The nature and paragenesis of natural bredigite and associated minerals from Carneal and Scawt Hill, Co. Antrim

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ABSTRACT. Bredigite is a constituent of the very high-temperature, low-pressure, exomorphic suite of Carneal, Co. Antrim. Although this mineral is very rare in nature, it is an important constituent of some slags and cement clinkers but there has been much controversy about its nature, most of the evidence having come from artificial materials. Chemical analysis of the Carneal mineral shows it to be remarkably similar to that from the type locality, Scawt Hill (also analysed here), and that it is an individual mineral species of generalized ionic composition $(Ca,Na)_{14}(Mg,Fe^{2+}Fe^{3+}Mn)_2(Si,P)_8O_{32}$. Ba (abundant in the original analysis of the slag mineral) is not a constituent. Accurate X-ray powder data of the natural mineral are given. Bredigite is not Ca_2SiO_4, nor is it part of a solid solution of variable composition between larnite and merwinite. Analyses are presented for the associated minerals larnite (allowing appraisal of its composition), spurrite, and spinels. The paragenesis is discussed.

KEYWORDS: bredigite, larnite, spurrite, spinel, Antrim, Northern Ireland.

FEW examples of the rare natural mineral bredigite have been described, although three occurrences are known from the United Kingdom. These are from Scawt Hill, Co. Antrim, from which the mineral was first described by Tilley and Vincent (1948); from Camas Mòr, Muck, mentioned by the same authors in a footnote; and from Carneal, Co. Antrim (Sabine, 1975; Sabine et al., 1982a; Griffith and Wilson, 1982). Uncertainty has long existed as to whether the natural mineral was a Ca, Ca–Ba–Mg, or Ca–Mg silicate, about the relationships with other silicates, and the polymorphism of it and the artificial analogues which may be of importance in cements and slags.

Numerous synthetic studies that bear on the problem of the composition have been reviewed among others by Biggar (1971), Midgley and

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Bennett (1971), Midgley (1974), Saalfeld (1974), Moore and Araki (1976), Essene (1980), Moseley and Glasser (1981, 1982), and Treiman and Essene (1983).

It is thus well established (from artificial materials) that bredigite essentially contains Mg but very few data are available from any natural material, and there is little indication of the range, if any, of its composition. Hitherto there has also been no indication of the significance of a unitary composition.

The present paper deals mainly with the Carneal occurrence and with comparative studies on the type minerals from Scawt Hill. It is confirmed that the natural mineral has a definite composition, for which refined chemical and X-ray data are provided. It is not a Ba-rich mineral, and is not Ca_2SiO_4.

The Carneal assemblage

At Carneal, Co. Antrim, the exomorphic larnite-bredigite-spinel assemblage was formed by the incorporation of blocks of underlying Cretaceous chalk brought up in a dolerite plug intruding Tertiary lavas at high temperature and low pressure (Sabine, 1975). The dense dark grey rock is composed essentially of an aggregate of larnite tablets commonly 0·1 mm or less across, showing fine polysynthetic twinning; spurrite plates, to which larnite may be altered and in which it is enclosed; bredigite, commonly in equidimensional crystals; abundant irregularly scattered cubes and aggregates of magnetite and other spinels; coarse prisms of gehlenite; a little calcite; and octahedra and irregular crystals of perovskite.

Analytical techniques. The minerals from Carneal and also from Scawt Hill (kindly provided from the Cambridge collection by Dr S. O. Agrell), were analysed using a Link systems, energy-dispersive X-ray analyser on a Cambridge Instruments Geoscan electron microprobe. The electron beam was

focused to approximately 5 μm diameter and an accelerating voltage of 25 kV and a specimen current of 5×10^{-9} amps were used throughout. Techniques and results are very similar to those described by Dunham and Wilkinson (1978). The energy dispersive analysis system checks for the presence of all elements of atomic number greater than 11 (Na) and only those given in the analysis tables were above the detection limit, which is approximately 0.2 wt. % oxide.

