Merwinite as an artificial mineral.[1]

(With Plate VIII.)

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IN the investigation of the system CaO–MgO–SiO_2 by Ferguson and Merwin[2] the orthosilicate $3CaO.MgO.2SiO_2$ was not observed, and the existence of this compound was first proved in 1921 by Larsen and Foshag[3] who detected it in a contact-altered limestone at Crestmore, California, and gave to it the name merwinite. Since then this compound has been found in contact-altered limestones at Scawt Hill, Antrim,[4] near Neihart in the Little Belt Mts. of Montana,[5] and at Velardeña, Mexico.[6] The history of the recognition of merwinite as an artificial mineral is less easy to trace, but it seems that research workers on refractory bricks were the first to recognize its existence. Thus U.S.A. Patents applied for in the years 1934 and 1935 and British Patents applied for on 11.10.1935 and 19.5.1936 by Non-Metallic Minerals Inc. specify merwinite and periclase as the essential constituents of a refractory brick produced by firing mixtures of dolomite and serpentine, dolomite and sand, or impure magnesite and dolomite at temperatures varying between 2700° and 2900° F. (that is, about 1500–1650° C.). The last Patent specifies the addition of mineralizers (oxides of boron, phosphorus, or chromium) to obviate deterioration of the merwinite bricks when used in circumstances permitting reaction with lime. The implication of this device is that merwinite and lime react readily with formation of β-calcium orthosilicate and periclase, the tendency of the former to 'fall' or 'dust' with consequent disintegration of the brick being counteracted by the mineralizing agents. No diagnostic properties of merwinite are communicated in these specifications, nor by Dr. Reinhart[7] who gives some details of the occurrence of

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[1] Communicated by permission of the Director, Geological Survey and Museum.

[2] J. B. Ferguson and H. E. Merwin, Amer. Journ. Sci., 1919, ser. 4, vol. 48, p. 81. [M.A. 1–321.]

[3] E. S. Larsen and W. F. Foshag, Amer. Min., 1921, vol. 6, p. 143. [M.A. 1–254.]

[4] C. E. Tilley, Min. Mag., 1929, vol. 22, p. 84.

[5] J. H. Taylor, Amer. Min., 1935, vol. 20, p. 124. [M.A. 6–125.]

[6] C. E. Tilley, Geol. Mag. 1928, vol. 65, p. 372. [M.A. 4–84.]

[7] Reinhart, Tonindustrie Zeitung, 1939, vol. 63, p. 29.

merwinite in refractory bricks. Reinhart states that merwinite has already begun to form at a temperature of 1375° C., that monticellite is also a constituent of the bricks, and that the calcium orthosilicate : merwinite ratio is controlled in firing mixtures of lime, magnesia, and silica by the ratio $CaO : SiO_2$. Between the limits $1{\cdot}4 < CaO : SiO_2 < 1{\cdot}8$ the product after firing will contain both β-$2CaO.SiO_2$ and $3CaO.MgO.2SiO_2$, merwinite being dominant between the limits $1{\cdot}4 < CaO : SiO_2 < 1{\cdot}6$.

In 1936 H. zur Strassen,[1] and later H. Schwiete and Strassen, described the results of experiments undertaken to test the reactions between lime and forsterite and lime and åkermanite. After firing at 1250° C. for two minutes åkermanite was completely and forsterite 80 % destroyed. In both cases the final products were β-$2CaO.SiO_2$ and MgO, but the intermediate compounds, monticellite and merwinite in the case of the experiment with forsterite, and merwinite in the case of åkermanite, were formed as transient products. The identification of the compounds was done by X-ray methods, and the authors report also as transient products mixed crystals between merwinite and β-$2CaO.SiO_2$ and between monticellite and β-$2CaO.SiO_2$. Tests were also made on a mixture of pure CaO, MgO, and SiO_2 in the proportions appropriate to the reaction $2CaO+2MgO+SiO_2 = \beta\text{-}2CaO.SiO_2+2MgO$, firing being at 1000° C. for periods increasing by half-hour intervals. For the shorter periods of firing 10–15 % of merwinite was found in the product; after 2½ hours some merwinite was still present, but after 18 hours (no observation having been made between these two periods) merwinite had disappeared.

