High-temperature condensates in chondrites and the environment in which they formed

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Abstract—Chemical compositions of melilites and titaniferous pyroxenes in calcium- and aluminum-rich inclusions in carbonaceous chondrites are consistent with their origin as high-temperature condensates from a gas of solar composition. Thermodynamic calculations indicate that the highest temperature minerals equilibrated with the gas at temperatures in excess of $1400°K$. The lack of evidence for direct condensation of gas to liquid enables us to set an upper limit to the pressure when the inclusions formed which may be as low as 2.2×10^{-3} atm. Glasses, which are commonly found in chondrules, are interpreted as quench products of liquids formed by secondary reheating of primary solid condensates. The high-temperature inclusions constitute evidence that accretion of grains to cm-sized objects occurred at a very early stage in the evolution of the solar nebula.

INTRODUCTION

IT HAS been realized for over 10 years that inclusions containing minerals commonly regarded as having a high-temperature origin occur in carbonaceous chondrites (see for example RINGWOOD, 1963), but only recently has it become clear that they belong to two distinct chemical classes. The most abundant class is composed mainly of ferromagnesian silicates, of which olivine predominates, with plagioclase as a widespread accessory. Less abundant by a factor of roughly 20 are whitish inclusions in which melilite, diopside, anorthite, spinel, perovskite, forsterite and a peculiar titaniferous pyroxene are the principal mineral constituents (CHRISTOPHE, 1968, 1969; KEIL et al., 1969; FUCHS, 1969). Chemical formulae of mineral names referred to in the text are given in Table 1.

LARIMER and ANDERS (1970) and MARVIN et al. (1970) suggested that the Ca, Al-rich inclusions (hereafter referred to as CAI) might represent early, high-temperature condensates from the solar nebula. This interpretation was based on calculations of the condensation sequence by LORD (1965). GROSSMAN (1972a) has extended Lord's calculations and in particular has taken account of the changes in composition of the nebular gas due to incorporation of large proportions of major elements in solid condensates. Certain similarities between phases predicted to be early condensates by Grossman and those observed in the CAI induced us to examine the observed and predicted mineralogies in some detail.

COMPOSITIONS OF MINERALS IN THE HIGH-TEMPERATURE INCLUSIONS

The melilites. Most investigators working with synthetic melilites have treated them as binary solid solutions between åkermanite and gehlenite. Soda-melilite, however, usually rivals these two components in importance in melilites from terrestrial igneous rocks (YODER, 1964; SAHAMA, 1967). The sodium content of igneous

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Table 1. Chemical formulae of mineral names referred to in the text.

Mineral name	Chemical formula
Plagioclase	
Anorthite	$CaAl_2Si_2O_8$
Albite	$NaAlSi_3O_8$
Melilite	
Gehlenite	$Ca_2Al_2SiO_7$
Åkermanite	$Ca_2MgSi_2O_7$
Soda-melilite	$NaCaAlSi_2O_7$
Clinopyroxene	
Diopside	$CaMgSi_2O_6$
Ca–Al-pyroxene	$CaAl_2SiO_6$
Ti-pyroxene	$CaTiAl_2O_6$
Orthopyroxene	
Enstatite	$MgSiO_3$
Ferrosilite	$FeSiO_3$
Olivine	
Forsterite	Mg_2SiO_4
Fayalite	Fe_2SiO_4
Corundum	Al_2O_3
Spinel	$MgAl_2O_4$
Perovskite	$CaTiO_3$
β-Al_2O_3	$CaO \cdot 6Al_2O_3$
Hibonite	β-$Al_2O_3 \pm MgO + TiO_2$
Wollastonite	$CaSiO_3$
Nepheline	$NaAlSiO_4$
Rutile	TiO_2

melilites increases with the sodium content of their host rocks and concentrations of up to 5 wt.% Na_2O in melilite have been reported.

SAHAMA (1967) has emphasized that in addition to their appreciable alkali content, igneous melilites commonly contain significant amounts of iron. Fe^{2+} replaces Mg in åkermanite, and Fe^{3+} replaces Al in gehlenite. Total iron oxide may exceed 8 per cent, and the Fe^{2+}/Fe^{3+} ratio may vary widely (SAHAMA, 1961).

Melilites from the CAI have neither of these chemical characteristics; alkalis and iron are commonly either rare in them or absent from them. For example, CLARKE et al. (1970) found neither Na nor Fe in a melilite from Allende, and KURAT (1970) reported 0·3 per cent FeO and <0·05 per cent Na_2O in one from Lancé. In fact, the melilites from the CAI commonly lie on or close to the åkermanite–gehlenite join, a fact that we shall show to be predictable if they are condensates from high-temperature gases.

There are no thermodynamic data for soda-melilite, and we require an estimate of its free energy of formation. YODER (1964) estimated that no more than four kilobars is required to stabilize soda-melilite at high temperatures relative to its low pressure breakdown products, nepheline + wollastonite. The molar volume for this pair is 94·11 cm³ (ROBIE et al., 1966) and that for soda-melilite is 88·69 cm³ as calculated by extrapolating the cell edges of binary melilite solid solutions reported by EDGAR (1965). The free energy difference at zero pressure is simply $P \Delta V$, where P is the transition pressure. Taking it to be 4 kbars gives 0·52 kcal/mol for the free

energy difference. This is probably less than the uncertainty in the thermodynamic data for nepheline + wollastonite, and we shall take the results for this pair of minerals to represent the free energy of formation of soda-melilite.

