## The origin of type C inclusions from carbonaceous chondrites

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Type C inclusions are plagioclase-rich, Ca-, Al-rich inclusions found in carbonaceous chondrites. They formed as solid condensates which were later melted in an event that destroyed the original condensate grains. Neither the melting event nor secondary alteration had a significant effect on bulk composition. Two stages in the condensation history can be discerned on the basis of major element bulk compositions. As in type A inclusions, the condensate phase assemblage originally consisted of melilite + spinel + perovskite ± hibonite. Type C's were, however, significantly enriched in spinel relative to unaltered portions of most type A's. In contrast to type A's, condensate grains of spinel and melilite in type C's reacted partially with a coexisting gas to produce anorthite + diopside. One-half to two-thirds of the silica now in type C inclusions was introduced by this process. The reactions involving melilite and spinel that are predicted by equilibrium condensation calculations for a cooling gas of solar composition did not occur, probably due to kinetic constraints.

Type C's may be related to Al-rich chondrules in ordinary chondrites by the addition of olivine and albite. Bulk compositions of Al-rich chondrules in enstatite chondrites are consistent with the addition of orthopyroxene and albite to type C inclusions. Thus, types A and C inclusions and Al-rich chondrules could represent sequences of condensates removed from interaction with the primitive solar nebula at progressively lower temperatures. If Al-rich chondrules represent the high-temperature component in chondritic material, then type C inclusions rather than the more common subgroups of CAIs could be the true parents of chondrites.

#### 1. Introduction

Considerable insight into the nature of processes occurring in the early solar nebula has been obtained from the study of Ca-, Al-rich inclusions (CAIs) from carbonaceous chondrites. Both finegrained and coarse-grained CAIs exist, but attention has focussed on coarse-grained inclusions because they can be studied by standard petrological techniques. In this study, the origin of type C inclusions, a class of coarse-grained CAIs, is constrained on the basis of bulk composition. The possibility that type C's are related to other Ca-, Al-rich objects in meteorites is also examined.

Coarse-grained CAIs were originally classified into types A, B and I [1]. The latter class was created because fassaite compositions from the single type I inclusion studied by Grossman [1] were intermediate between those of types A and B inclusions. This observation was later found to be incorrect [2] in that pyroxenes in type A inclusions analyzed by [1] were secondary. Wark [3] con-

cluded that Grossman's type I's are, in fact, a distinct class of CAIs. To avoid possible confusion with the misnomer "intermediate", however, he re-labeled type I's as type C's. The designation of Wark [3] is followed here.

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Primary phase assemblages of type C inclusions are characterized [3] by major anorthite (30–60 vol.%) and variable amounts (less than 30 vol.% each) of fassaite, melilite and spinel. In contrast, primary phase assemblages of type A inclusions consist mostly of melilite with no primary anorthite [1]. Those of type B's have less than 30 vol.% anorthite and more than 30 vol.% fassaite. Wark [3] has shown that bulk compositions of type C inclusions are distinct from those of types A and B.

Type A inclusions have been subdivided [4,5] into fluffy type A's (FTA's) and compact type A's (CTA's). The primary phase assemblage of FTA's consists of melilite with lesser amounts of spinel, hibonite and perovskite. FTA's are heavily altered and characterized by convoluted shapes. They are

generally thought to be vapor-to-solid condensates [5]. In CTA's, hibonite is generally restricted to rims and the inclusions are rounded in cross-section. As a rule, CTA's are much less altered than FTA's and the melilite is more akermanitic. CTA's probably crystallized from a melt [4].

All type C inclusions have "igneous" textures [3,6-8] and were at least partially melted at some time during their history. If this melting event was primary, then type C inclusions formed as liquid condensates [3,6]. If the melting event was secondary, then type C inclusions are re-melted condensates which may have undergone extensive volatilization. It is the latter possibility that is investigated in this paper. We do not disprove Wark's [3] suggestion that type C's formed as liquid condensates. However, his major supportive argument was that calculated bulk compositions of liquid condensates in a cooling gas of solar composition are very similar to those of type C's whereas calculated bulk compositions of solid condensates are not. In this paper, we show that bulk compositions of type C inclusions are in fact consistent with an origin as solid condensates under special circumstances, thus removing Wark's [3] principal objection to the idea. In addition, there are some basic problems with liquid condensation in the solar nebula that make alternative modes of origin worth considering. For example, high nebular pressures  $(10^{-1}-10^0)$  atm) are required to stabilize melts with compositions similar to those of type C's [3,9]. Such high pressures are not expected in the solar nebula. Furthermore, liquid condensation requires type C's to be unrelated to other classes of CAIs. This is certainly possible, but models for which type C's are readily related to other inclusion types would be preferable.