In 1938 the writer[2] and Belyankin and Korchemkin[3] reported independently the occurrence of merwinite as an essential constituent in blast-furnace slags. Review of the slags in the Tested Roadstone Collection of the Geological Museum shows that seven out of a total of 32 slags contain merwinite, and it is interesting to note that among the seven is the very first slag to arrive in this collection, in the year 1911. Merwinite is therefore a common mineral in British blast-furnace slags and indeed is second only to pseudowollastonite as the subordinate essential constituent, melilite being consistently the major constituent. Pseudowollastonite and merwinite have naturally not been observed in the same slag.

During a discussion on the constituent minerals of blast-furnace slags the writer drew the attention of Dr. F. M. Lea and his colleagues of the Building Research Station to the comparatively frequent presence of merwinite and Dr. Lea agreed to attempt the synthesis of this compound from the pure oxides. This was successfully accomplished and Dr. T. W. Parker has kindly supplied the following notes of its preparation:

> 'The starting materials were calcium carbonate (99·92 % purity), quartz (99·82 % purity), and magnesia (99·73 % purity), all in powder form, finer than a B.S. no. 170 sieve, and intimately mixed in the proportions required for $3CaO.MgO.2SiO_2$. Two mixes were made, one of them containing an 0·5 % admixture of B_2O_3. Both were heated in platinum boats in a platinum wire-

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[1] H. zur Strassen, Zement, 1936, vol. 25, p. 218; H. Schwiete and H. zur Strassen, Zement, 1936, vol. 25, pp. 849, 870.

[2] J. Phemister, Summ. Progr. Geol. Surv. Great Britain, 1938, for 1937, p. 87.

[3] D. S. Belyankin and L. I. Korchemkin, Trav. Inst. Pétrogr. Acad. Sci. U.R.S.S., 1938, no. 12, p. 203. [M.A. 7–286.]

wound electric muffle furnace for one hour at 1450° C. They were then cooled, re-ground to pass a B.S. no. 170 sieve, re-mixed and re-heated for one hour at 1500° C. The mix containing B_2O_3 gave a homogeneous product by check test under the microscope at the end of this treatment and was therefore considered to be fully reacted. The mix without B_2O_3 required a further 5 hours heating at 1500° C. before the product became homogeneous. In both cases the preparations were taken out of the furnaces at about 1450° C. and quenched by rapid cooling from this temperature to prevent any possibility of inversion or decomposition.'

From the above summary it is clear that up to the present merwinite, $3CaO.MgO.2SiO_2$, is known to have crystallized from a melt only in the case of blast-furnace slags where, in addition to CaO, MgO, and SiO_2, the oxides Al_2O_3 and FeO are also present, respectively in considerable and in minor proportions. The experiments by Strassen suggest that it is unlikely that merwinite can crystallize from a pure $CaO–MgO–SiO_2$ melt, but it may be recalled that in these experiments the proportion of SiO_2 is exactly that required for combination with lime to form $2CaO.SiO_2$. While, therefore, there exists at present no direct challenge to the accuracy of the equilibrium diagram prepared by Ferguson and Merwin it is worth remembering that the investigations on which this diagram is based were made before the existence of merwinite was suspected and its properties known, and also that, the optical properties of synthetic merwinite (see table I below) being very close to those of β-$2CaO.SiO_2$, the possibility of confusion between these two compounds is not to be disregarded.

The fact that merwinite can crystallize from blast-furnace slag is of the first importance from the economic standpoint. In contrast to the calcium orthosilicate, merwinite does not appear to undergo transformation in the solid state. It is well known that the former crystallizes as the α- or β-phase at high temperature and that at 675° C. the β-phase inverts to a γ-phase with great increase of volume. In consequence, slag containing the calcium orthosilicate as an important constituent is liable to disintegrate or 'fall'. Where, therefore, blast-furnace practice is such that an orthosilicate is present in the slag, the latter can be 'stabilized' by the use of a dolomitic, or some proportion of dolomitic, in place of a calcareous flux, and is then available (without fear of 'falling') for use in concrete aggregate and roadstone.

