

RELATIONSHIPS BETWEEN CALCIUM SILICATES AND CLAY MINERALS

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ABSTRACT

The crystal-chemical basis of the relationship between hydrated calcium silicate and clay minerals is discussed, and a review is given of recent work on the tobermorite minerals, the group of hydrated calcium silicates which most nearly resembles the clay minerals. New data are presented for the specific gravities, refractive indices, basal spacings, and dehydration isobars of synthetic tobermorite minerals, and a tentative explanation is proposed for the variability of Ca : Si ratio in these substances.

INTRODUCTION

Certain hydrated calcium silicates, belonging to the tobermorite group, present similarities to the clay minerals. The relationship can be traced back to that existing between the two metasilicates, enstatite and wollastonite. Both contain infinite $(\text{SiO}_3)_\infty$ chains, but these are kinked in different ways, which are determined by the respective sizes of MgO_6 and CaO_6 polyhedra (Fig. 1).

The existence in wollastonite of metasilicate chains of the type shown in Fig. 1B has recently been demonstrated independently by Dornberger-Schiff, Liebau, and Thilo (1954 and 1955), Buerger (1956), and Tolliday (1956). The previously accepted structure containing Si_3O_9 rings is thus discredited.

The more complex anions occurring in the amphiboles, and in clay minerals and other related phyllosilicates, are related to the pyroxene chain (Fig. 1A), and these groups of silicates therefore contain, as essential cationic constituents, magnesium or other ions of similar size. Calcium as a rule plays only a minor part in these structures, and most of the hydrated silicates in which it is the major or only electro-positive element appear to have structures (Fig. 1B) related to that of wollastonite.

Grudemo (1955) has obtained evidence for the existence of a calcium analogue of kaolinite as either a minor constituent or an unstable intermediate phase in a synthetic tobermorite preparation.

An analogue of the amphiboles thus occurs in xonotlite ($\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$). By extension of this analogy, it might be expected that layer-type calcium silicates similar to the clay minerals would exist having sheets formed from rings of four and eight tetrahedra (Fig. 1B). Sheets of this kind do occur in a distorted form