# 2. Bulk compositions of primary phase assemblages in type C inclusions

Bulk compositions of Allende type C inclusions ABC [7], 3655B [3,10], TS-26 [11], CG-5, 6/1, 10A-E, 160, 10B-X and 100 [3] are tabulated in Wark [3] and are used in this study. For 3655B, the bulk composition of Wark [3] was used in preference to that of Mason and Taylor [10] because of probable matrix contamination in the sample analyzed by the latter authors.

If type C inclusions formed by the condensation of solids followed by melting, then they no longer contain the original condensate crystals. Provided the inclusions did not undergo extensive volatilization and/or alteration, however, it is possible to constrain the original condensate mineralogy by means of bulk compositions. We first consider the contribution of alteration products to the bulk compositions of type C's, then show that these inclusions have not been significantly affected by volatilization and finally discuss the determination of condensate mineralogy.

## 2.1. Effect of secondary alteration products

For most CAIs, low-temperature alteration of melilite resulted in the introduction of FeO and Na<sub>2</sub>O into the inclusions and partial exchange of Ca, Mg and Si with the altering gas [12]. It is therefore difficult to determine bulk compositions prior to alteration for most CAIs. On the other hand, type C inclusions have little or no melilite and are substantially less altered than is typical of CAIs [3]. Bulk compositions of type C's are therefore very close to those of the primary inclusions. An exception may be inclusion 6/1 whose bulk composition [3] has twice as much Na<sub>2</sub>O (0.71 wt.%) and more FeO (0.86 wt.%) than that of any other type C. For this reason, inclusion 6/1 is not considered in the following discussion. For all other type C inclusions, the effect of alteration products on bulk composition is ignored.

### 2.2. Effect of volatilization

Wark [3] presented two substantive arguments against the possibility that type C inclusions were extensively volatilized during the melting event. First, bulk compositions of type C's have Si/Mg ratios that are much higher than those expected upon volatilization of chondritic material [13]. A precursor with an Si/Mg ratio higher than the chondritic value could be proposed, but chondrules, bulk chondrites and the most likely silicarich interstellar grains (e.g., olivine, enstatite) all have lower Si/Mg than do type C's [14]. Silica-rich chondrules [15,16] have high Si/Mg but CaO and Al<sub>2</sub>O<sub>3</sub> are trace constituents. It would be difficult to produce type C's with  $CaO + Al_2O_3 = 49-57$ wt.% from such a starting material. A second point made by Wark [3] is that Mg-isotope data [17] for a type C inclusion show a small enrichment in the light isotopes of Mg. A fractionation favoring heavy isotopes would be expected if type C's were volatilization residues. If silica-rich chondrules were the original precursor, then large positive Mg isotope fractionations would be expected. We agree with Wark [3] that type C inclusions were not extensively volatilized.

## 2.3. Determination of original condensate mineralogy

It was argued above that secondary processes which destroyed condensate grains in type C's did not strongly affect bulk compositions. If so, the bulk composition of each type C inclusion should be consistent with that of the primary phase assemblage regardless of what the current mineralogy may be. A convenient way of constraining what the original condensate mineralogy may have been is by projecting bulk compositions from those of minerals assumed to be in the primary phase assemblages. This reduces the complexity of compositional variations, making it easier to identify additional phases that may have been present. The geometrical and matrix basis for constructing pro-

jections is discussed in the literature [18–20]. In this study, a mineral name is capitalized when it refers to the composition of the pure end-member. Thus, GEHLENITE refers to the composition Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>. Gehlenite refers to a mineral whose composition can be described mostly in terms of Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> but which may contain Mg and small amounts of other elements.

Primary bulk compositions of type C inclusions can be described in terms of five oxides (CaO, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>). Type C's can be represented by projecting bulk compositions from the compositions of any two minerals in the primary phase assemblage onto the plane defined by three additional components. These latter three components need not correspond to those of minerals in the condensate phase assemblage. Compositions of all five of the selected components must, however, be linearly independent.

Spinel and perovskite. If type C inclusions were originally solid condensates, then spinel and perovskite were probably present. Spinel grains very close in composition to that of the pure end-mem-

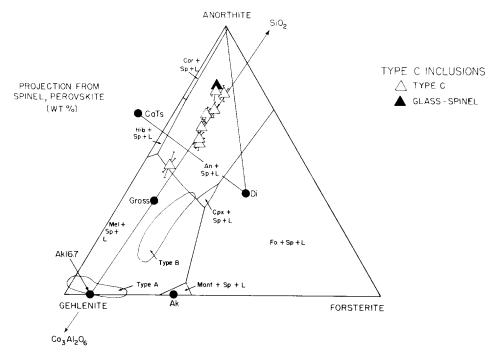


Fig. 1. Bulk compositions of type C inclusions and an Allende glass-spinel inclusion projected from SPINEL and PEROVSKITE onto the plane GEHLENITE-ANORTHITE-FORSTERITE. Spinel-saturated liquidus phase fields after [20] and composition fields for the primary phase assemblages of types A and B inclusions [11,12] are also shown.

ber MgAl<sub>2</sub>O<sub>4</sub> are found in nearly all CAIs. Spinel is also calculated to be a stable condensate in a wide variety of gas compositions and over a wide range in pressure and temperature [21–25].