Bredigite. The mineral occurs in equidimensional anhedral to scarce euhedral crystals typically 0.1 mm or less across. It is colourless (in normal thickness thin sections) and can be difficult to distinguish optically from larnite, but commonly shows the distinctive twinning described by Tilley and Vincent (1948), and may amount to perhaps 30% of the rock by volume.

One specimen from Carneal as well as four from Scawt Hill were analysed (Table I). The mean value for Scawt Hill (col. 6) makes allowance for the number of individual determinations whose results are shown in cols. 2–5. The specimens show a remarkable similarity in composition, with some variation in the content of Fe and its ratio to Mg. The oxidation state of iron has been shown as Fe^{3+}, as the whole rocks have a high Fe_2O_3 : FeO ratio (about 6 in the analysed larnite–spinel rock) although Fe is only present in small amounts. All the new analyses of bredigite contain small amounts of Na, commonly P, and a few contain Al just above the limit of detection (0.2 wt. % Al_2O_3). These elements may well play an important role in stabilizing the minerals, as has been suggested for larnite (Tilley and Vincent, 1948; Midgley and Bennett, 1971).

In the new Carneal and Scawt Hill analyses, Ba was below the detection limit (0.3 wt. %). Phosphorus (0.30% P_2O_5; 0.057 in the unit cell) reflects the phosphate content of the exomorphic rocks, e.g. the larnite–spinel rock (0.15% P_2O_5), and of the olivine-dolerite (0.15% P_2O_5). Flint contains a considerably smaller amount of P_2O_5 (about 0.02–0.03%) and most chalk about 0.04–0.11% P_2O_5 (Sabine *et al.*, 1982a), suggesting that the principal source of the phosphorus is the igneous rock.

Ionic formulae are shown in Table I, calculated on the basis of (O,F) = 32, Z = 2, following Moore and Araki's structural study (1976). FeO contents have not been determined and have been taken approximately as in the rocks as $\frac{1}{6}$ of the total iron oxide (Sabine, 1975). Clearly too much reliance cannot be placed upon the ionic contents calculated for the minor elements in view of the low and variable contents, close to the limits of detection.

The ionic formulae correspond well with the

structural formula of Moore and Araki (1976), $X_2^{[12]}X_4^{[9]}Y_8^{[10]}M_2^{[6]}(TO_4)_8$ (superscripts in square brackets are co-ordination numbers). In the natural mineral, X and Y are largely Ca,M = Mg, and T = Si, corresponding to $Ca_{14}Mg_2(SiO_4)_8$. The analyses show a slight deficiency in the tetrahedral T sites if only Si or Si + P is considered but this shortfall is lessened if other cations are included as in Table I. The ionic composition is $(Ca,Na)_{14.13}$ $(Mg,Fe^{3+},Fe^{2+},Mn)_{1.92}(Si,P)_{7.94}O_{32}$, close to the ideal formula. The new analyses presented here suggest that the M sites are not entirely filled by Mg, Fe, and Mn. This discrepancy is much greater than the anticipated analytical error. The slight excess of Ca + Na + K + Ba over 14.00 suggests that some of these ions enter the M site.

The remarkably close analyses of the Carneal and Scawt Hill natural occurrences (Table I, cols. 1 and 6) show this to be a specific mineral and supports the suggestion of Moore and Araki (1976) that bredigite has a well defined discrete composition rather than forming part of a solid solution of variable composition between Ca_2SiO_4 and merwinite. Ba, abundant in the analysis of the slag mineral (Tilley and Vincent, 1948) has not been detected in the natural minerals.

X-ray data. X-ray powder data (Table II) were obtained from diffractometer traces taken with Cu-$K\alpha$ radiation ($K\alpha_1$ = 1.54051 Å) at room temperature (around 20 °C) and a scanning speed of $\frac{1}{8}$° 2θ/min. Lead nitrate, $Pb(NO_3)_2$, cell dimension a = 7.855(8) Å at 20 °C was used as an internal standard. The powder data for bredigite from Carneal were refined using a program for the refinement of powder diffraction data (Appleman and Evans, 1973), giving cell dimensions a 10.9026 $\pm$ 0.0003 Å, b 18.3730 $\pm$ 0.0006 Å, c 6.7559 $\pm$ 0.0003 Å. These cell dimensions and the powder data are close to the values obtained by Moseley and Glasser (1981) from synthetic material. The space group is $P2nn$ or $Pmnn$, and the calculated density is 3.326 g cm^{-3}.

