

THE MINERALOGICAL MAGAZINE

AND

JOURNAL OF THE MINERALOGICAL SOCIETY

No. 222

September, 1953

Vol. XXX

Crestmoreite and riversideite.

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[Read June 12, 1952.]

A. INTRODUCTION.

THESE two minerals were described by Eakle² from the crystalline limestone at Crestmore, Riverside County, California. Both were shown to be hydrated monocalcium silicates, containing small amounts of P_2O_5 , SO_3 , and CO_2 , occurred with a fibrous habit, and had closely similar optical properties. They were distinguished chiefly by the higher water content (approx. 1.3 mol.) of crestmoreite as compared with riversideite (0.5 mol.), and by the fact that the former was included directly in the calcite, whereas the latter formed veins in masses of idocrase which were contained in it. The minerals had been produced under hydrothermal conditions caused by igneous intrusions. In both cases, the primary material was believed to have been wilkeite, which is an apatite mineral with much of the phosphorus replaced by sulphur, silicon, and possibly carbon. Due to the fibrous nature of both minerals, optical determinations are difficult; data are given by Eakle, Larsen,³ and Fairbanks.⁴

Flint and co-workers⁵ investigated one specimen of crestmoreite, and two described as riversideite, by X-ray powder photographs. They

¹ Now at Department of Chemistry, University of Aberdeen.

² A. S. Eakle, Bull. Dept. Geol. Univ. California, 1917, vol. 10, no. 19, p. 327. [M.A. 1-20.]

³ E. S. Larsen, Bull. U.S. Geol. Surv., 1921, no. 679, p. 280. [M.A. 1-367.]

⁴ E. E. Fairbanks, *in* Winchell, Optical mineralogy. 2nd edit., 1927, p. 227; 4th edit., 1951, p. 421.

⁵ E. P. Flint, H. F. McMurdie, and L. S. Wells, Journ. Res. Nat. Bur. Stand. U.S.A., 1938, vol. 21, p. 617. [M.A. 7-283.] H. F. McMurdie and E. P. Flint, *ibid.*, 1943, vol. 31, p. 225. [M.A. 9-45.]

found that the crestmorite gave a characteristic pattern, and that one specimen described as riversideite was identical with the crestmorite, whereas the other was in reality foshagite. They also found, contrary to Eakle's results, that most of the water in crestmorite in excess of that present in riversideite was lost at 110°, and that this did not alter the X-ray pattern. They concluded that riversideite was not a distinct species, and proposed that the name be dropped. Clark and Bunn¹ also obtained X-ray data for riversideite, which differ slightly from those of McMurdie and Flint. Data close to those in Clark and Bunn's paper are given on card II-1298 of the American Society for Testing Materials.²

Although a number of other hydrated calcium silicate minerals have been synthesized, material has never been obtained in the laboratory giving an X-ray pattern and optical data identical with those of natural crestmorite or riversideite. Alcock, Clark, and Thurston³ found, however, that a boiler scale gave an X-ray pattern similar to that of crestmorite.

Nomenclature.—The suggestion that the name riversideite be discarded in favour of crestmorite has met with general acceptance, and the latter name has therefore been adopted in the following account. The name tobermorite is used for the mineral discovered by Heddle⁴ and for the artificial product, 'calcium silicate hydrate (I)',⁵ which has been found⁶ to be substantially identical with it. It has been shown⁷ that this substance exists in several distinct states of hydration, which do not differ fundamentally from each other in crystal structure; and, pending the adoption of agreed nomenclature for the separate hydration states, the name tobermorite is used broadly to include all of them without further particularization.

B. EXAMINATION OF CRESTMOREITE.

I. *Material.*

A specimen labelled 'riversideite' (B.M. 1921,101) was made available by courtesy of the Trustees of the British Museum, and two others, also

¹ L. M. Clark and C. W. Bunn, *Journ. Soc. Chem. Indust.*, 1940, vol. 59, p. 155. [M.A. 8-116.]

² American Society for Testing Materials, first supplement to card file of X-ray diffraction data, 1944; from data supplied by Imperial Chemical Industries, Northwich, England.