Ti in type C inclusions now occurs in fassaite, but this phase crystallized from a melt after any condensation event. Perovskite is a plausible choice as the original carrier of Ti because it is the principal Ti-bearing phase in those CAIs most likely to be vapor-to-solid condensates [5]. It is also calculated to be a stable condensate in a cooling gas of solar composition [21,25]. It should be noted, however, that alternative carrier phases such as fassaite or a Ti-oxide cannot be rejected on the basis of bulk Ti concentrations.

Other major condensate minerals. In Fig. 1, bulk compositions of type C inclusions are projected from SPINEL (MgAl2O4; SP) and PEROVSKITE (CaTiO<sub>3</sub>; PV) onto the plane GEHLENITE (GE)-ANORTHITE (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>; AN)-FOR-STERITE (Mg<sub>2</sub>SiO<sub>4</sub>; FO). Also plotted is the glass composition from a glass-spinel inclusion described by Marvin et al. [26]. This inclusion is discussed later. Projected compositions of GROSSULAR (Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>; GROSS), SiO<sub>2</sub>, Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> (C3A), DIOPSIDE (CaMgSi<sub>2</sub>O<sub>6</sub>; DI), Ca-TSCHERMAK'S MOLECULE (CaAl<sub>2</sub>-SiO<sub>6</sub>; CaTs) and AKERMANITE (Ca<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>; Ak) are indicated. Spinel saturated liquidus phase fields [20] and primary bulk compositions of types A and B inclusions [11,12] are also shown. The projection plane GE-AN-FO was used by Stolper [20] in his study of type B inclusions. The conclusions of this work are not affected if alternative projection planes are used.

Except for CG-5, bulk compositions of type C inclusions lie near a line extending away from the ANORTHITE vertex in Fig. 1. Since anorthite is a near-liquidus phase in these inclusions [3,20,27], this is consistent with the possibility that most type C's are part of a fractional crystallization sequence from a single parent composition. To test this, bulk SPINEL contents of type C inclusions are plotted in Fig. 2 as a function of the amount of ANORTHITE component shown in Fig. 1. Also shown is the trace of the spinel saturation surface [20] which describes the composition of melts in equilibrium with anorthite and spinel. If type C's are products of fractional

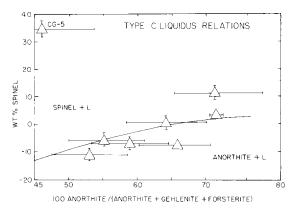


Fig. 2. Calculated wt.% SPINEL component in bulk compositions of type C inclusions as a function of projected ANORTHITE component in Fig. 1. Also shown is the trace of the anorthite-spinel liquidus surface in the vicinity of type C bulk compositions after [20].

crystallization, they should either plot along a line extending away from the ANORTHITE axis in Fig. 2 or along the spinel-anorthite liquidus saturation curve. Only CG-5 plots well away from the trace of the spinel saturation surface. Hence bulk compositions of most type C inclusions are consistent with being part of a fractional crystallization sequence from a single bulk composition. This suggests that fractional crystallization of spinel and anorthite may have modified the bulk compositions of some type C inclusions. It cannot be the sole process involved in the formation of type C's, however, for at least two reasons. First, it requires that CG-5 be an anomalous inclusion and second, even if most type C's are part of a fractional crystallization trend we are still left with the problem of how the original bulk composition was produced. Moreover, fractional crystallization is not a process that can result in a genetic relationship between type C's and other subgroups of CAIs.

In Fig. 1, bulk compositions of type C inclusions are very close to the line C3A-SiO<sub>2</sub>. This suggests that they can be described as a mixture of spinel and perovskite with two components whose compositions plot on the C3A-SiO<sub>2</sub> line. This line does not intersect any of the spinel-saturated invariant points in the system. Since most bulk compositions of type C inclusions have spinel on or near the liquidus ([3]; Fig. 2), this implies that type C's did not form as near-solidus partial melts.

The line C3A-SiO<sub>2</sub> also does not intersect the type B field. This means that type C's are not directly related to type B inclusions although indirect relationships are not precluded. There are a number of binary solid solutions in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> which intersect the C3A-SiO<sub>2</sub>-SP join (e.g., melilite, clinopyroxene). For none of these phases, however, do the compositions lie entirely within the C3A-SiO<sub>2</sub>-SP ternary. On the basis of the above observations, the original condensate phase assemblage of type C's contained spinel and perovskite mixed with variable amounts of at least two phases, one relatively rich in silica and the other relatively silica-poor.

