Al-rich pyroxene and melilite in a blast-furnace slag and a comparison with the Allende meteorite

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SUMMARY. Fassaitic diopside containing 22-23 wt% Al_2O_3 (approximately 41-43% calcium Tschermak's molecule, $CaAl_2SiO_6$) and melilite containing 69-43% gehlenite crystallized from a blast-furnace slag at atmospheric pressure between about 1450 °C and 1250 °C. The occurrence is of petrological interest because the association of pyroxene with gehlenite-rich melilite has not been recorded from experimental studies in the system $CaO-MgO-Al_2O_3-SiO_2$, and because of the similarity of the compositions of both minerals to pyroxene and melilite in the Ca-Al-rich inclusions of the Allende meteorite.

SLAG composition. The slag was produced at the Corby works of the British Steel Corporation in February 1973, and is within the normal range of compositions of blast-furnace slags being produced at Corby at that time. The slag was cast into an approximately hemispherical ladle 2 m in diameter and allowed to cool for a day before being tipped out. The nearly solidified 'ball' broke, leaving a central cavity from which some still-molten slag may have run out.

Samples were obtained from the chilled margin at the outermost 10 cm of the ball and from the coarse-grained interior at a point about 60 cm from the outside. Chemical analyses of the slag at 2-4 cm and at 60 cm from the outside are given in Table I. Estimates of cooling rates based on heat conduction show that the sample at 2-4 cm crystallized in a matter of minutes, while the sample at 60 cm crystallized over a period of a day, followed by rapid cooling when the ball was tipped out and broke open. The compositions of the two samples are closely similar, differing significantly only in the Al_2O_3 and MgO contents, and show that little differentiation occurred during cooling. Since both samples contain metallic iron (representing droplets of liquid iron entrained in the slag) it is possible that the titanium in the slag is in the trivalent state, although this could not be confirmed by chemical analysis. Titanium is quoted as Ti_2O_3 in Table I, but it makes little difference to the analysis totals or to the discussion of the data if the titanium is present as TiO_2.

Petrography. The outside surface of the slag, where it was quenched against the cold metal surface of the ladle, is a layer of aphyric green-brown glass less than 1 mm thick. This confirms

TABLE I. *Chemical compositions of two samples of blast-furnace slag*

	SiO_2	Al_2O_3	Ti_2O_3*	FeO*	MnO	MgO	CaO	Na_2O	K_2O	S	Fe*	Sum	$O \equiv S$	Total
1.	34·20	21·36	0·77	0·04	1·19	5·94	33·85	0·49	1·06	0·95	0·39	100·24	0·48	99·76
2.	33·98	22·35	0·77	0·02	1·06	5·43	33·87	0·47	1·07	0·93	0·30	100·25	0·47	99·78

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* Since both samples contain metallic iron, titanium is assumed to be present as Ti_2O_3, and FeO has been calculated from the mineral compositions (Table II).
1. Quenched slag, 2-4 cm from the surface.
2. Slowly cooled slag, 60 cm from the surface.

that the slag was wholly liquid at the time of casting. The slag is glassy or very fine-grained up to 5 mm from the surface; X-ray diffractometry shows only the presence of melilite in this zone, indicating that melilite was the first phase to crystallize. At 5–10 mm from the surface melilite was joined by pyroxene, both phases occurring as very fine dendrites.

At 2–4 cm from the surface, in the region corresponding to analysis 1, the melilite dendrites are up to 2 mm long parallel to {001} and 1 mm across parallel to the prism faces. The branches of the dendrites are 0·05 mm across and grow preferentially along a direction normal to the edge between the {001} and the prism faces. The crystals were found by electron-probe microanalysis to be homogeneous in chemical composition. Pyroxene occurs as needles 0·1 mm by 0·02 mm in size and rarely as dendritic crystals up to 0·5 mm in over-all dimensions. Minor phases are unidentified opaque needles or plates 0·05 mm by 0·001 mm, globules of metallic iron up to 0·2 mm in diameter, feathery and star-shaped dendrites of a sulphide mineral (probably old-hamite, calcium sulphide), and rare patches of pale-yellow glass between the branches of the melilite dendrites.