At 10^{-3} atm total pressure GROSSMAN (1972a) found that melilite is a stable condensate in equilibrium with a gas of solar composition (CAMERON, 1968) between 1625°K and 1450°K. Assuming ideal solid solution, it was also calculated that the åkermanite content of the melilite increases continuously with falling temperature, rising from essentially pure gehlenite at 1625°K to 81 mol per cent åkermanite at 1450°K, at which temperature the melilite breaks down to diopside + spinel.

We estimate the soda-melilite content by assuming that it enters into ideal solid solution with åkermanite and gehlenite, and that its free energy is the same as that of nepheline + wollastonite. From these assumptions and the gas compositions in equilibrium with the high-temperature condensates (GROSSMAN, 1972a) we can find an upper limit to the soda-melilite concentration. It also increases with decreasing temperature, reaching a maximum value of 2×10^{-4} mol per cent at 1450°K.

Thus the low soda content of the CAI is just what we would expect if they are condensates from a vapor. The chemical differences between melilites from the CAI and from igneous rocks are wholly attributable to their different modes of origin. The low soda content predicted for the condensate melilite is hardly surprising, since it has already been established that other alkali-bearing phases do not condense until the temperature has dropped to 1100°K or so (GROSSMAN, 1972a).

The low iron content of these melilites is also to be expected if they originate as condensates. The first ferromagnesian silicate to condense is an iron-free diopside, and forsterite and enstatite, both containing virtually no iron, are amongst the early condensates (WOOD, 1963; GROSSMAN, 1972a). The chemical potential of iron in the gas becomes buffered by crystallization of the metal, and oxidized iron does not occur in crystalline phases until the temperature has dropped far below the values indicated by the mineralogy of the CAI.

The titaniferous pyroxenes. FUCHS (1969) reported a peculiar pyroxene, rich in Ti and Al and very poor in Fe, from a CAI in Allende. His discovery was confirmed by MARVIN et al. (1970) and later by CLARKE et al. (1970), and they used the name fassaite for this mineral. Actually it bears no close chemical resemblance to any pyroxene for which a name is recognized. Virtually all terrestrial pyroxenes carry more total iron ($FeO + Fe_2O_3$) than TiO_2 (see, for example, DEER et al., 1963, and the references compiled by WILKINSON, 1956). Yet the titaniferous pyroxenes from the CAI have virtually no iron, and up to 18 per cent TiO_2.

The compositions of the titaniferous pyroxenes can be closely approximated by taking them to be solid solutions between $CaMgSi_2O_6$, $CaAl_2SiO_6$ and the hypothetical end member $CaTiAl_2O_6$ proposed by YAGI and ONUMA (1967). The occurrence in Allende of a pyroxene containing over 50 per cent of this last end member is probably the best mineralogical evidence of its validity (see Table 2). Besides the principal end members, small amounts of wollastonite, quartz and in two cases rutile are calculated from the analyses. These may reflect minor analytical error, although slight solid solution towards wollastonite is certainly possible. It is also possible that some of the Ti is in the +3 state, in an end member like $CaTi_2SiO_6$ for example. Converting some of the $CaTiAl_2O_6$ to this compound consumes the excess silica and

Table 2. Analyses (recalculated to 100 per cent) of titaniferous pyroxenes and their pyroxene norms (weight per cent).

	Allende (Clarke et al., 1970, p. 39)	Allende (Fuchs, 1971, p. 2062)	Allende (Fuchs, 1971, p. 2055)	Vigarano (Christophe et al., 1970, p. 211)	Allende (Marvin et al., 1970, p. 347)
SiO_2	40·4	31·0	33·7	27	37·7
TiO_2	5·5	17·5	17·0	17	9·3
Al_2O_3	18·5	21·8	17·3	26	18·5
MgO	9·8	5·0	7·8	4	9·6
CaO	25·8	24·7	24·2	25	24·9
Diopside	52·6	26·8	41·7	21·4	51·6
Ti-pyroxene	16·7	50·9	40·5	50·7	27·6
Ca–Al-pyroxene	24·2	0	0	9·2	14·2
Wollastonite	4·3	12·1	8·1	10·8	3·0
Quartz	2·4	9·9	6·4	6·4	3·7
Rutile	0	0·4	3·4	0	0

releases Al_2O_3 to combine with wollastonite and form more $CaAl_2SiO_6$. There is theoretical support for the suggestion of trivalent titanium in the calculations of Grossman (1972a), who found that if Ti is assumed not to be a component in pyroxene, perovskite reacts with the gas to form Ti_3O_5 as the temperature falls.

Yagi and Onuma (1967) found that the maximum extent of stable solid solution on the join $CaMgSi_2O_6$–$CaTiAl_2O_6$ was 11 per cent $CaTiAl_2O_6$. We do not know whether a similar limit applies in the $CaMgSi_2O_6$–$CaAl_2SiO_6$–$CaTiAl_2O_6$ plane, nor do we know what effects wollastonite and Ti^{3+} might have. Nevertheless it seems probable that the titaniferous pyroxenes in the CAI are metastable with respect to solid breakdown products. The ease with which metastable pyroxenes can be quenched and their stubborn persistence at temperatures well below the solidus have been well-documented (O'Hara and Schairer, 1963; Yagi and Onuma, 1967). Above the solidus the presence of a small amount of liquid catalyzes reaction, and stable pyroxene compositions are achieved comparatively rapidly. The possibility also exists that the titaniferous pyroxenes in the CAI formed in the absence of liquid, by condensation from a vapor phase.

