MINERALOGICAL MAGAZINE

Some observations on Assarsson's Z-phase and its structural relations to gyrolite, truscottite, and reyerite

J. A. GARD, T. MITSUDA,[1] and H. F. W. TAYLOR

Department of Chemistry, University of Aberdeen, Meston Walk,
Old Aberdeen, AB9 2UE, Scotland

SUMMARY. Z-phase was obtained hydrothermally at 120 °C by decomposition of Al-substituted tobermorite and by reaction of lime and colloidal silica. X-ray and electron diffraction show that the structural element is hexagonal, with a 9·65, c 15·3 Å, and good {0001} cleavage. Reversible water loss and lattice shrinkage occur on heating, the layer thickness (c) decreasing to 12·1 Å at 400 °C. For material in equilibrium with air of normal humidity, the composition is probably between $CaO.2SiO_2.1·7H_2O$ and $CaO.2SiO_2.2H_2O$; $Z = 8$ for the structural element. New t.g. and infra-red absorption data are presented; the infra-red spectrum closely resembles that of gyrolite, but OH ions attached only to Ca appear to be absent. Conditions of formation are discussed; if Z-phase has any stability field, it is below 120 °C. Crystal structures for Z-phase, gyrolite, and truscottite are suggested, based on the known structure of reyerite.

FUNK and Thilo (1955) described a new phase of composition $CaO.2SiO_2.2H_2O$, which they had prepared by autoclaving a calcium silicate hydrate gel at 180 °C. Assarsson (1957, 1958, 1960, 1962) obtained a product of similar composition by autoclaving mixtures of lime and amorphous silica at 140–240 °C, and called it Z-phase. Funk (1961) and Taylor (1962) concluded that these products were identical. Z-phase was later obtained by Harker (1964), who autoclaved a mixture of lime and silicic acid at 195 °C. It is characterized by a strong X-ray powder spacing of about 15·2 Å and is formed as an intermediate in the formation of gyrolite, to which Taylor (1962) suggested it was structurally related. X-ray powder data, electron micrographs, t.g. and d.t.a. curves, density, and mean refractive index have been reported. Z-phase has not been found pure as a natural mineral, but some specimens of gyrolite probably contain small amounts of it as an intergrown impurity (Assarsson, 1957; Taylor, 1962). In this paper we show that Z-phase can be produced by decomposition of Al-substituted tobermorite and present results of thermal, electron-optical, and infra-red

[1] Permanent address: Materials Research Laboratory, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Japan

studies, which confirm the relationship to gyrolite; possible structures for Z-phase and related minerals are suggested.

Formation. The Z-phase was obtained accidentally, in an attempt to make tobermorite by prolonged hydrothermal reactions in glass flasks at 120 °C; reaction with the glass caused the Ca/Si ratio to decrease and tobermorite to be converted into Z-phase. The starting materials were mixtures of CaO with either aluminosilicic gels or colloidal silica, and are described elsewhere (Mitsuda and Taylor, 1975). The gels had Al/(Si+Al) = 0·05—0·15 and contained substantial amounts of Na_2O. The mixtures, which had Ca/(Si+Al) = 0·8, were autoclaved for 4 hr at 120 °C in stirred suspensions, followed by processing at the same temperature in closed vessels without stirring for times up to 1 year. If the gels were used with stainless-steel vessels, an Al-substituted-tobermorite was gradually formed over a period of 4 weeks (Mitsuda and Taylor, 1975). If glass vessels were used, and reaction was continued for longer periods, the tobermorite was gradually converted into Z-phase. The latter was never obtained free from tobermorite. The highest content of Z-phase was obtained from a 1-year run using a gel with Al/(Si+Al) = 0·05 and Na/Si = 0·24; Ca/(Si+Al) decreased to 0·53 and X-ray diffraction showed Z-phase with only a little tobermorite. This preparation was used in the subsequent work; analysis gave SiO_2 52·09, Al_2O_3 2·26, CaO 27·15, Na_2O 0·18, loss 18·18, total 99·86 %. Mixtures made using the colloidal silica underwent conversion into Z-phase more slowly; in a typical run, the Ca/Si ratio after 1 year was 0·62 and only a little Z-phase was detected. We have also made some preliminary experiments using mixtures of CaO and colloidal silica at Ca/Si = 0·56 in steel vessels; at 120 °C a 3-week run gave Z-phase, and a 6-week run, Z-phase mixed with gyrolite. At 200 °C only gyrolite was detected.

