

*The hydrated calcium silicates riversideite, tobermorite,
and plombierite.*

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INTRODUCTION.

IN a recent paper Taylor has shown that three distinct hydration levels exist within the 'calcium silicate hydrate (I)' group of artificial preparations (Taylor, 1953*a*, p. 168). The individual hydrates may be distinguished from the position of the 002 reflection in X-ray powder photographs. The *d* spacings corresponding to the three hydrates of this group examined during the present investigation are 14.6, 11.3, and 9.6 Å. These hydrates have H₂O:SiO₂ molar ratios of approximately 2.0, 1.0, and 0.5 respectively.

A recent examination of the minerals crestmoreite and riversideite (Taylor, 1953*b*) has shown that both these minerals are intimate intergrowths of members of the above hydrate series with the mineral wilkeite. Both the artificial preparations and the crestmoreite-riversideite intergrowths have failed to provide material suitable for detailed optical study.

During a mineralogical investigation of rocks from a dolerite-chalk contact at Ballycraigy, Larne, County Antrim, a mineral was examined and subsequently identified, from X-ray powder photographs, with the 11.3 Å. hydrate referred to above. Optical and X-ray studies on single crystals of this mineral were made and subsequently both the 14.6 and 9.6 Å. hydrates were prepared from this material experimentally.

X-ray powder photographs of a gelatinous material collected at Ballycraigy showed that this material could also be identified with the 'calcium silicate hydrate (I)' group. A chemical analysis of this substance showed that, in composition, it was closely comparable to the mineral plombierite, a gelatinous material originally described by Daubrée (Daubrée, 1858*b*). That plombierite, as defined by Daubrée, is a gelatinous member of the 'calcium silicate hydrate (I)' group is thought to be highly probable.

NOMENCLATURE.

Precise determination of the optical properties of the individual crystalline hydrates of this group led, inevitably, to the problem of their future nomenclature. In discussing the nomenclature used in the past three facts must be considered:

(1) In the absence of a suitable technique, now provided by X-ray examination, the presence of several hydration states in any hydrate sample could not be readily appreciated. The present investigation has shown that the optical properties of mixed hydrates are mean values.

(2) The instability of the crystalline hydrates of low 002 spacing at normal room-temperature and humidity was not formerly recognized. This instability makes it imperative that specimens of the pure hydrates, once examined, should be stored under conditions which prevent further hydration.

(3) Both crestmoreite and riversideite as described by Eakle (1917) have now been shown to be intimate intergrowths of the hydrate minerals with wilkeite (Taylor, 1953*b*).

As a direct consequence of the fact that no special precautions were taken by Eakle to preserve the riversideite specimens examined by him these now contain only minor amounts of the 9.6 Å hydrate. Thus the high water content of the riversideite specimens examined by Flint (Flint and others, 1938) and Taylor (1953*b*, p. 156) was correctly taken to indicate that the specimens of riversideite examined could be identified with crestmoreite, as defined by Eakle. The conclusion reached by Flint that crestmoreite and riversideite, as defined by Eakle, were identical was, however, invalid on the basis of the present reasoning. Distinctive optical and X-ray characteristics have now been demonstrated for the 9.6 Å hydrate, which is thought to have been the primary hydrate component of the intergrowths described by Eakle as riversideite. Accordingly it is here suggested that the name riversideite be reserved for the 9.6 Å hydrate, should this be found and preserved in an unhydrated state. It should be noted that the chemical composition given by Eakle for riversideite approximates to that of the 9.6 Å hydrate (Eakle, 1917, p. 347).

Claringbull and Hey (1952) have shown, from X-ray powder data, that the mineral tobermorite as described by Heddle (1880) may be identified with the 'calcium silicate hydrate (I)' group of artificial preparations. The 002 reflection recorded by these authors indicates that this mineral is in the 11.3 Å hydration state. Accordingly the mineral name tobermorite will be used in the present account to describe material in

this hydration state. The relative stability of tobermorite from Skye in hydration experiments will be discussed later in the present paper in relation to its alkali content.

