

The hydration of larnite (β -Ca₂SiO₄) and bredigite (α_1 -Ca₂SiO₄) and the properties of the resulting gelatinous mineral plombierite.

(With Plate XVII.)

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INTRODUCTION.

IN this paper the formation of a gelatinous hydrate phase from the natural dicalcium silicate minerals larnite and bredigite is described. Detailed study of the gel so formed indicates that the process of hydration is a solid reaction which is effected by diffusion. The preferred orientation of the hydrate phase suggests that the hydration is facilitated by a relationship between the structure of the anhydrous silicate and that of the hydrate phase produced.

In this investigation the variations in density, mean refractive index, and chemical composition of the natural gels have been determined and the characteristics of the adsorbed water studied by isothermal dehydration and rehydration. In discussing the mechanism of hydration it has been assumed that this obtains at constant volume. This assumption is based on the study of gel pseudomorphs after single crystals of larnite and bredigite in thin section.

The orientation of the hydrate phase relative to the original crystallographic directions of the parent silicate has been determined from single-crystal X-ray photographs of gel pseudomorphs after bredigite.

The hydration mechanism, as deduced from the experimental evidence presented below, is thought to have considerable bearing on the hydration reactions of β -Ca₂SiO₄, and of gel formation from this compound, in the hydration of portland cement clinker.

OCCURRENCE.

The gels examined during the present investigation were collected at the dolerite-chalk contacts at Ballycraig and Scawt Hill, both of which

are near Larne, County Antrim. In a previous paper the natural gel from Ballycraigy was briefly described, and identified with the mineral plombierite and also with a synthetic preparation 'calcium silicate hydrate (I)' (McConnell, 1954, p. 302). The gels have been formed through the hydration, under natural conditions, of the minerals larnite and bredigite. Accounts of the occurrence of these minerals at the Scawt Hill contact have been given by Tilley (1929, p. 77; 1948, p. 257). An account of the dolerite-chalk contact at Ballycraigy is in course of preparation.

Larnite rocks occur in the endogenous zones at both contacts. At Scawt Hill they have been formed through the magmatic silicification of the chalk rock at the immediate contact, and also through the metasomatic reaction of flint nodules with the surrounding

chalk at a distance of several feet from the contact. The larnite nodules formed in the latter instance are extremely pure and are invariably surrounded by a sheath of gelatinized larnite up to five centimetres in radial thickness. A diagrammatic section through one such nodule is shown in fig. 1. The gel sheath is homogeneous and has an extremely sharp contact with the unhydrated larnite core. The outer contact between the gel and the recrystallized chalk is less well defined and appears to represent the original boundary of the flint nodule.

The gel is a transparent to translucent solid. It is brittle and breaks with a conchoidal fracture. In colour it ranges from pink to red-brown and its hardness is approximately 4.

REFRACTIVE INDEX AND DENSITY DETERMINATIONS.

The natural gel has a birefringence varying between 0.001 and 0.003. In any sample from a single location at the contact a small range in refractive index was observed in the crushed material. On such a sample

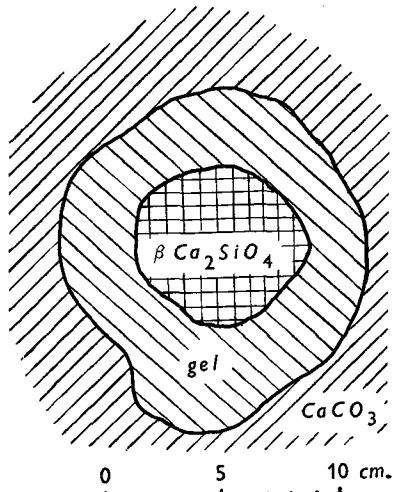


FIG. 1. Diagrammatic section through a metasomatized flint nodule from Scawt Hill, Co. Antrim.

a mean refractive index could be determined, and in samples from different locations at the contact a considerable range in the mean refractive index, thus defined, was observed. In fig. 2 the mean refractive indices