Larnite. Several grains of larnite adjacent to bredigite grains have been analysed with the results given in Table III (cols. 1–4). These new microprobe results allow a better assessment of the earlier and fuller analysis of Carneal larnite (Sabine, 1975). The absence of Al_2O_3 in the microprobe analyses (less than the detection limit, 0.2 wt %) indicates that it cannot be present as a main constituent. Recalculation of the earlier analysis to remove Al_2O_3 and related elements as gehlenite and ferrian chlorospinel, but to retain P_2O_5, yields the results shown in Table III, col. 5. The newer analyses show no significant variation from grain to grain. Small amounts of Na and P are present in the larnite at

TABLE I. *Chemical analyses of bredigite*

	1	2	3	4	5	6	7
SiO_2	34.91	35.23	35.24	35.61	35.08	35.22	33.08
TiO_2	< 0.2	< 0.2	< 0.2–0.22	< 0.2	< 0.2	0.05	0.34
Al_2O_3	< 0.2	< 0.2–0.23	< 0.2	< 0.2–0.33	< 0.2–0.22	0.19	—
Fe_2O_3*	1.47	1.90	1.02	1.30	1.37	1.47	0.12
MnO	< 0.2–0.25	< 0.2	< 0.2	< 0.2–0.27	< 0.2	0.05	3.38
MgO	4.82	4.92	5.22	5.20	5.09	5.08	6.78
CaO	57.86	57.99	58.22	58.13	57.81	58.02	49.23
BaO	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	6.91
Na_2O	0.31	0.35	0.29	0.38	0.30	0.33	—
P_2O_5	0.30	< 0.2–0.22	0.33	0.24	< 0.2	0.20	—
F	—	—	—	—	—	—	0.16
Total	99.67	100.39	100.32	100.86	99.65	(100.61)	(100.00)
Number of ions on basis of 32 oxygens							
Si	7.886	7.877	7.886	7.898	7.918	7.886	7.815
Al	—	0.061	—	0.086	0.058	0.050	—
Ti	—	—	0.038	—	—	0.008	0.061
P	0.057	0.042	0.062	0.046	—	0.038	—
Fe^{3+}‡	0.204	0.258	0.138	0.175	0.189	0.202	0.021
Fe^{2+}‡	0.048	0.061	0.032	0.042	0.043	0.047	—
Mn	0.048	—	—	0.050	—	0.009	0.676
Mg	1.621	1.638	1.741	1.718	1.711	1.693	2.385
Ca	13.996	13.887	13.954	13.808	13.974	13.914	12.456
Ba	—	—	—	—	—	—	0.640
Na	0.136	0.152	0.126	0.162	0.131	0.143	—
F	—	—	—	—	—	—	0.119
$Si+Al+Ti+P+S$	7.943	7.980	7.985	8.030	7.976	7.982	7.876
$Fe^{3+}+Fe^{2+}+$ $Mn+Mg$	1.920	1.957	1.911	1.986	1.943	1.951	3.082
$Fe^{3+}+Fe^{2+}+$ $Mn+Mg+Ca+$ $Na+K+Ba$	16.052	15.996	15.992	15.956	16.048	16.008	16.178
$Ca+Na+K+Ba$	14.132	14.039	14.081	13.970	14.105	14.057	13.096

1. Carneal (NI 1596; mean of 8 determinations).
2. Scawt Hill (NI 4128, S350/51931; mean of 8 determinations).
3. Scawt Hill (NI 4129, S371/51927; mean of 5 determinations).
4. Scawt Hill (NI 4130, S409(A)/47756; mean of 4 determinations).
5. Scawt Hill (NI 4131, S377/51934; mean of 5 determinations).
6. Scawt Hill, weighted mean of 22 determinations (cols. 2–5).
7. Spiegeleisen slag, Middlesbrough (Tilley and Vincent, 1948: this was the original description of bredigite).