³ T. C. Alcock; L. M. Clark, and E. F. Thurston, *Journ. Soc. Chem. Indust.*, 1944, vol. 63, p. 292. [M.A. 9-103.] L. M. Clark, *Min. Mag.*, 1948, vol. 28, p. 362.

⁴ M. F. Heddle, *Min. Mag.*, 1880, vol. 4, p. 119.

⁵ H. F. W. Taylor, *Journ. Chem. Soc. London*, 1950, p. 3682. [M.A. 11-314.]

⁶ G. F. Claringbull and M. H. Hey, *Min. Mag.*, 1952, vol. 29, p. 960.

⁷ H. F. W. Taylor, *Journ. Chem. Soc. London*, 1953, p. 163. [M.A. 12-172.]

labelled 'riversideite', were kindly supplied by Professor A. Pabst from Eakle's original collection at California University. In each case the material was soft, white, and fibrous in accordance with Eakle's description. The British Museum specimen was supplied free from adjacent minerals, although microscopic and X-ray single-crystal investigation revealed the presence of minute traces of idocrase, and of a second fibrous species which could not be identified; rotation photographs showed that the repeat distance along the fibre axis of the latter was 6.86 Å. The crestmoreite in the two specimens from Eakle's collection was present as veins a few millimetres thick. These were of irregular shape, and the fibres of which they were composed only remained parallel over small regions. Idocrase, diopside, calcite, and wollastonite were present in close proximity to each other and to the crestmoreite.

2. *Optical examination.*

All three specimens broke down, on rough crushing, into flakes which were apparently composed of approximately parallel fibres. Unless very thin, they were almost opaque, and only incomplete optical data could be obtained. Flakes from any of the specimens, when lying on the principal cleavage, had mean refractive indices within the range 1.59–1.60, with very low birefringence. Extinction was uneven, but always broadly parallel to the fibre direction. Some flakes had positive elongation and others negative elongation; the latter was observed chiefly in the case of flakes from either of the specimens from Eakle's collection. Satisfactory observations could not be made on flakes in other orientations. These results agree with those given by Eakle, except for the signs of elongation, which he states to be positive for both crestmoreite and riversideite.

3. *X-ray powder investigation.*

X-ray powder photographs were taken of each of the crestmoreite specimens, using cameras of 6 cm. and 19 cm. diameter with Cu- $K\alpha$ radiation. The results (table I) are in substantial agreement with those of earlier investigators. Agreement is best with the data on card II-1298 of the A.S.T.M. index, and worst with those of McMurdie and Flint, but there can be little doubt that in every case the same substance was being examined.

A comparison with photographs of wilkeite and of synthetic 'calcium silicate hydrate (I)' (table I) shows that, with certain minor exceptions, all the crestmoreite lines can be accounted for, if this substance is a

TABLE I. X-ray data for synthetic tobermorite, crestmoreite, and wilkeite. Spacings in Å.

Synthetic tobermorite. ¹	Specimen labelled 'Riversideite' (B.M. 1921,101).	Specimen labelled 'Riversideite' (Eakle's collection).	Wilkeite (B.M. 1914,1129). ²
—	14.0 vs	14.0 s	—
11 s	11.2 mw	11.2 w	—
—	8.2 mw	8.2 m	8.2 mw
5.6 ms	5.6 m	5.6 mw	—
—	—	—	5.1 vw
—	4.7 w	—	—
—	—	4.1 vvw	4.1 vw
—	3.90 vvw	3.90 vw	3.90 vw
3.55 vvw	3.73 vw	—	—
—	3.45 ms	3.45 ms	3.45 ms
3.28 vvw	3.25 mw	—	—
—	—	—	3.16 vw
3.07 vvs	3.07 vs	3.07 ms	3.07 vw
2.97 s	2.97 s	2.97 mw	—
2.80 s	2.80 vvs	2.81 vvs	{ 2.82 vs 2.79 ms
—	2.72 vs	2.72 vs	2.72 s
—	2.62 m	2.62 ms	2.62 ms
2.52 vw	—	—	—
2.48 vw	—	—	—
2.28 ms	2.29 ms	2.29 mw	—
—	2.27 m	2.27 ms	2.27 ms
2.15 m	2.15 mw	2.15 w	2.15 w
2.07 m	2.07 s	2.07 w	2.07 vw
—	—	2.03 vw	2.03 vvw
2.00 m	2.00 mw	2.00 vw	2.00 vw
1.93 vvw	1.94 s	1.94 vs	1.94 ms
—	1.88 w	1.88 vw	1.88 m
1.83 vs	1.83 vs	1.83 vs	1.83 s
1.81 vvw	1.80 mw	1.80 ms	1.80 mw
—	1.77 w	1.77 m	1.77 mw
1.76 vvw	—	—	—
—	1.74 w	1.74 m	1.74 mw
1.71 vvw	1.71 mw	1.71 ms	1.71 m
1.67 s	1.67 ms	1.67 w	—
—	1.63 vw	1.63 mw	1.63 w

