202. *Hydrothermal Chemistry of the Silicates. Part X.* A Partial Study of the Field* $CaO–Al_2O_3–SiO_2–H_2O$.

By R. M. Barrer and P. J Denny.

A hydrothermal study has been made of part of the $CaO–Al_2O_3–SiO_2–H_2O$ system in the range 125—450°. The crystalline products depended to some extent upon whether the silica was introduced as a sol or as powdered silica glass. These products included boehmite, corundum, and two calcium aluminate hydrates as silica-free species; and cristobalite, and small amounts of wollastonite and foshagite, as alumina-free species. A series of grossularite-hydrogarnets was prepared, and also a number of zeolites (tetragonal and cubic analcites, thomsonite, harmotome, epistilbite, and a little mordenite). Anhydrous phases formed included anorthite and its hexagonal dimorph. By sintering reactions the hydrated phases were transformed for the most part into anorthite, its hexagonal dimorph, and $12CaO,7Al_2O_3$. A number of the phases have been characterised by thermogravimetry, differential thermal analysis, *X*-ray diffraction, and electron and optical microscopy; and crystallisation fields have been delineated. Crystallisation is normally less complete than for alkali-metal aluminosilicates under comparable conditions. Addition of tetramethylammonium hydroxide to the calcium aluminosilicate gels resulted in the appearance of bayerite, a sodalite-type structure, a zeolite of the gmelinite-chabazite family, and a montmorillonoid as additional phases.

Of the various calcium silicates a number have been synthesised by hydrothermal methods,[1] and the majority have been characterised by *X*-ray and optical methods.[2] Aluminates of calcium have also received attention [3] and have been produced hydrothermally together with hydrated forms of alumina such as gibbsite and boehmite. The system $CaO–Al_2O_3–SiO_2–H_2O$ has been examined in part by various workers. Goldsmith and Ehlers [4] crystallised compositions $CaO,Al_2O_3,2SiO_2$ + aq. over the temperature range 220—504°, with glasses and oxide mixtures as starting materials. Anorthite, a hexagonal dimorph of this felspar, and the fibrous zeolite thomsonite were reported. Ehlers [5] also prepared thomsonite, and at higher temperatures grossularite, anorthite, and its hexagonal dimorph, the parent mixtures of oxides and of glass being of composition $4CaO,3Al_2O_3,6SiO_2$. Davis and Tuttle [6] made anorthite and its hexagonal and orthorhombic polymorphs by the pyrolytic method.

Ames and Sand [7] recently synthesised the zeolites calcium analcite (wairakite) and calcium mordenite from co-precipitated gels and calcined nitrates. The wairakite was formed from mixtures of composition $CaO,Al_2O_3,5SiO_2$ + aq. Mordenite was prepared from hydrous mixtures $CaO,Al_2O_3,10SiO_2$ (at 340—380°/1000 atm.), and at 455° anorthite and cristobalite were found as crystalline products. Ellis [8] also studied the hydrothermal crystallisation of calcium aluminosilicate glasses and oxide mixtures of composition $CaO,Al_2O_3,8SiO_2$ between 200° and 450°. From glasses, quartz, anorthite, epistilbite, analcite, mordenite, and heulandite were reported, but from oxide mixtures only cristobalite, anorthite, analcite, and mordenite. Using glass of composition $3CaO,Al_2O_3,nSiO_2$

---

* Part IX, preceding paper.

[1] See *e.g.*, Corwin, Yalman, Edwards, and Shaw, *J. Phys. Chem.*, 1957, **61**, 941; Assarsson, *J. Phys. Chem.*, 1958, **62**, 223; Heller and Taylor, *J.*, 1951, 2397; Taylor, *J.*, 1953, 163.

[2] Heller and Taylor, " Crystallographic Data for the Calcium Silicates," D.S.I.R. and H.M.S.O., London, 1956.

[3] *E.g.*, Majumdar and Roy, *J. Amer. Ceram. Soc.*, 1956, **39**, 434; Schneider and Thorvaldson, *Canad. J. Res.*, 1941, **19**, *B*, 123; Johnson and Schneider, *ibid.*, 1943, **21**, *B*, 236.

[4] Goldsmith and Ehlers, *J. Geol.*, 1952, **60**, 386.

[5] Ehlers, *J. Geol.*, 1953, **61**, 233.

[6] Davis and Tuttle, *Amer. J. Sci.*, Bowen Vol., 1952, p. 107.

[7] Ames and Sand, *Amer. Mineral.*, 1958, **43**, 476.

[8] Ellis, Ph.D. Thesis, Otago, N.Z.

(n = 1—3), Flint, McMurdie, and Wells[9] made members of the hydrogrossular series, which were solid solutions of composition intermediate between the end-members $3CaO,Al_2O_3,6H_2O$ and $3CaO,Al_2O_3,3SiO_2$, but the anhydrous end-member $3CaO,Al_2O_3,3SiO_2$ could not be synthesised. Stability relations of hydrogrossulars were also examined by Yoder.[10]

The CaO–Al_2O_3–SiO_2–H_2O system continues to attract attention[11] on account of its importance both geologically and technically, but even so exploration has been partial only, and it appears that the products often depend on the nature of the starting materials.[8] It was, therefore, of considerable interest to examine this system further, especially with active hydrous aluminosilicate gels as reactants. In the sodium aluminosilicate field crystallisation from active gels can occur at 100° or below;[12] but less reactive materials crystallise only above about 150°.[13] The crystalline products then vary according to the temperature of growth. In the present paper we record the results of a further partial exploration of the lime–alumina–silica–water system, in which the reactivity of the starting materials is varied, and in which additional chemical aspects of crystallisation have been examined.

EXPERIMENTAL

Two forms of silica were used: "Syton 2X," a stable sol containing 30% by weight of silica; and finely powdered "Vitreosil" silica glass, of purity greater than 99·8%. The alumina was a freshly prepared amorphous gel, made as described elsewhere.[14] The calcium oxide was obtained by ignition of finely powdered "AnalaR" calcium carbonate. When silica sol was used, the gels were made by first grinding solid calcium oxide and alumina gel together. Distilled water was added and the suspension stirred. "Syton 2X" was then added and the mixture stirred for a further 15 min. With silica glass as a starting material the three components were mixed in the correct proportions and ground while dry. The charge was placed in the autoclave, and distilled water was added.

Stainless-steel autoclaves of about 16 c.c. internal capacity were employed as reaction vessels. Preparations on a larger scale were made in an electrically heated 1 l. autoclave supplied by C. W. Cook and Sons Ltd. In all syntheses the ratio of water to solid was near 10 c.c. per 0·75 g. The degree of filling was always 0·5. Electrically heated ovens, thermostatically controlled within ±1°, were used for heating up to 300° c, and an electrically heated furnace for heating between 300° and 450°. The furnace could hold nine autoclaves simultaneously and was maintained at constant temperature within ±2°. Seven chromel–alumel thermocouples were placed at different points of the copper heating-block to check that no appreciable thermal gradients appeared.

After the appropriate heating period the autoclaves were air-cooled or water-quenched. The pH's of the cold mother-liquors were measured, and the products were then filtered or centrifuged off and washed with distilled water until neutral to indicators. They were then air-dried, or dried in an oven at 75°, or in a vacuum-desiccator. The white powders were then examined by *X*-ray diffraction, optically, by electron microscopy and electron diffraction, and by differential thermal analysis and thermogravimetry.

In *X*-ray work, a Guinier camera, and also a 9 cm. Debye–Scherrer powder camera, were variously used, with filtered Cu-K_α radiation, supplied either by a Raymax *X*-ray diffraction unit or by a Hilger HRX *X*-ray unit. A Leitz polarising microscope and a Vickers projection microscope were employed in optical work, and a Philips electron microscope for the further examination of the crystals. The differential thermal analyser and thermogravimetric equipment have been described elsewhere.[15] The rate of heating in both differential thermal analysis and thermogravimetry was 10° per min.

[9] Flint, McMurdie, and Wells, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 13.
[10] Yoder, *J. Geol.*, 1950, **58**, 221.
[11] Glasser and Roy, *Amer. Mineral.*, 1959, **44**, 447; Roy, *J. Amer. Ceram. Soc.*, 1958, **41**, 293.
[12] Barrer, Baynham, Bultitude, and Meier, *J.*, 1959, 195.
[13] Barrer and White, *J.*, 1951, 1167.
[14] *E.g.*, Weiser and Milligan, *J. Phys. Chem.*, 1937, **41**, 1029.
[15] Barrer and Langley, *J.*, 1958, 3804.

RESULTS

Although the calcium aluminosilicate gels did not crystallise as readily as did those of the alkali metals it was possible to obtain major or minor yields of the species given in Table 1. The ease of crystallisation diminished with falling temperature, and as the silica content increased relative to the amount of alumina and base. Rather surprisingly, the reactive gels prepared from " Syton 2X " silica sols often crystallised less readily than did mixtures containing powdered silica glass. This behaviour may be attributed to the large surface of the reactive gels, which adsorbed calcium hydroxide strongly[16] and so lowered the pH of the mother-liquor and reduced the solubility of the gel, which is always higher in alkaline media. Attempts to saturate the crystallising gels with calcium by adding calcium chloride to the mother-liquors resulted in no noticeable improvement. The products frequently contained proportions of non-crystalline gel, or were non-crystalline altogether, even after long reaction times. Where partial crystallisation had occurred several species often appeared together.

TABLE 1. *Crystalline species formed from calcium aluminosilicate gels and mixtures.*

Reference letter	Identification	Maximum yield *
Ca-A	Boehmite, Al_2O_3,H_2O	Major
Ca-B	Corundum, Al_2O_3	Major
Ca-M	$4CaO,3Al_2O_3,3H_2O$	Major
Ca-D	Tetragonal Ca-analcite, $CaO,Al_2O_3,4SiO_2,2H_2O$	Major
Ca-E	Cubic Ca-analcite, $CaO,Al_2O_3,4SiO_2,2H_2O$	Major
Ca-F	Anorthite, $CaO,Al_2O_3,2SiO_2$	Major
Ca-P	Hexagonal dimorph of anorthite, $CaO,Al_2O_3,2SiO_2$	Major
Ca-H	α-Cristobalite, SiO_2	Major
Ca-I	Ca-thomsonite, $CaO,Al_2O_3,2SiO_2,2H_2O$	Minor
Ca-J	Ca-epistilbite, $CaO,Al_2O_3,6SiO_2,5H_2O$	Major
Ca-K	Hydrogrossular series, $3CaO,Al_2O_3,6H_2O$ to $3CaO,Al_2O_3,3SiO_2$	Major
Ca-L	Ca-harmotome, $CaO,Al_2O_3,3SiO_2,5H_2O$	Major
Ca-N	Tricalcium aluminate hexahydrate, $3CaO,Al_2O_3,6H_2O$	Major
Ca-O	Unidentified	Major
Ca-Q	Ca-mordenite, $CaO,Al_2O_3,10SiO_2,6{\cdot}7H_2O$	Very minor
Ca-R	Foshagite, $4CaO,3SiO_2,H_2O$	Very minor
Ca-S	Wollastonite, CaO,SiO_2	Very minor
Ca-X	Unidentified	Very minor
Ca-Y	Unidentified	Very minor
Ca-Z	Unidentified	Very minor

* A " major " yield is one in which a crystalline product appears more abundant than any other species, or gel, under microscopic examination.