Merwinite in blast-furnace slag.—The slags which carry merwinite always contain melilite as their major constituent as prisms or tables which are usually strongly zoned. The melilite is optically negative gehlenite with birefringence moderate in the core and decreasing towards a peripheral zone, which may be isotropic for all or part of the visible spectrum. In some specimens zoning to optically positive åkermanite is continued beyond the isotropic layer. Merwinite shows a variety of habit. When very abundant it has separated out from the molten slag at as early a stage as the gehlenite with which it sometimes forms a graphic intergrowth (pl. VIII, fig. 1). It may occur also as optically continuous drops and as idiomorphic crystals within gehlenite or as poikilitic plates enclosing melilite, these plates attaining a length of 5 mm. in the slag E 19006. When less abundant it may act as an interstitial mineral, the irregular grains of which interfere with the outermost zone of the melilite, or it may form acicular crystals stretching through several melilite tables and the interstitial isotropic matter

(? glass) (pl. VIII, figs. 1 and 2). The minor constituents of the slags are calcinm sulphide (oldhamite) in clusters of tiny octahedra, colourless spinel, and arborescent isotropic growths (of ?) which are typically enclosed in melilite but appear also within merwinite.

Merwinite is recognized by its high refractive index, moderate birefringence, biaxial positive character, moderately large 2V, and complex twinning. In the accompanying table there are given the optical constants of the mineral in slags E 19543, 19008 of the Geological Survey collection and of synthetic merwinite prepared at the Building Research Station. The values agree well with those determined by Belyankin and Korchemkin for merwinite from a Ural slag, but the birefringence is almost double that recorded by Larsen and Foshag for merwinite from Crestmore, the difference being due mainly to the higher value of γ in the artificial compound. The refractive indices of Crestmore merwinite were therefore studied, by the immersion method, on material supplied by Mr. F. A. Bannister, Deputy Keeper of Minerals, Natural History Museum, and values (reproduced in the table) closely comparable with those of the slag merwinite were obtained. Professor C. E. Tilley very kindly checked the values for Crestmore merwinite in his collection, obtaining α 1·706, β 1·712, γ 1·724. Concurrently he made full determinations on the Scawt Hill merwinite, for which approximate values only were recorded hitherto, and has given me permission to publish the figures here. The new values for the natural mineral agree closely with those for the artificial compound; the higher values for the merwinite of slags E 17543 and 19008 probably indicate a material content of ferrous oxide.

TABLE I. Optical properties of merwinite from various sources.

	Blast-furnace slag.			Natural mineral.		
	E 17543. E 19008.	Ural. (±0·003).	Synthetic, prepared at the Building Research Stn.	Crestmore, determined by J. Phemister.	Scawt Hill, determined by C. E. Tilley.	Montana determined by J. H. Taylor.
α ...	1·708	1·705	1·706	1·707	1·706	1·710
β ...	1·714	1·711	1·711 or 1·712	1·712	1·712	1·712
γ ...	1·728	1·724	1·724	1·725	1·724	1·718
$\gamma - \alpha$ ...	0·020	0·019	0·018	0·018	0·018	0·008
2V ...	69°±2° (56°)	75°	71°±2°	67°±1°	—	70°

In the first column of the table two values of the optic axial angle are given. The lower value was observed in three broadly twinned grains; in all three one portion gave the lower angle, the other gave a normal angle.

Two sets of polysynthetic twinning are characteristic of merwinite and in sections normal, or nearly so, to the twinning the two sets of lamellae make an angle of 42½° (pl. VIII, fig. 4). The acute positive bisectrix bisects the obtuse angle between the two lamellar groups. Grains suitable for the measurement of this angle directly on the microscope stage can be found, but are not very common in thin sections of slag. Sections showing only one set of lamellae are by far the more common and the lamellae usually appear as very narrow streaks traversing the crystal or grain. Larsen and Foshag believe the mineral to be monoclinic with $\gamma = b$, $\alpha : c = 36°$, c the twinning axis, and (110) the composition-plane.