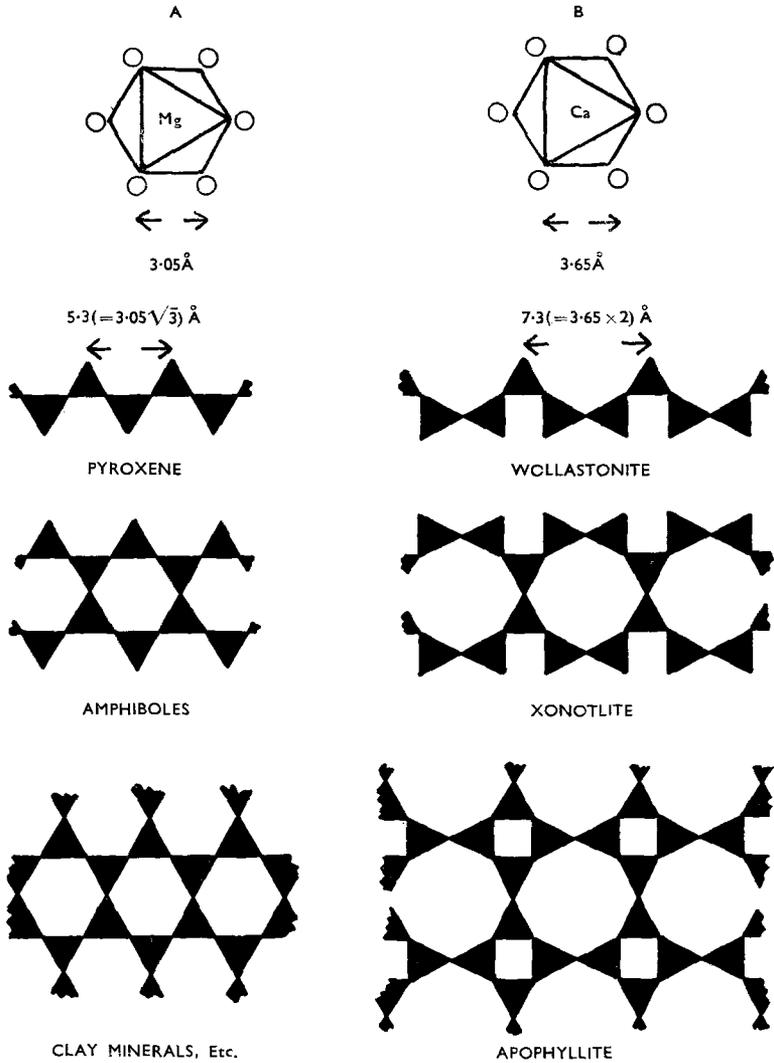


FIG. 1—Some groupings of SiO_4 tetrahedra giving rise to chain or sheet structures with repeat distances related to the dimensions of MgO_6 or CaO_6 polyhedra. A (left); MgO_6 polyhedron and dimensionally related structures. B (right); CaO_6 polyhedron and dimensionally related structures. The representations are idealized, especially in the case of apophyllite.

in apophyllite, but seem to be uncommon, and the tobermorite minerals, which in other respects are the closest known calcium analogues of the clay minerals, contain metasilicate chains similar to those in wollastonite.

THE STRUCTURE OF TOBERMORITE

Relatively perfect and macroscopic crystals of tobermorite are known to occur in Northern Ireland (McConnell, 1954). Their composition is probably $\text{Ca}_4(\text{Si}_6\text{O}_{18}\text{H}_2)\cdot\text{Ca}\cdot 4\text{H}_2\text{O}$, and their crystal structure has been shown by Megaw and Kelsey (1956 a and b) to be of a 2:1 layer type, with some similarities to that of vermiculite.

The similarity between artificial tobermorite or "calcium silicate hydrate (I)" and clay minerals was pointed out by Taylor (1950), and the resemblance to vermiculite in particular was noted by McConnell (1954).

The central part of each layer, equivalent to the octahedral layer in a clay mineral, could be described as a distorted calcium hydroxide sheet divested of all its hydrogen atoms. This sheet is flanked on both sides by parallel rows of wollastonite-type chains, which are kinked in a plane perpendicular to that of the sheets. Only two-thirds of the tetrahedra in each chain are linked directly to the central CaO_2 sheet by sharing of oxygen atoms. The other third, which are held away from the CaO_2 sheet, will be called "bridging" tetrahedra. The composite 2:1 sheets so far described have the composition $\text{Ca}_4\text{Si}_6\text{O}_{18}$. Between them are the remaining or inter-layer calcium atoms, and water molecules. The distribution of the hydrogen is uncertain. There may be more SiOH than is implied by the formula $\text{Ca}_4(\text{Si}_6\text{O}_{18}\text{H}_2)\cdot\text{Ca}\cdot 4\text{H}_2\text{O}$, with corresponding replacement of interlayer water by hydroxyl.

To a good approximation, tobermorite from the above localities is orthorhombic with $a=11\cdot23$, $b=7\cdot37$, $c=22\cdot6$ Å, $Z=4$. The crystals are laths with length b (parallel to the chains) and cleavage (001) (the plane of the layers); a and b are both strongly pseudo-halved, and for many purposes a pseudo-cell with $Z=1$ may be used. This pseudo-cell is body centred. The longest observed basal spacing is therefore 002 ($d=11\cdot3$ Å), and corresponds to the thickness of a single 2:1 layer.

Tobermorite is thus recognisably similar to the clay minerals in crystal structure. Other characteristics in which it resembles them to varying degrees are variability of basal spacing with water content, wide variability in degree of crystallinity, and variability in Ca:Si ratio. These characteristics will be discussed and some new observations included.