* Total Fe shown as Fe_2O_3. † SO_2. ‡ For calculation of Fe^{2+}, Fe^{3+}, see text. n.d. not detected. tr. trace.

Carneal and Scawt Hill and the potassium and strontium previously found probably also occur in the mineral. The refined cell dimensions at 20 °C are: $a = 5.500 \pm 0.002$ Å, $b = 6.762 \pm 0.001$ Å, $c = 9.311 \pm 0.002$ Å, $\beta = 94° 31' \pm 2'$.

Gehlenite. Gehlenite is abundant in coarse tablets and prisms up to 1 mm long, showing no zoning. It has already been described (Sabine *et al.*, 1982*b*) and yields the formula $Ca_{2.04}Mg_{0.06}Fe^{3+}_{0.11}Al_{1.75}$ $Si_{1.06}O_7$. This may be interpreted as gehlenite, 83.3 mol. %; ferri-gehlenite, 10.8 mol. %, åkermanite, 5.9 mol. %, showing it to be perhaps the most highly gehlenitic terrestrial melilite recorded. It is to be contrasted with the very different melilite (humboldtilite) of the complementary endomorphic melilite–titanaugite suite (the contaminated dolerite: Sabine, 1975), which contains 64.9 % of the Mg–Fe end-member åkermanite, only 6.4 % gehlenite, and has the formula $(Ca,Na,K)_{2.99}Mg_{0.42}(Fe^{2+}, etc.)_{0.24}$ $Al_{0.41}Si_{1.93}O_7$.

TABLE II. X-ray powder data for bredigite from Carneal, Co. Antrim

I/I_1	d_{obs}(Å)	d_{calc}(Å)	hkl	I/I_1	d_{obs}(Å)	d_{calc}(Å)	hkl
1	6.34	6.341	011	12	2.073	2.073	072
2	4.69	4.688	220	5	2.030	2.030	223
2	4.595	4.593	040			2.030	371
5	3.852	3.852	221	10	2.021	2.022	043
4	3.797	3.798	041			2.020	281
7	3.484	3.487	231	14	2.004	2.004	432
		3.482	150	5	1.954	1.9542	091
8	3.378	3.378	002	4	1.950	1.9493	461
7	3.229	3.228	051	38	1.926	1.9258	442
1	3.116	3.116	241	22	1.899	1.8992	082
15	2.958	2.958	032	12	1.837	1.8373	0.10.0
35*	2.837*	2.837	212			1.8371	452
		2.837	331	5	1.747	1.7472	092
25b	2.783	2.789	061	5	1.725	1.7252	192
		2.778	251	9	1.708	1.7091	073
100	2.740	2.741	222			1.7059	423
95	2.724	2.726	400	6	1.689	1.6890	004
		2.721	042	5	1.670	1.6703	433
90	2.670	2.670	260	5	1.650	1.6498	472
3	2.640	2.640	142	3	1.623	1.6232	363
14	2.600	2.600	232	12	1.6104	1.6103	134
7	2.584	2.584	350	10	1.6075c	1.6079	083
7	2.551	2.552	170			1.6071	214
7	2.487	2.487	052	1	1.5943	1.5942	612
12	2.451*	2.452	312	6	1.5893	1.5890	224
15	2.447	2.447	071	5	1.5852	1.5852	044
7	2.425	2.425	152	7	1.5764	1.5765	622
10	2.344	2.344	440	9	1.5627	1.5627	660
15	2.297	2.297	080	12	1.5593	1.5601	234
20	2.234	2.235	013			1.5583	482
		2.232	271	10	1.5476	1.5476	2.10.2
20	2.214	2.214	441	7	1.5312	1.5311	0.12.0
20	2.174	2.174	081	3	1.5236	1.5235	4.10.0
14	2.113	2.114	033	4	1.4356	1.4357	404
8	2.083	2.083	451	5	1.3628	1.3628	800
10	2.075†	2.075	501				
		2.075	133				

b = broad;   * 'shoulder' on gehlenite peak, intensity uncertain;
† 'shoulder' on bredigite 072 peak; ¢ Intensity enhanced by 134α₂ peak.
The intensities are the observed relative peak heights.