The cleavage is perfect parallel to (010), but is not conspicuous in thin sections of slag and was observed only in sections normal to β. In crushed preparations of the mineral the presence of this cleavage is, however, responsible for the large numbers of fragments which show the emergence of the acute bisectrix. Traces of a cleavage parallel to (100) have been noted by the writer.

The synthetic merwinite prepared at the Building Research Station is in the form of a powder which under the microscope is seen to be composed of shapeless grains up to 0·2 mm. in length, but usually considerably smaller. They are patchily coated by glass and some of the larger grains contain veinlets of glass. A broad lamellar twinning is common and there is a tendency for some grains to have edges parallel to the trace of the twinning planes. Dr. T. W. Parker notes that 'the product is in effect the form stable at 1500° C. We do not know whether there are any other forms or whether merwinite decomposes at lower temperatures. Similarly, we do not know whether it has a congruent melting-point or not. Its melting-point is higher than 1500° C.' The optical properties of the synthetic merwinite are given in the table. No difference beyond the range of observational error was found between the values for the pure product and that prepared in the presence of boric oxide.

In pl. VIII, figs. 5 and 6 are reproduced X-ray powder photographs, taken by Mr. F. A. Bannister, of synthetic β-$2CaO.SiO_2$ and $3CaO.MgO.2SiO_2$ prepared at the Building Research Station. The spacing data are given in table II.

TABLE II. Spacings in Ångström units and estimated intensities of the principal lines of powder photographs of artificial merwinite and larnite (pl. VIII, figs. 5 and 6), taken with copper radiation.

Merwinite (fig. 6).		Larnite (fig. 5).	
2·94 w	1·75 vw	3·03 w	1·80 w
2·83 w	1·69 vw	2·76 s (2·751)	1·70 vw
2·73 w	1·61 w	2·69 s (2·703)	1·63 mw
2·65 s (2·646)	1·57 w	2·66 w	1·61 mw
2·41 vw	1·53 m (1·532)	2·58 vw	1·57 vw
2·30 w	1·43 vw	2·45* w	1·55 vw
2·20 w	1·39* vw	2·25 w	1·52 vw
2·16 w	1·34 w	2·18 m (2·170)	1·48 vw
2·03 w	1·32 w	2·02 w	1·39 vw
1·90 m (1·901)	1·23 vw	1·98 m (1·969)	1·37 vw
1·87 mw	1·19 vw	1·89 w	

* Unresolved doublets.

The spacings of the strongest lines have also been measured on powder photographs taken with iron radiation and are given in brackets. These lines provide a satisfactory distinction between the two compounds and appear on relatively short exposure X-ray photographs.

In conclusion, the writer wishes to express his thanks to Professor C. E. Tilley for the loan of thin sections of Scawt Hill rocks containing larnite, and to Mr. F. A. Bannister for a gift of merwinite-bearing rock from Crestmore. To both these gentlemen and to the officers of the Building Research Station he is indebted for their most helpful co-operation in obtaining the data recorded in this paper.

APPENDIX by R. W. NURSE, M.Sc.

Note on the melting relations of Merwinite.[1]

From the constancy of the figures given by Dr. Phemister for the optical constants of merwinite, it is almost certainly a pure compound; it is therefore to be expected that it should be found in the system $CaO–MgO–SiO_2$. A few experiments carried out by the writer in the course of work at the Building Research Station show that the synthetic merwinite, the method of preparation and optical properties of which are described in Dr. Phemister's paper, decomposes at 1590° C. into melt and a phase which resembles $2CaO.SiO_2$, except that the refractive indices are lower (α 1·708, γ 1·735) and the axial angle is very small, being nearly uniaxial. When examined under the microscope in polished sections, with vertical illumination, the decomposition product is etched by HF vapour, 10 % $MgSO_4$ solution, and alcoholic nitric acid solution, reactions which are characteristic of $2CaO.SiO_2$, whereas merwinite is not etched by 10 % $MgSO_4$. From the limited data available it may be concluded that merwinite does in fact occur in the system $CaO–MgO–SiO_2$ as an incongruently melting compound.