X-ray powder data. Table I, col. 3, gives the X-ray powder pattern, obtained using a diffractometer and Guinier camera with copper radiation. Si was used as a standard for spacings (a = 5·4301 Å). The pattern is similar to those given by Funk and Thilo (1955) and Assarsson (1960) (cols. 1 and 2 respectively). Many of the peaks can be indexed as either $000l$ or $hki0$ reflections for a hexagonal lattice with a 9·65, c 15·3 Å, but the true c-axis could well be either a multiple of this or else indefinite due to complexities of layer stacking, and these parameters should be regarded as those of a structural element and not necessarily of the true unit cell.

Patterns were also obtained for specimens that had been heated at various temperatures. For heating conditions up to 20 hr at 700 °C they indicated an essentially similar structural element but with a shorter c-axis; Table I, col. 4, gives data for a specimen that had been heated for 66 hrs at 500 °C, and Table II gives basal spacings for specimens heated under other conditions. For specimens that had been heated at 200 to 300 °C, the basal spacing quickly reverted to 15·2 Å on standing in air; for that heated at 400 °C it increased slowly to 14 Å on wetting with water for 3 days; for those heated at 500 to 700 °C it did not change on wetting. A specimen heated for 4 days at 700 °C gave pseudowollastonite (α-$CaSiO_3$); this confirms an earlier observation of Funk and Thilo (1955) and is similar to the behaviour of gyrolite (Mackay and Taylor, 1953). The X-ray pattern of the unheated material did not change on treatment with ethylene glycol.

TABLE I. *X-ray powder data for Z-phase*

1		2		3			4		
Funk and Thilo‡ (1955)		Assarsson (1960)		This investigation					
				Unheated*			500 °C/66 hr*		
d(Å)	I	d (Å)	I	d (Å)	I	hkil	d (Å)	I	hkil
—	—	15·1	s	15·3	vs	0001	11·8	s	0001
8·32	w	8·35	m	8·38	mw	101̄0	8·24	vw/b	101̄0
—	—	—	—	—	—	—	5·90	m/b	0002
5·02	vvw	5·070	m	5·10	w	0003	—	—	—
—	—	—	—	4·83	vvw	112̄0	—	—	—
—	—	4·390	w	—	—	—	—	—	—
4·18	mw	4·165	vw	4·18	ms	202̄0	4·16	w/b	202̄0
—	—	—	—	—	—	—	3·91	w/b	0003
3·82	vw	3·786	w }d	3·81	mw	0004	—	—	—
3·35	vw	3·357	mw	3·32	vvw†	—	—	—	—
		3·142	vw }d	3·16	vvw	123̄0	—	—	—
3·05	s	3·033	ms	3·05	m	0005	—	—	—
—	—	—	—	—	—	—	2·95	w/b	0004
—	—	—	—	2·89	mw	—	—	—	—
2·77	vw	2·778	w/b	2·80	m†	303̄0	2·76	w/b	303̄0
2·52	vvw	2·410	w	2·41	vvw	—	—	—	—
2·26	vvw	—	—	—	—	—	—	—	—
2·08	vvw	—	—	2·09	vvw†	—	—	—	—
1·92	vw	1·911	w	1·916	vvw	—	—	—	—
1·87	vvw	—	—	—	—	—	—	—	—
1·82	s	1·817	s	1·823	ms	415̄0	1·82	w/b	415̄0
		—	—	1·619	vvw				
		—	—	1·577	vvw				
		—	—	1·525	vvw				
		1·336	w/b	1·338	vw				
		—	—	1·222	vvw				
		1·192	w	1·195	vvw				

* Peaks attributed wholly to tobermorite omitted.
† Peaks due partly or wholly to tobermorite.
‡ Later work (Funk, 1961; Taylor, 1962) showed that this and similar preparations also gave a spacing of about 15·2 Å.
s = strong, m = moderate(ly), w = weak, v = very, b = broad, d = diffuse band.