¹ Sample 58, of approximate composition $\text{CaSiO}_3 \cdot \text{H}_2\text{O}$, prepared by L. Heller and H. F. W. Taylor (Journ. Chem. Soc. London, 1951, p. 2397; 1952, p. 1018. [M.A. 11-471]), and described there as 'calcium silicate hydrate (I)'. The data in column 1 are slightly more accurate than those given in the original paper, and are the same as those quoted by Claringbull and Hey (1952).

² Data separately determined for a specimen of wilkeite.

Relative intensities: s = strong, m = moderate, w = weak, v = very, d = diffuse.

TABLE I (continued).

Synthetic tobermorite.	'Riversideite' (B.M. 1921,101).	'Riversideite' (Eakle's collection).	Wilkeite (B.M. 1914,1129).
1·61 vw	1·61 vw	1·61 vvw	1·61 w
1·59 vvw	—	—	—
1·53 m	1·53 w/d	1·53 w/d	—
—	1·50 w	1·50 mw	1·50 w
—	1·47 w	1·47 m	1·47 mw
—	1·45 mw	1·45 m	1·45 m
1·43 vw	1·43 mw	1·43 m	1·43 mw
1·405 w } 1·395 w }	1·40 w/d	1·40 mw	—
1·370 vvw	—	—	—
—	—	1·36 vw	1·36 vvw
—	1·33 vw	1·33 vw	1·33 vw
—	1·32 vw	1·32 vw	1·32 vvw
—	1·28 vw	1·28 vw	1·28 vvw
1·260 vvw	1·26 vw	1·26 vw	1·26 w
—	1·24 w	1·24 w	1·24 w
1·225 vw	1·23 vw	1·23 w	1·23 vw
1·185 vvw	1·180 vvw	—	—
1·160 vvw	1·155 vw	1·155 vw	1·155 vw
—	1·145 vw	1·145 vw	1·145 vw
—	1·135 vvw	1·135 vvw	1·135 vvw
—	1·115 vw	1·115 vw	1·115 vw
—	1·105 vw	1·105 vvw	1·105 w
1·110 w	1·100 vw	1·100 w	—
1·075 vw	1·075 vw	—	—

mixture of tobermorite and wilkeite. The proportion of the latter constituent appears to be lower in the British Museum specimen than in the two specimens from Eakle's collection, which gave almost identical photographs.

4. X-ray single-crystal investigation.

Rotation and zero-layer Weissenberg photographs (figs. 1 and 2 respectively) were taken about the fibre axis of a flake from the British Museum specimen. They show two distinct and superimposed patterns, viz.:

(i) A pattern of relatively sharp spots, which could be indexed on a hexagonal cell having $a\ 9.45 \pm 0.05$, $c\ 6.90 \pm 0.05$ Å. The c -axis was parallel to the fibre direction. These conclusions were confirmed by taking oscillation photographs about c and a , a first-layer Weissenberg photograph about c , and a Laue photograph with the X-ray beam parallel to c . The parameters obtained agree with those found by

McConnell¹ for wilkeite (a 9.48, c 6.91 and a 9.40, c 6.89 Å. for specimens containing respectively 14.4 and 32.2% of P_2O_5). Comparison of the photographs with corresponding ones of wilkeite (B.M. 1914,1129) showed close agreement as regards intensities of corresponding reflections.