Cell dimensions: *a* 10.9026 ± 0.0003Å,   *b* 18.3730 ± 0.0006 Å,   *c* 6.7559 ± 0.0003 Å, V 1353.3 ± 0.1 Å³.

Spurrite. Spurrite occurs in large plates enclosing and altered from larnite and possibly bredigite. Two grains were analysed with results shown in Table IV, cols. 1-3. Phosphorus is present in significant quantity. In molecular terms the Carneal mineral corresponds to $Ca_{4.31}(Si_{0.98}P_{0.03}O_{4.13})_2$ $(CaCO_3)_{0.91}$. Since the determination of CO_2 on the Carneal specimen was only by difference, the figure for CaO may be a little too high and carbonate too low.

Spinels. Minerals of the spinel group are abundant in the rock, amounting to 5–10% by volume, and are largely magnetite. Crystals have a grain size of 10–50 μm, rarely up to 150 μm. A typical composition is given in Table V, col. 1. The Fe_2O_3 content of all the spinels has been obtained by recalculating the analysis on a basis of approximately 24 cations and making the sum of 3+ cations approximately equal to 16 and the 2+ cations to 8. Analysis shows that the magnetite contains substantial Al and Mg. Theoretical end-member molecules have been calculated for the spinel group minerals from the ionic formulae of

the respective mineral analyses (Table V) and are given in Table VI. The distribution of the 3+ cations Al^{3+} and Fe^{3+} and the 2+ cations Mg and Fe^{2+} has been according to the ratios in the ionic formulae after the subtraction of Fe^{2+} to form ülvospinel. Approximate mineral analysis is shown in Table VI, col. 1.

This mineral is thus a magnetite, near the join magnetite($Fe^{2+}Fe^{3+}O_4$)–magnesioferrite ($MgFe_2^{3+}O_4$) in the classification of Hey (1950, p. 46), these two end-members accounting for 82% of the composition.

A few larger grains, approximately 300–400 μm in diameter, have cores of a dark greenish-brown spinel, and opaque rims. This variation is clearly shown by analyses of the centres and edges of two grains (Table V, cols. 2c and E, 3c and E). The cores are an aluminous spinel similar to the ferrian chlorospinel from Carneal (Sabine, 1968), Table V, col. 4, but containing more Al and consequently less Fe^{3+} and more Fe^{2+} in the calculated composition. The spinel thus appears to be a ferrian variety in the general chemical field of chlorospinel.

TABLE III. *Chemical analyses and ionic composition of larnite*

	1	2	3	4	5
SiO$_2$	33.36	33.88	34.44	33.89	34.63
CaO	65.52	65.23	65.93	65.56	64.92
Na$_2$O	0.39	0.40	0.30	0.36	0.17
K$_2$O	—	—	—	—	0.05
P$_2$O$_5$	0.24	0.29	0.44	0.32	0.14
SrO	—	—	—	—	0.09
Total	99.51	99.80	101.11	100.13	(100.00)

Number of ions on basis of 16 oxygens					
Ca				8.080	7.984
Sr				—	0.006
Na				0.080	0.037
K				—	0.007
Si				3.900	3.976
P				0.032	0.014

1-3. Carneal, Co. Antrim, this paper.
4. Carneal, mean of cols. 1-3.
5. Carneal, Co. Antrim (Sabine, 1975, recalculated as stated in text).