TABLE 2. *Syntheses in the lime–alumina system.*

Anhyd. gel composition (oxide formula)	Time (days)	Temp.	Products	pH of cold mother-liquor
CaO,Al_2O_3	18	300°	Ca-A + Ca-M	>10·5
CaO,Al_2O_3	18	425	Ca-B + Ca-M	9·2
CaO,Al_2O_3	2	445	Ca-B + Ca-M	>10·5
$3CaO,Al_2O_3$	26	125	Ca-N	>10·5
$3CaO,Al_2O_3$	9	200	Ca-N + $Ca(OH)_2$ (?)	>10·5
$3CaO,Al_2O_3$	9	220	Ca-M + $Ca(OH)_2$	>10·5
$3CaO,Al_2O_3$	18	300	Ca-M	>10·5
$3CaO,Al_2O_3$	3	410	Ca-M + $Ca(OH)_2$	>10·5
$3CaO,Al_2O_3$	18	430	Ca-M	>10·5

Lime–alumina gels free from silica crystallised more readily than calcium aluminosilicate gels, a behaviour ascribed to the higher pH's of the mother-liquors (compare Table 2 with Tables 3—5). At the silica-rich end crystallisation was always more sluggish still. For the formation of calcium silicates a higher lime content would be desirable.

The Lime–Alumina System.—The lime–alumina system under hydrothermal conditions yielded the products shown in Table 2. Crystalline calcium hydroxide was often a product from the lime-rich compositions, and Ca-M ($4CaO,3Al_2O_3,3H_2O$) was universally present in

---

[16] Greenberg, *J. Phys. Chem.*, 1956, **60**, 325.

TABLE 3. *Hydrothermal crystallisation of gels* $CaO,Al_2O_3,nSiO_2$ *prepared by using* SiO_2 *sol.*

Temp. and times (days)

n	180° 8	200° 10—30	225° 41	245° 34	252° 11	260° 29	280° 39	285° 8
1	Fair Ca-M (8·9) *	Poor Ca-P Poor Ca-A (9·8)	Fair Ca-P Fair Ca-I (7·6)	Fair Ca-P Fair Ca-I (6·8)	Good Ca-P (10·0)	Good Ca-F Poor Ca-A (8·5)	Fair Ca-P V. poor Ca-P Fair Ca-A (6·8)	Fair Ca-M (8·9)
2	Fair Ca-M (9·6)	U † (7·9)	U (10·0)	Fair Ca-P Fair Ca-I (6·7)	Good Ca-P (10·5)	Good Ca-F Poor Ca-M (5·8)	Good Ca-F Poor Ca-P (6·4)	Fair Ca-D Poor Ca-M (9·6)
3	Fair Ca-M (7·3)	U (8·0)	U (10·0)	U (10·0)	Fair Ca-L (6·5)	Fair Ca-D Fair Ca-F (5·6)	Good Ca-D V. poor Ca-P (6·2)	Fair Ca-M (7·3)
4	Fair Ca-M (8·5)	U (8·5)	Poor Ca-J (6·2)	Fair Ca-J (6·8)	Fair Ca-L (9·0)	Good Ca-D (5·6)	Fair Ca-D (6·0)	Fair Ca-M (8·5)
5	Poor Ca-M (6·9)	U (8·5)	U (7·3)	Fair Ca-J (8·5)	U (6·6)	Fair Ca-J (5·8)	U (5·6)	Fair Ca-M (6·9)
6	Poor Ca-M (6·9)	U (8·5)	U (7·4)	Fair Ca-J (6·5)	U (6·5)	U (5·8)	U (5·5)	Fair Ca-M (6·9)
7	Poor Ca-M (6·8)	U (8·0)	U (7·4)	U (9·0)	U (6·5)	U (5·8)	U (7·0)	Fair Ca-M (6·8)
8	Fair Ca-M (8·5)	U	—	U (6·6)	U (6·5)	U (5·8)	U (5·6)	Poor Ca-M (8·5)
9	Fair Ca-M (8·7)	U	—	U (6·8)	U (6·5)	U (5·8)	U (5·6)	Poor Ca-M (8·7)

Temp. and times (days)

n	300° 32	351° 12	390° 8	410° 3	425° 3	440° 5	450° 6
1	Fair Ca-A Fair Ca-P Poor Ca-F (10·0)	Good Ca-F Fair Ca-P Fair Ca-A (5·6)	Fair Ca-A Fair Ca-F Fair Ca-P (6·8)	Good Ca-F Fair Ca-P Fair Ca-A (6·7)	Fair Ca-A Fair Ca-F Poor Ca-P (7·0)	Good Ca-B Poor Ca-F V. poor Ca-P (6·5)	Good Ca-B Poor Ca-F V. poor Ca-P (6·7)
2	Fair Ca-P Fair Ca-F (10·5)	Good Ca-F Poor Ca-P (5·6)	Good Ca-F Fair Ca-P (5·7)	Good Ca-F Fair Ca-P Poor Ca-E V. poor Ca-A (5·7)	Good Ca-F Fair Ca-P Poor Ca-A (6·5)	Good Ca-F Fair Ca-A Fair Ca-P (6·0)	Good Ca-F Poor Ca-P (6·5)
3	Good Ca-D Poor Ca-F V. poor Ca-P (6·5)	Fair Ca-F Fair Ca-E Poor Ca-P (5·6)	Good Ca-E Poor Ca-F Poor Ca-P (5·5)	Good Ca-E Poor Ca-F Poor Ca-P (5·6)	Good Ca-F Poor Ca-P V. poor Ca-E (5·7)	Good Ca-F Fair Ca-P (5·4)	Fair Ca-F Fair Ca-P Poor Ca-H (6·0)
4	Good Ca-D Poor Ca-F (9·0)	Good Ca-E Poor Ca-F V. poor Ca-P (5·5)	Good Ca-E Poor Ca-F Poor Ca-P (5·4)	Fair Ca-E V. poor Ca-F V. poor Ca-P (10·5)	Fair Ca-E Fair Ca-F Poor Ca-P (5·5)	Fair Ca-E Fair Ca-F Poor Ca-P (5·5)	Fair Ca-F Fair Ca-P Fair Ca-H (5·4)
5	U (6·6)	Good Ca-E V. poor Ca-F (5·6)	Good Ca-E Poor Ca-F Poor Ca-P (5·5)	Poor Ca-F (5·7)	Good Ca-E Poor Ca-F Poor Ca-P (5·7)	Good Ca-E Fair Ca-F Poor Ca-P (5·5)	Fair Ca-F Fair Ca-P Fair Ca-H (5·5)
6	U (6·5)	Poor Ca-E (5·5)	Good Ca-E V. poor Ca-F Poor Ca-P (5·5)	V. poor Ca-E (5·7)	Poor Ca-H V. poor Ca-F (5·7)	Fair Ca-F Poor Ca-P Fair Ca-H (5·5)	U (7·2)
7	U (6·5)	U (5·5)	Good Ca-E V. poor Ca-F Poor Ca-P (5·7)	U (5·7)	U (5·7)	Fair Ca-F Poor Ca-P Fair Ca-H (5·5)	Good Ca-H Poor Ca-P Poor Ca-F
8	U (6·5)	U (7·9)	Good Ca-E V. poor Ca-F V. poor Ca-P (5·5)	U (10·5)	U (5·5)	Good Ca-H Poor Ca-P V. poor Ca-F (5·5)	Good Ca-H Poor Ca-P Poor Ca-F (5·5)
9	U (6·5)	U (5·5)	Good Ca-E V. poor Ca-F V. poor Ca-P (5·5)	U (10·0)	U (5·5)	Good Ca-H Poor Ca-P V. poor Ca-F (5·5)	Good Ca-H Poor Ca-P Poor Ca-F (5·5)

* Figures in brackets are the pH's of the cold mother-liquors after reaction.

† U denotes non-crystalline. The terms " poor," " fair," and " good " in this and similar Tables refer to the yields of the crystals. Yields were estimated visually, and from the intensities of the *X*-ray diffraction patterns.

TABLE 4. *Hydrothermal crystallisation of gels* $3CaO,Al_2O_3,nSiO_2$ *prepared by using* SiO_2 *sol.*

	Temp. and times (days)				
n	200°	220°	250°	295°	300°
	20	9	30	8	26
1	Good Ca-K(N) (10·5) *	Good Ca-K V. poor Ca-P (7·5)	Good Ca-O (10·5)	Poor Ca-K Poor Ca-O (10·5)	Poor Ca-O Poor Ca-F (7·6)
2	Fair Ca-K(N) (6·9)	Good Ca-K Poor Ca-P (8·2)	Poor Ca-O Fair Ca-F (9·8)	Fair Ca-K (8·8)	Fair Ca-K Poor Ca-F (7·2)
3	Good Ca-K(N) (9·4)	Fair Ca-P (8·0)	Good Ca-E Poor Ca-F V. poor Ca-O	Poor Ca-K Good Ca-P (6·0)	Good Ca-F + poor ? (5·7)
4	Good Ca-K(N) (10·5)	Fair Ca-P (8·0)	Good Ca-E Fair Ca-F (6·4)	—	Good Ca-F (5·5)
5	Poor Ca-K(N) (10·0)	V. poor Ca-D V. poor Ca-P (5·8)	Fair Ca-O Fair Ca-F (5·8)	Good Ca-P V. poor Ca-D (5·8)	Good Ca-D Poor Ca-F (6·0)
6	V. poor Ca-K(N) (6·0)	—	Fair Ca-E Poor Ca-F (5·8)	Fair Ca-O (5·5)	Good Ca-D V. poor Ca-F (5·6)
7	V. poor Ca-K(N) (6·5)	Poor Ca-D (6·0)	—	—	Good Ca-E Poor Ca-F (6·0)
8	—	U † (6·7)	U (5·8)	Good Ca-E (5·5)	Good Ca-D (6·0)
9	—	U (6·7)	U (5·5)	—	U (6·0)