At 60 cm from the surface of the slag, in the region corresponding to analysis 2, the mineral phases are the same as in sample 1, but the crystal size, morphology, and composition of the melilite are very different. The melilite occurs as euhedral plates with planar faces 1·5 mm long parallel to {001} and 1 mm long parallel to the prism faces, with no trace of dendritic habit. The melilites are strongly zoned, with a continuous variation of birefringence from 0·006 at the cores to nearly isotropic at the rims; the compositional zoning is confirmed by electron-probe microanalysis (see next section). The cores of the crystals are clear or contain minute rod-like inclusions of an unidentified opaque mineral, but the rims frequently contain inclusions, well known in blast-furnace slag melilites, of oldhamite, which was found by electron-probe microanalysis to contain up to about 25 % Mn and 8 % K, giving a composition of the form (Ca, Mn, K_2)S. The oldhamite occurs as a comb-like pattern of closely-spaced bifurcating needles 0·1–1·0 μm thick orientated perpendicular to the faces of the melilite crystals, and as irregularly distributed star-shaped dendrites. Pyroxene occurs as dendritic crystals filling the spaces between the melilites and as anhedral crystals included in the outer parts of the meli-lite crystals. It also occurs rarely as individual prisms up to 0·1 mm long and 0·025 mm across. Compositional zoning could not be detected in the pyroxene. Pale-yellow glass is sometimes found between the pyroxene crystals. Metallic iron occurs as small globules in all the phases.

The petrography of the two slag samples can be interpreted in the same way as the petrography of an igneous rock, with the added advantages that the 'magma' was known to be a homogeneous liquid at the start of crystallization, and that the thermal history is known fairly accurately. The samples also have the advantage of being mineralogically simple, consisting of only two major phases.

In both slags melilite crystallized as the primary phase, followed by pyroxene. Sample 1, 2 cm from the outer surface of the ball, can be regarded as a quenched melt, as indicated by the estimated cooling rate and by the dendritic habit and homogeneous composition of the melilite. The euhedral melilites in sample 2, 60 cm from the cooling surface, are analogous to phenocrysts; the strong zoning indicates that they crystallized at a rate faster than the rate of equilibration, possibly even approaching a perfect fractionation condition. The inclusion of pyroxene crystals in the outer zones of the melilites indicates that pyroxene (together with oldhamite) nucleated after the melilite. There is no petrographic evidence of a reaction relationship between melilite and pyroxene, and no other Ca–Mg–Al silicate or oxide phases except for the trace amounts of glass have been detected in either the quenched or the slowly cooled slag.

Chemistry of the phases. The compositions of the phases were determined using a Cambridge Scientific Instruments Microscan 9 electron-probe microanalyser; conventional ZAF computer correction procedures were used to derive the chemical analyses. The accuracy of the analytical procedure was checked by determining the compositions of olivine (Fo_{90}), pure diopside, and plagioclase (An_{100} and An_{80}). Errors were not greater than 0·5 wt % for SiO_2, Al_2O_3, MgO, and CaO.

The compositions of the melilite and pyroxene in samples 1 and 2 and the glass in sample 2 are given in Table II. Since metallic iron is present in both samples, it is assumed that some or all of the titanium is present in the trivalent state and it is therefore quoted as Ti_2O_3 in the analyses. It makes little difference to the analysis totals or to the structural formulae of the pyroxenes if titanium is calculated as TiO_2.

TABLE II. *Electron-probe microanalyses of pyroxene, melilite, and glass from blast-furnace slag*

Quenched slag			Slowly cooled slag				Atomic ratios of the pyroxenes (6 oxygens) and melilites (7 oxygens)					
	1a Pyroxene	1b Melilite	2a Pyroxene	2b Melilite core	2c Melilite rim	2d Glass		1a	1b	2a	2b	2c
SiO_2	39·56	30·37	39·33	30·14	35·88	43·34	Si	1·45	1·39	1·44	1·37	1·63
Al_2O_3	22·29	23·87	22·98	25·31	16·02	26·20	Al^Z	0·55	0·61	0·56	0·63	0·37
Ti_2O_3	2·34	0·02	2·92	0·01	0·01	0·32						
FeO	0·05	0·04	0·01	0·04	0·01	0·04	ΣZ	2·00	2·00	2·00	2·00	2·00
MnO	0·46	0·15	0·25	0·14	0·08	0·11						
MgO	9·21	4·34	9·13	4·07	7·35	1·18	Al^Y	0·41	0·68	0·43	0·72	0·49
CaO	26·07	40·05	24·96	39·71	39·32	10·82	Ti	0·07	0·00	0·09	0·00	0·00
Na_2O	0·03	0·37	0·05	0·38	0·63	1·53	Fe	0·00	0·00	0·00	0·00	0·00
K_2O	—	—	—	—	—	10·28	Mn	0·01	0·01	0·01	0·01	0·00
							Mg^Y	0·50	0·30	0·48	0·28	0·50
Sum	100·01	99·21	99·63	99·80	99·30	93·82						
							ΣY	0·99	0·99	1·01	1·01	0·99
							Mg^X	—	—	0·02	—	—
							Ca	1·02	1·96	0·98	1·93	1·92
							Na	0·00	0·03	0·00	0·03	0·06
							ΣX	1·02	1·99	1·00	1·96	1·98