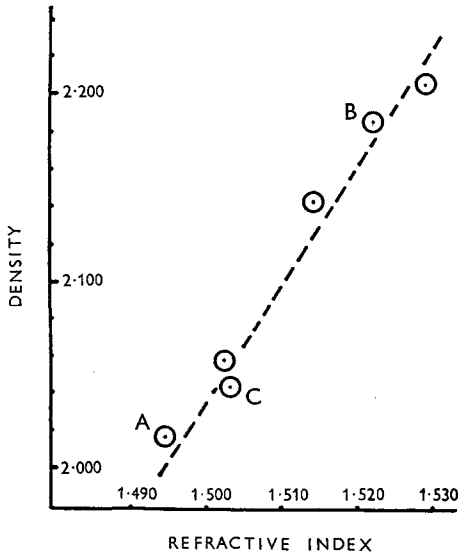


FIG. 2. Plot of density against mean refractive index for a series of gel samples. Points A, B, and C correspond to analyses A, B, and C in table I.

of a series of samples have been plotted against their density, as determined by suspension in liquid. This plot illustrates a linear relationship between the mean refractive index of the gel and its density. The total variation in the latter corresponds to a factor of 10% approximately. Later in the present paper chemical analyses of two of these gel samples are compared (samples A and B on fig. 2). The comparison indicates that density variation is not, in the main, a function of variable chemical composition. The graph presented approximates to the classical equation,

$$(\mu - 1)/\rho = K_G,$$

given by Gladstone and Dale, where μ is the refractive index, ρ the density, and K_G a constant. From this relationship it is evident that the gel behaves optically in a manner analogous to compressible liquids.

THIN-SECTION STUDY OF THE GEL AND THE REPLACEMENT PROCESS.

In thin section the gel is seen to pseudomorph both larnite and bredigite. The pseudomorphs have low birefringence and moderately sharp extinction. In suitably orientated sections pseudomorphs after bredigite yield a perfect biaxial interference figure; $2V$ being positive and equal to that of the parent silicate. Examination of a number of partly hydrated bredigite crystals by means of the Berek compensator indicated that the birefringence of the bredigite was reduced by a factor of five on gelatinization, regardless of the orientation of the original section.

The formation of gel pseudomorphs after larnite in a larnite-spinel-rock from Ballycraigy is illustrated in pl. XVII, and the relationships between the several zones present are shown on the overlay over fig. 1. The hydration interface between the larnite and gel is sharp and crosses individual crystals without respect to their orientation, and no preferential hydration along grain boundaries was observed in this or other sections. Under crossed nicols relict lamellar twinning can be seen in crystals marked L, alternate lamellae extinguishing together. Examination of a large number of thin sections suggests that the hydration process is effected without appreciable volume change.

X-RAY EXAMINATION.

X-ray powder data for the gel have been presented previously (McConnell, 1954, p. 297). During the present study powder photographs of material representing the limits in density variation were compared and found to be identical.

A single crystal of bredigite, pseudomorphed by gel, was examined by single-crystal X-ray techniques. The original crystallographic directions of the bredigite were determined from an optical examination of the pseudomorph. The single-crystal photographs showed that the reflections given by the pseudomorph were orientated and these were subsequently indexed, indicating that the b^* direction of the hydrate phase was orientated parallel to the c^* direction of the parent bredigite (Douglas, 1952, p. 878), and that the a^* direction of the hydrate was randomly orientated in the plane normal to this direction. The existence of preferred orientation in the hydrate phase suggests that the original structure of the bredigite is inherited to some degree.

CHEMICAL COMPOSITION AND DEHYDRATION OF THE GEL.

An analysis of plombierite from Ballycraigy has already been given (McConnell, 1954, p. 302) and this is shown together with a second analysis in table I. In an earlier section it has been noted that the chemical composition of the gel is sensibly independent of variation in the density of the gel. The third analysis in table I was carried out on a larger sample of the gel collected from a hydrated larnite nodule at Scawt Hill.

Part of the last sample was used for the adsorption experiments now to be described. The apparatus used for these experiments was extremely simple; 100 mg. samples of the gel, graded between 90 and 150 mesh, were placed in a shallow boat and suspended on a helical glass spring in a vertically mounted cylindrical desiccator. Movement of the

TABLE I. Chemical analyses of plombierite gels from Ballycraigy and Scawt Hill, Co. Antrim.