We can use the same approach as in the case of the melilites to estimate the composition of the first-condensing pyroxene. Assuming ideal solid solution, using the thermodynamic data of Robie and Waldbaum (1968) for $CaAl_2SiO_6$ and treating the free energy of $CaTiAl_2O_6$ as equivalent to that of the isochemical mixture perovskite + corundum, we calculate the following composition by weight: 67 per cent $CaMgSi_2O_6$, 12 per cent $CaAl_2SiO_6$ and 21 per cent $CaTiAl_2O_6$ at 1455°K. The calculated of $CaTiAl_2O_6$ is an upper limit, since Yagi and Onuma (1967) have shown that the pair perovskite + corundum is stable instead. We are unable to determine by how much we have overestimated the Ti content, but this upper limit composition for the first pyroxene to condense is likely to be metastable, as are the pyroxenes in the CAI. This pyroxene will change its composition as the temperature falls and higher Ti contents are possible. Kurat (1970) has reported pyroxenes from CAI in Lancé which are much closer in composition to pure $CaMgSi_2O_6$ than those listed in Table 2. Such pyroxenes could form by the reaction of melilite with the vapor at

1450°K if perovskite, the source of Ti, is trapped inside the growing CAI and thereby prevented from equilibrating.

The ferromagnesian silicates. CLARKE *et al.* (1970) presented a histogram of the fayalite contents of olivines from chondrules in Allende. Its remarkable features are a conspicuous peak in frequency at 0-1 per cent fayalite and a more or less uniform scatter of values between 10 and 45 per cent fayalite. The corresponding histogram for olivine from terrestrial igneous rocks would have an altogether different appearance. The peak in frequency would be closer to 10 per cent fayalite and compositions between 10 and 20 per cent would be distinctly commoner than more iron-rich ones. Results similar to those of CLARKE *et al.* (1970) have been found for olivine and pyroxene from chondrules in Type II carbonaceous chondrites (WOOD, 1967). And in the Type I carbonaceous chondrites, single crystals of iron-poor olivine and orthopyroxene (REID *et al.*, 1970a) suggest that the chemical peculiarities of the minerals in Types II and III are not simply due to some special chemical effects accompanying chondrule formation.

As stated earlier, the ferromagnesian minerals condensing at the highest temperatures are expected to be virtually iron-free. At lower temperatures the equilibrium iron content increases continuously. The presence of olivine and pyroxene grains of differing iron content in a single meteorite shows conclusively that chemical equilibrium has not been reached. Crystals that could be in equilibrium with the gas at low temperatures are mixed with those that could only coexist at very high temperatures. The very low iron content of the ferromagnesian silicates, which is the one most commonly encountered, is naturally explained as a consequence of high-temperature condensation.

Origin of the inclusions. The compositions of melilites and titaniferous pyroxenes from CAI and the iron contents of magnesium silicates in carbonaceous chondrites have been shown to be compatible with their origin by condensation processes. Pyroxenes so rich in Ti and melilites so poor in Na and Fe have never been found in terrestrial igneous rocks. GROSSMAN (1972a) has also pointed out the low åkermanite contents of the melilites in the CAI and the relative scarcity of such compositions among their terrestrial counterparts.

It can be demonstrated that, because of their Na–Fe-poor, Ca–Al-rich compositions, the CAI, if igneous in origin, could only be the crystallization products of liquids formed by the melting of Na–Fe-poor, Ca–Al-rich assemblages such as high-temperature condensates. Attributing their genesis to igneous processes (RINGWOOD, 1963) does not solve the problem of their ultimate origin.

Sometimes, CAI are observed which contain accessory alkali–halogen-rich feldspathoid minerals (CHRISTOPHE, 1969; FUCHS, 1969; MARVIN *et al.*, 1970; CLARKE *et al.*, 1970; KURAT, 1970) and some have been reported which contain spinels bearing moderate amounts of FeO (CHRISTOPHE, 1968; KURAT, 1970). Such observations are inconsistent with the high-temperature condensate origin of the CAI proposed here since neither FeO, nor the volatile alkali elements nor the halogens should have condensed over the same range of high condensation temperatures as the major minerals of the CAI. GROSSMAN (1972a) has suggested that these characteristics were produced after condensation by reaction between the CAI and their host matrices.

PRESSURE VARIATION OF THE CONDENSATION TEMPERATURES OF THE CAI

Using trace element fractionation patterns in chondrites, ANDERS (1968) has suggested that the gas pressure was between 10^{-2} and 10^{-6} atm during the formation of the ordinary chondrites. CAMERON and PINE (1972) have proposed a range of pressures between 10^{-2} and 10^{-5} atm for the inner solar nebula (1–10 AU) based on hydrodynamic models of its formation. These pressures are in the same range as those prevailing in cool circumstellar envelopes, 10^{-7} atm to 10 atm (LORD, 1965; GILMAN, 1969; FIX, 1970). Detailed calculations of the condensation temperatures of the phases in the CAI at 10^{-3} atm have been presented by GROSSMAN (1972a). Here we estimate the condensation temperatures of these phases at pressures of 10^{-2} and 10^{-4} atm.