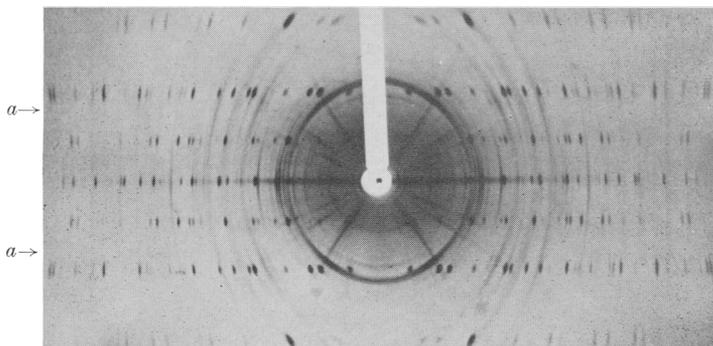


FIG. 1. X-ray photograph of crestmoreite (B.M. 1921,101). Rotation about the fibre axis. a,a : second layer-line of the tobermorite constituent.

(ii) A preferred orientation pattern, consisting of arcs in the oscillation and rotation photographs (fig. 1), and of streaks in the Weissenberg photographs (fig. 2). Direct comparison showed that this preferred orientation pattern, as seen in the oscillation and rotation photographs, was in substantial agreement with the powder pattern of synthetic tobermorite

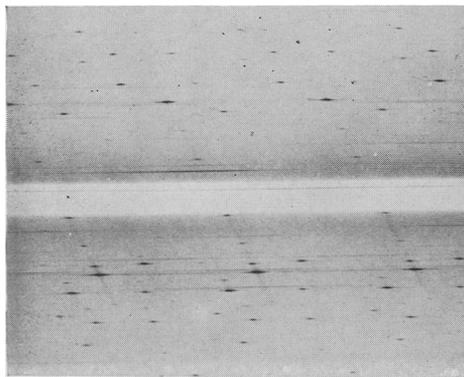


FIG. 2. X-ray photograph of crestmoreite (B.M. 1921,101). Zero-layer Weissenberg about the fibre axis.

(fig. 3), although certain discrepancies were observed which corresponded with those noted in connexion with the powder investigation. It has been shown elsewhere (Taylor, 1953, loc. cit.) that variations

¹ D. McConnell, Amer. Min., 1937, vol. 22, p. 977. [M.A. 7-14.]

in the X-ray pattern of 'calcium silicate hydrate (I)' are caused by differences in the hydration state, and inspection of the photographs showed that this provided a satisfactory explanation of the dis-

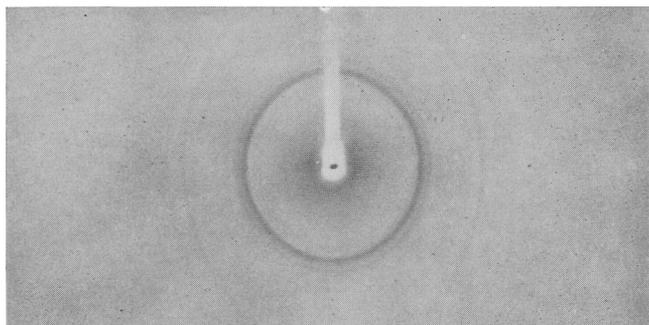


FIG. 3. X-ray powder photograph of synthetic tobermorite (specimen for which data are listed in table I).

crepancies in the present case. The preferred orientation patterns showed a repeat distance in the *b*- or fibre direction of 7.30 \AA . The odd layer-lines on rotation about this axis are very weak, and cannot be seen in the reproduction (fig. 1).

5. *Qualitative mineral composition.*

The effects described above might be ascribed to the chance association of crystals, or fibres, of the two minerals. However, certain facts exclude this explanation. Twelve crystals, taken from different parts of all three specimens, and varying in size from under 100μ to 800μ in length, were studied, and in all cases the same effect was observed. The *c*-axis of the wilkeite, the fibre direction, and the mean direction of the crestmorite *b*-axis always coincided. Among crystals from any one specimen no significant differences could be observed either in the relative intensities of the two patterns, or in the degree of orientation of the crestmorite, although, in accordance with the powder data, the British Museum specimen appeared to be richer in the latter constituent than were those from Eakle's collection. Finally, no crystals of wilkeite were visible under the microscope.

