs}	<i>I</i>	<i>d</i> _{obs}
110	2	8.51 Å	8.51 Å	1	2.471 Å	2	1.713 Å
020	2	7.71	7.71	1	2.366	2	1.704
101	2	5.70	5.69	2	2.295	2	1.701
111	1	5.36	5.34	1	2.293	4	1.672
121	3	4.59	4.58	1	2.283	1	1.658
201	3	4.10	4.10	1	2.238	1	1.599
211	4	3.96	3.96	3	2.210	2	1.588
040	1	3.85	3.85	4	2.175	2	1.565
131	1	3.81	3.81	1	2.141	2	1.555
221	1	3.62	3.62	1	2.085	4	1.531
012	6	3.35	3.35	3	2.066	3	1.514
231	5	3.20	3.20	1	2.025	3	1.490
141	4	3.19	3.19	3	2.019	3	1.388
022	3	3.13	3.13	5	1.962	5	1.372
301	4	3.05	3.05	1	1.953	3	1.354
122	3	3.00	3.00	1	1.931	2	1.334
311	2	2.990	2.990	5	1.899	1	1.326
150	1	2.945	2.952	5	1.896	1	1.318
032	10	2.855	2.851	1	1.851	3	1.274
202			2.846	3	1.841	1	1.246
330	7	2.838	2.838	2	1.825	1	1.235
321			2.835	2	1.820	1	1.196
132	2	2.752	2.747	3	1.808	1	1.170
151	1	2.712	2.711	2	1.783	1	1.137
331	6	2.622	2.622	2	1.778	1	1.126
060	6	2.571	2.570	4	1.759	1	1.115
042	2	2.565	2.562	3	1.750	1	1.108
232	1	2.488	2.490	3	1.742		

X-ray data. Weissenberg photographs show calcium sulphosilicate to have the same systematic extinctions as silicocarnotite which is classified as *Pnma* by Dickens and Brown (1971). The conventional orientation ($c < a < b$) of *Pcmm* is used in this paper for calcium sulphosilicate.

The powder X-ray data, Table II, was measured on films from a Guinier–Hagg focusing camera using Cu-K α_1 radiation and ThO $_2$ internal standard. A parameter refinement using the method described by Pryce (1970) gave a 10.183 ± 0.001 , b 15.408 ± 0.005 , c 6.852 ± 0.001 Å, axial ratios 0.6609:1:0.4447, approximately $\frac{2}{3}:1:\frac{1}{3}$, V 1075 Å 3 . Interchanging the a and b axes shows a close comparison with the

unit cell reported by Gutt and Smith (1971), b 10.18 ± 0.01 , a 15.41 ± 0.02 , c 6.84 ± 0.01 Å. Interchanging the a and c axes shows a close comparison with the axes of silico-carnotite, c 10.132 , b 15.508 , a 6.737 Å, reported by Dickens and Brown (1971).

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