In order to calculate approximate condensation temperatures at 10^{-2} and 10^{-4} atm, it was assumed that the distribution of each element between its major gaseous species is the same at these pressures as that given by the equilibrium calculations at 10^{-3} atm at the same temperature. Thus, at high temperatures, P_{Mg}, P_{Al} and P_{Ca} are proportional to the total pressure at constant temperature but P_O was found to remain constant. Consequently P_{Si} and P_{Ti} are proportional to the pressure at constant temperature. Free energy data for corundum, perovskite, gehlenite and spinel are taken from ROBIE and WALDBAUM (1968) and that for diopside from KRACEK et al. (1953). Of these five condensates, corundum was found to condense first by the method described by GROSSMAN (1972a) over the entire pressure range investigated. Below the condensation point of corundum, if gas–solid equilibrium is assumed,

$$2 \log P_{Al} = \log K_{eq} - 3 \log P_O$$

where K_{eq} is the equilibrium constant for the decomposition reaction of corundum into its monatomic gaseous component elements. Since both P_O and K_{eq} are practically independent of pressure, P_{Al} is a function of temperature only, after corundum appears. Perovskite was found to be the second condensate, then gehlenite, spinel and finally diopside. The condensation point of each phase was calculated by assuming that each mineral crystallizes from a vapor which is in equilibrium with all phases which condensed at higher temperatures. The results of these calculations are shown in Fig. 1, from which it is apparent that the sequence of condensation of these four phases is the same from 10^{-2} to 10^{-4} atm. This treatment assumes that the five crystalline phases considered are the only condensates in the temperature range of interest, whereas the detailed calculations at 10^{-3} atm were able to eliminate 88 other crystalline phases (GROSSMAN, 1972a, Table 2) at these temperatures. This assumption seems justified by the near-parallelism of the condensation lines in Fig. 1, and the fact that, at 10^{-3} atm, no other phases were found to condense within at least 25° of each of these five minerals. The only exception to this is forsterite, which condenses at a lower temperature than diopside over this pressure range (GROSSMAN, 1972a). The reader is cautioned against extrapolation of the condensation lines in Fig. 1 to greater pressure extremes, as the predicted condensation temperatures would be subject to considerable uncertainty due to the possible breakdown of either of the major assumptions upon which the calculations presented in this section are based. The presence of these condensate phase assemblages in the CAI is strong evidence that gas temperatures in the primitive solar nebula exceeded 1400°K. The textural
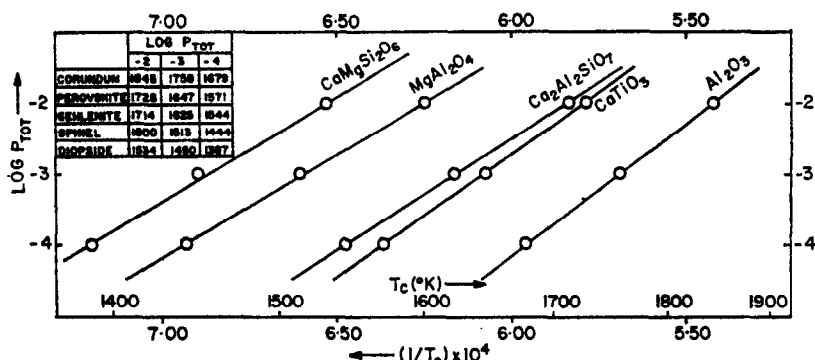
Fig. 1. Pressure variation of the condensation temperatures of the predominant minerals in the CAI. The condensation sequence does not change over the pressure interval 10^{-2} to 10^{-4} atm.

relations of these minerals in the CAI suggest that accretion processes in the centimeter size range were well under way very early in the history of the solar system, while temperatures were still this high.

UPPER LIMITS TO THE PRESSURE IN THE NEBULA

UREY (1952) and WOOD (1963) have previously considered the pressure–temperature conditions under which oxidized material might condense directly to liquid rather than solids. They assumed that the oxidized condensates were magnesium silicates, and consequently their calculations are completely inapplicable to the compositions of condensates considered here. We are concerned with compositions having higher condensation temperatures than magnesium silicates, and, because of their greater chemical complexity, probably having considerably lower solidus temperatures than those encountered in the system MgO–SiO_2. Thus the question of the conditions under which liquids can condense must be reopened, and if we can argue convincingly that no liquids in fact condensed, then we can establish an upper limit to the pressure in the nebula.

GROSSMAN (1972a) showed that the mineralogical compositions and textural relations displayed by the CAI are consistent with the sequence of condensation and reaction predicted from a model in which only crystalline phases are allowed to condense. We have shown here that the compositions of melilite, pyroxenes and olivine are also predicted by this model. The presence of metastable, Ti-rich, subsolidus pyroxenes in the CAI is direct evidence that they did not equilibrate with a liquid phase. Such pyroxenes are known to equilibrate relatively rapidly with silicate melts, a process which leads to formation of their stable breakdown products.

The arguments developed in this section assume complete chemical equilibrium between crystals and vapor and assume that all major compounds have been included in the equilibrium calculations (see GROSSMAN, 1972a).

Chemical compositions predicted for condensates at temperatures above $1300°K$ and at a pressure of 10^{-3} atm are given in Table 3 (GROSSMAN, 1972a). We have ignored iron, since it condenses as a metal which is inert to oxides and silicates under these conditions. We have also neglected Ti, since it is a minor constituent of the condensates at temperatures below $1550°K$.

Above $1550°K$ condensate compositions can be considered in terms of the system CaO–Al_2O_3–SiO_2 (see Fig. 2). The first phase to condense is corundum, and the condensate composition

Table 3. Compositions of condensates (except Fe and TiO_2) at 10^{-3} atmospheres (weight per cent).