TABLE II. *X-ray results for heated specimens*

Treatment	Basal spacing (Å)	Remarks
Unheated	15·3 vs	
200 °C/1 hr	14·9 vs	
300 °C/1 hr	12·4 s	Basal spacing reverted to 15·2 Å on standing in air
400 °C/1–19 hr	12·1 s	Basal spacing increased to 14 Å on wetting with water for 3 days
500 °C/1 hr	11·7 m	
500 °C/2 days	11·8 m	
500 °C/3 days	11·9 m	No change in basal spacing on wetting
700 °C/20 hr	11·9 m	
700 °C/4 days	—	Altered to pseudowollastonite

For comparison, X-ray data were obtained for gyrolite (natural specimen from Bombay; Mackay and Taylor, 1953) before and after heating at 400 °C. The basal spacing was 22·1 Å for the unheated, and 19·1 Å for the heated material. If the heated specimen was wetted with water, the basal spacing reverted to 22·1 Å.
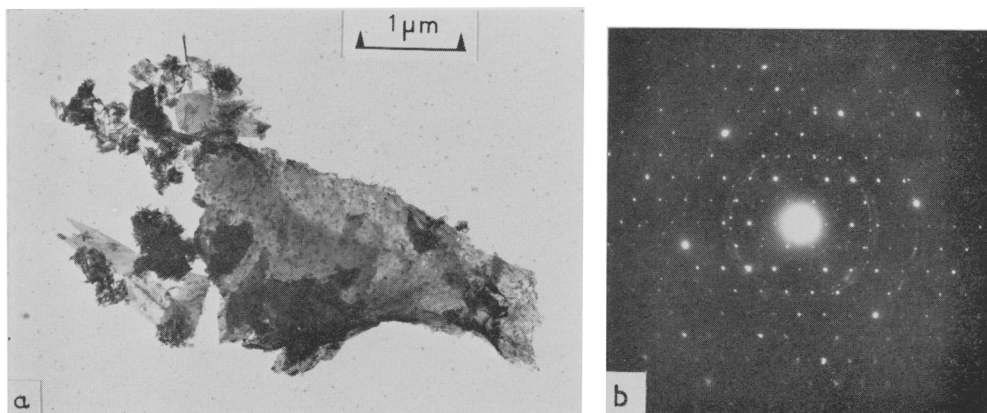

FIG. 1. A: An electron micrograph of a crystal of Z-phase. The plate has irregular edges, and the surface is covered with small particles. A few crystals of tobermite can be seen in the lower left-hand corner. B: An electron-diffraction pattern of Z-phase. The spots can be indexed on a hexagonal unit cell with $a = 9.65$ Å. The $\{41\bar{5}0\}$ reflections indicate a hexagonal sub-cell with $a_s = 3.65$ Å, rotated $19.1°$ with respect to a.

Electron microscopy and diffraction. Funk (1961) has reported electron micrographs of Z-phase; he described the particles as undulating foils ('Folien, gewellt'; 'gebogene Folien'). For the present investigation, a suspension in isopropyl alcohol was allowed to dry on specimen grids carrying thin carbon films. Aluminium was evaporated in vacuum on some specimens as a standard for electron diffraction. Two distinct types of particle were observed. The first comprised somewhat elongated plates with straight edges, often approximating to hexagonal shapes. Electron-diffraction patterns from tilted crystals represented clearly defined zones, in which all d-spacings corresponded to those of 11 Å tobermorite. Fig. 1A shows an example of the second type of particle, considered to be of Z-phase, and fig. 1B its electron diffraction pattern. The particles were irregular plates with maximum dimension about 3 μm. The edges were uneven, and the surfaces were covered with much smaller particles, about 50 nm in diameter. The diffraction pattern could be indexed on a hexagonal unit cell with $a = 9.65$ Å, but the strong set of $\{41\bar{5}0\}$ reflections suggested a sub-lattice with $a_s = 3.65$ ($= 9.65 \times 7^{-\frac{1}{2}}$) Å, for which a_s was rotated $19.1°$ with respect to a. The pattern, including the general distribution of intensities, is similar to that reported for a synthetic truscottite (Gard, 1965). Crystals were tilted around various rows of spots in an attempt to determine the c-period, but this was unsuccessful for all except one crystal, because clear zones were not observed, possibly due to disorder in the layer stacking. Faint powder rings on some patterns were probably due to the small particles on the surface