Note on nomenclature. Because of the characteristics just mentioned, wide variations are possible within the framework of the tobermorite structure. To avoid use of the mineral name "tobermorite" over too wide a range, or alternatively, the introduction of a multiplicity of names, the generic term "tobermorite minerals" is suggested, to include *inter alia*, the synthetic products also known as "calcium silicate hydrate (I)," "CSH(I)," or "CSH(B)" (synonyms), and the slightly different "calcium silicate hydrate (II)" ($C_2SH(II)$, C_2SH_2). The names "calcium silicate hydrate (I)" and "calcium silicate hydrate (II)" will be retained where it is desirable to distinguish between them.

VARIABILITY OF BASAL SPACING

Early studies on tobermorite minerals (Taylor, 1953 a; McConnell, 1954) showed the existence in well-crystallized material of three distinct hydration states, with 002 spacings of 14-14.6 Å, 10.4-11.3 Å, and 9.3-9.6 Å, and corresponding $H_2O:Si$ ratios of 2-3, 0.8-1.0, and about 0.5 respectively. Recent work indicates that additional hydration states are possible. Available data are collected together in Table 1. Within some, if not all, of the hydration states appreciable variations in the 002 spacing occur, and it seems unlikely that these can be wholly explained by experimental errors.

Megaw and Kelsey (1956 a, 1956 b) showed that in the 11.3 Å hydrate, adjacent layers are packed with the metasilicate chains back-to-back, and they suggested that dehydration to the 9.6 Å state caused a change in packing to an arrangement in which the chains on one sheet fitted into the grooves between those on the next. Incomplete observations (Heller and Taylor, 1956) and further work now in progress on the symmetry of the 9.6 Å hydrate conform with this view, and suggest also that the packing in the 10.3 Å hydrate is similar to that in the 9.6 Å hydrate. The 10.3 Å and 11.3 Å hydrates may therefore differ chiefly in the way the layers are packed; it is possible that the 12.4 Å and 14.6 Å hydrates are similarly related.

Poorly crystallized synthetic preparations made and dried at room temperature show a broad basal spacing with an indefinite maximum usually between 11 Å and 12.5 Å, although values ranging from 10.0 Å (Taylor, 1950) to 13.7 Å approximately (Grudemo, 1955) have been reported. (Spacings of 8.2 Å (Greenberg, 1954) and 7.2-7.4 Å (Kalousek, 1955) have also been reported but whether these are basal spacings is uncertain). The significance of these broad spacings is uncertain; the possibility of random interstratification has been suggested (Heller and Taylor, 1956).

VARIABILITY IN THE DEGREE OF CRYSTALLINITY

Tobermorite minerals vary widely in crystallinity from the relatively large and perfect crystals occurring in Northern Ireland to the nearly

TABLE 1. Basal spacings reported for tobermorite minerals (better-crystallized specimens).

<i>d</i> 002	Observer.	Locality.	Comments.
17.7	Brindley (1954)	Crestmore	Very weak line
14.9	McMurdie and Flint (1943)	Crestmore	Alteration product
14.6	McConnell (1954)	N. Ireland	
14.5	Greenberg (1954)	Synthetic	
14.0	Taylor (1953)	Crestmore	
13.72	I.C.I.(N) (1950)	Crestmore	
12.5	Heller and Taylor (1956)	Crestmore	Minor constituent
12.4	Brindley (1954)	Crestmore	Very weak line
12.3	Greenberg (1954)	Synthetic	
11.5	Heller and Taylor (1956)	Crestmore	
11.3	McConnell (1954), Megaw and Kelsey (1956 a and b)	N. Ireland	
11.3—11.5	Greenberg (1954)	Synthetic	
11.2—11.4	Claringbull and Hey (1952)	Mull and Skye (Scotland)	
11.21	I.C.I.(N) (1950)	Crestmore	
11.0—11.2	Kalousek (1955)	Synthetic	
11.0	Heller and Taylor (1951)	Synthetic	(hydrothermal)
10.4	McMurdie and Flint (1943)	Crestmore	
10.2—10.4	Brindley (1954)	Crestmore	
10.25	Heller and Taylor (1956)	Crestmore	
9.61	Brindley (1954)	Crestmore	
9.6	McConnell (1954)	N. Ireland	Alteration product
9.54	I.C.I.(N) (1950)	Crestmore	
9.3	Taylor (1953)	Crestmore	
9.2	Greenberg (1954)	Synthetic	

amorphous material formed in the setting of Portland cement or tricalcium silicate-water pastes. Some typical stages in a probably continuous range of crystallinity are listed in Table 2, which shows the influence of this factor on the morphology and on the diffraction patterns. Some other properties affected by the degree of crystallinity are as follows:

(i) *The length of the b-axis*; the strong 040 spacing is 1.84-1.85 Å in well-crystallized specimens and 1.82-1.83 Å in badly-crystallized specimens (Kalousek, 1955; Megaw and Kelsey, 1956 b).

(ii) *Specific gravity and refractive index*; these are discussed later.

(iii) *Specific surface*; measured using nitrogen adsorption. Kalousek (1955) found 60-69 sq m/g for well-crystallized synthetic specimens and 120-180 sq m/g for badly-crystallized material. Other values reported are 25-90 sq m/g for the very badly-crystallized product formed on setting of tricalcium silicate pastes (Brunauer, Copeland, and Bragg, 1956). These results can be used to calculate the number of individual layers occurring in the thickness of each crystal. If it is assumed that the specimens consist of sheets large in extent relative to their thickness, and that they have specific gravity 2.4 and basal spacing 11 Å, the lowest value (25 sq m/g) indicates an average thickness of 30 layers (330 Å) and the highest value (220 sq m/g) one of 3.5 layers (38 Å). This model is probably substantially correct for the better-crystallized specimens, but for some of the badly-crystallized ones a fibrous habit has been observed (Table 2). The minimum value of 3.5 given above is therefore possibly low. These estimates are in general agreement with those derived from electron-microscopy (Gaze and Robertson, 1956).

VARIABILITY IN Ca:Si RATIO

Early investigations on poorly-crystallized synthetic tobermorite minerals, reviewed by Steinour (1947 and 1954) showed that the Ca:Si ratio can vary widely without apparent change in X-ray pattern or appearance of a second phase. There is now fairly general agreement that the lower limit for the tobermorite or calcium silicate hydrate (I) phase is about 0.8. The upper limit is less certain, values of 1.33 (Kalousek, 1954 a) and about 1.5 (Grudemo, 1955; van Bemst, 1955) having been reported in recent investigations. Some evidence exists for a closely related but distinct phase of higher Ca:Si ratio ("calcium silicate hydrate (II)"). The most recent studies indicate that this has Ca:Si—1.75 (Kalousek, 1954 b and 1955), or 1.7-2.0 (van Bemst, 1955).

TABLE 2. Variability in the degree of crystallinity of tobermorite minerals. Some typical specimens arranged in order of decreasing crystallinity.

Locality or conditions of preparation.	Size and form of crystals.	Disorder as shown in single-crystal X-ray or electron-diffraction patterns.	Disorder apparent in X-ray powder pattern.
1. Ballycraigy } (N. Ireland) Scawt Hill } { (McConnell, 1954.) { (Megaw & Kelsey, 1956.)	Laths with (001) cleavage and length b , up to 0.35 mm long.	Minor, affecting principally weak reflections not indexable on the pseudo-cell.	None.
2. Loch Eynort, Scotland (Claringbull & Hey, 1952.) (Gard and Taylor, 1957.)	Laths or fibres, length b , cleavage usually (100); usually a few μ long.	Similar to above though more complex.	None.
3. Synthetic: well-crystallized hydrothermal preparations. (Heller & Taylor, 1951.) (Kalousek, 1955.) (Gard and Taylor, 1957.)	Thin sheets or foils (001) with no marked elongation, usually a few μ in each direction.	Similar to 1.	None.
4. Ciestmore, California. Oriented, sub-microscopic intergrowths with apatite minerals (Taylor, 1953 b.)	Fibres up to several mm long. The individual constituents have not yet been separated.	Tobermorite constituents give preferred orientation patterns. No spreading of reflections indexable on pseudo-cell except along lines of constant θ .	None, though the presence of the apatite constituent obscures the finer details.
5. Synthetic: typical poorly-crystallized material precipitated from dilute suspensions at room temperature. (Taylor, 1950.) (Kalousek, 1955.) (Grudemo, 1955.) (van Bemst, 1955.)	Usually foils similar to 3 but smaller. Minute fibres in some cases, possibly rolled foils, have also been reported, especially with "calcium silicate hydrate (II)."	No data.	Few reflections occur except 002 and $hk0$ reflections indexable on pseudo-cell.
6. Ballycraigy. "Plombierite" gel (McConnell, 1955.)	Shapeless material resembling silica gel.	No data.	As 5 but no basal spacing visible.
7. Synthetic: extremely poorly-crystallized material formed in tricalcium silicate pastes and in some hydrothermal preparations. (Brunauer, Copeland and Bragg, 1956) (van Bemst, 1954)	No data.	No data.	Only 220 and 040, and sometimes also 002 and 400, are visible.