The only possible explanation is that the flakes are very close intergrowths of crestmorite and wilkeite. This probably accounts for their opacity, a characteristic that was observed by Eakle. The individual regions occupied by the two minerals are apparently sub-microscopic, and ordinary methods of separation are likely to be impracticable.

6. *Chemical analysis.*

The results of a chemical analysis of one of the specimens (labelled 'riversideite') from Eakle's collection are given in table II, column 1.

TABLE II. Chemical analyses of crestmoreite.

	1.	2.	3.	4.	5.	6.
SiO ₂	27.4	3.0	35.3	1.00	38.30	1.00
TiO ₂	< 0.1	—	< 0.1	< 0.002	—	—
Al ₂ O ₃	0.9	—	1.3	0.02	—	—
Fe ₂ O ₃	0.3	—	0.4	0.005	—	—
MgO	1.0	—	1.4	0.06	—	—
CaO	48.8	11.3	48.2	1.46	41.20	0.97
P ₂ O ₅	4.9	4.9	—	—	3.50	—
SO ₃	4.0	4.0	—	—	1.25	—
CO ₂	3.3	—	—	—	—	—
H ₂ O(110°)	3.7	—	13.3	1.26	15.17	1.35
H ₂ O(450°)	5.1					
H ₂ O(1000°)	0.4					
	99.9	23.2	100.0		99.42	

1. Crestmoreite, Crestmore, California, from A. S. Eakle's collection. Analyst, F. J. McConnell, on 0.47 gm. Sp. gr., 2.45. Total iron as Fe₂O₃. H₂O loss at 110° under water-vapour pressure 6 mm. to reach equilibrium; at 450° also at 6 mm.; at 1000°, loss after deduction of CO₂.

2. Oxides allocated to wilkeite.

3. Column 1 after deduction of wilkeite (23.2 %) and calcite (7.5 %), and calculated to 100%.

4. Molecular ratios calculated from column 3.

5. One of three closely agreeing analyses of crestmoreite (A. S. Eakle, 1917). Eakle also gave an analysis of riversideite, as do Clark and Bunn (1940), whose results, however, show that the material analysed was really crestmoreite.

6. Molecular ratios from column 5 after deducting wilkeite.

Portions of this material had been used in the X-ray work already described. The material had been carefully selected, fibre by fibre, under the microscope, and except for a small proportion of calcite, no other minerals could be detected. In order to interpret the results, it was necessary to correct for the presence of the wilkeite, and as the composition of this mineral is very variable, this could only be done approximately. It was assumed that the wilkeite contained all the P₂O₅ and SO₃, together with amounts of CaO and SiO₂ required by the formula 3Ca₃(Si,P,S)₂O₈.CaO. By allowing for the oxides thus allocated to wilkeite (column 2), and deducting also CO₂ as calcite, an approximate estimate of the composition of the hydrated calcium silicate was obtained (columns 3 and 4). For comparison, one of Eakle's three analyses of

crestmoreite is included, together with the molar ratios calculated from it on the assumption that the P_2O_5 and SO_3 are present as wilkeite (columns 5 and 6).

Due to the assumptions which have to be made, it would be wrong to place too much reliance on these results. They nevertheless support the conclusion reached from the X-ray work, that the specimen contains wilkeite together with a hydrated calcium silicate, and suggest further that this has a composition comparable to that of Eakle's crestmoreite.

C. EXAMINATION OF SPECIMENS LABELLED 'CRESTMOREITE'.

Two specimens labelled 'crestmoreite' were examined. One (B.M. 1919,2) was from the British Museum collection, and the other, supplied by courtesy of Professor A. Pabst, was from Eakle's original collection. Both consisted of inclusions of soft, white, fibrous material in blue calcite, in agreement with the original description. X-ray powder and single-crystal photographs showed, however, that both consisted mainly of an apatite mineral, with unit-cell dimensions near to those of wilkeite. This was confirmed by chemical analysis in the case of the specimen from Eakle's collection, which consisted of a mixture of calcite and wilkeite.