$T(^{\circ}K)$	1650	1600	1550	1500	1450	1400	1350	1300
CaO	0	30·8	37·7	35·0	19·4	6·1	4·8	4·1
MgO	0	0	0	6·8	21·9	45·7	46·8	41·6
Al_2O_3	100	52·8	42·6	38·3	20·4	6·4	5·1	4·3
SiO_2	0	16·4	19·7	19·9	38·2	41·8	43·3	50·0

remains at the Al_2O_3 corner of the diagram until gehlenite appears at 1625°K. As the temperature falls further the composition of the condensate moves along the join corundum–gehlenite until Mg begins to condense at 1550°K and the composition moves off the ternary plane.

GROSSMAN (1972a) was unable to consider the phase β-Al_2O_3 because of a lack of thermodynamic data. β-Al_2O_3 occurs naturally as the mineral hibonite which has been found terrestrially and in CAI in at least four meteorites (KEIL and FUCHS, 1971). These meteoritic occurrences raise the possibility that hibonite is a stable condensate that replaces corundum with falling temperature. The discovery of a virtually pure Al_2O_3 (corundum) phase in Lancé by KURAT (1970) is consistent with this hypothesis since it can be interpreted as a high-temperature relict that failed to equilibrate with the gas at lower temperatures. Alternatively we could suppose that hibonite is the primary condensate instead of corundum. In this case Kurat's corundum would have to be a metastable phase under all nebular conditions.

If either of the foregoing possibilities is correct, the trajectory of the condensates in the CaO–Al_2O_3–SiO_2 plane should follow the compatible join β-Al_2O_3–gehlenite. The lowest-freezing liquid along this join occurs at the composition of the reaction point between $CaAl_4O_7$, β-Al_2O_3 and gehlenite at 1748°K (point R of Fig. 2). If condensation had proceeded along this join at temperatures above the solidus, $CaAl_4O_7$ would have crystallized from the resulting condensate liquid. So far, this phase has never been observed in the CAI and its absence may imply that this liquid played no part in their origin and, therefore, that condensation of gehlenite took place below 1748°K. Using Fig. 1, we see that this means that the total pressure
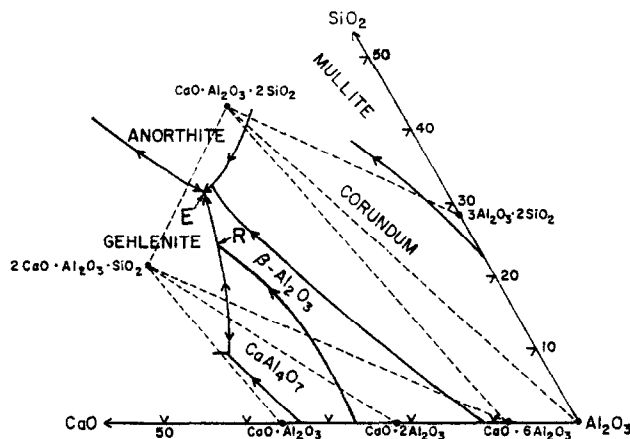

FIG. 2. Primary phase fields, cotectic liquid compositions and stable joins in the Al_2O_3-rich portion of the system CaO–Al_2O_3–SiO_2 (GENTILE and FOSTER, 1963). Condensation along the $CaO·6Al_2O_3$–gehlenite composition join at temperatures above the solidus leads to liquid R which solidifies to a mixture of gehlenite, hibonite and $CaAl_4O_7$. Along the corundum–gehlenite join, liquid E results from condensation above the solidus and the assemblage anorthite–gehlenite–hibonite will crystallize from it.

in that region of the nebula where they originated could not have exceeded 2.2×10^{-2} atm. To this date, however, very few CAI have been described in detail and it is possible that $CaAl_4O_7$ may be discovered in the future.

But there is yet a third possibility. If hibonite is a lower temperature product of the reaction of Al_2O_3 with Ca-rich phases, and if condensation occurred in the manner outlined by GROSSMAN (1972a), that is along the corundum–gehlenite composition join, then another, more SiO_2-rich liquid is possible. This eutectic liquid disappears at $1653°K$ (point E of Fig. 2). Had condensation occurred along this join at temperatures above the solidus, the resulting liquid would have crystallized to a mixture of hibonite, gehlenite and anorthite. Although it must be stressed again that the mineralogy and texture of very few CAI have been studied in detail, this assemblage has only been reported in a single CAI from Leoville (KEIL and FUCHS, 1971). But the presence of this assemblage does not necessarily mean that it crystallized from a liquid. Hibonite could be a relict high-temperature condensate while anorthite could be the product of the condensation reaction between spinel and diopside which occurs at $1362°K$ at 10^{-3} atm (GROSSMAN, 1972a). Of more significance are several reports of the occurrence of hibonite in CAI from which anorthite is absent: Vigarano (CHRISTOPHE et al., 1970) and Allende (KEIL and FUCHS, 1971; FUCHS, 1971) or from which gehlenite is absent: Allende (FUCHS, 1969) or from which both gehlenite and anorthite are absent: Murchison (FUCHS et al., 1970). In these cases, crystallization from the proposed liquid condensate could not have occurred, which in turn implies that the condensation of gehlenite took place below $1653°K$. The data of Fig. 1 suggest that this could have happened only if the pressure in the nebula were less than 2.2×10^{-3} atm.