	Temp. and times (days)			
n	350°	380°	415°	450°
	10	7	6	3
1	Good Ca-O (10·5)	Good Ca-O V. poor Ca-K (10·5)	Fair Ca-K Fair Ca-O (10·5)	Good Ca-O Poor Ca-K (10·5)
2	Good Ca-K Poor Ca-O (5·0)	Good Ca-K Poor Ca-O (8·5)	Good Ca-K Poor Ca-O (9·4)	Good Ca-O Poor Ca-K (8·0)
3	Fair Ca-K Fair Ca-P (5·6)	Fair Ca-K Fair Ca-P (6·4)	Good Ca-K V. poor Ca-O (5·8)	Good Ca-K Poor Ca-F (5·7)
4	Good Ca-P (5·5)	—	Fair Ca-P Fair Ca-F (5·5)	Fair Ca-F Fair Ca-K (5·6)
5	Good Ca-E Poor Ca-P (5·5)	U (7·6)	Poor Ca-E Fair Ca-F (5·5)	Fair Ca-F V. poor Ca-K (5·6)
6	Good Ca-E V. poor Ca-P (5·5)	—	Good Ca-E Poor Ca-F (5·5)	—
7	Good Ca-E V. poor Ca-P (5·5)	—	Fair Ca-O Poor Ca-F V. poor Ca-E (5·6)	—
8	Good Ca-E V. poor Ca-P (5·5)	Good Ca-E (5·6)	—	Poor Ca-O (5·5)
9	Good Ca-E Poor Ca-H V. poor Ca-P (5·5)	Fair Ca-O (5·5)	—	V. poor Ca-O (5·5)

* See footnotes to Table 3.

all crystalline products formed at 220° or above. At lower temperatures the more highly hydrated Ca-N ($3CaO,Al_2O_3,6H_2O$) appeared, the transition temperature Ca-N to Ca-M being between 200° and 220°. Yields were satisfactory but, especially for shorter reaction times, non-crystalline gel was often observed, and the crystals were small and irregular.

Calcium Aluminosilicate Crystallisation Fields.—The investigation was carried out by using hydrous gels of oxide formula $CaO,Al_2O_3,nSiO_2$ ($1 < n < 9$), silica sol being used to prepare the initial compositions. In a second investigation gels of oxide formula $3CaO,Al_2O_3,nSiO_2$ ($1 < n < 9$) were employed, also made with silica sol. A third study used the same compositions as the first, but with powdered silica glass as the source of silica. The experimental conditions and products are summarised in Tables 3—5.

(*a*) Species obtained from the gels $CaO,Al_2O_3,nSiO_2$ of Table 3 included mainly thomsonite, epistilbite, anorthite, its hexagonal dimorph, cristobalite, and cubic and tetragonal forms of Ca-analcite. The cubic form of analcite appeared at higher, and the tetragonal form at lower temperatures. The crystals obtained were very small and often anhedral. The growth and variety of crystals became more marked at higher temperatures and lower silica content. The reproducibility of crystal formation was found to be good, and the fields of crystal growth for several species are indicated in Figs. 1*a*, *b*, and *c*. Gels crystallised at 180° and 285° for the relatively short time of 8 days gave the calcium aluminate hydrate Ca-M as the main product for most values of *n*, but gels crystallised at similar temperatures and for longer times (about 30 days) normally failed to yield this species, which may therefore be a metastable intermediate. Calcium harmotome (Ca-L) appeared on two occasions only, after relatively shorter crystallisation times (11 days at 252°), and so may also here be metastable.

(*b*) When the more lime-rich gels $3CaO,Al_2O_3,nSiO_2$, also prepared by using silica sol, were treated hydrothermally the crystallisation times were still long (Table 4), but crystallisation proceeded more readily. Analcites again appeared over much of the field of composition, but epistilbite (Ca-J) and thomsonite (Ca-I) were absent and also cristobalite (Ca-H) was less common. Two new phases were formed, namely, Ca-O, which was not identified, and Ca-K which represented a series of grossularite hydrogarnets. The crystallisation fields are shown in Figs. 2*a*—*c*. Comparison with Fig. 1 shows that the central regions of formation of several species (Ca-E, Ca-D, Ca-P, and Ca-F) are displaced to compositions corresponding to higher silica contents. Despite the additional lime, the pH's of the cold mother-liquors (Table 4) were not noticeably above those recorded in Table 3.

TABLE 5. *Hydrothermal crystallisation of oxide mixtures* $CaO,Al_2O_3,nSiO_2$, *using powdered* SiO_2 *glass.*

Temp. and times (days)

n	150°	200°	250°	275°	292°
	20	24	31	18	31
1	Fair Ca-N V. poor $Ca(OH)_2$ (10·5) †	V. poor Ca-N Fair Ca-L V. poor $Ca(OH)_2$ (8·5)	Poor Ca-A Poor Ca-P Poor Ca-F (10·5)	Fair Ca-A Fair Ca-P (8·7)	Poor Ca-F Fair Ca-A +? (6·7)
2	Fair Ca-N V. poor $Ca(OH)_2$ (10·5)	Fair Ca-L V. poor Ca-N V. poor $Ca(OH)_2$ (8·5)	V. poor Ca-L Poor Ca-P Poor Ca-F (6·9)	Fair Ca-F Fair Ca-P (6·0)	Fair Ca-F (6·7)
3	Fair Ca-N V. poor $Ca(OH)_2$ (8·5)	Good Ca-L V. poor $Ca(OH)_2$ (6·5)	Good Ca-L (6·7)	Poor Ca-L Poor Ca-P (6·0)	Fair Ca-E Fair Ca-F (6·7)
4	Fair Ca-N V. poor $Ca(OH)_2$ (10·5)	Good Ca-L (6·5)	Good Ca-L (6·5)	Poor Ca-P V. poor Ca-J(?) (6·0)	Good Ca-E (6·7)
5	Fair Ca-N V. poor $Ca(OH)_2$ (10·0)	Fair Ca-L V. poor $Ca(OH)_2$ (6·5)	—	V. poor Ca-J(?) Poor Ca-P (6·0)	Good Ca-E (6·7)
6	Fair Ca-N V. poor $Ca(OH)_2$ (10·0)	Poor Ca-L V. poor $Ca(OH)_2$	Good Ca-J (6·5)	Fair Ca-P (6·0)	Good Ca-E (6·7)
7	Poor Ca-N V. poor $Ca(OH)_2$ (10·0)	Poor Ca-L V. poor $Ca(OH)_2$ (6·5)	Good Ca-J (6·5)	Fair Ca-P (6·0)	Good Ca-E (6·7)
8	Poor Ca-N V. poor $Ca(OH)_2$ (9·5)	Fair Ca-L V. poor $Ca(OH)_2$ (6·5)	—	Fair Ca-P (6·0)	Good Ca-E (6·7)
9	Poor Ca-N V. poor $Ca(OH)_2$ (9·0)	Poor Ca-L V. poor $Ca(OH)_2$ (6·5)	—	Poor Ca-P (6·0)	Fair Ca-E (6·7)

TABLE 5. (*Continued.*)

n	Temp. and times (days) 300° 5	 300° 12	 350° 7	 420° 6	 450° 4
1	—	—	Fair Ca-F Poor Ca-A (9·5)	Fair Ca-F Fair Ca-P V. poor Ca-A (6·7)	Fair Ca-O Fair Ca-K V. poor $Ca(OH)_2$ (6·5)
2	—	—	Good Ca-F Poor Ca-P (7·0)	—	Good Ca-F V. poor Ca-P V. poor Ca-O V. poor Ca(OH) (6·5)
3	Poor Ca-L (6·3)	Fair Ca-L (6·7)	Fair Ca-E Poor Ca-F Poor Ca-P (6·7)	Fair Ca-P Fair Ca-F (5·8)	Fair Ca-F Fair Ca-P Fair Ca-E Poor Ca-H (6·5)
4	—	—	V. good Ca-E (6·7)	—	Poor Ca-F Fair Ca-E Poor Ca-P Fair Ca-H (6·5)
5	—	—	Good Ca-E (6·7)	Good Ca-E Fair Ca-P Poor Ca-F (6·0)	Fair Ca-E Poor Ca-F V. poor Ca-P Fair Ca-H (6·5)
6	—	—	Fair Ca-E (6·7)	Good Ca-H Poor Ca-P Poor Ca-E V. poor Ca-F (5·8)	Fair Ca-H Fair Ca-E V. poor Ca-F(?) V. poor Ca-P (6·5)
7	—	—	Poor Ca-E (6·7)	U * (10·5)	Fair Ca-H Fair Ca-E V. poor Ca-P (6·5)
8	—	—	V. poor Ca-E (6·7)	—	Fair Ca-H Poor Ca-E V. poor Ca-P (6·5)
9	—	--	V. poor Ca-E (6·7)	—	Fair Ca-H Poor Ca-E V. poor Ca-P (6·5)

See footnotes to Table 3.

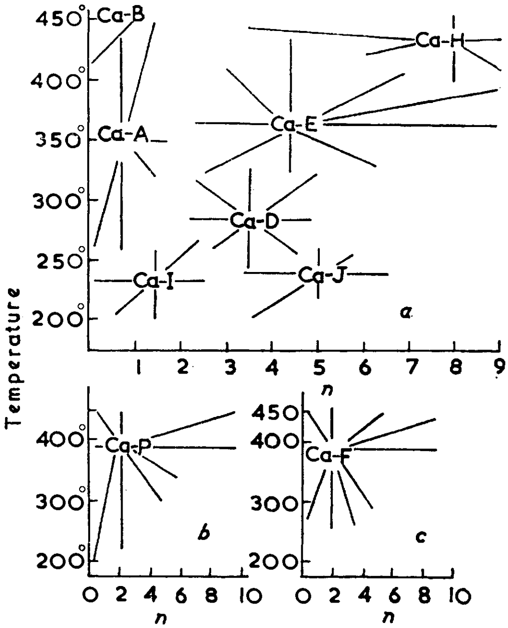
TABLE 6. *Products of crystallisation of gels* $CaO,Al_2O_3,nSiO_2,3NMe_4{\cdot}OH + aq.$

Reference letter	Identification	Reference letter	Identification
(Ca,N)-A	Boehmite, Al_2O_3,H_2O	(Ca,N)-P	Hexagonal dimorph of anorthite
(Ca,N)-C	Bayerite, $Al_2O_3,3H_2O$	(Ca,N)-V	Montmorillonite-type phase
(Ca,N)-T	Sodalite-type phase	(Ca,N)-G	Gmelinite-type phase
(Ca,N)-L	Cubic harmotome		

(*c*) When mixtures of oxide composition $CaO,Al_2O_3,nSiO_2$ ($1 < n < 9$) were made with silica glass powder in place of the silica sol, better yields of crystals were obtained. Ca-harmotome (Ca-L) appeared over much of the lower temperature field, but Ca-analcite was still an important phase. Species Ca-N, or hydrogrossulars Ca-K poor in silica and therefore near the non-siliceous end member Ca-N, appeared below 210° instead of aluminosilicates. This indicates that the silica glass is unreactive at these low temperatures, so that the system behaves as though the silica component was not present. At about 300° harmotome (Ca-L) crystallised first, and then recrystallised to analcite (Ca-E) after a time greater than 12 days. The products and conditions of crystallisation are shown in Table 5, and crystallisation fields are given in Fig. 3*a*—*c*.