X-ray single-crystal photographs of the British Museum specimen showed, in addition to the strong pattern of spots characteristic of the apatite mineral, a number of weak powder-lines. The spacings and relative intensities of these showed a general resemblance to those of the micas and other minerals containing $(Si_2O_5)_n$ sheets of hexagonal type. A small proportion of a second species was thus present, unoriented and intergrown with wilkeite. Insufficient material was available for analysis, and it was not therefore possible to establish whether this species was a hydrated calcium silicate; but this might be considered unlikely, in view of the fact that the calcium ion is apparently too large to occupy the octahedral positions in structures of this type.

D. DISCUSSION.

The present results show that all three of the specimens labelled 'riversideite' were sub-microscopic intergrowths of tobermorite and wilkeite. The X-ray powder data for these specimens are in agreement with those found for 'crestmoreite' by Flint, McMurdie, and Wells, and with those found for 'riversideite' by the same investigators and by Clark and Bunn. Hence, if the two specimens labelled 'crestmoreite' that were examined in the present investigation can be discounted, all

specimens described as crestmorite or riversideite for which X-ray data are available have been composed of tobermorite and wilkeite. It is probable that in all cases the two constituents were intergrown in the same way, as any coarser mixture could hardly have escaped detection.

The appearance of the hand-specimens, the optical properties, and the chemical analyses (given by Clark and Bunn and in the present investigation) are sufficient to establish that all the above specimens consisted of essentially the same material as the crestmorite and riversideite originally examined by Eakle. All the evidence is thus consistent with the view that the specimens from the Crestmore locality, which have been called crestmorite or riversideite, are sub-microscopic intergrowths of tobermorite and wilkeite.

Some observations on the state of hydration of the crestmorite in one of the specimens described here have been reported elsewhere.¹ They showed that the crestmorite was a mixture of two hydration states having water contents of approximately 2.5 and 1.0 molecules respectively. Further examination now in progress suggests that a small proportion of the hemihydrate is probably also present and that still other hydrates may also exist in the material. The crestmorite in the intergrowths from Crestmore is thus a complex mixture as regards hydration state, and it is reasonable to conclude that the differences between the water contents of various specimens, including Eakle's original crestmorite and riversideite, are due to differences in the relative proportions of the several hydrates present.

Due to the presence of wilkeite, the optical and X-ray data which have been attributed to crestmorite differ appreciably from those of pure tobermorite, as found (in the case of natural material) by Claringbull and Hey. This accounts for the fact that attempts to synthesize material with properties similar to those attributed to crestmorite have not succeeded, since in all cases the starting materials have contained only lime, silica, and water. On the other hand, tobermorite is readily obtained in the laboratory under hydrothermal conditions,² and its formation at Crestmore may therefore be understood. Alcock, Clark, and Thurston's observation that a boiler scale gave an X-ray pattern similar to that of crestmorite may also be explained, since a mixture of

¹ H. F. W. Taylor, *Journ. Chem. Soc. London*, 1953, p. 165. [M.A. 12-172.] The specimen was of crestmorite from A. S. Eakle's collection, labelled 'riversideite', by which name it was (incorrectly) described in that paper.

² L. Heller and H. F. W. Taylor, *Journ. Chem. Soc. London*, 1951, p. 2397; 1952, pp. 1018, 2535. [M.A. 11-471, 12-83.]

tobermorite and some apatite mineral could well have been formed in the scale. This mixture would give an X-ray powder pattern similar to that of crestmoreite.

Acknowledgements.—I thank Professor J. D. Bernal, F.R.S., for his interest and advice; the Trustees of the British Museum, and Professor A. Pabst, for the mineral specimens; and Mr. F. J. McConnell (Building Research Station, Watford, Hertfordshire) for the chemical analysis. The work was carried out as part of an extra-mural contract for the Building Research Board, and I thank the Director of Building Research for permission to publish this paper.