At temperatures below $1550°K$, when Mg becomes important and the condensate composition moves into the quaternary system, nearly all of the Ca and Al have condensed. It is a quirk of the solar abundances that CaO and Al_2O_3 are nearly equally abundant when expressed in weight per cent (CAMERON, 1968). Thus we can focus our attention on the composition plane $CaO + Al_2O_3–MgO–SiO_2$, with CaO and Al_2O_3 equal by weight. Fields of solid phases appearing on the liquidus of this plane can be constructed from the data of OSBORN et al. (1954). The light dashed lines on Fig. 3 show the intersections of the planes on which OSBORN et al. (1954) give data with the plane of the figure.

The trajectory of the condensates as a function of temperature is also shown in Fig. 3. MgO begins to enter the condensed phases slowly at first. But between 1451 and $1450°K$ a dramatic increase in both MgO and SiO_2 occurs because of the reaction of melilite with the gas to form diopside. We estimate that this part of the trajectory approaches the solidus most closely. As the compositions move closer to the $MgO–SiO_2$ join, the solidus temperatures probably rise (SCHAIRER and YODER, 1969), and the temperature of condensation drops. Thus we are most concerned with the part of the trajectory lying in the spinel field at temperatures close to $1450°K$.

Three pseudobinary compositional joins, diopside–spinel, åkermanite–spinel and diopside–$CaAl_2SiO_6$ pierce the plane of Fig. 3 in the compositional range of most interest. They are labeled ds, as and dc, respectively, in the figure. At the piercing points the three joins ds, as and dc solidify completely at $1238 \pm 3°C$ (roughly $1510°K$) according to SCHAIRER and YODER (1969). According to O'HARA and BIGGAR (1969), these same temperatures of solidification range from 1230 to $1233.5°C$, indicating fair agreement. Referring to Fig. 1, we see that diopside condenses 120° and 60° below this temperature at 10^{-4} and 10^{-3} atm, respectively. The CAI cannot condense as liquids at these pressures. At 10^{-2} atm, however, diopside crystallizes at $1534°K$, above the solidus temperature in this composition range. Thus, at 10^{-2} atm, the condensation of diopside is expected to generate a small amount of liquid where diopside, melilite and spinel grains are in intimate contact. In addition to spinel, anorthite or melilite, and a pyroxene, forsterite should also precipitate from this liquid. Forsterite is not commonly observed in the CAI (FUCHS, 1969) and, when seen, it is never associated with diopside (CLARKE et al., 1970) which is a common constituent of most CAI (KURAT, 1970). The lack of evidence for the widespread coexistence of diopside and forsterite in the CAI suggests that these minerals did not crystallize from the proposed condensate liquid. This means that CAI having the composition of the equilibrium condensate assemblage could not have crystallized from a gas whose pressure exceeded $\sim 5.6 \times 10^{-3}$ atm, the pressure at which diopside condenses at $1510°K$.

The actual temperatures for diopside condensation may be slightly lower than those shown in Fig. 1 since P_{Mg} is lower than that used in the calculations due to the fact that Mg goes into solid solution in melilite. This effect is offset by the increased stability of diopside due to solid solution of Al and Ti. Because there is some textural and mineralogical evidence in the CAI for disequilibrium condensation (CROSSMAN, 1972a), it is possible for them to have condensed at pressures slightly higher than this limit, the exact increase depending on the degree of departure from equilibrium and on how much this depresses the condensation temperature of diopside.
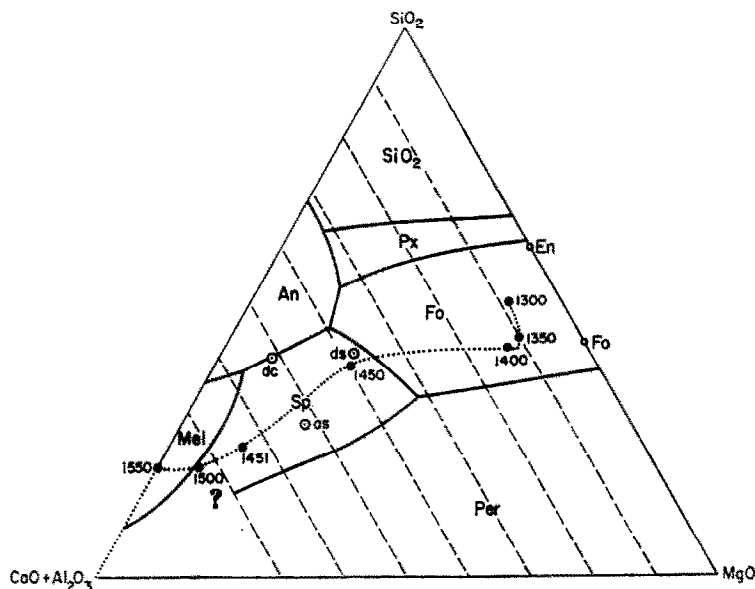

Fig. 3. Primary phase fields in the quaternary system CaO–Al$_2$O$_3$–MgO–SiO$_2$ where CaO = Al$_2$O$_3$ (taken from OSBORN *et al.*, 1954). The composition–temperature trajectory of the equilibrium condensates at 10^{-3} atm total pressure is shown by the dotted line. Note that significant amounts of MgO are present in the condensates only below 1550°K. The trajectory comes closest to the minimum solidus temperatures in the spinel field where pseudobinary compositional joins pierce the plane at *ds*, *as* and *dc*. These three joins solidify completely at ~1510°K, 60° above the temperature at which the condensates approach these compositions at this pressure.