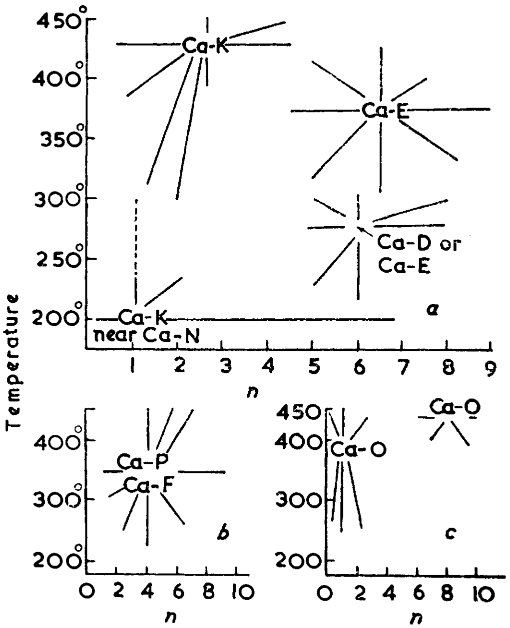
Crystallisation of Calcium Aluminosilicate Gels in Presence of Tetramethylammonium Hydroxide.—Because of the low pH often found in the cold mother-liquors after reaction (Tables

Fig. 1.



(*a*), (*b*), (*c*) *Crystallisation fields of some species grown hydrothermally from the four-component system* $CaO–Al_2O_3–SiO_2–H_2O$. *The parent gels were of oxide composition* $CaO,Al_2O_3,nSiO_2$ + aq. *The value of n is the abscissa in the Figure.*

Fig. 2.



(*a*), (*b*), (*c*) *Crystallisation fields from the four-component system* $CaO–Al_2O_3–SiO_2–H_2O$. *The parent gels were of oxide composition* $3CaO,Al_2O_3,nSiO_2$ + aq. *The value of n is the abscissa in the Figure.*

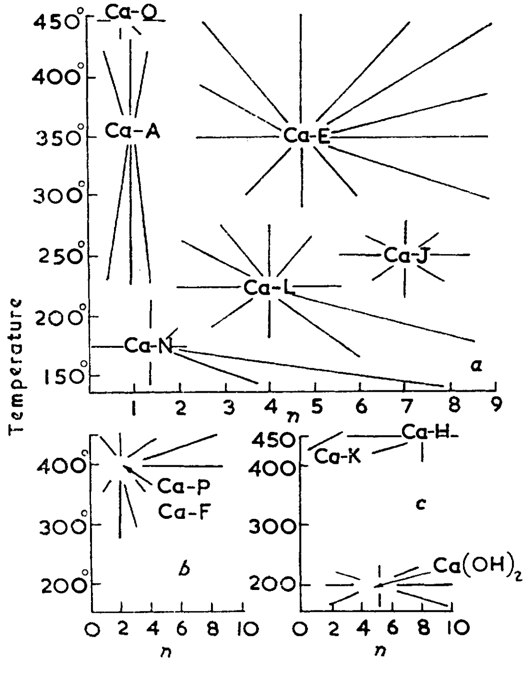


Fig. 3.

(*a*), (*b*), (*c*) *Crystallisation fields from the four-component system* $CaO–Al_2O_3–SiO_2–H_2O$. *The reaction mixtures were lime + aluminium hydroxide in the molar ratio* 1 : 1 *together with n molar parts of powdered silica* + aq. *The value of n is the abscissa in the Figure.*

3—5), tetramethylammonium hydroxide was added to maintain the pH and so to act as a possible mineraliser. Gels of composition $CaO,Al_2O_3,nSiO_2,\frac{1}{2}NMe_4{\cdot}OH$ + aq. (n = 2 or 4) were first studied. However, little or no crystallisation occurred at 200° in times up to 16 days. Gels of composition $CaO,Al_2O_3,nSiO_2,3NMe_4{\cdot}OH$ + aq. were then found to crystallise within 7 days at 100°, and so were examined further. The organic base became in part a constituent of some of the crystals so that its function was not just that of a mineralising catalyst. The tetramethylammonium ion tended to be hydrolysed under the conditions employed,[17] so that the actual organic ions incorporated are not known. However, all are derived from amine bases, and are given the symbol N. The species formed are summarised in Table 6. The extent to which nitrogenous ions are incorporated must vary from phase to phase. No ions are present in the hydrated aluminas, but nitrogenous sodalites, harmotomes, and montmorillonite-type phases have been synthesised in entire absence of metallic inorganic ions,[17] so that the organic ions can compete with Ca^{2+} for lattice sites. In (Ca,N)-P there may, however, be little nitrogenous material, because the lattice is less open [18] and so less able to provide sites for the larger alkylammonium ions. The bayerite, sodalite, and montmorillonite of Table 6 did not appear in absence of the organic base (cf. Table 1).

Table 7 records the experimental conditions under which the phases of Table 6 appeared. Two methods of making the reaction mixtures were used. In method (*a*) quicklime and alumina gel were ground together, silica sol was added with stirring, and finally the tetramethylammonium hydroxide was also added. In method (*b*) the organic base was first mixed with alumina gel, the silica sol next stirred in, and finally the solid calcium oxide added. Use of method (*b*) resulted, *inter alia*, in the appearance of the montmorillonite-type phase (Ca,N)-V.

TABLE 7. *Crystallisation of mixtures* $CaO,Al_2O_3,nSiO_2,3NMe_4{\cdot}OH$ + aq.*

	Method of mixing and conditions			
	Method (*a*)		Method (*b*)	
n	4 days 150°	7 days 200°	3 days (*n* = 1—4) 200°	2 days (*n* = 5—8) 250°
1	Fair (Ca,N)-C Poor (Ca,N)-T	Good (Ca,N)-A	Fair (Ca,N)-A	Fair (Ca,N)-A Fair (Ca,N)-P
2	Poor (Ca,N)-C Fair (Ca,N)-T	Good (Ca,N)-P Poor (Ca,N)-A	Good (Ca,N)-G Poor (Ca,N)-T	Fair (Ca,N)-P
3	Poor (Ca,N)-C Fair (Ca,N)-T	Fair (Ca,N)-P Good (Ca,N)-G Fair (Ca,N)-T	Good (Ca,N)-T Poor (Ca,N)-G	Poor (Ca,N)-L Poor (Ca,N)-T V. poor (Ca,N)-P
4	Poor (Ca,N)-C Fair (Ca,N)-T	Fair (Ca,N)-G Fair (Ca,N)-T	Fair (Ca,N)-T V. poor (Ca,N)-G	Fair (Ca,N)-T Poor (Ca,N)-L
5	Poor (Ca,N)-C	Fair (Ca,N)-G Fair (Ca,N)-T	Poor (Ca,N)-T	Fair (Ca,N)-L Poor (Ca,N)-T
6	Poor (Ca,N)-C	U	U	Poor (Ca,N)-V
7	Poor (Ca,N)-C	U	U	Poor (Ca,N)-V
8 and 9	Poor (Ca,N)-C	U	U	Poor (Ca,N)-L Fair (Ca,N)-T

* U denotes non-crystalline. In every crystallisation, in addition to compounds listed, a very weak *X*-ray pattern of crystalline $Ca(OH)_2$ was recorded.

The *d*-spacings of (Ca,N)-G, are recorded in Table 11. This crystal has pronounced similarities to gmelinite and also to chabazite, though there are some differences.[12] The properties of the individual species in Table 7 are not, however, further described since their counterparts produced from nitrogenous aluminosilicate gels free from Ca-ions are discussed elsewhere [17] [with the exception of (Ca,N)-G].

Some Characteristic Synthetic Ca-*aluminates and Aluminosilicates*.—The synthetic boehmite (Al_2O_3,H_2O), corundum (Al_2O_3), bayerite ($Al_2O_3,3H_2O$), and cristobalite (SiO_2) will not be further characterised in this section. Various compounds are, however, considered below.

Species Ca-M ($4CaO,3Al_2O_3,3H_2O$). This species was not obtained free of gel, as indicated by the thermogram in Fig. 4, curve *c*. The small endothermic peaks between 20° and 500° appear as a result of the presence of alumina gel mixed with $Ca(OH)_2$. The peak at 705° is also considered to be due to gel. The main peaks at 767° and 850° are attributed to Ca-M,

---

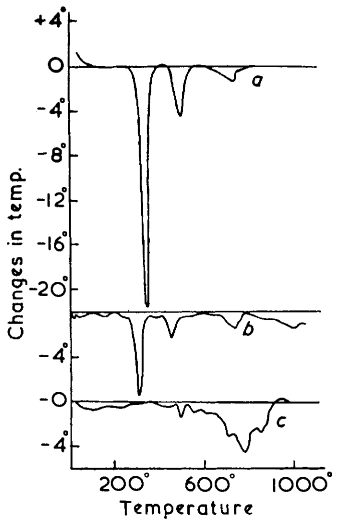
[17] Barrer and Denny, preceding paper.

[18] Takeuchi and Donnay, *Compt. rend.*, 1959, **248**, 265.