of the crystal. Three of these powder spacings (3·07, 2·82, and 1·83 Å) agree with the strongest $hk0$ spacings of tobermorite, but the others do not seem to be attributable to this phase and the nature of the surface particles must be considered uncertain. Only one crystal was found with a 'three-dimensional' reciprocal lattice. An initial tilt of 40° was required to give an hexagonal diffraction pattern. Relatively clear zones of spots were observed by tilting around an a^*-axis through angles up to 78°, when a centred net was observed from which $d_{1.1.\bar{2}.10}$ was estimated at 1·51 Å. $d_{11\bar{2}l}$ was
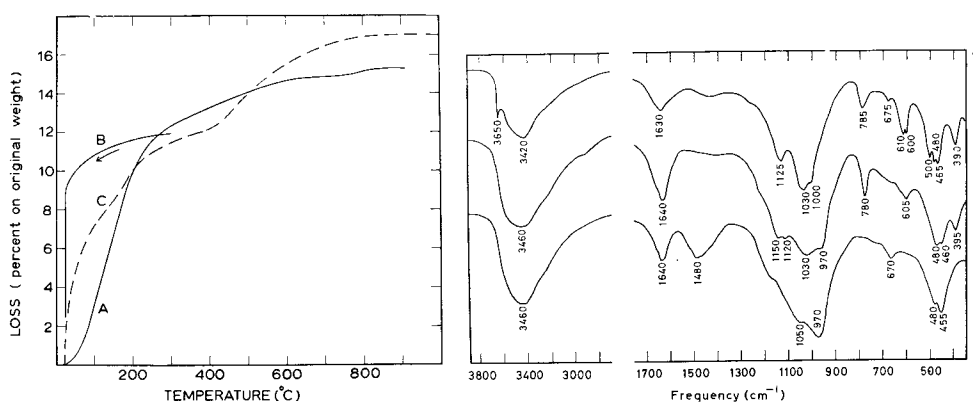
FIGS. 2 and 3: FIG. 2 (left). Thermal weight-change curves. A: heating curve, obtained in air at 15 deg C min⁻¹, for a preparation of Z-phase containing a little tobermorite. B: same sample as above; cooling curve obtained in moist air after heating for 1 hr at 300 °C. C: Static heating curve for 'CaH₄Si₂O₇' (Z-phase; Funk and Thilo, 1955) obtained in N₂ at $P(H_2O) = 20$ mm. FIG. 3 (right). Infra-red absorption spectra for (G) synthetic gyrolite, (Z) Z-phase containing a little tobermorite, and (T) synthetic tobermorite.

measured for each zone, and a projection of the reciprocal lattice down a^* was constructed; a mean c-period of between 15 and 16 Å was estimated, in agreement with the X-ray data. However, spots on the individual zones comprised networks that were slightly distorted from orthogonal; the distortion increased with the angle of tilt. Using a procedure described elsewhere (Gard, 1971; Cliff et al., 1975), the angle between c and c^* was estimated at 4±1°. Z-phase is therefore only pseudohexagonal, but it is not certain whether it has monoclinic or triclinic symmetry.

Comparison between micrographs recorded in this investigation and those reported by Funk (1961) is difficult because the magnifications of the latter were not given. In the present work, stereomicrographs were recorded by tilting the particles between exposures. They suggested that the plates were composite, but that the individuals of which they were composed were flat with {0001} cleavage; they showed no sign of the undulations reported by Funk.