TABLE V. *Chemical analyses and ionic composition of spinels*

	1	2(C)	2(E)	3(C)	3(E)	4
SiO$_2$	0.32	—	0.40	—	0.31	—
TiO$_2$	0.62	—	0.53	—	0.92	0.21
Al$_2$O$_3$	5.24	50.23	7.34	50.96	8.65	43.7
Fe$_2$O$_3$*	64.44	20.36	63.96	20.36	63.64	30.2
FeO*	19.97	7.41	19.18	7.83	18.97	4.2
MnO	1.96	0.60	2.18	0.71	2.06	0.62
MgO	6.31	20.51	7.54	20.52	8.01	21.0
Total	98.86	99.11	101.13	100.38	102.56	99.93

Number of ions on basis of 32 oxygens						
Si	0.092	—	0.109	—	0.084	—
Ti	0.135	—	0.109	—	0.186	0.03
Al	1.775	12.710	2.389	12.746	2.749	11.2
Fe^{3+}*	13.937	3.289	13.291	3.251	12.913	4.94
Fe^{2+}*	4.799	1.330	4.429	1.390	4.277	0.76
Mn	0.477	0.110	0.509	0.127	0.470	0.12
Mg	2.703	6.562	3.103	6.458	3.219	6.82

1. Magnetite, Carneal.
2-3. Spinel, Carneal; (C) = Centre of grain; (E) = Edge of grain.
4. Ferrian chlorospinel, Carneal (Sabine, 1968). There are also minor amounts of Co, Ni, and Zn present.
* Fe$_2$O$_3$, FeO calculated: see text.

Possible molar percentages of end-members shown in Table VI, col. 3 may be compared with the calculated composition for the ferrian chlorospinel shown in col. 4.

The rims are a magnetite very similar to those in the rest of the rock, as may be seen from comparison of the percentages of the end-members Table VI, col. 1 (magnetite) and col. 2 (edges of the composite grains). This variation from core to rim tends to suggest that the aluminous spinel later changed by loss of alumina to magnetite, perhaps accompanied by the growth of gehlenite, the only other aluminous phase in the rock.

Paragenesis

The rocks containing bredigite from Carneal (and Scawt Hill) are mineralogically variable and

TABLE IV. *Chemical analyses and ionic composition of spurrite, Carneal*

	1	2	3		4
SiO$_2$	26.39	26.16	26.28	Ca	5.118
CaO	64.46	63.41	63.93	Si	1.964
P$_2$O$_5$	0.89	0.95	0.92	P	0.058
CO$_2$	(8.26)	(9.48)	(8.87)	C	0.905
				O	11.000

1-2. Spurrite, Carneal, CO$_2$ determined by difference.
3. Mean of analyses 1 and 2.
4. Ionic composition, Carneal, on basis of 11 oxygens.

texturally complex. The textures suggest that the rocks were originally the normal fine-grained and equigranular type, composed largely of larnite-spinel aggregate. Subsequent reaction has caused the transformation of the aluminous spinels to magnetite, accompanied by the formation of abundant bredigite, and gehlenite which occurs either as porphyroblasts or very fine-grained intergrowths. A fine granular aggregate of bredigite and

TABLE VI. *Molar percentages of end-members from spinel analyses*

	1	2E	2C	4
Spinel (MgAl$_2$O$_4$)	3.94	5.98	65.15	65.18
Hercynite (FeAl$_2$O$_4$)	6.65	8.11	13.19	6.78
Magnesioferrite (MgFe$_2^{3+}$O$_4$)	30.42	33.14	16.84	23.73
Magnetite (Fe^{2+}Fe$_2^{3+}$O$_4$)	51.21	44.98	3.45	2.35
Jacobsite (MnFe$_2^{3+}$O$_4$)	5.38	5.44	0.28	0.46
Galaxite (MnAl$_2$O$_4$)	0.69	0.98	1.09	1.11
Ulvospinel (Fe$_2^{2+}$TiO$_4$)	1.70	1.37	—	0.39

1. Magnetite, Carneal, Table V, analysis 1.
2. Spinel, edges of grains, Carneal, Table V, analysis 2E.
3. Spinel, centres of grains, Carneal, Table V, analysis 2C.
4. Ferrian chlorospinel, Carneal, Table V, analysis 4.
Calculations as described in text.