Examination of the X-ray powder photographs of the 14.6 Å. hydrate from Ballycraigy, where it results through the hydration of the 11.3 Å. hydrate, shows that its formation is accompanied by a decrease in the number and clarity of the reflections observed. This is associated with a breakdown of the relatively perfect crystal structure of the 11.3 Å. hydrate, and the 002 reflection recorded may be regarded as inherited from the ordered structure of the parent 11.3 Å. hydrate. The natural gels studied correspond in composition to the 14.6 Å. hydrate. In the gels crystallization is extremely imperfect and no 002 reflection has been recorded. Consequently the presence or absence of the 002 reflection is thought merely to be indicative of the degree of crystallization. In the event of plombierite being recognized as a member of the 'calcium silicate hydrate (I)' group this mineral name may be adopted to describe the hydrates of the series in which the $H_2O:SiO_2$ molar ratio approximates to 2.0. The present nomenclature is set out in table I.

TABLE I. Distinguishing characters of the calcium silicate hydrates.

	$H_2O:SiO_2$ molar ratio (approximate).	002 spacing.	Refractive indices.
Riversideite	0.5	9.6 Å.	α 1.600 β 1.601 γ 1.605
Tobermorite	1.0	11.3	α 1.570 β 1.571 γ 1.575
Plombierite	2.0	14.6	β 1.550
Gels	variable	absent	variable

THE 11.3 Å. HYDRATE FROM BALLYCRAIGY, LARNE, Co. ANTRIM.

This mineral occurs in cavities in contact-rocks at Ballycraigy. The dolerite-chalk contact from which these rocks were obtained is similar to that at Scawt Hill (Tilley, 1931) and was exposed in a temporary trench. The dolerite intrusion at Ballycraigy, one mile north of Larne, has no connexion with the Scawt Hill plug, six miles north of Larne. The hydrate mineral was found in association with the mineral scawtite in vugs in larnite-rocks from the endogenous zone of the contact, where it occurs as minute radiating aggregates of fibres. In hand-specimens the mineral is characterized by a distinctive silky lustre on cleavage faces and is seen to alter readily to a fine white powder, which

has been identified as the 14.6 Å. hydrate. In some cases the mineral is completely pseudomorphed by calcite. The occasional preservation of the unaltered 11.3 Å. hydrate is ascribed to the compact nature and desiccating action of the enclosing larnite-rocks. The mineral is preserved in the laboratory by storing it over silica gel.

The hydrate dissolves in hydrochloric acid leaving a gelatinous residue of silica, and qualitative microchemical tests indicate abundant calcium. The mineral has a hardness of $2\frac{1}{2}$ and its specific gravity, as determined by suspension, was found to be 2.44.

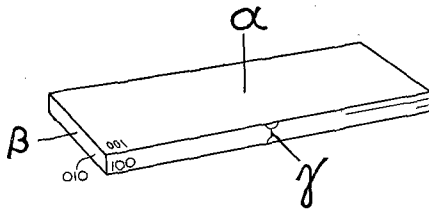


FIG. 1. Optical orientation of the 11.3 Å. hydrate.

In thin section, radiating fibres of the hydrate were found to have positive or negative elongation and straight extinction. The maximum birefringence observed was 0.005. From fibre aggregates in thin section, $2V$ was found to be small and positive, the optic axial plane lying normal to the length of the fibres. Single crystals of the hydrate were isolated and these were invariably found to be elongated flakes which lay on a perfect cleavage and showed a second cleavage parallel to the length. Crystals in this orientation were found to be negatively elongated. The refractive indices of the hydrate were determined as α 1.570, β 1.571, γ 1.575, all ± 0.002 . Weak dispersion was noted. The optical orientation of single crystals is illustrated in fig. 1. The crystallographic axes chosen from the single-crystal X-ray study had the following relationship to the optical directions: $a = \gamma$, $b = \beta$, $c = \alpha$. The perfect cleavage is consequently (001) and the second cleavage (100).