In summary, the absence of critical phases or assemblages in the CAI implies that they condensed below the solidus. Since the condensation temperatures of the major phases of the CAI increase markedly with the total pressure, subsolidus condensation can be used to fix upper limits to the nebular pressure. The absence of CaAl$_4$O$_7$ requires that the total pressure was less than 2.2×10^{-2} atm in that part of the nebula where the CAI originated if condensation took place along the hibonite–gehlenite join. The lack of evidence for the coexistence of diopside and forsterite in the CAI lowers the upper limit to 5.6×10^{-3} atm. Finally, if condensation occurred along the corundum–gehlenite join, the upper limit is constrained to be even lower than this (2.2×10^{-3} atm) since hibonite is rarely associated with gehlenite and anorthite. These pressures are some 4 or 5 orders of magnitude lower than the pressures estimated by WOOD (1963) to be required to produce liquid condensates in the system MgO–SiO$_2$.

GLASSY EQUIVALENTS OF THE CAI

Glassy chondrules have been found in Allende and Vigarano, and some of them have close chemical affinites to the CAI that we have been considering (MARVIN et al., 1970; REID et al., 1970b; CLARKE et al., 1970). These affinities can be brought out by calculating the analyses into "condensate norms," in which the mineral assemblages are chosen to coincide as closely as possible with calculated equilibrium condensate assemblages (GROSSMAN, 1972a). This is done in Table 4, which contains the

Table 4. Analyses (recalculated to 100 per cent) of glasses in chondrules and their "condensate norms" (weight per cent).

	1 Vigarano (REID et al., 1970b)	2 Allende (MARVIN et al., 1970)	3 Allende (MARVIN et al., 1970)	4 Allende (MARVIN et al., 1970)	5 Allende (MARVIN et al., 1970)	6 Allende* (CLARKE et al., 1970)
SiO$_2$	21	21·7	42·1	45·3	44·5	48·1
TiO$_2$	1	0	4·8	0	0	0
Al$_2$O$_3$	40	38·1	14·6	26·4	35·1	25·0
Fe$_2$O$_3$	0	0	0	0	0·3	0
MgO	14	0·5	13·7	5·4	0	6·4
FeO	0	0	0	1·9	0	0·7
CaO	24	39·7	24·7	21·0	20·0	17·7
Corundum	12·4	2·2				
Perovskite	1·8					
Gehlenite	18·1	95·0				
Åkermanite	38·7	1·9				
Spinel	29·2	0·7				
Diopside			64·3	25·9		23·1
Wollastonite					1·3	
Ca–Al-pyroxene			18·1	3·9		
Ti-pyroxene			14·3			
Forsterite			2·8	3·2		4·4
Enstatite			0·4			
Anorthite				67·0	96·4	58·5
Albite						9·5
Nepheline						4·5
Quartz					2·2	

* Also includes 2·0 per cent Na$_2$O and 0·2 per cent K$_2$O.

norms as well as the original analyses recalculated to 100 per cent. The analyses are listed in approximately the order of decreasing condensation temperatures, to the extent that they can be deduced from the "normative" mineralogies. The valence state of the Fe is conjectural because these are microprobe analyses. It was taken to be Fe^{3+} in 5 because there is no MgO in this glass and the norm is practically pure anorthite, in which Fe$_2$O$_3$ might substitute for Al$_2$O$_3$.

The normative mineralogies listed in Table 4 are consistent with assemblages predicted from condensation calculations and with the mineral assemblages in the CAI. There is a general decrease in condensation temperature as one moves across the table, but there are no cases where radically incompatible condensates need be chosen to account for a particular glass composition. Although no uniqueness can be

claimed for possible mineralogies, the possibilities are nevertheless restricted to some degree by the bulk chemical compositions. For example, an attempt to calculate glass 3 into perovskite + spinel + diopside + melilite, a univariant assemblage that is stable only at 1450°K at a pressure of 10^{-3} atm (GROSSMAN, 1972a), led to a negative amount of åkermanite.

The chondrules consisting of euhedral crystals of spinel in glass reported by MARVIN et al. (1970) are of special interest. Since the proportion of spinel to glass is not reported, the bulk compositions of these chondrules cannot be determined with any accuracy. But it is highly probable that they lie within the field of primary crystallization of spinel in Fig. 3. If this is true, these chondrules may represent equilibrium assemblages close to the liquidus temperatures in this field. MARVIN et al. (1970) report experiments suggesting that the observed liquid–spinel equilibria could only exist above 1500°C (1773°K). This enables us to make a very persuasive argument against their origin as primary liquid condensates. Reference to Fig. 1 shows that spinel can be an equilibrium condensate at 1773°K only if the pressure exceeds one atmosphere. Such pressures are so far outside the pressure limits predicted for the primitive solar nebula (CAMERON and PINE, 1972) that significant reheating of the precursors of these glassy CAI must be considered as an important event in their genesis. Glassy equivalents of the CAI were probably formed by the reheating, melting and quenching of original solid condensates.

Alternatively, if they are interpreted as quenched primary liquid condensates, formed at higher nebular pressures than their primary crystalline counterparts, then models for the early evolution of the nebula must be derived which feature at least two regions characterized by pressures differing by nearly an order of magnitude. In addition, these two regions must be close enough together so that transport mechanisms compatible with this model allow condensates from one region to mingle with those from the other within time periods which are short compared to the agglomeration times of meteoritic material. Otherwise both liquid and solid condensates could not accumulate on a single body such as Allende. Such restrictive boundary conditions may effectively rule out the possibility that the glassy equivalents of the CAI had a primary liquid condensate origin.