gehlenite has a grain size of about 5 μm; the minerals were identified by electron probe. Grains of the same minerals also form equidimensional aggregates about 80 μm across that may represent earlier larnite, and also substantial relic porphyroblasts perhaps themselves after gehlenite and possibly merwinite. Other parts of the rocks are of normal larnite-spinel aggregate; some aggregates of magnetite are associated with gehlenite (NI 4128). Spurrite is locally abundant: it usually occurs as large porphyroblasts commonly with inclusions of larnite, bredigite and gehlenite, and is clearly replacing them, but also occurs as veins (NI 1596). This spurrite does not appear to have been part of the initial larnite-spinel or the re-equilibrated bredigite-gehlenite assemblage but probably formed during a later addition of CO_2-rich fluids.

The principal chemical components and constituent minerals in these rocks can be represented graphically by a tetrahedron with apices CaO, SiO_2, Al_2O_3, MgO. The calc-silicate minerals, essentially free from Al_2O_3, can be represented on the CaO-SiO_2-MgO face (fig. 1). Alumina enters separate phases, viz. spinels and gehlenites which are also important constituents: their relationships are more clearly shown on the projection from SiO_2 on to the CaO-Al_2O_3-MgO face (figs. 2 and 3).

Another significant component, Fe_2O_3 is present as magnetite and other spinel. The natural rocks differ from the simple systems (CaO-MgO-SiO_2-CO_2: Essene, 1980; Treiman and Essene, 1983) by containing significant amounts of Al_2O_3 and Fe_2O_3 that affect the mineral assemblages formed. However, if analogy is made with these studies, some estimate of the temperature of formation can be made.

The composition of the fluid (H_2O-CO_2) phase in the retrograde metamorphism and metasomatism, during which spurrite appears to have formed, markedly affected the conditions of crystallization of the solids. Wyllie and Haas (1966) pointed out that in the system CaO-SiO_2-CO_2-H_2O the addition of a few percent of CO_2 in the vapour phase is sufficient to raise the melting temperature by several hundred degrees. The presence of this fluid phase and the greater number of components in the natural systems reduce the validity of direct comparison with dry synthetic systems. The phase relations proposed by Treiman and Essene (1983, Fig. 8) suggest that both magnetite-bearing and larnite-spinel assemblages must have been formed at temperatures greater than 970 °C for larnite to be present at the pressure of 0.2 kbar proposed by Sabine (1975) for the Carneal rocks. If, as is suggested from petrographic observations, the spurrite is retrograde, it implies a temperature for the larnite-spinel assemblage above its upper stability limit, in excess of 1080 °C. These temperatures are within the experimentally determined stability field of bredigite, 979–1372 °C (Schlaudt and Roy, 1966; Lin and Foster, 1975). However, Essene (1980) suggests that the lower limit of 979 °C may be a synthesis rather than an equilibrium boundary and that bredigite may be stable down to
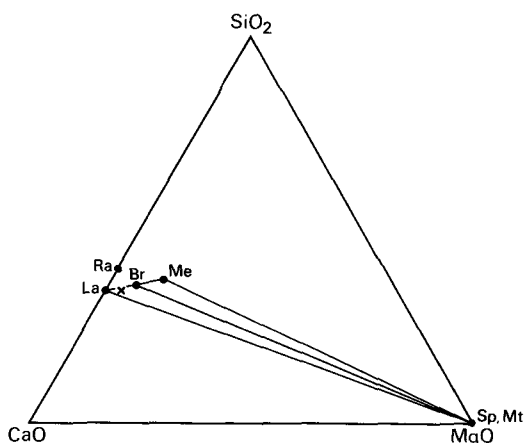