Determination of the refractive indices of partly hydrated crystals showed that these were appreciably lower than those given above, which were the values consistently obtained on fresh material. Partial hydration was invariably indicated by the opacity of the hydrated material. The results of a single-crystal X-ray study carried out on carefully selected material are given below (table II).

TABLE II. X-ray powder spacings of the calcium silicate hydrates.

A.		B.		C.		D.	
<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.
11.3	vvs	11.4	vvs	11	s	—	
5.55	vs	5.47	mw	5.6	ms	5.48	w b
3.84	vw	—	—	—	—	—	
3.57	ms	3.50	mw	3.55	vvw	—	
3.34	vw	3.34	vw	—	—	—	
3.24	vw	—	—	3.28	vvw	3.17	} ms b
3.11	ms	3.10	s	3.07	vvs	3.01	
2.99	ms	2.99	m	2.97	s	—	
2.83	vvs	2.82	ms	2.80	s	2.81	ms
2.75	vw	2.74	vvw	—	—	—	
2.53	m	2.52	vw	2.52	vw	—	
2.45	mw	2.45	vw	2.48	vw	—	
2.32	ms b	—	—	—	—	—	
2.29	m	2.30	w b	2.28	ms	—	
2.15	m	2.15	w	2.15	m	—	
2.10	m	2.09	vw	—	—	2.07	w
2.01	ms	2.01	mw	2.00	m	—	
—	—	—	—	1.93	vvw	—	
1.85	vs	1.847	m	1.83	vs	1.83	ms
—	—	—	—	1.81	vvw	—	
1.74	mw	—	—	1.76	vvw	—	
—	—	—	—	1.71	vvw	—	
1.676	ms	1.673	mw	1.67	s	1.67	w
1.627	ms	1.622	vw	1.61	vw	—	
1.570	w	—	—	1.59	vvw	—	
1.547	w	1.550	w	1.53	m	—	
1.511	vvw	1.503	vvw	—	—	—	
1.469	vvw	—	—	—	—	—	
1.442	vvw	1.442	vw	1.43	vw	—	
1.408	vvw	—	—	1.405	w	1.403	vw
1.401	vvw	1.402	vvw	1.395	w	—	
1.381	vvw	1.380	vvw	1.370	vvw	—	
1.293	vvw	1.290	vvw	—	—	—	
1.267	vvw	1.268	vvw	—	—	—	
1.261	vvw	1.258	vvw	1.260	vvw	—	
1.220	vvw	1.220	vvw b	1.225	vw	—	
1.198	vvw	—	—	—	—	—	
1.181	vvw	1.185	vvw	1.185	vvw	—	
1.168	vvw	1.170	vvw	1.160	vvw	—	
1.114	vvw	1.117	vvw b	1.110	w	—	
1.073	vvw	—	—	1.075	vw	—	
1.066	vvw	—	—	—	—	—	
1.029	vvw	—	—	—	—	—	
0.937	vvw	—	—	—	—	—	
0.921	vvw	—	—	—	—	—	
0.875	vvw	—	—	—	—	—	
0.836	vvw	—	—	—	—	—	
0.792	vvw	—	—	—	—	—	
0.780	vw	—	—	—	—	—	

A. Tobermorite from Ballycraig, County Antrim.

B. Tobermorite from Tobermory pier, Mull. (Claringbull and Hey, Min. Mag., 1952, vol. 29, p. 961.)

C. Artificial tobermorite, (Sample 58, Taylor, Min. Mag., 1953, vol. 30, p. 158.)

D. Natural 'calcium silicate hydrate (I)' gel (plombierite) from Ballycraig.

Scale of decreasing intensities: vvs, vs, s, ms, m, mw, w, vw, vvw, vvww, b = broad from visual estimation.