The pyroxenes in the quenched (1a) and the slowly cooled (2a) samples are similar in composition, with Al_2O_3 and Ti_2O_3 slightly higher in the slowly cooled sample. They correspond to titaniferous fassaites. Adding the small amounts of Fe and Mn to Mg and calculating these elements as $CaMgSi_2O_6$ (diopside, Di), and calculating the Al^Y as $CaAl_2SiO_6$ (calcium-Tschermak's molecule, CTs) and the Ti as either $CaTi^{3+}AlSiO_6$ or $CaTi^{4+}Al_2O_6$ (titanium pyroxene, Tp), the contents of the Y (octahedral cation) group of the pyroxenes can be expressed in terms of end members as:

$$1a: Di_{52}CTs_{41}Tp_7, \qquad 2a: Di_{48}CTs_{43}Tp_9.$$
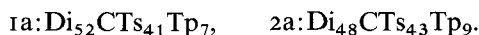
The pyroxene composition is close to the limit of solid solution of CTs in Di as determined experimentally by Sakata (1957) and by de Neufville and Schairer (1962).

The compositions of the melilites can be expressed in terms of the end-members $Ca_2MgSi_2O_7$ (åkermanite, Åk), $Ca_2Al_2SiO_7$ (gehlenite, Geh), and $NaCaAlSi_2O_7$ (sodium-gehlenite, Ng) as:

$$1b: Åk_{31}Geh_{66}Ng_3, \qquad 2b: Åk_{28}Geh_{69}Ng_3, \qquad 2c: Åk_{51}Geh_{43}Ng_6.$$
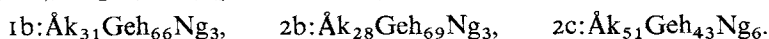
All these compositions lie on the gehlenite-rich side of the minimum in the melting curves for the system åkermanite-gehlenite (Osborn and Schairer, 1941). In relation to this system the compositions of the melilite in sample 2 can be described as normal zoning, with the lower-temperature composition forming the outer part of the crystal.

The composition of the glass (2d), which forms less than 1 % of the slowly cooled sample, represents the residual liquid after crystallization of the melilite and pyroxene. Since negligible amounts of K_2O crystallize in the two main phases, the residual liquid is strongly enriched in this component. The four major components of the glass composition, SiO_2, Al_2O_3, CaO, and K_2O, can be expressed normatively as melilite + anorthite + leucite, and may represent a composition near a eutectic in this system. The presence of the glass could be the result of either quenching during the rapid cooling or vitrification during the slow cooling of the sample. In either case it indicates that the phases present correspond to those of the final liquidus temperature of the slag.

Physical properties of the minerals. The β refractive index of the pyroxene in sample 2 is 1.70 ± 0.01. The unit-cell dimensions, computed from a powder photograph using the indices of reflections given by de Neufville and Schairer (1962), are a 9·66 Å, b 8·84 Å, c 5·28 Å, β 73·89°. The ω refractive index of the cores of melilites from sample 2 is 1.652 ± 0.002. The d_{211} spacing of the homogeneous melilite in sample 1 was determined by diffractometry of the slag sample, using NaCl as an internal standard, as 2.854 ± 0.005 Å. These data are in good agreement with physical properties for the compositions of these minerals estimated by interpolation from the available data on the respective solid solution series (Deer, Howie, and Zussman, 1962 and 1963).