TABLE 8. *Some* d-*spacings (in* Å*) of aluminates and of* Ca-N *and* Ca-K, *and of a natural grossularite garnet.*

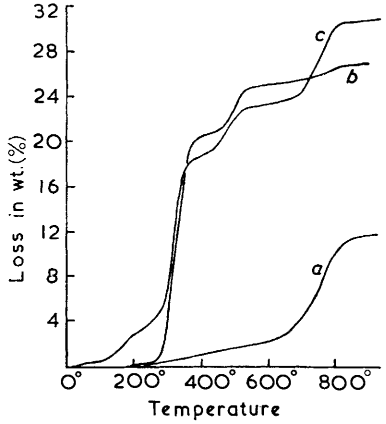
Ca-N			$(3CaO,Al_2O_3,6H_2O)$ [9]		Ca-K		Ca-K		Ca-K		Ca-K		Grossul-arite [9] garnet		Ca-M $(4CaO,3Al_2O_3,3H_2O)$		$12CaO,7Al_2O_3$ (A.S.T.M. index)		Ignited Ca-N	
d	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
5·11	vs	211	5·16	vs	5·16	m	5·09	m	—	—	—	—	—	—	5·06	vw	4·85	100	4·91	s
4·42	m	220	4·47	m	4·44	mw	4·39	w	—	—	—	—	4·14	vw	4·84	w	—	—	3·95	vw
3·35	ms	321	3·37	m	3·37	s	3·30	w	—	—	—	—	—	—	$3{\cdot}71_5$	w	3·77	20	3·68	vw
$3{\cdot}13_1$	m	400	3·15	m	$3{\cdot}14_9$	s	$3{\cdot}10_5$	w	$2{\cdot}99_9$	w	2·98	s	2·98	s	3·57	vs	3·20	20	3·2	w
$2{\cdot}80_0$	vs	420	2·81	m	$2{\cdot}81_7$	vs	$2{\cdot}78_5$	m	$2{\cdot}68_1$	s	$2{\cdot}66_2$	vs	2·65	vs	$3{\cdot}45_2$	m	2·98	50	3·04	w
$2{\cdot}66_9$	vw	332	—	—	—	—	—	—	—	—	$2{\cdot}52_9$	vw	2·51	w	$3{\cdot}32_2$	w	2·67	100	2·68	vs
$2{\cdot}55_5$	w	422	2·56	vw	$2{\cdot}56_9$	vw	—	—	$2{\cdot}44_8$	vw	$2{\cdot}42_8$	w	2·42	m	$3{\cdot}24_6$	s	2·43	50	2·44	w
$2{\cdot}45_8$	mw	431	2·46	w	$2{\cdot}46_9$	w	—	—	$2{\cdot}35_3$	w	$2{\cdot}33_6$	w	2·33	m	$3{\cdot}07_8$	m	2·18	50	2·18	m
$2{\cdot}28_8$	vs	521	2·30	vs	$2{\cdot}30_2$	s	$2{\cdot}27_7$	w	$2{\cdot}19_0$	vw	—	—	$2{\cdot}16_5$	m	$3{\cdot}00_8$	vs	1·93	40	—	—
—	—	440	$2{\cdot}22_0$	vw	—	—	—	—	—	—	—	—	$2{\cdot}09_3$	vw	$2{\cdot}84_4$	s	1·66	40	1·69	m
$2{\cdot}03_3$	vs	611	$2{\cdot}03_9$	s	$2{\cdot}04_2$	s	$2{\cdot}02_1$	w	$1{\cdot}94_7$	mw	$1{\cdot}93_1$	mw	$1{\cdot}92_8$	s	$2{\cdot}78_0$	m	1·59	40	1·60	m
$1{\cdot}98_1$	vw	620	$1{\cdot}99_2$	vw	—	—	—	—	—	—	—	—	$1{\cdot}87_1$	vw	$2{\cdot}60_8$	s				
$1{\cdot}80_8$	w	444	$1{\cdot}81_2$	vw	—	—	—	—	$1{\cdot}73_3$	vvw	$1{\cdot}71_6$	w	$1{\cdot}71_1$	m	$2{\cdot}53_4$	vs				
$1{\cdot}73_7$	m	640	$1{\cdot}74_1$	w	$1{\cdot}74_7$	m	$1{\cdot}72_2$	w	$1{\cdot}66_3$	w	$1{\cdot}64_7$	w	$1{\cdot}64_5$	s	$2{\cdot}40_0$	vw				
$1{\cdot}70_5$	m	633	$1{\cdot}71_1$	w	$1{\cdot}71_4$	w	—	—	—	—	—	—	—	—	$2{\cdot}38_0$	vw				
$1{\cdot}67_5$	ms	642	$1{\cdot}68_0$	m	$1{\cdot}68_2$	m	$1{\cdot}65_1$	w	$1{\cdot}60_2$	mw	$1{\cdot}58_8$	mw	$1{\cdot}53_8$	vs	$2{\cdot}28_0$	s				
$1{\cdot}59_1$	mw	651	$1{\cdot}60_0$	vw	—	—	—	—	—	—	—	—	—	—	$2{\cdot}21_6$	s				
$1{\cdot}56_6$	mw	800	$1{\cdot}57_1$	w	—	—	—	—	—	—	$1{\cdot}48_4$	vw	$1{\cdot}48_6$	m	$2{\cdot}15_4$	m				
$1{\cdot}47_7$	vw	822	—	—	—	—	—	—	—	—	—	—	—	—	$2{\cdot}08_0$	vvs				
$1{\cdot}40_1$	w	840	$1{\cdot}40_5$	w	—	—	—	—	—	—	—	—	—	—	$1{\cdot}91_6$	s				
		752	—	—	—	—	—	—	$1{\cdot}33_6$	vvw	—	—	$1{\cdot}33_7$	m	$1{\cdot}79_2$	m				
		833	—	—	—	—	—	—	$1{\cdot}30_9$	vvw	$1{\cdot}29_6$	vw	$1{\cdot}29_6$	s	$1{\cdot}73_3$	m				
															$1{\cdot}67_9$	w				
															$1{\cdot}59_5$	vs				
															$1{\cdot}56_7$	s				
															$1{\cdot}54_7$	s				
															$1{\cdot}50_5$	m				
															$1{\cdot}40_3$	m				
															$1{\cdot}37_1$	s				
															$1{\cdot}32_6$	m				
a = 12·53 Å			a = 12·56 Å		a = 12·60 Å		a = 12·41 Å		a = 12·00 Å		a = 11·89 Å		a = 11·84 Å							

FIG. 4.



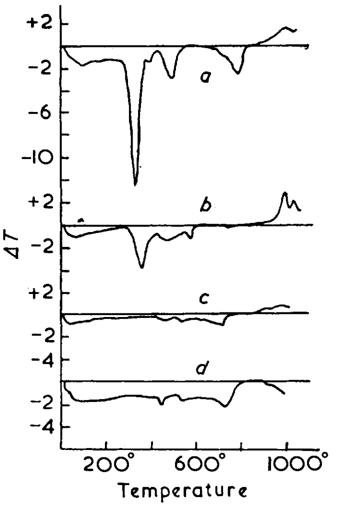
(*a*) *and* (*b*): *Thermograms of* Ca-N ($3CaO,Al_2O_3,6H_2O$) *prepared* (*a*) *at* 125° *for* 26 *days and* (*b*) *at* 200° *for* 9 *days.* (*c*) *Thermogram of* Ca-M ($4CaO,3Al_2O_3,3H_2O$).

FIG. 5.



(*a*) *Thermogravimetric curve of* Ca-M. (*b*) *and* (*c*) *Thermogravimetric curves of two* Ca-N *samples of differing purity.*

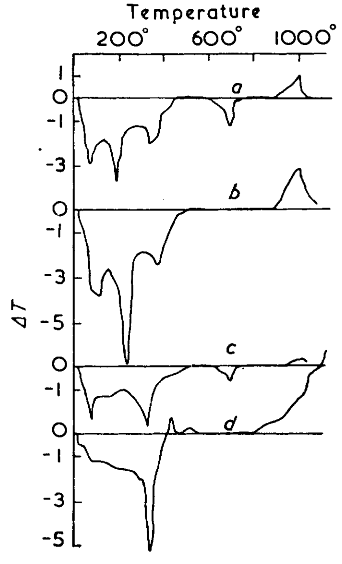
FIG. 6.



(*a*), (*b*), (*c*) *Thermograms of some synthetic hydrogarnets, of differing* $Al_2O_3 : SiO_2$ *ratios. Samples* (*a*) *and* (*b*) *are very poor in silica and approach* Ca-N *in composition. Sample* (*c*) *is rich in silica* (*Table* 9). *Curve* (*d*) *gives the thermogram of a natural hydrogarnet.*

a: $3CaO,Al_2O_3,SiO_2$ *at* 200° *for* 20 *days.*
b: $3CaO,Al_2O_3,SiO_2$ *at* 220° *for* 19 *days.*
c: $3CaO,Al_2O_3,3SiO_2$ *at* 450° *for* 4 *days.*

FIG. 7.



(*a*) *and* (*b*) *Thermograms of synthetic and naturally occurring* Ca-*thomsonite respectively.* (*c*) *and* (*d*) *Thermograms of synthetic and naturally occurring* Ca-*epistilbite respectively.*

a: $CaO,Al_2O_3,3SiO_2$ (*glass*) *at* 250° *for* 31 *days.*
b: $CaO,Al_2O_3,6SiO_2$ (*glass*) *at* 250° *for* 31 *days.*

although a thermogram previously given for this compound [3] shows only one smooth endothermic peak at about 730°. The thermogravimetric curve is shown in Fig. 5*a*, and the characteristic *d*-spacings are summarised in Table 8. The 12% loss in weight in the thermogravimetric curve further suggests the presence of gel, since the water content of pure Ca-M is only 9%.

Species Ca-N ($3CaO,Al_2O_3,6H_2O$). This compound is the non-siliceous end-member of the hydrogrossular series designated as Ca-K. As for Ca-M, this phase was not obtained free from gel, the best yield being from the mixture $3CaO,Al_2O_3$ + aq. heated at 125° for 26 days. Thermogravimetric curves of two samples of Ca-N are shown in Fig. 5*b*, *c*. The purer sample (curve *b*) shows negligible water loss up to the first sharp dehydration step starting at about 250° and so indicates absence of gel. 25% of water is lost in the first two steps and since the pure phase Ca-N contains 28·6% by weight of water, the purity of the sample examined may be ~87%. The second sample of Ca-N (curve *c*) is considerably less pure and contains hydrous gel.

The thermograms and differential thermogravimetric curves of Ca-N (Fig. 4*a*, *b*) show good correspondence of peaks indicating that the processes observed in the thermograms are associated with water loss. The main endothermic peaks are at 340° and 500° and the water is lost in steps. The differential thermal analyser was then calibrated by using salt hydrates ($BaCl_2,2H_2O$ and $CuSO_4,5H_2O$) [19] which have known heats of hydration, and was then used to obtain approximate heats of reaction for the purer sample. In the main dehydration step, corresponding to the loss of nearly 5 mol. of water per formula weight, the heat absorbed was ~20·1 kcal. per mole of water lost, and in the second step this heat was ~22·6 kcal. for the loss of the sixth molecule. One of the products of water loss was the phase $12CaO,7Al_2O_3$.[20]

The *d*-spacings of Ca-N are given in Table 8. The cubic unit-cell dimension was 12·56 Å, and the refractive index determined in sodium light was 1·608 ± 0·002.