| | A. | B. | C. | C ₁ . | C ₂ . |
|---------------------------------------|-------|-------|-------|------------------|------------------|
| SiO ₂ | 40.4 | 39.9 | 41.76 | 6.00 | 5.96 |
| Al ₂ O ₃ | 2.4 | 4.3 | 0.23 | ... | ... |
| Fe ₂ O ₃ | 0.8 | 0.5 | 0.47 | ... | ... |
| MgO | 0.3 | 0.0 | 0.30 | ... | ... |
| CaO | 32.6 | 31.9 | 31.18 | 4.80 | 4.76 |
| Na ₂ O | n.d. | n.d. | 0.18 | ... | ... |
| K ₂ O | n.d. | n.d. | 0.10 | ... | ... |
| TiO ₂ | n.d. | n.d. | 0.20 | ... | ... |
| Mn ₂ O ₃ | n.d. | n.d. | 0.05 | ... | ... |
| H ₂ O - (110°) | 23.3 | 23.0 | 14.76 | ... | ... |
| H ₂ O + (1000°) | | | | 10.72 | ... |
| | 99.8 | 99.6 | 99.95 | ... | ... |
| Density | 2.018 | 2.186 | 2.042 | ... | ... |
| Mean ref. ind. | 1.495 | 1.523 | 1.503 | ... | ... |

A. Natural gel from Ballycraigy. (McConnell, 1954, p. 302.)

B. Ditto. New analysis by author on 0.30 gm.

C. Gel from Scawt Hill. Analyst, L. J. Larner, Building Research Station, Garston, Herts.

C₁. Molecular ratios CaO:SiO₂ on basis 6SiO₂ from analysis C.

C₂. Number of silicon and calcium atoms in the volumetrical equivalent of half the unit cell of bredigite from the same sample of material.

spring with respect to a fixed reference point, coaxial with the desiccator, was measured by means of a travelling microscope. The method allowed of the determination of weight change of the order of 0.05 % of the total weight of the gel sample. In practice the desiccator was permanently evacuated and sulphuric acid solutions of known concentration were introduced, in turn, and time-weight loss curves plotted for the gel sample. From these curves the relative rates of diffusion at different vapour pressures, and the final degree of approach to equilibrium, were estimated. The diffusion coefficient was found to decrease rapidly with decreasing vapour pressure and at low vapour pressures near equilibrium was attained only after a period of weeks.

Two different experiments were carried out. In the first of these the sample was dehydrated from 80 % relative humidity to near zero humidity and then rehydrated. In the second experiment dehydration was taken to 15 % relative humidity and the sample rehydrated from this point. Different samples were used in each experiment. The adsorption curves are given in fig. 3 and the most important features shown by them are listed below:

1. A marked break in the desorption curves occurs at 40 % relative humidity.

2. Rehydration after complete dehydration is accompanied by marked hysteresis.
3. Dehydration and rehydration between the limits of 40 and 15 % relative humidity appear to be strictly reversible.

In its general characteristics this adsorption curve is similar to that obtained for silica gel. A desorption curve with similar characteristics

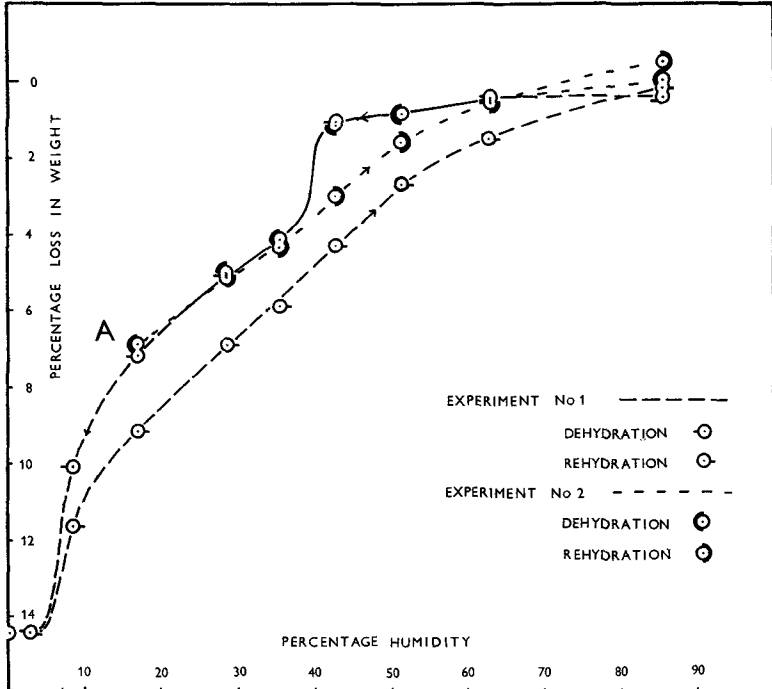


FIG. 3. Adsorption isotherms for plombierite gel. Temperature 16° C.

has been given by Giertz-Hedström for portland cement hydration products (1938, p. 517).