Some important characteristics of the variability in Ca:Si ratio are as follows:

Increase above the minimum value is associated with poor crystallization. The natural specimens from N. Ireland and from Scotland, which are the best-crystallized tobermorite minerals known to exist, all have Ca:Si ratio near 0.83 (5:6). Kalousek (1955) could prepare badly-crystallized specimens of calcium silicate hydrate (I) with Ca:Si up to 1.33, but for well-crystallized specimens the ratio did not exceed 1.0. (Kalousek considered that it might be possible to obtain well-crystallized material with higher values of Ca:Si. Heller and Taylor (1951) in fact obtained such material with Ca:Si 1.5. It was, however, less readily prepared than that with Ca:Si 1.0). The lack of agreement as to the upper limit of Ca:Si can therefore possibly be explained by differences in the degree of crystallinity of preparations made using different methods.

The $H_2O:Si$ ratio, for specimens dried at temperatures around 100°C and at a fixed humidity, is substantially independent of Ca:Si ratio. Earlier indications to this effect have now been confirmed by the authors, using a silica spring balance in an atmosphere of controlled humidity and very low CO_2 content. Results for specimens made at room temperature from calcium hydroxide and silica sol are given in Fig. 2. With one exception, the isobars for specimens of differing Ca:Si ratio agree closely below 200°C. Such differences as exist between the curves cannot be correlated with differences in Ca:Si, and must therefore be attributed to some other cause.

All preparations with Ca:Si ratio below 1.5 yield an exothermic d.t.a. peak at 800-900°C, which, at least when $Ca:Si \leq 1$, corresponds to transition to β - $CaSiO_3$. The temperature of this peak increases with Ca:Si ratio (Kalousek, 1954 a).

Synthetic preparations, if placed in calcium hydroxide solution, undergo transfer of lime to or from the solution according to a fairly definite equilibrium curve (Steinour, 1947 and 1954). Attainment of equilibrium is slow, especially with solids of high Ca:Si ratio, days or weeks often being needed. This contrasts with the rapidity of typical cation-exchange reactions of clay minerals.

Data for variation in basal spacing with Ca:Si fluctuation are conflicting. Kalousek (1956) reported no differences between poorly-crystallized specimens having Ca:Si ratio 1.0, 1.25, and 1.33, but Grudemo (1955) observed a decrease with increasing Ca:Si for similar material. New data are given in Table 3; because of the breadth of the lines, the spacings are rarely accurate to better than $\pm 0.5 \text{ \AA}$. The

hydrothermal preparations show a slight and uncertain tendency to shorter basal spacings with increase in Ca:Si ratio. This tendency is more definite for the specimens made at room temperature and dried at 108°C. For the specimens made at room temperature and dried at 236°C, no trend with Ca:Si variation can be discerned.