While a re-examination of Ferguson and Merwin's diagram in the region adjacent to the monticellite and åkermanite primary phase fields would be necessary to confirm that merwinite can occur as a primary phase in the ternary system, there is a strong possibility that it does do so in that part where final melting temperatures are below 1590°. The compositions shown as having been examined by Ferguson and Merwin in the construction of their ternary diagram include only a few in this area.

As a matter of interest, blast-furnace slags melt completely at temperatures lower than that of the decomposition temperature of merwinite, and the latter can therefore occur as a phase in contact with melt in blast-furnace slag systems.

EXPLANATION OF PLATE VIII.

Photomicrographs of merwinite in blast-furnace slags (figs. 1–4).

FIG. 1. E 17543. Needles of merwinite in stout tables of melilite which contain arborescent growths of isotropic material spreading from the *c*-axis towards the pinakoidal faces. Ordinary light. × 50.

FIG. 2. E 17543C. Needles of merwinite in a slag composed mainly of melilite. Nicols nearly crossed. × 40.

FIG. 3. E 19008. Intergrowth of merwinite in a thick table of melilite which shows the basal cleavage. Nicols crossed. × 30.

FIG. 4. E 19008B. In the centre of the photograph a crystal of merwinite shows the two sets of lamellar twinning inclined at 42½°. Nicols crossed. × 60.

FIGS. 5 and 6. X-ray powder photographs of artificial larnite, β-$2CaO.SiO_2$ (fig. 5), and artificial merwinite, $3CaO.MgO.2SiO_2$ (fig. 6), taken with unfiltered copper radiation and with the same cylindrical camera diameter 6 cm. Actual size.

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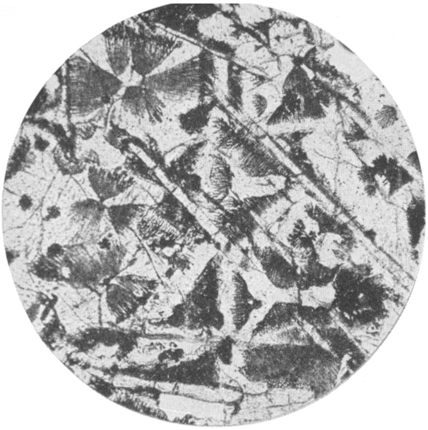
[1] Communicated by permission of the Director, Building Research Station.



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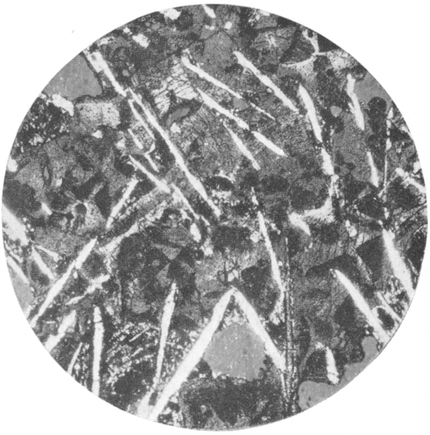

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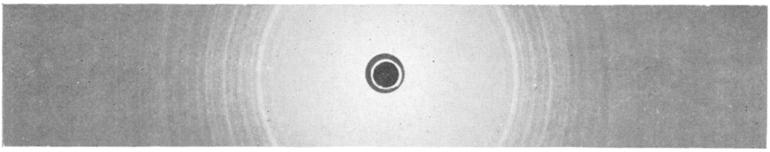

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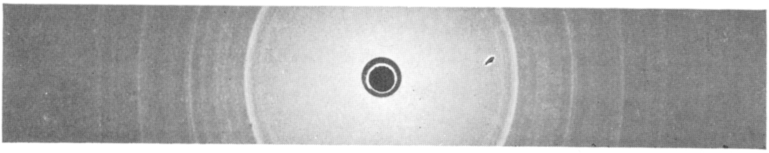

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J. PHEMISTER: MERWINITE IN SLAGS