All photographs taken with $\text{Cu-K}\alpha$ radiation and *d* spacings given in Å. units.

Oscillation photographs taken for all three axes confirmed the orthorhombic symmetry of the mineral and indicated the following values for the dimensions of the unit cell: a 11.3, b 7.33, and c 22.6 Å. The space-group was found to be $C222_1$ as determined from zero, first, and second layer-line Weissenberg photographs taken about the b -axis. A zero layer-line photograph was also taken on rotation about the a -axis. Reflections with h and k odd were found to be weak and diffuse, and the direction of spread of these spots was found to be along the c^* -axis in reciprocal space, indicating that the mineral is built up of perfect structural slabs normal to c with structural mistakes occurring between these slabs. Since the reflections with h and k odd are extremely weak a smaller pseudo-cell may be defined with $a' = a/2 = 5.65$, $b' = b/2 = 3.66$, and $c' = c = 22.6$ Å. The lattice of the pseudo-cell is body-centred and possible space-groups are $Immm$, Imm , $I222$, and $I2_12_12_1$. A list of the d spacings of tobermorite from Ballycraigy is given in table II together with those of tobermorite from Mull and a sample of 'calcium silicate hydrate (I)' prepared by Taylor.

CHEMICAL COMPOSITION OF THE 11.3 Å. HYDRATE FROM BALLYCRAIGY.

The pure 11.3 Å. hydrate from Ballycraigy has not been analysed. Its composition has, however, been determined indirectly from the analysis of a mixed 11.3–14.6 Å. hydrate. The latter occurs in some abundance in the contact-zone at Ballycraigy, where it has been formed through the hydration of tobermorite. X-ray examination of this material shows that both the 11.3 Å. and 14.6 Å. hydrates are present. In thin sections the mixed hydrate was opaque and the mean of determined refractive indices was 1.550. The following analysis was made by the author on 0.500 gram of material.

TABLE III. Chemical analysis of a mixed calcium silicate hydrate from Ballycraigy.

			Molar ratio. $5CaO, 6SiO_2, 5H_2O$.		
SiO ₂	44.86	1.00	1.00
CaO	36.02	0.86	0.83
Na ₂ O	0.05	—	—
K ₂ O	0.05	—	—
H ₂ O+	11.10	0.82	0.83
H ₂ O-	8.32	—	—
			100.40		

The analysis (table III) shows that the mixed hydrate is essentially a pure hydrated calcium silicate. Assuming that the loss of water at 105° C. corresponds to the dehydration of all the material present to the

11.3 Å. hydration state the molar ratios given in the second column above correspond to the 11.3 Å. hydrate. From the density and cell dimensions already given the contents of the pseudo-cell may be written: $5\text{CaO} \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$. The cumulative dehydration curve given in a later section suggests that part of the water present in the 11.3 Å. hydrate occurs as hydroxyl groups. The above formula may then be written $(\text{OH})_2\text{CaCa}_4\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$. In this formula an attempt has been made to satisfy the symmetry of the pseudo-cell.

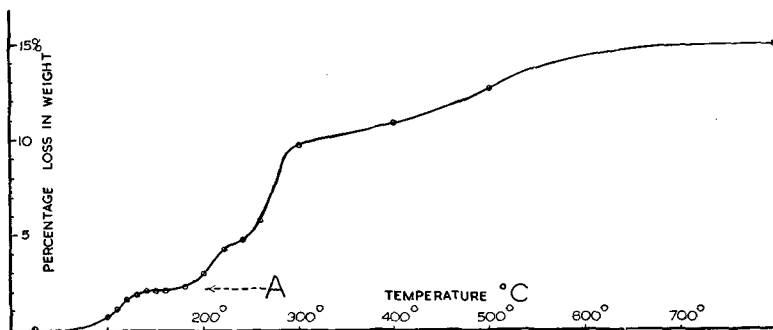


FIG. 2. Cumulative dehydration curve drawn for the 11.3 Å. hydrate.