Comparison with the mineralogy of the Ca–Al-rich inclusions of the Allende meteorite. Some carbonaceous chondrites, of which Allende (Clarke et al., 1970) is the best-known example, contain inclusions composed of Ca- and Al-rich minerals, among which the assemblage melilite–pyroxene–plagioclase–spinel is common. The mineralogy of these inclusions has been studied in detail by Grossman (1975). The melilite is gehlenite-rich, varying from $Åk_{15}Geh_{85}$ to approximately the minimum melting composition at $Åk_{72}Geh_{28}$, and the pyroxene is also very rich in Al_2O_3 (up to 21 %) and titanium oxide (up to 17 %). Dowty and Clark (1973) showed that some of the titanium in these pyroxenes is likely to be in the trivalent state.

The analyses of the pyroxene and the melilite core and rim from the blast-furnace slag (Table II) can be matched almost exactly with analyses from Allende (cf. Grossman, 1975, Table 4, pyroxene TS12 F3 8, and Table 1, melilites TS12 F1 116 and TS2 F1 30). The minerals of the Ca–Al-rich inclusions of Allende and similar meteorites have been suggested by Marvin et al. (1970) and other workers to be a high-temperature condensate from a cooling solar nebula in which the pressure at the time of formation would have been of the order of 10^{-3} atm (Grossman, 1972). An alternative hypothesis (Blander and Fuchs, 1975), which may be a closer analogy to the conditions of formation of the blast-furnace slag, is that the mineral assemblages of the Allende inclusions were formed by metastable crystallization from sub-cooled liquids. The point in making this comparison of meteorite and blast-furnace slag mineralogy is that the assemblage of Geh-rich melilite and CTs-rich pyroxene was formed in the first case probably and in the second case definitely at low pressure. This is of importance in relation to the next section of this paper.

Comparison with experimental petrology. Ninety-five per cent of the chemical composition of the slag consists of the four components of the system $CaO–MgO–Al_2O_3–SiO_2$. The products of crystallization of the slag should therefore be comparable with the equivalent composition in the experimentally determined quaternary system at atmospheric pressure. The principal end-

members of the two major phases, melilite and pyroxene, define a plane Åk–Geh–CTs–Di in this system.

Projection of the slag composition (Table I) on to the liquidus diagrams for the system $CaO-MgO-Al_2O_3-SiO_2$ (Osborn et al., 1954) shows that it lies in the melilite field at a temperature of about 1450 °C, and that crystallization of melilite would produce a final liquid on the melilite–pyroxene cotectic at a temperature of about 1250 °C. The temperatures in the actual slag would of course be lower than this because of the presence of additional components, particularly the alkalis.

The compositions of the melilites (Table II, anals. 1b, 2b, and 2c) are consistent with quenching (sample 1) and fractionation (sample 2) of a bulk composition that can be expressed in terms of the system åkermanite–gehlenite–diopside (Gee and Osborn, 1969) as approximately $Åk_{25}-Geh_{50}-Di_{25}$. However, cooling a melt of this composition does not lead to cotectic crystallization of Geh-rich melilite and diopside, though this can occur in the adjacent, nearly coplanar, and more silica-saturated system Geh–Di–anorthite.

Discrepancies with the results of experimental petrology are also found when the details of the mineral compositions are considered. The only compositions listed in Table II known from petrographic evidence to coexist are the pyroxene 2a and the rim melilite 2c, whose compositions projected into the $CaO-MgO-Al_2O_3-SiO_2$ system are $Di_{53}CTs_{47}$ and $Åk_{54}Geh_{46}$ respectively, together with liquid of composition 2d. However, the occurrence in the Allende meteorite inclusions of a wider range of compositions of both pyroxene and melilite is an additional indication that CTs-rich pyroxene and Geh-rich melilite can coexist at atmospheric or low pressures, though in an alkali-poor environment, and associated with other minerals.