Specific gravity and refractive index determinations are also given in Table 3. The specific gravities were determined by suspension; care was taken to remove trapped air by preliminary boiling of the liquid

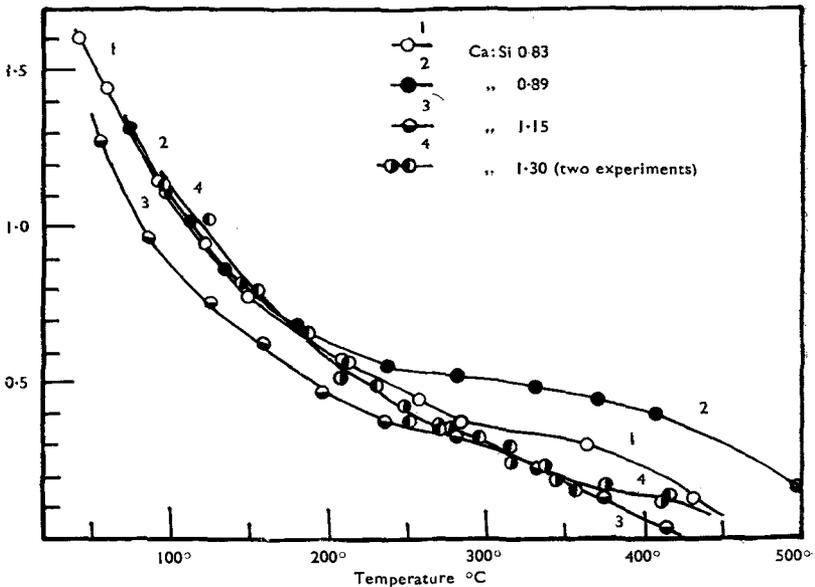


FIG. 2.—Dehydration isobars, obtained at 6 mm partial pressure of water vapour, for some synthetic tobermorite minerals prepared at room temperature. Values of Ca:Si corrected for CO_2 assumed present as CaCO_3 .

under reduced pressure. Values for the specific gravity were also calculated from the mean refractive indices using the Lorentz-Lorenz equation as described elsewhere (Howison and Taylor, 1956), and with a few exceptions agree moderately well with the observed values. For comparison, values from the literature for some other specimens are included. Table 3 also gives the weight of the pseudo-cell contents for each specimen; these values were calculated from the observed specific gravity and basal spacing, assuming mean values for a and b of 5.6 Å and 3.6 Å respectively. The results suggest that

TABLE 3. Basal spacings, specific gravities and refractive indices of some tobermorite minerals. New data except where otherwise stated.

Conditions of Preparation (or locality)	Ca:Si*	H ₂ O:Si Spacing	Basal Spacing	Mean Refractive index (<i>n</i>)	Observed Specific Gravity	Specific Gravity calculated from (<i>n</i>)	Pseudo-cell weight
Synthetic, hydrothermal. Prepared at 110-150°C and afterwards dried to constant weight at 65°C and p(H ₂ O) 6 mm.	0.83	1.42	12.1	1.555	2.34	2.33	689
...	0.89	1.40	11.5	1.580	2.48	2.42	693
...	0.96	1.48	11.9	1.570	2.43	2.27	703
...	1.00	1.18	11.5	1.565	—	2.41	674†
...	1.15	2.44	12.1	1.575	2.40	2.30	706
...	1.49	1.35	11.0	1.555	1.92	2.40	642†
...	1.50	1.48	11.5	1.575	2.49	2.45	696
...	1.50	1.57	10.9	1.580	2.46	2.45	652
...	1.50	1.57	10.0	1.575	2.42	2.44	589
Synthetic. Prepared at room temperature from Ca(OH) ₂ and SiO ₂ sol, and dried to constant weight at 108°C and p (H ₂ O) 6 mm.	0.81	0.95	10.7	1.530	2.32	2.32	604
...	0.83	1.03	11.1	1.525	2.23	2.28	601
...	0.89	1.07	11.3	1.520	2.26	2.26	621
...	0.96	1.06	11.3	1.530	2.16	2.32	594
...	1.15	0.86	9.1	1.545	2.28	2.41	504
...	1.30	1.12	9.9	1.540	2.37	2.38	570
...	1.36	1.11	10.2	1.540	2.25	2.36	557
Synthetic. Prepared at room temperature from Ca(OH) ₂ and SiO ₂ sol, and dried to constant weight at 236°C and p(H ₂ O) 6 mm.	0.81	0.58	9.7	1.545	2.37	2.43	558
...	0.83	0.51	9.7	1.545	2.31	2.46	545
...	0.89	0.58	9.9	1.545	2.44	2.44	586
...	0.96	0.59	9.8	1.555	2.28	2.49	543
...	1.15	0.38	9.0	1.555	2.42	2.53	529
...	1.30	0.47	9.7	1.565	2.45	2.55	577
...	1.36	0.48	9.7	1.560	2.34	2.54	551
Natural mineral from Ballycraiga (McConnell, 1954)	0.86	0.82	11.3	1.572	2.44	2.50	688‡
Hydrated tricalcium silicate paste (Brunauer, Copeland and Bragg, 1956)	1.5§	1.5§	11.0	1.56	2.44§	2.38	651