PREPARATION OF THE 9.6 Å. AND 14.6 Å. HYDRATES.

The cumulative dehydration curve shown in fig. 2 was prepared from data obtained on a very small quantity of the 11.3 Å. hydrate from Ballycraigy. The initial loss of part of the water present in the sample was thought to indicate that a small quantity of the 14.6 Å. hydrate was present. On this assumption the level, marked A on the diagram, was thought to correspond to the 11.3 Å. hydrate. The dehydration curve also shows a marked point of inflexion below 300° C. corresponding to the formation of the 9.6 Å. hydrate. Dehydration was considered complete at a temperature of 800° C. A similar dehydration curve for natural intergrowths of the hydrate minerals with wilkeite has been given by Taylor (1953*a*, p. 165).

Examination of powder photographs of the 11.3 Å. hydrate held at 300° C. for a short time showed that the 002 spacing had been reduced to 9.6 Å. Single crystals of the 9.6 Å. hydrate thus produced were examined optically. The optical orientation of the single crystals was found to be unchanged, but a general increase in the refractive indices was recorded. These were α 1.600, β 1.601, γ 1.605, all ± 0.002 , and

increased dispersion was noted. The d spacings of the artificial 9.6 Å. hydrate are given in table IV below.

TABLE IV. X-ray powder spacings of the 9.6 Å. hydrate.

d .	Int.	d .	Int.
9.67	s	2.10	vw
4.83	s	2.02	vw
3.62	w	1.834	w
3.16	ms	1.659	w
3.04	vs	1.526	w
2.79	ms	1.393	vvw
2.35	ms	1.106	vvw
2.17	vw	1.067	vvw

As already noted, the 11.3 Å. hydrate alters readily to the 14.6 Å. hydrate when exposed to the atmosphere. A direct attempt to demonstrate this hydration process in the laboratory was made as follows. A small quantity of the 11.3 Å. hydrate, in which seawite was present as an impurity, was photographed on a low-angle focusing X-ray camera. The resulting photograph showed a strong but diffuse 002 reflection corresponding to a d spacing of 12.0 Å. This was taken to indicate that the 11.3 Å. hydrate was partly hydrated. The material on the camera was subsequently moistened with water and re-photographed. Two very sharply defined reflections were recorded. The first of these which was very strong corresponded to a d spacing of 14.6 Å. The second was a very faint reflection and corresponded to a d spacing of 11.3 Å. The presence of the latter reflection was taken to indicate that the cores of some of the larger crystals present remained unhydrated. An account of a similar hydration experiment on the mineral tobermorite from Skye is given in the following section.

COMPARISON OF TOBERMORITE FROM SKYE WITH THAT FROM BALLYCRAIGY.

X-ray powder data for tobermorite from Mull and tobermorite from Ballycraigy are compared in table II. A specimen of tobermorite from Loch Eynort in Skye supplied by the British Museum (specimen number B.M. 1952,35) was examined by the present author. Optical examination confirmed the data already given for this mineral by Claringbull and Hey (1952, p. 962). The birefringence of the minute crystals present was found to be 0.005 approximately, and the limits of refringence were 1.545 and 1.565. Claringbull and Hey noted that the refractive indices of this material varied with its opacity. Increase in opacity is now correlated

with decrease in the mean refractive index, a condition already noted in examination of tobermorite from Ballycraigy. Accordingly, it is suggested that the Loch Eynort material is not perfectly homogeneous in respect of its water content.

Attempts were made, in the manner outlined in the previous section, to alter the strong 11.3 Å. spacing of tobermorite from Skye by further hydration. The strong 11.3 Å. reflection given by this material was unaltered even after it had been ground up with water. The significance of the stability of tobermorite from Skye will be discussed in a later section in relation to the alkali content of this mineral and to the inter-layer structure of the hydrates.