Complete analysis of the adsorption isotherms presented is not possible at present. It is evident, however, that the marked break in the desorption curves at 40 % relative humidity corresponds to the loss of a large water fraction from equivalent energy positions within the gel structure. Less generally this water may be regarded as occupying a capillary system of defined dimensions within the gel. The X-ray evidence already presented suggests that the gel pseudomorphs consist

of small orientated hydrate units and the possibilities of defined dimensions in such a system are twofold. They may represent interlayer distances in the hydrate units of structure, or the distance between the individual structural units. Regarded as a laminar capillary system, the classical theory, due to Kelvin, suggests that the spacing is of the order of 10 Å. It has been found experimentally that the bulk volume of the gel does not change to an appreciable extent on complete dehydration.

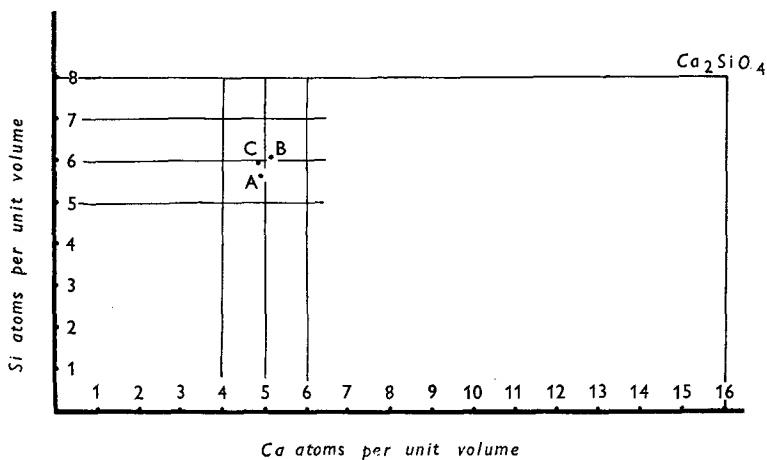


FIG. 4. The volume relationships of the hydration process. Points A, B, and C correspond to the analyses in table I.

THE VOLUME RELATIONSHIPS OF THE HYDRATION PROCESS.

The limits of variation in density and chemical composition of the gels have already been discussed, and it has been suggested that the process of hydration obtains at constant volume. The volume relationships of the process are represented in fig. 4, where the number of silicon and calcium atoms in unit volume of the parent silicate and the gel have been plotted. The unit volume chosen was that of half the unit cell of bredigite (Douglas, 1952, p. 882) or twice the volume of the larnite unit cell (Midgley, 1952, p. 307). From this diagram it is evident that the hydration process involves the removal of both calcium and silicon atoms from the structure, and that the volumetrical equivalent of half the bredigite unit cell contains 5 calcium and 6 silicon atoms. The formula unit of the crystalline hydrates of this group has the form $5\text{CaO} \cdot 6\text{SiO}_2 \cdot x\text{H}_2\text{O}$ (McConnell, 1954, 298), which suggests again that a

simple relationship may exist between the structure of the hydrate and that of the parent dicalcium silicate minerals.

Descriptions of silica hydrogels formed through the leaching of natural minerals have been given by a number of authors. In most cases some degree of ordering in the leached structure is observed. This is reflected in the retention of optical symmetry directions. Skeletonized apophyllite has been described by Bailey (1941, p. 565). In this case X-ray powder photographs showed that, in its structure, the silica hydrogel was essentially amorphous. Leaching experiments on gillespite ($\text{BaFeSi}_4\text{O}_{10}$) were carried out by Schaller (1929, p. 319) and later repeated by Pabst (1943, p. 388). The Fe and Ba atoms were removed from the mineral by acid leaching and the residual silica hydrogel formed was found to occupy the same volume as the parent silicate structure. A Laue photograph of a leached crystal of gillespite was taken by Pabst and this showed that the tetragonal symmetry of the parent silicate was preserved, but powder photographs of the silica hydrogel failed to show any reflections, indicating that the gel was amorphous.