*Unit-cell taken as *a* 11.23, *b* 7.37, *c* 22.6, Å.

‡After correction for presence of calcium hydroxide.

*After correction for CO₂ assumed present as CaCO₃.

†Specific gravity calculated from refractive index employed.

the specific gravity and refractive index vary with the degree of crystallinity and with $H_2O:Si$ ratio, but that where these factors are both approximately constant there is little or no systematic variation with $Ca:Si$ ratio.

The high-lime phase "calcium silicate hydrate (II)," with $Ca:Si$ ratio probably 1.75, also differs from calcium silicate hydrate (I) or tobermorite in details of its X-ray powder pattern (Taylor, 1950; Toropov, Borisenko and Shirokova, 1953), and in habit; it is fibrous and not lamellar (Grudemo, 1955; van Bemst, 1955). Van Bemst found that it differs also in infra-red spectra, in decomposing at $800^\circ C$ to give Ca_2SiO_4 and not wollastonite, and in giving a basal spacing of 10 \AA and not 13.6 \AA . This last property, however, may not be characteristic, as some specimens of calcium silicate hydrate (I) show a 10 \AA basal spacing. Van Bemst (1954) considers that calcium silicate hydrate (II) is formed on setting of tricalcium silicate pastes, but Brunauer, Copeland and Bragg (1956) and Pressler, Brunauer, and Kantro (1956) consider that the product is calcium silicate hydrate (I).

DISCUSSION

The variability of $Ca:Si$ ratio in tobermorite minerals has most frequently been attributed to adsorption of calcium hydroxide by a compound of low $Ca:Si$ ratio. The present results show that this theory is unsatisfactory, for several reasons:

(i) Adsorption of calcium hydroxide implies addition of one molecule of water in the form of hydroxyl for every atom of calcium added. The dehydration isobars of preparations of high $Ca:Si$ ratio would therefore be expected to show higher values of $H_2O:Si$ ratio at all temperatures below that at which this water was expelled; above this temperature the curves should be identical with those given by preparations having $Ca:Si=0.83$. In fact, no such effect is observed (Fig. 2).

(ii) In order to raise the $Ca:Si$ ratio from 0.83 to the probable upper limit of 1.5, four calcium atoms would have to be added for every five originally present. Such a large addition could only be accommodated if adsorption occurred between the layers as well as on external surfaces. (This statement is based on the estimates of crystal thickness already given). The weight of the pseudo-cell contents would therefore be expected to increase markedly with increasing $Ca:Si$ ratio; a product with $Ca:Si=1.5$ might be expected to have a pseudo-cell weight about 40% greater than that of one with $Ca:Si=$