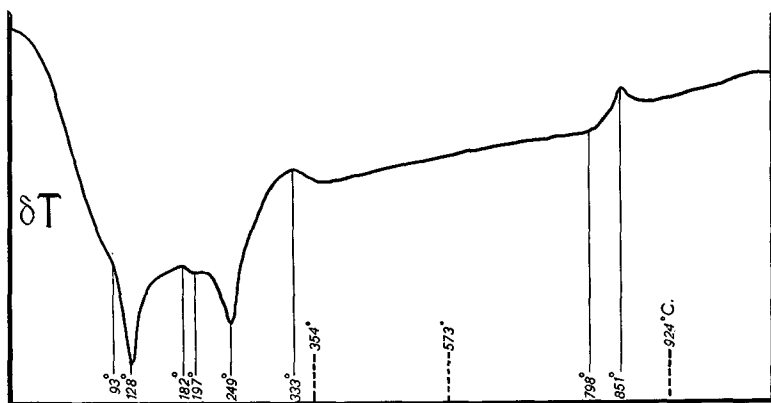


FIG. 3. Differential thermal curve of an 11.3–14.6 Å. hydrate mixture from Ballycraigy, Co. Antrim.

DIFFERENTIAL THERMAL ANALYSIS OF THE 11.3–14.6 Å. HYDRATE MIXTURE.

The chemical composition of this mixed hydrate has already been given in the section on the composition of the 11.3 Å. hydrate. A differential thermal analysis of the mixed hydrate was carried out by Dr. R. J. W. McLaughlin of the Department of Mineralogy and Petrology, Cambridge. The resulting differential thermal curve is shown in fig. 3. The most important features of this curve are the marked endothermic peaks at 128° and 249° C. Exothermic reactions are indicated by peaks at 333° and 851° C. The last was shown to correspond to the formation of CaSiO_3 by taking a powder photograph of material held at a temperature in excess of 900° C. for a short period.

Comment will be made in a later section of the present paper on the close similarity which exists between the above differential thermal analysis curve and that of Ca-substituted vermiculite. In the same section the relationship between the interlayer structure of the hydrates studied and the vermiculite minerals will be discussed.

A NATURAL GELATINOUS MEMBER OF THE 'CALCIUM SILICATE
HYDRATE (I)' GROUP.

X-ray powder data for a gelatinous material found at Ballycraigy are given in table II. This material has been identified with the 'calcium silicate hydrate (I)' group from the reflections observed in powder photographs. These compare closely with those of a poorly crystalline artificial hydrate prepared at room-temperature by Taylor. The composition of the latter sample, which was prepared from $\text{Ca}(\text{OH})_2$ and SiO_2 gel, was $1.3\text{CaO}:\text{SiO}_2:2.1\text{H}_2\text{O}$.

In thin section the gelatinous material from Ballycraigy is seen to replace both larnite and bredigite and has a low birefringence thought to be due to the partial orientation of the crystallites present. In the pseudomorphs after larnite the delicate twinning of the latter mineral is preserved.

In attempting to identify the natural gel with some known mineral its composition was compared with that given for the mineral plombierite, described originally by Daubrée (1858). Analyses of plombierite and the natural gel are compared below.

TABLE V. Chemical analyses of plombierite and the Ballycraigy gel.

	A.	B.
SiO_2	40.6	40.4
CaO	34.1	32.6
Al_2O_3	1.3	2.4
Fe_2O_3	—	0.8
MgO	—	0.3
H_2O	23.2	23.3
	99.2	99.8

A. Plombierite, Plombières, Vosges, France. (G. A. Daubrée, 1858*b*, p. 245.)

B. Analysis, on 0.200 gm., of the natural gel from Ballycraigy, County Antrim, by the author. Iron present was determined as Fe_2O_3 . The alkali content was not determined.