Infra-red absorption. Fig. 2 gives spectra obtained using the KBr disc method for a preparation of Z-phase containing a little tobermorite, and also for the synthetic gyrolite specimen mentioned earlier and for a synthetic tobermorite similar to those converted into Z-phase in the present work. The spectrum of Z-phase resembles that

of gyrolite, but is not particularly like that of tobermorite. It differs from that of gyrolite most obviously in the absence of a sharp peak at 3650 cm^{-1} attributable to OH groups coordinated only to Ca. The shoulder at 970 cm^{-1} could be due to tobermorite. Spectra were also obtained, using Nujol mulls, for preparations of Z-phase that had been heated. Heating at 300 to 400 °C caused little change apart from a marked weakening of the bands at 1640 and 3460 cm^{-1}, attributable to loss of molecular water. Heating at 500–700 °C caused the spectra to become weak and diffuse; the 780 cm^{-1} peak moved to 810 cm^{-1}.

Thermogravimetry. Fig. 3, curve A, shows a t.g. curve for the present specimen, obtained in air at a heating rate of 15 deg min^{-1}. It is sufficiently similar to typical curves for tobermorite that any correction for the presence of the latter in the specimen would be small. Curve B gives results for reabsorption of water by a sample that had been heated for 1 hr at 300 °C and then cooled in moist air; the basal spacing at the end of the run was 15·2 Å. A static weight-loss curve obtained by Funk and Thilo (1955) is included for comparison (curve C); these workers also recorded curves obtained in N$_2$ at $P(H_2O)$ = 2 mm and over P$_4$O$_{10}$. Funk (1961) reported that the d.t.a. curve showed an endotherm at 175 °C and an exotherm at 804 °C; these probably correspond respectively to loss of water and formation of pseudowollastonite.

Discussion

Formation and equilibria. The previous investigations have shown that Z-phase can be obtained from gels at 150 or 180 °C, or from mixtures of lime with amorphous silica or silicic acid at 140 to 240 °C, and that, at the higher temperatures at least, it forms as an intermediate stage in the crystallization of gyrolite. Assarsson (1958) could not prepare it at 120 °C, and concluded that if it had any field of stability, this was at about 130 to 150 °C. The present results show that it can be obtained at 120 °C either from Al-substituted tobermorite or from mixtures of lime and colloidal silica, and that even at this temperature it is an intermediate in the formation of gyrolite. If any stability field exists for Z-phase, it is therefore below 120 °C.

Composition, density, and refractive index. All the available evidence is consistent with a Ca/Si ratio of 0·5. The water content is indefinite, as much of the water is readily lost and regained. Funk (1961) concluded that, for material dried in a vacuum over silica gel, the composition was 2CaO.4SiO$_2$.3H$_2$O. For material in equilibrium with air of ordinary humidity the analytical and thermogravimetric evidence indicate a water content of 15 to 17 %, which corresponds approximately to a compositional range of CaO.2SiO$_2$.1·7—2·0H$_2$O.

Funk and Thilo (1955) found that material dried using liquid ammonia had a density of 2·23 g cm^{-3} and a mean refractive index of 1·52. For reasons given later, the structural element probably contains sixteen atoms of Si; assuming also the a and c parameters found in the present work and the composition 8CaO.16SiO$_2$.14H$_2$O, this gives a calculated density of 2·24 g cm^{-3}. The density may also be calculated from the refractive index using the Lorentz–Lorenz equation with atomic refractivities Ca = 3·25, O = 3·65, H = Si = zero, which have been found to give good results

for a wide range of calcium silicate phases (Howison and Taylor, 1957); assuming the same composition, this gives $2 \cdot 26$ g cm^{-3}.

The contents of the structural element for material in equilibrium with air of ordinary humidity are thus probably between $8CaO \cdot 16SiO_2 \cdot 14H_2O$ and $8CaO \cdot 16SiO_2 \cdot 16H_2O$.

Constitution and structure; relations to gyrolite, truscottite, and reyerite. The present results support the view that Z-phase is structurally related to gyrolite, truscottite, and reyerite, all of which are hexagonal or trigonal with a-axes of $9 \cdot 72$ $-9 \cdot 76$ Å and good (0001) cleavage. The resemblance to gyrolite in particular is shown by the infrared spectrum and the reversible shrinkage in the c-direction of about $3 \cdot 0$ Å that occurs on heating at 300–400 °C. The phases differ in their compositions and in the thicknesses of their structural elements, which are about $22 \cdot 1$ Å for gyrolite, $19 \cdot 1$ Å for reyerite, $18 \cdot 8$ Å for truscottite, and $15 \cdot 3$ Å for Z-phase.