Experimental data on the pyroxene join Di–CTs by de Neufville and Schairer (1962, with additional work by Schairer and Yoder, 1970) show that pyroxene at the limit of solid solution of CTs in Di at atmospheric pressure should coexist with melilite of composition $Åk_{89}Geh_{11}$, together with anorthite and possibly forsterite. Data on the melilite join Åk–Geh by Biggar and O'Hara (1972) place the limit of composition of melilite coexisting with diopside (plus one or two of the phases anorthite, spinel, and forsterite) as approximately $Åk_{80-83}Geh_{20-17}$. In both these studies the composition of the melilite is on the Åk side of the minimum melting point at $Åk_{72}Geh_{28}$ in the melilite solid solution series. This is confirmed by the work of Gee and Osborn (1969), who show that a thermal valley extends from the minimum melting point across the melilite field in the system melilite–diopside, thus precluding the cotectic crystallization of Geh-rich melilite and pyroxene except in relatively silica-saturated compositions with anorthite as an additional phase.

Extrapolation of multi-component rock compositions into simple binary, ternary, and quaternary oxide systems is common practice in petrogenetic interpretation. In most cases natural rocks are in good accord with the results of experimental petrology. In the case of the blast furnace slag described here the bulk composition of the slag is very close to the corresponding quaternary $CaO-MgO-Al_2O_3-SiO_2$, but the products of crystallization of the slag, melilite + pyroxene, do not correspond to the products of crystallization of the corresponding quaternary composition, which would be melilite + anorthite + forsterite + spinel (Osborn et al., 1954) or melilite + diopside + spinel (O'Hara and Biggar, 1969).

A possible explanation is that the slag is not composed of an equilibrium-phase assemblage. Petrographic evidence shows that melilite is the first phase to crystallize; comparison of the data in Tables I and II shows that crystallization of melilite will produce a liquid enriched in SiO_2 and MgO and depleted in CaO, but with the Al_2O_3 content virtually unchanged. If pyroxene should nucleate as a metastable second phase, or if a stable phase such as spinel should fail to nucleate,

all the major components of the slag composition could be represented by a Geh-rich melilite and a CTs-rich pyroxene. This hypothesis could account for the mineralogy of the slag, which crystallized over a short period of time, but seems less likely to apply to the Ca-Al-rich inclusions of the Allende meteorite, which have possibly been metamorphosed (Grossman, 1975) and should therefore have had an opportunity to recrystallize to the equilibrium subsolidus phase assemblage.

An alternative possibility is that the minor components of the slag composition have a relatively drastic effect on the geometry of the planar quaternary system Åk–Geh–CTs–Di, shifting the position of the melilite–pyroxene cotectic so that it lies within the melilite–pyroxene system for both åkermanite-rich and gehlenite-rich melilite compositions.

Of the minor components of the chemistry of the slag and its mineral phases, such a shift cannot be attributed to Fe or S, which form metal and sulphide phases respectively. The very small amount of FeO and the crystal-chemical similarity of MnO to MgO make it unlikely that these components have a great effect on the quaternary system. The remaining components are Na_2O, mainly in melilite, titanium, mainly in pyroxene, and K_2O.

In relation to melilite, the binary systems åkermanite-sodium-gehlenite and gehlenite-sodium-gehlenite are known (Nurse and Midgley, 1953), but the ternary system of all three melilite end-members has not been investigated. It is possible that addition of sodium-gehlenite to the åkermanite-gehlenite system converts it from a solid solution with a minimum to a solid solution without a minimum, similar to the plagioclase series. Such an effect could account for the observed mineralogy of the blast-furnace slag, but not for the Ca–Al-rich inclusions in the Allende meterorite, which have a very low Na_2O content.

Experimental work on systems containing titaniferous pyroxene and melilite is limited. Onuma and Yagi (1971) studied the system diopside-åkermanite-$CaTiAl_2O_6$ and showed that titaniferous pyroxene can coexist with åkermanite. Gupta et al. (1973) showed that in the system diopside-$CaTiAl_2O_6$ -SiO_2 the amount of Ti substitution in diopside increases with decreasing SiO_2. From this it can be suggested that increasing silica-undersaturation (as in melilite-bearing assemblages) could stabilize the high-titanium diopsides in the blast-furnace slag and the Allende meteorite. This effect might be further extended for the blast-furnace slag by the presence of K_2O because of extreme silica-undersaturation of the residual liquid (Table II, anal. 2d).

Experimental work at atmospheric pressure on systems containing sodium-bearing melilites and titanium-bearing pyroxenes would be a valuable contribution to understanding the mineral assemblages of compositions such as the blast-furnace slag described here and, more important for petrology and geochemistry, the Ca–Al-rich inclusions of the Allende meteorite.

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