Comparison of the chemical analyses given above together with Daubrée's comments on the gelatinous character of plombierite suggest that plombierite and the gel from Ballycraigy are identical. Confirmation of the identity postulated may eventually be provided by X-ray powder photographs of Daubrée's material which is at present unavailable.

Considerable experimental work has been done on the gelatinous members of the 'calcium silicate hydrate (I)' group and methods of preparation have been listed by Taylor (1950, p. 3689). These include the hydration of tricalcium silicate. The artificial gels are characterized by variable $\text{CaO}:\text{SiO}_2$ molar ratio, and the general formula indicated by Bessey (1938, p. 209) is $1-1.5\text{CaO}.\text{SiO}_2.n-x\text{H}_2\text{O}$. The chemical composition of the natural gel from Ballycraigy indicates that the lower limit of the $\text{CaO}:\text{SiO}_2$ molar ratio in the above formula may be reduced to 0.85 approximately.

A more detailed account of the optical and physical properties of the natural gels will be given in a later paper. Further study of the natural gels is justified by the fact that the formation of similar material is thought to be a primary factor producing 'set' in portland cement hydrated at room-temperature.

GENERAL CONCLUSIONS ON THE INTERLAYER STRUCTURE OF THE HYDRATES.

Taylor has suggested (1953*a*, p. 169) that the water present in the hydrates in excess of one molecule is loosely held between the primary structural sheets, and an analogy with the clay minerals is postulated. The present investigation indicates that a close analogy exists between the hydrate minerals and vermiculite, in the same connexion. In vermiculite the normal 002 spacing is 14 Å. Loss of part of the interlayer water at 110° C. reduces this spacing to 11.8 Å. and the spacing is further reduced to 9.3 Å. on the loss of the remaining water at still higher temperature. These two water fractions are described as 'unbound' and 'bound' water respectively (Walker, 1951, p. 206). Differential thermal analysis curves for normal vermiculite show two strong endothermic peaks at low temperature corresponding to the loss of these water fractions (Barshad, 1948, p. 664). Current theory suggests that Mg ions are present in the interlayer zones in normal vermiculite and that these are surrounded by hydration shells of water molecules. Part of the water present is in an 'unbound' condition and is liberated from the interlayer zone at a temperature of 110° C. (Walker, 1951, p. 206).

Recent work by Barshad (1948) has shown that the Mg ions in interlayer positions in vermiculite may be replaced by other cations and that the cation substituted controls the character of the differential thermal analysis curve and the 002 spacing of the substituted vermiculite in different hydration states. Examination of the effects of Ca-substitution on the 002 spacing and the differential thermal analysis curve is of

interest in the present discussion. At normal temperature the 002 spacing of Ca-substituted vermiculite is 15.07 Å. On complete dehydration this spacing is reduced to 9.55 Å. As in normal Mg-vermiculite two endothermic peaks are present in the differential thermal analysis curve of Ca-vermiculite indicating the presence of 'unbound' and 'bound' water fractions. These peaks occur at slightly lower temperature than the corresponding peaks for Mg-vermiculite. In Na-substituted vermiculite only one endothermic peak is recorded, and the 002 spacing of air-dried material is 12.5 Å.

A close analogy between the interlayer structure of the hydrates at present studied and that of the vermiculite minerals is indicated by:

(1) The close similarity between the 002 spacings of the hydrates and the hydration states of Ca-vermiculite.

(2) The close similarity between the differential thermal analysis curve of the mixed 11.3–14.6 Å. hydrate from Ballycraigy and that of Ca-vermiculite.

The above comparisons suggest that Ca ions are present in the interlayer zones of the hydrate minerals from Ballycraigy. The persistence of the 11.3 Å. spacing in the mineral tobermorite from Skye is explained as being due to the presence of alkali ions in the interlayer positions. It is proposed to test the validity of the above hypothesis by cationic exchange experiments on the hydrate minerals.

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