Merlino (1972) determined the crystal structure of reyerite $((Na,K)_2Ca_{14}(Si_8O_{20})$ $(Si_{14}Al_2O_{38})(OH)_8 \cdot 6H_2O)$. The suggestions about the structure made by Clement and Ribbe (1973), which were not based on a structure determination, are only partly correct. Merlino showed that reyerite has a layer structure with two different kinds of anionic layer, designated T1 (Si_8O_{20}) and $T2\overline{T2}$ $(Si_{14}Al_2O_{38})$. Fig. 4*a* shows the layer sequence. The OH ions occur in interstices in the surfaces of the T1 and $T2\overline{T2}$ layers and complete the octahedral coordination of the Ca ions; the H_2O molecules and alkali cations occur in other interstices, and are not shown. The structure of reyerite provides a clue to the probable structures of truscottite, gyrolite, and Z-phase, suggested structures for which are shown in fig. 4*b–d*. It is proposed that the structure of truscottite (fig. 4*b*) is derived from that of reyerite essentially by replacement of the Al by Si and omission of the alkali cations and some of the H_2O molecules to give $Ca_{14}(Si_8O_{20})(Si_{16}O_{38})(OH)_8 \cdot 2H_2O$. The evidence regarding the Ca/Si ratio of truscottite is not clear-cut, some analyses and density measurements tending to suggest a lower value than 7:12; possibly 1 Ca ion in 7 and an equivalent amount of OH are missing from the structure.

The $T2\overline{T2}$ layer can be cleaved into two separate layers (T2 and $\overline{T2}$) by breaking 2 Si–O–Si linkages per $Si_{16}O_{38}$ unit, giving $(Si_8O_{20})_2$. If this occurs, and additional H_2O molecules and Ca ions are inserted between the T2 and $\overline{T2}$ layers, a formula of $Ca_{16}(Si_8O_{20})_3(OH)_8 \cdot 14H_2O$ could result, and it is suggested that this represents the situation in gyrolite (fig. 4*c*). The uncoupling of the T2 and $\overline{T2}$ layers would allow variations in stacking sequence, which could explain the occurrence of polytypism in this mineral.

A structure derived from that proposed for gyrolite by omission of the T1 layers, their associated OH ions, and alternate layers of Ca ions would have approximately the correct layer thickness and composition for Z-phase (fig. 4*d*). The probable Ca/Si ratio of $0 \cdot 5$ and absence of OH ions could be explained by assuming that 1 Ca ion in 7 is absent, as suggested above as a possibility for truscottite. The poor quality of X-ray patterns given by Z-phase, and the appearance of the crystals in the electron microscope, suggest that the crystal structure is imperfect; this might account for the reduction in a-axial length to $9 \cdot 65$ Å. Wieker (1967) concluded from a chemical method for investigating the degree of anion condensation that a preparation similar
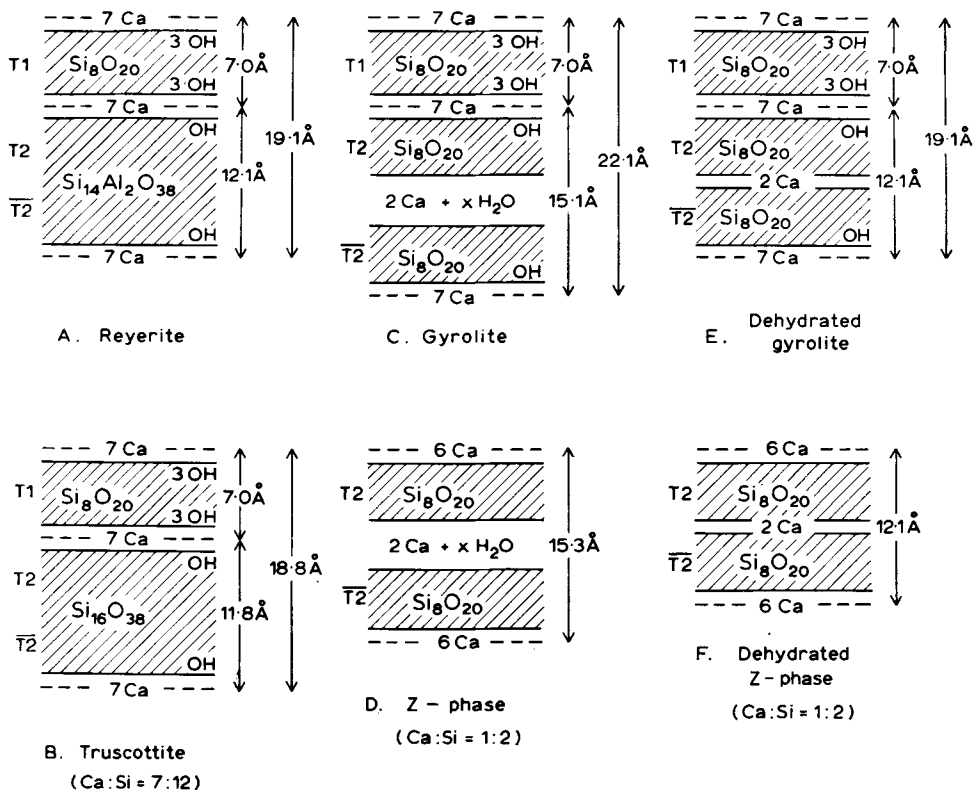
FIG. 4. Layer sequences for some lamellar calcium silicate phases. That of reyerite (A) is based on the results of Merlino (1972); the others are suggested. Water molecules present in interstices of the silicate layers are omitted, as are alkali cations in the case of reyerite.