A typical, primitive CAI in Allende is shown in Fig. 4. Note its irregular shape and large size compared to the surrounding ferromagnesian chondrules. A large cavity containing subhedral crystals of what is probably gehlenite is visible in the CAI, suggesting crystal growth under relatively low pressure. A perfectly spherical chondrule (Fig. 5) contains the same mineral assemblage as the CAI but lacks their irregular shape. It is interpreted as the product of devitrification of a Ca–Al-rich glass sphere such as glass 1 (Table 4). The evidence presented here supports the theory that sudden melting of primitive condensates into rapidly-crystallized liquid droplets (NELSON et al., 1972) is the mechanism for the formation of chondrules of all compositions, as previously proposed by WHIPPLE (1966, 1972), CAMERON (1966, 1972), LARIMER and ANDERS (1967), REID et al. (1970b), KING et al. (1972) and ONUMA et al. (1972).

GROSSMAN (1972b) found that the CAI in Allende were enriched in refractory trace elements such as Sc, the rare earths and Ir by a factor of approximately 23 relative to Cl chondrites. KURAT (1970), having noted enrichments of refractory Zr,
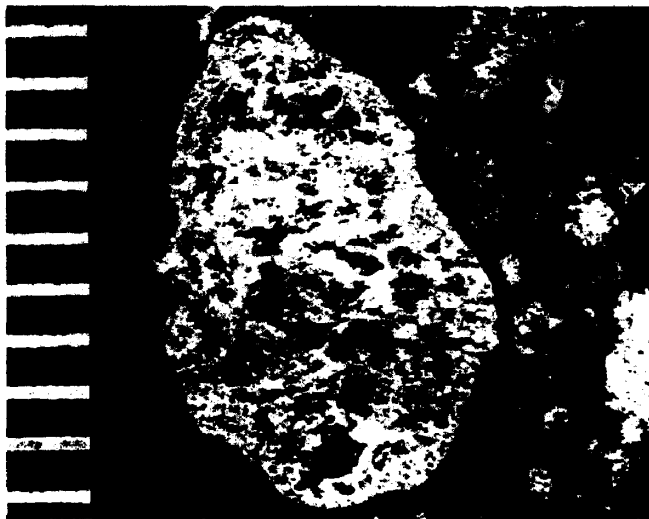
Fig. 4. A typical, primitive CAI in Allende. Note its irregular shape and the large grain sizes. Crystals in the cavity are probably gehlenite. A mm scale is shown for reference.

Fig. 5. A typical, Ca–Al-rich chondrule in Allende. Note its spherical shape and large size compared to the surrounding ferromagnesian chondrules. A smaller CAI is also visible. A mm scale is shown for reference.

Y and Ti in CAI from Lancé, proposed an evaporation, rather than condensation, origin for them as he saw no mechanism whereby the refractories could have been so concentrated by condensation processes. GROSSMAN (1972b) attributed these enrichments to the co-condensation of these trace elements with the Ca-Al-rich oxides silicates. According to this model, the observed enrichments can be explained by postulating that the minerals of the CAI condensed only where there already existed crystalline nuclei of the more refractory trace metals, many of which (Os, Sc_2O_3, Re, Ta, ZrO_2) would otherwise have been supersaturated by factors of 10 to 10^3 in the range of condensation temperatures of the minerals of the CAI.

In particular, the average concentration of Ir in the Allende CAI is 10·9 ppm. In a trace element study of 300 individual chondrules from ordinary chondrites, OSBORN et al. (1972) discovered, in the H-group chondrites, a sub-population of chondrules with substantially higher-than-average Al and Ir contents, although still factors of 5 lower than those in the CAI. Furthermore, the Ir and Al abundances in these chondrules correlate with one another, suggesting the presence of varying amounts of a high-temperature condensate component. Also, DODD's (1971) description of Ca-Al-rich micro-inclusions of monticellite, spinel and "fassaite" within an iron-bearing (Fa_{22}) olivine chondrule in the Sharps H-3 chondrite may be interpreted as the direct incorporation of partially melted and reacted high temperature condensates into chondrules. These observations are consistent with the theory that chondrules were formed by the melting of pre-existing mixtures of high- and lower-temperature primitive condensates.

CONCLUSIONS

1. Compositions of titaniferous pyroxenes and melilites in the CAI and iron contents of magnesium silicates in carbonaceous chondrites are consistent with a condensation origin.

2. The sequence of condensation of the Ca-Al-rich, high-temperature condensates does not vary over the pressure range 10^{-2} atm to 10^{-4} atm.

3. Formation of these condensates in the primitive solar nebula indicates temperatures in excess of 1400°K at the pressures thought to have prevailed in the inner solar system.

4. Accretion of condensate grains to cm-size objects was well under way at a very early stage of evolution of the solar nebula.

5. The metastable pyroxene compositions, the absence of the mineral $CaAl_4O_7$ and the scarcity of the assemblages hibonite-gehlenite-anorthite and forsterite-diopside in the CAI indicate that their condensation temperatures were below the solidus.

6. Subsolidus condensation of the CAI implies upper limits to the total pressure in the nebula as low as 2·2 × 10^{-3} atm.

7. Both glassy and crystalline chondrules in C-3 chondrites have bulk chemical compositions similar to those of the CAI, suggesting chondrule formation by melting of primitive condensates.

8. C-3 chondrites are mechanical mixtures of chondrules and relatively unaltered primitive condensates which ceased to equilibrate with the vapor at different temperatures over a range in excess of 1000°K.

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