Species Ca-K (*grossular hydrogarnets of variable* $Al_2O_3 : SiO_2$ *ratios*). A series of solid solutions is believed to exist [9] between the cubic iso-structural compounds $3CaO,Al_2O_3,6H_2O$ (Ca-N) and $3CaO,Al_2O_3,3SiO_2$, for which series the unit cells and *d*-spacings vary continuously with composition from the hydrous aluminate to the anhydrous aluminosilicate (grossular). The temperatures of crystallisation and unit-cell sizes of some hydrogarnets prepared in this work are given in Table 9. From the relation between unit-cell dimensions and composition given by Flint, McMurdie, and Wells [9] the compositions of the hydrogarnets of Table 9 have been estimated. These compositions fall into a high- and a low-silica field. The high field has composition limits 1·81 < SiO_2 < 2·79 per residue $3CaO,Al_2O_3$, the low field has limits 0 < SiO_2 < 0·51, and it is therefore possible that an immiscibility gap exists. The less hydrated crystals were obtained at higher temperatures. Species Ca-K was not prepared in a pure state, and was commonly admixed with Ca-P, Ca-F (anorthite), or Ca-O. The thermograms of several hydrogarnets are shown in Fig. 6*a*—*c*, curve *d* referring to a natural hydrogrossular. They should be compared with the thermograms of Fig. 4 for Ca-N.

TABLE 9. *Preparation of hydrogarnets from gels* $3CaO,Al_2O_3,nSiO_2$ + aq.

Temp.	*n*	Unit cell edge (Å)	Composn. of product (mol. per $3CaO,Al_2O_3$)		Temp.	*n*	Unit cell edge (Å)	Composn. of product (mol. per $3CaO,Al_2O_3$)	
			SiO_2	H_2O				SiO_2	H_2O
200°	1	12·60	0(?)	6·0	350°	3	11·91	2·71	0·58
200	2	12·61	0(?)	6·0	380	1	11·95	2·55	0·90
200	3	12·61	0(?)	6·0	380	2	11·92	2·68	0·64
200	4	12·57	0·05	5·90	380	3	11·92	2·68	0·64
220	1	12·52	0·18	5·64	415	1	11·96	2·51	0·98
220	2	12·50	0·23	5·54	415	2	11·95	2·55	0·90
237	2	12·49	0·27	5·46	415	3	11·92	2·68	0·64
237	2,1	12·06	2·07	1·86	450	2	11·94	2·60	0·80
265	1	12·11	1·81	2·38	450	3	11·97	2·47	1·06
265	2 *	12·41	0·51	4·98	455	2	11·94	2·60	0·80
300	2	12·00	2·35	1·30	450	3	11·89	2·79	0·42
350	2	11·90	2·75	0·50					

* SiO_2 glass as source.

---

[19] Barrer and Langley, *J.*, 1958, 3817.

[20] A.S.T.M. index.

TABLE 10. *Some* d-*spacings of synthetic* Ca-*zeolites and of their natural counterparts.*

Harmotome				
Tetragonal Ca-harmotome [21]			Ca-L	
hkl	*d*	*I*	*d*	*I*
110	7·1	s	7·14	vs
002	4·94	s	4·96	ms
211	4·12	s	4·14	s
112	4·05	ms	4·07	w
311	3·22	m	$3{\cdot}24_0$	m
103	3·12	s	$3{\cdot}14_2$	vs
222	2·87	m	—	—
213	2·66	s	$2{\cdot}67_4$	ms
400	2·55	mw	$2{\cdot}56_8$	vw
303	2·33	m	$2{\cdot}33_2$	vw
204	2·20	w	—	—
323	2·12	w	$2{\cdot}12_3$	vw
422	2·06	mw	$2{\cdot}07_1$	vw
224	2·02	w	—	—
005	$1{\cdot}97_5$	mw	$1{\cdot}98_7$	vw
314	$1{\cdot}93_0$	mw	$1{\cdot}94_4$	vw
215	$1{\cdot}80_5$	mw	$1{\cdot}81_6$	vw
440	$1{\cdot}77_0$	mw	$1{\cdot}78_3$	mw
522	$1{\cdot}73_5$	mw	$1{\cdot}74_3$	vw
433	$1{\cdot}70_5$	mw	$1{\cdot}71_6$	w
600	$1{\cdot}66_5$	w	$1{\cdot}67_5$	vw
610	$1{\cdot}64_0$	mw	$1{\cdot}65_0$	vw
116	$1{\cdot}60_3$	w	—	—
800	—	—	$1{\cdot}26_1$	w
	a = 10·01 Å c = 9·87 Å		a = 10·01 Å c = 9·89 Å	

Thomsonite				
Natural (A.S.T.M. index)			Ca-I	
hkl [b]	*d*	*I*	*d*	*I*
022	4·63	67	4·63	m
312	—	—	3·50	m
132	3·45	53	—	—
322,232	3·18	40	$3{\cdot}19_7$	w
204,024	2·93	100	$2{\cdot}94_3$	m
412,142	2·84	13	$2{\cdot}85_8$	m
242,422	2·66	43	$2{\cdot}67_2$	m
	2·24	27	$2{\cdot}25_0$	w
	2·17	33	$2{\cdot}17_9$	w
	1·81	36	—	—
	1·74	23	$1{\cdot}76_9$	vw
	1·61	8	$1{\cdot}62_6$	vw
	1·46	36	—	—

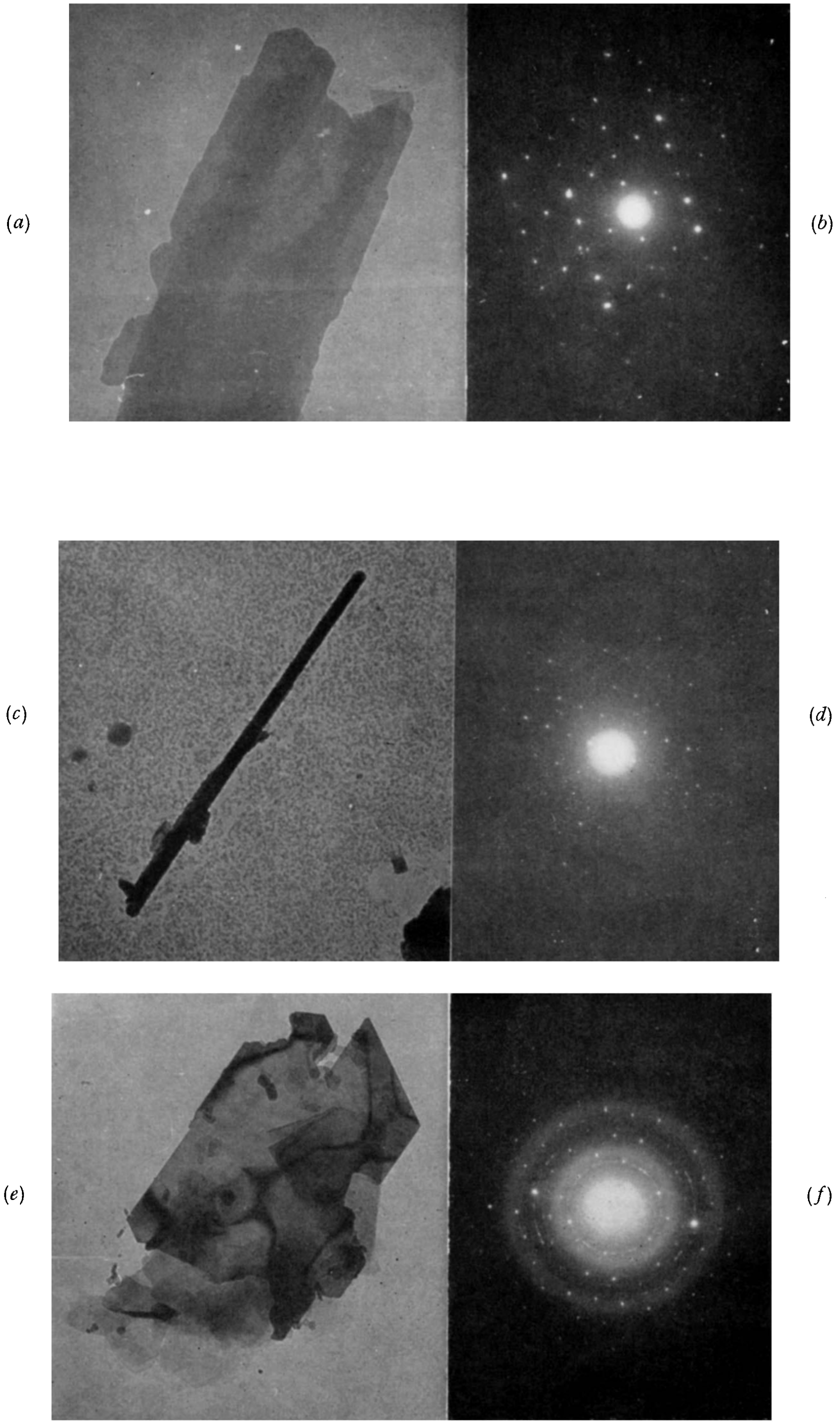
Epistilbite				
Natural			Ca-J	
hkl	*d*	*I*	*d*	*I*
020	8·85	m	8·89	s
210	6·85	m	6·88	s
—	—	—	[5·54	mw]
002	4·89	s	4·89	s
230,102	4·63	vw	—	—
040	4·47	vw	4·48	w
022	4·32	m	4·31	mw
240,212	3·98	vw	—	—
141	3·90	vw	—	—
240,330	3·84	s	3·87	s
032	3·78	w	—	—
400,222	3·71	w	—	—
312	3·42	vs	$3{\cdot}44_4$	vs
042	3·31	vw	$3{\cdot}33_4$	w
	3·24	w	$3{\cdot}25_1$	w
	3·19	ms	$3{\cdot}20_5$	ms
	3·03	vw	—	—
	2·90	m	$2{\cdot}91_5$	mw
	2·84	m	$2{\cdot}85_3$	m
	2·76	vw	$2{\cdot}78_7$	w
	2·68	w	$2{\cdot}68_4$	m
	2·66	w	—	—
	2·54	w	$2{\cdot}50_9$	m
			$2{\cdot}41_7$	w
			$2{\cdot}21_1$	vw
			$2{\cdot}09_3$	vw
			$1{\cdot}86_6$	vw
			$1{\cdot}77_6$	w
	a = 14·9 Å [e] b = 17·87 Å c = 10·32 Å β = 90° 40′		a = 15·0 Å [c,d] b = 17·0 Å c = 10·25 Å β = ~90°	