FIG. 1. Phase relationships in the system CaO-MgO-SiO_2. The magnetite plots in the MgO corner since it contains a small amount of MgO but almost no SiO_2 and CaO. Br, bredigite; Ge, gehlenite; La, larnite; Mt, magnetite; Me, merwinite; Ra, rankinite; Sp, spinel. ×, composition of analysed larnite-spinel rock.
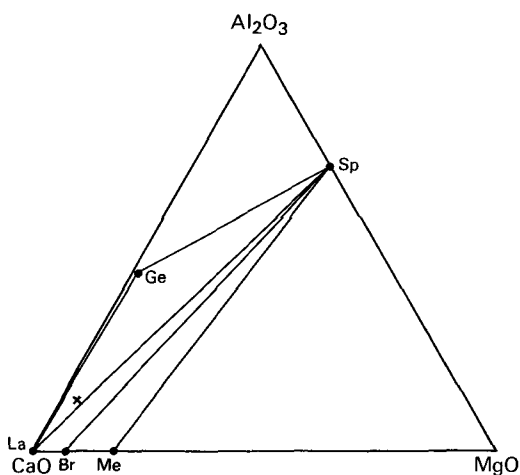

FIG. 2. Phase relationships in the system CaO-MgO-Al_2O_3, before the breakdown of spinel to magnetite. For abbreviations see fig. 1.

500 °C, but the rocks studied here throw no light on this problem.

The rankinite phase found necessary by Essene (1980) and not recorded at Carneal, lies on the SiO_2-rich side of the larnite-merwinite tie-line, and would only be expected to occur in the more siliceous rocks under the conditions thought to have occurred at Carneal. Tilleyite has also not been found.
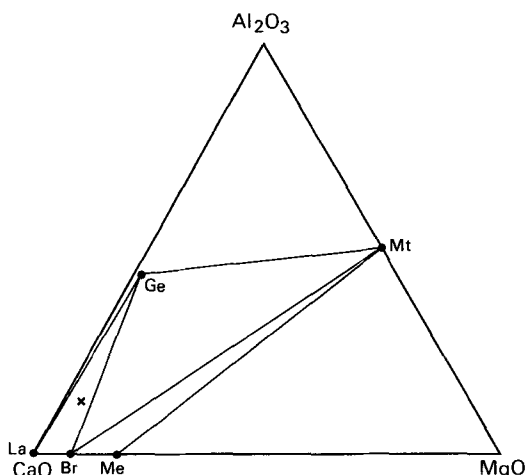

FIG. 3. Phase relationships in the system CaO-MgO-Al_2O_3 after the breakdown of spinel to magnetite. For abbreviations see fig. 1.

The change from chlorospinel to magnetite (Table V) cannot be allowed for in figs. 2 and 3, since the components are widely different. If an attempt is made to allow for this, for example if the apex from which the Al_2O_3-MgO-CaO plane of figs. 2 and 3 is plotted is treated as Fe_2O_3, both chlorospinel and magnetite lie near to the Fe_2O_3-Al_2O_3-MgO face of the tetrahedron and project on or near the Al_2O_3-MgO side. The introduction of these additional components does not thereby greatly move the position of the points shown on figs. 2 and 3 or the topology of the lines.

The possible initial mineral assemblages of the larnite-spinel rocks are shown in fig. 2 with the analysed rock of this assemblage (Sabine, 1975) plotting very close to the larnite-spinel tie-line. This is to be expected since only small quantities of other minerals are present. Small amounts of gehlenite, or in slightly more magnesian rocks, bredigite, might be expected, and for significantly more magnesian compositions, merwinite-spinel-bredigite, as exemplified in thin section NI 4128. In

fig. 3 the observed mineral assemblages after the breakdown of spinel to magnetite are shown. In this diagram the bulk composition of larnite-spinel rock plots close to the bredigite-gehlenite tie-line, showing that a rock of this composition would form these minerals in abundance. The two diagrams show the classical crossed tie-line relationship of the reacting phases. Bredigite-gehlenite-magnetite is the stable assemblage for a wide range of compositions. Larnite is only stable in rocks relatively low in Al and Mg, as seen in parts of the larnite-spinel rock (NI 1596) where it co-exists with abundant bredigite and gehlenite.

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