A considerable amount of experimental work has been carried out on the hydration products of the portland cement clinker compounds $\beta\text{-Ca}_2\text{SiO}_4$ and Ca_3SiO_5 . Both are known to hydrate at normal temperatures to give gelatinous hydration products. One of the most important of these is 'calcium silicate hydrate (I)', which, as noted previously in this paper, corresponds to the natural gelatinous mineral described in the present communication. The mechanism of gel formation, as outlined here, may have considerable bearing on the formation of calcium silicate hydrogels in the setting of portland cement.

Study of the natural materials suggests that such a hydrogel would be stable for an indefinite period of time in the presence of unhydrated clinker particles, and that, at high density, the gel would be competent to act as a rigid bonding medium in set cement.

Acknowledgements.—The author is indebted to the director of the Building Research Station, Garston, Herts., for permission to publish the analysis shown in table I. This research was carried out in the Department of Mineralogy and Petrology at Cambridge under the direction of Professor C. E. Tilley.

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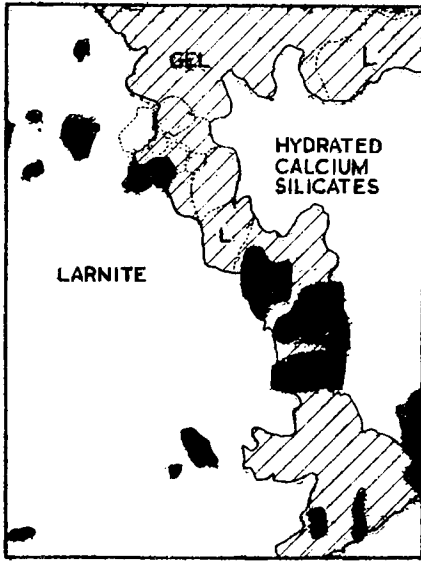
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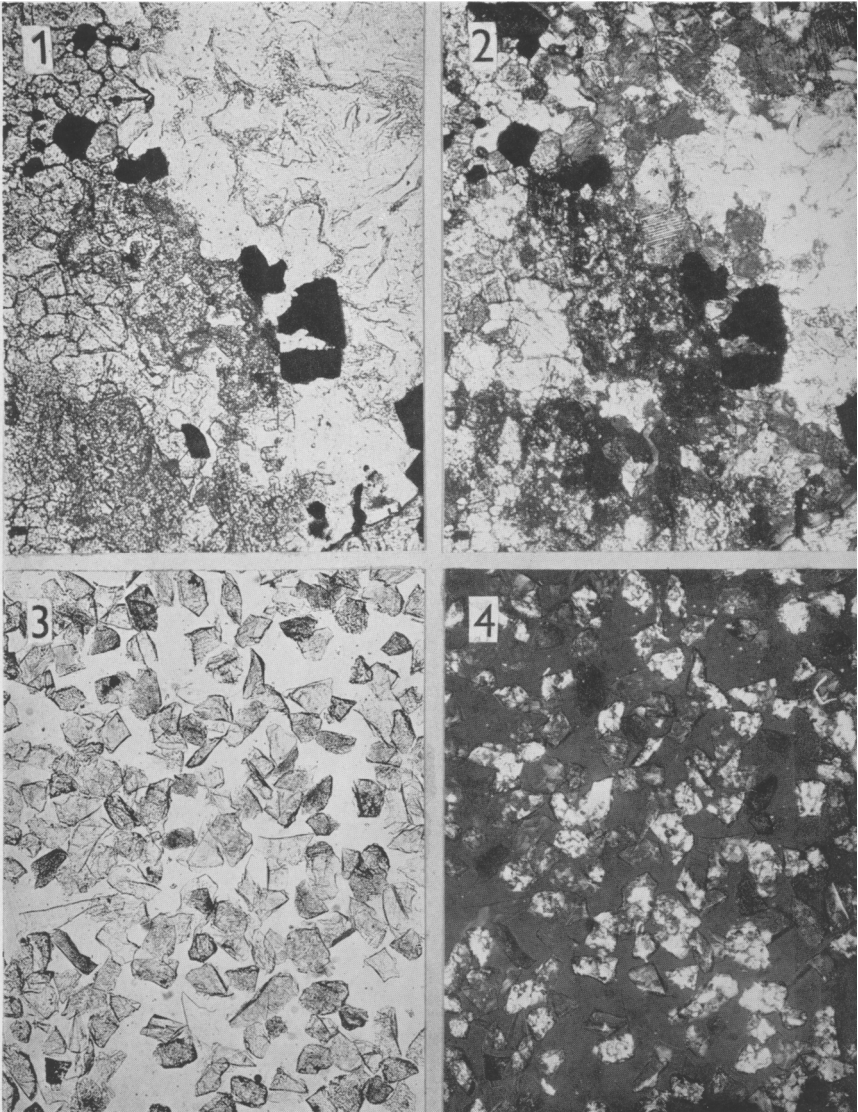
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EXPLANATION OF PLATE XVII.