to that described by Funk and Thilo (1955) contained layer-type anions. The constitution $CaH_4Si_2O_7$ proposed by Funk and Thilo (1955) is unlikely to be correct.

The hypothetical nature of these structures must be stressed, though they appear to satisfy all the available data. The reversible lattice shrinkage that occurs on heating gyrolite or Z-phase can be attributed to the loss of a layer of water molecules from between the T2 and $\overline{T2}$ layers (fig. 4e and f).

REFERENCES

Assarsson (G. O.), 1957. J. Phys. Chem. 61, 473.
—— 1958. Ibid. 62, 223.
—— 1960. Ibid. 64, 328.
—— 1962. Proc. 4th Int. Symp. Chem. Cement, Washington 1960, 1, 190.

CLEMENT (S. C.) and RIBBE (P. H.), 1973. *Amer. Min.* **58,** 517.

CLIFF (G.), GARD (J. A.), LORIMER (G. W.), and TAYLOR (H. F. W.), 1975. *Min. Mag.* **40,** 113.

FUNK (H.), 1961. *Zeits. anorg. allg. Chem.* **313,** 1.

—— and THILO (E.), 1955. Ibid. **278,** 237.

GARD (J. A.), 1965, *The Chemistry of Cements* (H. F. W. TAYLOR, ed.), **2,** ch. 21, p. 266 and Pls. 31 and 32. London and New York (Academic Press).

—— 1971. *The Electron Optical Investigation of Clays* (J. A. Gard, Ed.), ch. 2, p. 55. London (Mineralogical Society).

HARKER (R. I.), 1964. *Journ. Amer. Ceram. Soc.* **47,** 521.

HOWISON (J. W.) and TAYLOR (H. F. W.), 1957. *Mag. Concrete Res.* **9,** 13.

MACKAY (A. L.) and TAYLOR (H. F. W.), 1953. *Min. Mag.* **30,** 80.

MERLINO (S.), 1972. *Nature,* **238,** 124.

MITSUDA (T.) and TAYLOR (H. F. W.), 1975. *Cement Concrete Res.* **5,** 203.

TAYLOR (H. F. W.), 1962. *Proc. 4th Int. Symp. Chem. Cement, Washington 1960,* **1,** 167.

WIEKER (W.), 1967. *Proc. Symp. Autoclaved Calcium Silicate Building Products, London 1965,* 205.

[Manuscript received 7 November 1974]