0.83. No such variation is observed (Table 3). Apart from these considerations, it appears misleading to describe part of the interlayer calcium as adsorbed, and the rest as part of the structure. It appears preferable to attempt to calculate the total atomic contents of the unit-cell, from the specific gravity, cell dimensions and chemical analysis, for each of a series of values of Ca:Si. In practice, interpretation of the data is complicated because even with the relatively well-crystallized specimens from Northern Ireland, the pseudo-cell weight of 688 calculated from the observed data (Table 3) is appreciably less than the theoretical value of 730 calculated for $\text{Ca}_5\text{Si}_6\text{O}_{22}\text{H}_{10}$. The discrepancy could be caused by a true deficiency in the average contents of the pseudo-cell, or by a lowering in the apparent specific gravity caused by gaps between crystallites, and the relative importance of these two possible causes is unknown. Dependent on the extent of occurrence of the second possibility, the absolute values of the pseudo-cell weights given in Table 3 will tend to be low. It is nevertheless probably justifiable to compare relative values within groups of specimens that are approximately identical in degree of crystallinity and in $\text{H}_2\text{O}:\text{Si}$ ratio. For each such group the values show either no consistent trend with Ca:Si ratio, or if anything, a slight and indefinite decrease. This suggests that variation in Ca:Si ratio occurs by a replacement of silicon by calcium. As already stated, increase in Ca:Si ratio caused by addition of calcium without removal of silicon would cause a large increase in the pseudo-cell weight. If, on the other hand, it was caused by removal of silicon without corresponding addition of calcium there would be a comparably large decrease in the pseudo-cell weight.

Various hypothetical ways in which Si^{4+} might be replaced by Ca^{2+} have been examined, and only one has been found that seems to be in accordance with all the facts. Two kinds of modification to the tobermorite structure are postulated:

(i) Removal of "bridging" tetrahedra not directly attached to the central CaO_2 sheet. Since two of the oxygen atoms in each of these tetrahedra are common to adjacent groups, the alteration can be described as removal of SiO_2 with possible transfer of hydrogen to other positions in the structure.

(ii) Replacement of two hydrogen atoms by calcium, the latter occupying an interlayer position made available by removal of silica.

If these two modifications occurred to about equivalent extents, so causing replacement of SiO_2H_2 by Ca, variation in Ca:Si ratio would have relatively little effect on either the pseudo-cell weight, or the

H₂O:Si ratio. This is shown by comparison of the suggested formulae I and II below:

Pseudo-cell contents	CaO : SiO ₂ : H ₂ O	Pseudo-cell weight
I. Ca ₄ Si ₆ O ₁₈ . CaO ₄ H ₁₀	0.83 : 1 : 0.83	730
II. Ca ₄ Si _{4½} O ₁₅ . Ca _{2½} O ₄ H ₇	1.44 : 1 : 0.78	697
III. Ca ₄ Si ₄ O ₁₄ . Ca ₃ O ₄ H ₆	1.75 : 1 : 0.75	686

Such a replacement might also be expected to occur without marked effect on the unit-cell dimensions. It would also explain the other main characteristics of variability in Ca:Si ratio.

(i) A relatively perfect crystalline structure is only possible at the minimum Ca:Si ratio of 0.83.

(ii) The upper limit of about 1.5 and probable existence of a high-lime phase related to tobermorite can be explained if it is assumed that a certain proportion of the bridging tetrahedra must be retained to maintain the tobermorite structure, or else none at all, allowing collapse to a different but related structure. If 25% of the bridging tetrahedra are retained, as in case II above, Ca:Si is 1.44, which is about the upper limit for calcium silicate hydrate (I). If none are retained, Ca:Si becomes 1.75 (case III). This is the most probable value for calcium silicate hydrate (II).

(iii) The slowness with which equilibrium is reached between synthetic tobermorite preparations and calcium hydroxide solution is explained, because alteration in Ca:Si ratio of the solid phase would involve formation or removal of layers from the crystals. The fact that equilibrium is reached so slowly provides further evidence against the adsorption hypothesis, since a simple process of gain or loss of calcium and hydroxyl might be expected to occur more rapidly.

It must be stressed that any single explanation of the variability of Ca:Si ratio in tobermorite minerals is probably an oversimplification. The present evidence seems to indicate that the hypothesis suggested above represents the most important effect. It would, however, be surprising if with such poorly crystallized material, other factors did not play contributory parts. Among these, a limited amount of surface adsorption can probably be included.

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