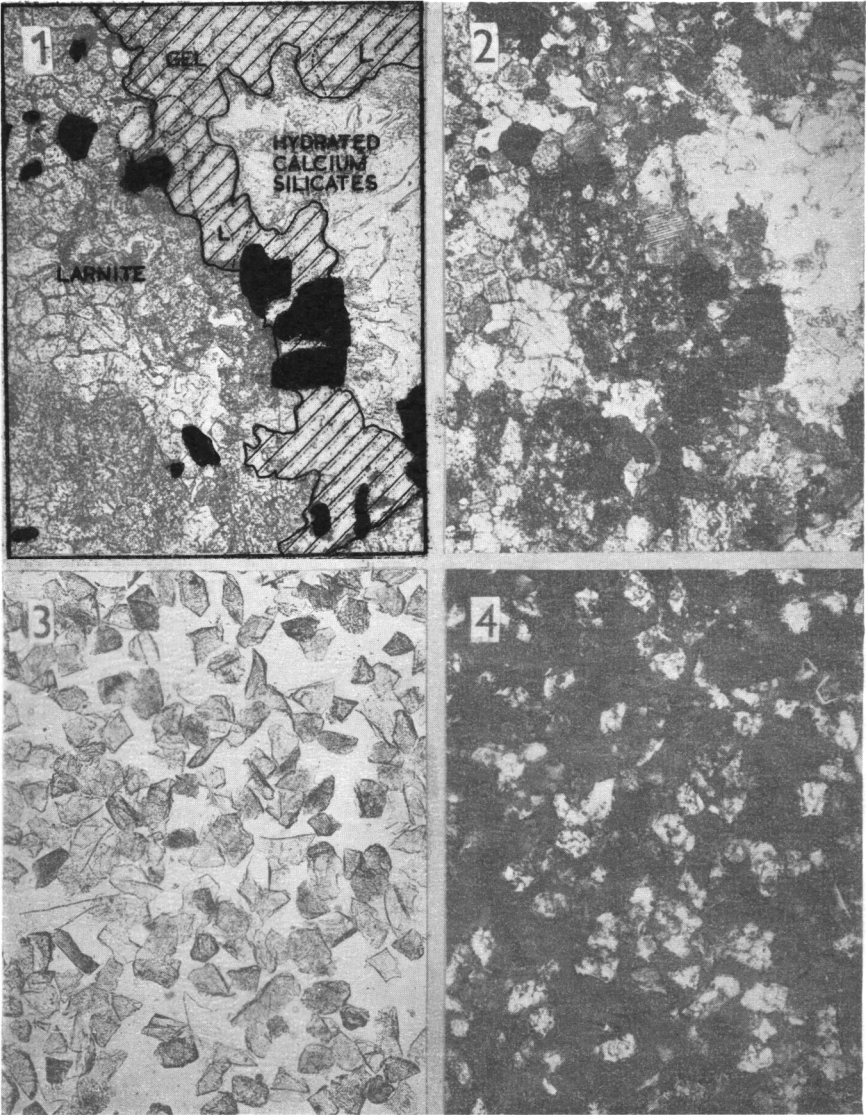
Photomicrographs of larnite-rock and hydration products.

- FIG. 1. Larnite-rock in thin section, showing a hydration zone of gel surrounding a vug containing afwillite and portlandite. $\times 85$.
On the overlay the area of gelatinized larnite is shaded, and the outlines of some of the larnite crystals are indicated. Relict lamellar twinning is shown under crossed nicols (fig. 2) in the crystals marked L. The black areas are spinel.
- FIG. 2. The same as of fig. 1 under crossed nicols showing the relict twinning in gel pseudomorphs after larnite. $\times 85$.
- FIG. 3. A crushed sample of plombierite gel from Scawt Hill. $\times 25$.
- FIG. 4. The same as fig. 3 under crossed nicols, showing birefringence effects in the gel. $\times 25$.
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J. D. C. McCONNELL: PHOTOMICROGRAPHS OF LARNITE-ROCK AND HYDRATION PRODUCTS.



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