Ca-Analcites						
	Wairakite [a]		Ca-E		Ca-D	
hkl	*d*	*I*	*d*	*I*	*d*	*I*
200	6·85	m	6·80	m	6·82	m
211	5·57	vs	5·54	vs	5·56	vs
220	4·84	m	4·80	m	4·82	m
321	3·64	m	3·63	w	3·63	m
400	3·42	s	$3{\cdot}40_2$	vs	$3{\cdot}40_8$	vs
004	3·39	vs	—	—	$3{\cdot}37_1$	s
332	$2{\cdot}90_9$	s	$2{\cdot}90_3$	vs	$2{\cdot}90_7$	s
323	$2{\cdot}89_7$	m	—	—	$2{\cdot}89_3$	m
431	$2{\cdot}68_0$	m	$2{\cdot}67_0$	m	$2{\cdot}66_9$	w
—	2·67	vw	—	—	—	—
125	$2{\cdot}48_9$	m	$2{\cdot}48_8$	m	$2{\cdot}47_9$	w
440	$2{\cdot}41_8$	w	$2{\cdot}40_9$	w	$2{\cdot}40_7$	w
116	$2{\cdot}21_5$	m	$2{\cdot}21_2$	w	$2{\cdot}20_4$	vw
640	$1{\cdot}89_5$—	m (diff)	$1{\cdot}88_9$	w	$1{\cdot}88_9$	vw
	$1{\cdot}88_6$					
633	$1{\cdot}85_7$	w	$1{\cdot}85_5$	w	$1{\cdot}85_3$	vw
327	$1{\cdot}73_2$—	m (diff)	—	—	$1{\cdot}72_5$	vw
	$1{\cdot}72_2$					
741	$1{\cdot}68_0$	w (diff)	$1{\cdot}68_0$	w		
(811,554)						
831,743	$1{\cdot}58_6$	w	$1{\cdot}58_4$	w		
(750)						
	a = 13·68 Å b = 13·56 Å		a = 13·62 Å c = 13·56 Å		a = 13·62 Å	

[a] Steiner, *Min. Mag.*, 1955, **30**, 691; Coombs, *ibid.*, p. 699. [b] Indexing on the basis of a unit cell a = 13·0, b = 13·1, c = 13·2 Å. [c] Near orthorhombic pseudo-cells; a somewhat smaller monoclinic unit cell can also be given (Strunz and Tennyson, *Neues Jahrb. Min.*, 1956, **1**, 1). [d] Obtained from the electron-diffraction pattern of another sample.

TABLE 11. *Some* d-*spacings of synthetic* Ca-*aluminosilicates.*

Anorthite (A.S.T.M. index)		Ca-F		Ignited Ca-harmotome		Ignited Ca-analcite		Ca-P Davis and Tuttle [6]			Ca-P This work		Ca-O		(Ca,N)-G	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*hkl*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
6·39	40	—	—	6·40	w	—	—	002	7·37	85	7·33	vw	3·59	s	11·6	vw
—	—	[5·55]	vs	[5·4]	w	—	—	100,010	4·43	7	4·42	s	3·11$_6$	vw	9·21	vs
4·61	40	[4·80]	w	—	—	—	—	102,012	3·80	30	3·79	vs	3·02$_7$	m	7·62	m
4·04	60	4·07	vw	4·10	w	4·09	vw	004	3·68	100	3·67	s	2·78$_7$	vs	6·67	mw
—	—	—	—	3·99	m	3·96	mw	104,014	2·84	40	2·83$_2$	vs	2·54$_3$	m	6·32	vs
3·70	40	3·69	s	3·69	m	3·69	m	110	2·55$_5$	9	2·55$_6$	vs	2·35$_3$	m	5·39	mw
3·57	60	—	—	—	—	—	—	006	2·45$_6$	14	—	—	2·20$_2$	w	4·60	m
—	—	3·42	vvs	3·45—3·34	m (diff)	3·48	vw	112	2·41$_4$	3	2·41$_5$	vw	2·07$_5$	m	4·48	s
—	—	—	—	—	—	3·34	w	106,016	2·14$_7$	11	—	—	1·86$_5$	vw	4·20	ms
3 19	100	3·19$_6$	vs	3·18	vs	3·18	vs	202,022	2·11$_9$	4	2·11$_9$	w	1·79$_6$	vw	3·78	vs
2·96	60	2·93$_6$	s	2·87	vw	2·96	m	008	1·84$_2$	100	1·84$_2$	m	1·74$_2$	vw	3·32$_2$	w
2·79	60	2·84$_8$	s	2·82	w	2·83	w	116	1·77$_0$	9	1·77$_0$	w	1·55$_6$	ms	3·17$_0$	m
2·65	40	2·67$_6$	m	2·67	w	—	—	118	1·49$_5$	14	—	—	1·51$_2$	w	2·95$_7$	w
2·51	70	2·50$_4$	m	2·53	w	2·52	vw	1,0,10;	1·39$_9$	12	—	—	1·43$_0$	vw	2·87$_2$	mw
—	—	—	—	2·50	w	—	—	0,1,10							2·70$_0$	mw
2·38	20	—	—	2·41	w (diff)	—	—	2,0,10;	1·27$_7$	9	—	—			2·50$_6$	m (diff)
2·24	20	2·21$_0$	w	2·20	w	2·17	vw	0,2,10							2·39$_2$	vw
2·13	50	2·11$_6$	s	2·14	w	2·13	vw								2·34$_4$	vw
2·08	40	2·08$_4$	w	2·07	w	—	—								2·21$_7$	vw
2·02	40 (diff)	2·00$_2$	vw	—	—	—	—								2·00$_1$	vw
1·94	40 (diff)	1·88$_6$	m	1·90	vw	—	—								1·79$_0$	m
1·84	20	1·84$_0$	s	1·83	w (diff)	1·82	vvw								1·66$_6$	mw
1·79	50	1·78$_9$	s	—	—	—	—								1·59$_6$	vvw
1·76	60	1·74$_7$	m	1·76$_1$	m	1·76	vvw								1·41$_7$	vw
1·71	40	—	—	—	—	1·71	vvw								1·29$_0$	vw
1·62	40	1·62$_7$	vw	1·60$_0$	vw										1·21$_8$	vw
1·54	20	1·55$_8$	vvw	—	—											
1·48	60	1·48$_5$	m	1·51$_5$	vw											
1·45	20	1·46$_0$	vs	1·46$_8$	vw											
1·41	20	—	—	1·43$_5$	vw											
1·39	50	1·40$_1$	m													
1·36	60	—	—													
1·34	60	1·34$_3$	m													
1·32	20	—	—													
1·30	20	1·29$_8$	w													
1·27	40	1·27$_3$	s													
1·24	20	1·25$_3$	vw													
1·21	40	1·21$_0$	m													
1·08	20	1·10$_5$	vw													



(a), (c), and (e) are electron micrographs of synthetic epistilbite, mordenite, and the hexagonal dimorph of anorthite, respectively; (b), (d), and (f) are the corresponding electron-diffraction patterns.

Some *d*-spacings of Ca-N, of several samples of Ca-K, and of a natural grossular are compared in Table 8. The refractive index of a hydrogarnet having a unit-cell edge of 11·97 Å was 1·665 ± 0·004.

Zeolites. The zeolites formed belonged to the analcite, harmotome, thomsonite, epistilbite, and mordenite groups. Several of these species are described below.

Species Ca-L (*calcium harmotome*). This zeolite was most readily prepared, in good but not 100% yield, from mixtures $CaO,Al_2O_3,nSiO_2$ when silica glass was the source of silica (Table 5). The thermograms of this mineral and of a Ca-harmotome prepared by ion-exchange from synthetic Na-harmotome [12,21] are shown in Fig. 7*a* and *b* respectively. The peak for Ca-L at about 700° is associated with the presence of gel, but otherwise the similarity is clear. The thermogram and differential thermogravimetric curves corresponded closely so that the endothermic peaks are all associated with water loss. By considering the water loss in the range 20—460° to be from Ca-harmotome only, the heat of dehydration was evaluated, as for Ca-N. It was about 28·4 kcal. per mole of water lost.

The Ca-harmotome sample examined by *X*-ray powder photograph was tetragonal with $a = 10{\cdot}10$ and $c = 9{\cdot}89$ Å. The *d*-spacings are compared in Table 10 with those of the Ca-harmotome prepared by ion exchange.[21] The refractive index of a specimen prepared from a mixture $CaO,Al_2O_3,3SiO_2$ + aq. at 250° was 1·510 ± 0·003.

Species Ca-I (*calcium thomsonite*). Calcium thomsonite (Table 3) was admixed with gel, Ca-P, or boehmite. Although the yield was low the thermogram resembled that of natural thomsonite. The comparison of peak heights suggests about a 20% yield of synthetic thomsonite. The peak at about 745° is due to gel. The *d*-spacings are compared with those of natural thomsonite in Table 10.

Species Ca-J (*calcium epistilbite*). This zeolite was obtained from systems $CaO,Al_2O_3,nSiO_2$ + aq., both sol and powdered glass being used as source of the silica (Tables 3 and 5), although the better yields were obtained from the latter. The thermogram of a sample of synthetic Ca-J is compared with that of a natural epistilbite in Fig. 7*c*, *d*. The peak with its maximum at about 700° is due to a small amount of gel. The thermogravimetric curve, shown in Fig. 8, gives a maximum water loss of 16%. The heat associated with the first 13·2% water loss was evaluated as ~21·3 kcal./mole. The *d*-spacings of Ca-J are given in Table 10. The electron-diffraction pattern and an electron micrograph are shown in Plate *b* and *a*, for a specimen of Ca-epistilbite obtained from a gel $CaO,Al_2O_3,4SiO_2$ + aq. crystallised at 225°. The diffraction pattern corresponds to a monoclinic but nearly orthorhombic unit cell $a = 15{\cdot}0$, $b = 17{\cdot}0$, $c = 10{\cdot}25$ Å, and $\beta \sim 90°$. The *X*-ray powder pattern of a natural epistilbite gave $a = 14{\cdot}9$, $b = 17{\cdot}87$, $c = 10{\cdot}32$ Å, and $\beta = 90° 40'$; an alternative monoclinic unit cell with $a = 9{\cdot}1$, $b = 17{\cdot}87$, $c = 10{\cdot}32$ Å, and $\beta = 125° 3'$ can also be chosen, analogous to that given by Strunz and Tennyson.[22] The micrograph shows the lamellar habit of the crystals.

Species Ca-Q (*calcium mordenite*). Plate *d*, *c* shows the electron diffraction pattern and micrograph of a crystal of Ca-mordenite from a sample obtained by crystallising a gel $CaO,Al_2O_3,7SiO_2$ + aq. at 390°. The crystals are acicular in habit, and the electron-diffraction pattern gives an orthorhombic unit cell of dimensions $a = 18{\cdot}5$, $b = 20{\cdot}3$, and $c = 7{\cdot}55$ Å. Na-mordenite has been prepared in good yield at lower temperatures,[13,23] and it has also been made under conditions similar to those noted above.[7,8]

Species Ca-D (*tetragonal calcium analcite*). Species Ca-D was a variety of analcite similar to the natural mineral, wairakite.[24] It was common over a wide range of temperature and composition, although admixed with gel, Ca-F or Ca-P. The thermogram shows similarity with that of wairakite (Fig. 9*a*, *b*). The thermogravimetric curve of Ca-D in Fig. 10 refers to a sample containing some gel, so that it appears to contain more water (11·2%) than wairakite (8·35%). The *d*-spacings are compared in Table 10 with those of wairakite and of Ca-E. The tetragonal unit cell had dimensions $a = 13{\cdot}62$, $c = 13{\cdot}56$ Å. The factor $c/a = 0{\cdot}995$ was the same for samples prepared at different temperatures. The refractive index of Ca-D was 1·496.

Species Ca-E (*cubic calcium analcite*). Species Ca-E was best synthesised at 350° from mixtures $CaO,Al_2O_3,4SiO_2$ + aq. with powdered silica glass as the source of silica. Thermogram

---

[21] Barrer, Bultitude, and Kerr, *J.*, 1959, 1521.
[22] Strunz and Tennyson, *Neues Jahrb. Min.*, 1956, **1**, 1.
[23] Barrer, *J.*, 1948, 2158.
[24] Steiner, *Min. Mag.*, 1955, **30**, 691; Coombs, *ibid.*, p. 699.

and thermogravimetric curves are shown in Figs. 9 and 10, curves *c*. The thermogram shows distinct differences from those of Ca-D or wairakite. The thermogravimetric water loss is 6·80%, and the yield of Ca-E in the sample is therefore estimated at 80%, since the thermogram showed an absence of gel in the product. The *d*-spacings are given in Table 10; the cubic unit-cell edge was 13·62 Å, and the refractive index of the small, often irregular crystallites was 1·493 ± 0·004.

Additional Aluminosilicates.—Characteristics of several additional Ca-aluminosilicates are given below.

Species Ca-F (*calcium felspar*). Calcium felspar was of common occurrence in all crystallisation fields, above about 250° (Tables 3—5, Figs. 1—3). It was usually mixed with gel or another crystalline phase, often Ca-P. The *d*-spacings of Ca-F are compared in Table 11 with those of anorthite, and of some related products prepared by ignition of other species. Some interesting differences arise in these *d*-spacings and their intensities.

FIG. 8. *Thermogravimetric curves of (a) synthetic* Ca-*epistilbite and (b) synthetic* Ca-*harmotome.*

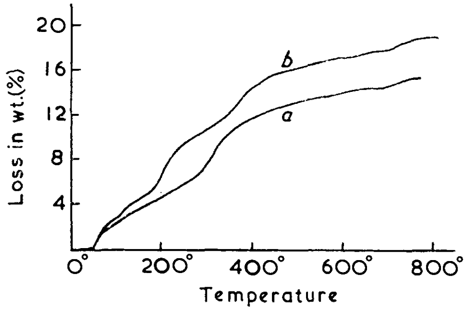


FIG. 10. *Thermogravimetric curves of (a) tetragonal* Ca-*analcite (+ some gel), (b) natural wairakite, and (c) cubic synthetic* Ca-*analcite.*

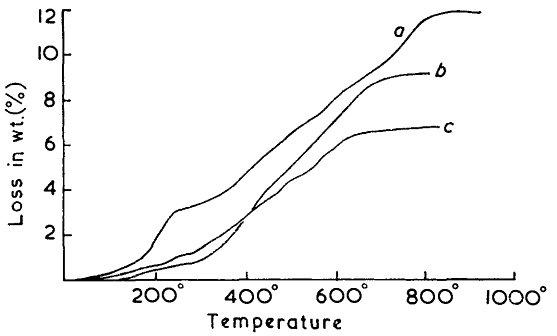
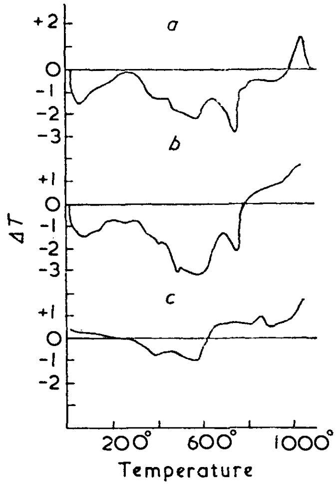


FIG. 9. *Thermograms for (a) synthetic tetragonal* Ca-*analcite (b) a natural wairakite, and (c) synthetic cubic* Ca-*analcite.*



a: $CaO,Al_2O_3,3SiO_2$ *at* 300° *for* 31 *days.*
b: $CaO,Al_2O_3,4SiO_2$ *at* 300° *for* 12 *days.*

Species Ca-P. This phase was a hexagonal dimorph of anorthite,[6] which was also common in all aluminosilicate crystallisation fields, and which first appeared at temperatures as low as 200° (Tables 3—5 and Figs. 1—3). The electron-diffraction pattern and electron micrograph of Plate *f*, *e* clearly show the hexagonal symmetry of this compound. *d*-Spacings are summarised in Table 11, and are compared with those of a preparation by Davis and Tuttle.[6] The latter preparation was stated to be preferentially orientated, the strongest lines all being 00*l*. Orientation may thus account for the differences in observed relative intensities between their preparation and that in Table 11 obtained in our work. Species Ca-P was stable to heating in the differential thermal analysis apparatus up to at least 1050°.

Species Ca-O. The *d*-spacings of this unidentified phase, obtained in major yield, are given in Table 11, to permit its subsequent identification and characterisation.

DISCUSSION

The hydrothermal study reported in this paper has shown that a number of hydrated minerals may be formed under controlled conditions. It has, however, also been possible to prepare anhydrous phases such as corundum, cristobalite, Ca-P, and Ca-F, and it was of interest to find whether other anhydrous materials can be made by sintering the hydrated species. Table 12 summarises the results of such experiments. From the aluminosilicates only Ca-F or Ca-P are formed, often with amorphous material. The calcium aluminate hydrates can yield an aluminate of composition $12CaO,7Al_2O_3$, and CaO. The *d*-spacings of the phase $12CaO,7Al_2O_3$ are given in Table 8.

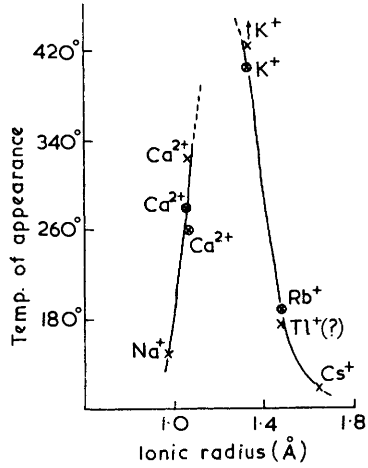


FIG. 11. *Apparent correlation between the lowest temperatures observed for hydrothermal analcite formation from gels, and the radius of the cation present.*

× *Cubic analcites.* ⊗ *Tetragonal analcites.*

The alkali-metal aluminosilicates crystallised most readily when the source of silica in the gel was a sol of high surface area;[12,13] the calcium aluminosilicates, however, have as a rule been shown to behave in the opposite way. Our observation that the crystals formed may depend on the nature and history of the parent gel or mixture is confirmed

TABLE 12. *Ignition products from hydrated calcium aluminates and aluminosilicates.*

Materials ignited	Temp. ignition	Products
Ca-analcites (cubic and tetragonal) + trace of Ca-P	840°	Amorphous and v. poor Ca-P
	1030	Ca-P + near anorthite
	1080	Ca-P + near anorthite
Natural thomsonite	1030	Near anorthite
Synthetic thomsonite (+ gel + Ca-P)	1030	Near anorthite + Ca-P
Natural epistilbite	1050	Amorphous
Synthetic Ca-epistilbite and gel (from mix using silica sol)	1050	Near anorthite
Synthetic Ca-epistilbite (from mix using powdered silica glass)	1020	Mainly amorphous + v. poor Ca-P + a trace of anorthite (?)
Synthetic Ca-harmotome	850	Mainly amorphous
Synthetic Ca-harmotome (from mix using SiO_2 sol)	1000	Near anorthite
Synthetic Ca-harmotome (from mix using powdered SiO_2 glass)	1020	Near anorthite
Synthetic hydrogrossular ($3CaO,Al_2O_3,2{\cdot}45SiO_2,1{\cdot}1H_2O$)	1000	No change
Natural grossular	1000	No change
Ca-M ($4CaO,3Al_2O_3,3H_2O$) + gel	1030	Unidentified product
Ca-N ($3CaO,Al_2O_3,6H_2O$) + gel	410	$12CaO,7Al_2O_3$ + (?)
	560	$12CaO,7Al_2O_3$ + (?)
	1040	$12CaO,7Al_2O_3$ + CaO + (?)
Non-crystalline product from gel $CaO,Al_2O_3,3SiO_2$ + aq at 225° C.	1030	Near anorthite

by a similar observation by Ellis.[8] The zeolites produced most readily in the Ca-aluminosilicate crystallisation fields differ on the whole from those most easily formed in crystallisation fields of the alkali-metal aluminosilicates. Analcites, however, are of universal occurrence in all fields, except that of the lithium aluminosilicates.[25] By direct synthesis, analcitic phases of sodium, potassium (two forms), rubidium (two forms), cæsium, thallium, ammonium, and calcium (two forms) have been prepared. A correlation exists between unit-cell dimensions of various forms of the analcitic phases, the diameter of the cation, and whether or not the water is also present in the crystal lattice.[26]

The lowest crystallisation temperatures of analcites appear to vary greatly, and again a correlation is found between these temperatures and the ionic radius, as shown in Fig. 11. The correlation, for lower crystallisation temperatures, is of course likely to be influenced in part by the reactivity of the parent gel or mixture. It is noteworthy that so far the largest ion forming an analcite is Cs^+. Various methylammonium aluminosilicate gels have been crystallised, but analcites were not found in the products.[17] There is probably insufficient room in the analcite-type of aluminosilicate framework to accommodate such large cations. The correlation shown in Fig. 11 is in part related to the basigenic character of the metal, but this is not the only factor, since it appears more difficult to form potassium analcites than it is to make calcium analcites.

PHYSICAL CHEMISTRY DEPARTMENT,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
S. KENSINGTON, LONDON, S.W.7.

[*Received, June 2nd*, 1960.]

---

[25] Barrer and White, *J.*, 1951, 1167.
[26] Barrer, *Trans. Brit. Ceram. Soc.*, 1957, **56**, 155.