The silica-rich end-member is most likely SiO<sub>2</sub> since it is the only single phase on C3A-SiO<sub>2</sub> in Fig. 1 on the silica-rich side of type C bulk compositions. Quartz has been calculated to be a stable condensate in the Si-rich zone of supernovae [23] but not together with spinel. It is more likely that the "SiO<sub>2</sub>" in type C's came from a gas that reacted with silica-poor condensates. The identity of the dominant Si-bearing molecule in the vapor cannot, however, be determined on the basis of the present calculations. The alternative, that the silica-rich end-member is a mixture of two discrete phases is unlikely because an extremely homogeneous mixture of the two phases would be required.

Possible end-members on the silica-poor end of C3A-SiO<sub>2</sub> include a pyroxene on the join DI-CaTs (~ CaTs67), grossular, melilite on the join AK-GE (~ Ak17) and C3A. Of these four possibilities, only melilite is a reasonable candidate. Pyroxene is very unlikely to be the precursor phase because pyroxenes as aluminous as CaTs67 are unstable in the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> at low pressures [28]. Moreover, the bulk composition of inclusion CG-5 is inconsistent with CaTs67 as the silica-poor end-member because it plots on the wrong side of the DI-CaTs join in Fig. 1. Grossular has never been calculated to be a stable condensate in a cooling gas of solar composition. It does occur as an alteration phase in CAIs [12,29,30] and is calculated to be a stable condensate in Si-rich zones in supernovae [22,23] but in neither case is grossular ever in equilibrium with spinel. If type C inclusions originally consisted of grossular plus spinel, then they must either have formed under non-equilibrium conditions or in a non-solar environment. Similar arguments make C3A an unlikely candidate as a primary phase in type C inclusions. C3A may be stable in a gas which is Al-poor, Ca-rich relative to a gas of solar composition but condensates from such a gas would have higher than solar  $CaO/Al_2O_3$  ratios. Bulk compositions of type C inclusions have  $CaO/Al_2O_3$  ratios  $(0.7 \pm 0.2)$  consistent with that of a solar gas (0.77; [31]).

In contrast to CaTs67, grossular or C3A, melilite plus spinel plus perovskite is a commonly observed phase assemblage and Ak17 a typical melilite composition in type A inclusions [5]. In a cooling gas of solar composition, melilite is calculated to be a stable condensate over a wide range of pressure and temperature. Bulk compositions of type C's are consistent with condensation of inclusions containing melilite + spinel + perovskite, which we will refer to as type C precursors, followed by reaction with SiO<sub>2</sub> in a coexisting gas. Possible products of such a reaction include (Fig. 1) anorthite plus diopside and anorthite plus olivine. The fact that bulk compositions of type C's do not lie on the silica-rich side of the join AN-DI is consistent with a reaction product of anorthite plus diopside.

Reaction of melilite plus spinel with SiO<sub>2</sub> in a coexisting gas to form anorthite plus diopside can be described by the two equilibria:

$$2GE + SP + 6SiO2(g) = 3AN + DI$$
 (1)

and:

$$2AK + SP + 4SiO2(g) = AN + 3DI$$
 (2)

It is assumed here that perovskite was not an important reactant, although this possibility cannot be rejected. In order to determine modes of condensates prior to reactions (1) and (2), bulk compositions of type C inclusions were re-calculated in terms of GE-AK-SP-PV-SiO<sub>2</sub>. Cast in this form, the components which were present in the precursor phase assemblages (GE, AK, SP, PV) can be distinguished from those introduced by later reaction (SiO<sub>2</sub>). If it is assumed that "SiO<sub>2</sub>" was introduced into type C's according to reactions (1) and (2), then 42-91% of the melilite and 10-79% of the spinel in the type C precursor reacted to form anorthite plus diopside. It should be noted that the relative proportions of spinel

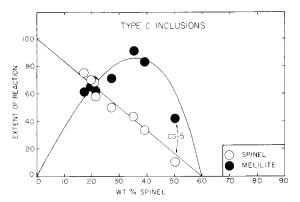


Fig. 3. Calculated proportions of spinel and melilite in type C precursors consumed by reactions (1) and (2) as a function of calculated wt.% SPINEL in the precursor phase assemblage.

and melilite that reacted are fixed by the stoichiometries of reactions (1) and (2), a consequence of the precursor consisting almost entirely of melilite + spinel. In Fig. 3, percentages of melilite and spinel in the type C precursor that reacted with SiO<sub>2</sub> are plotted against wt.% SPINEL for each of eight inclusions. For all eight inclusions, there is a strong negative correlation between the proportion of spinel that reacted and wt.% spinel in the precursor assemblage. A least squares line for SPINEL is drawn through calculated positions for type C's such that there is 100% extent of

reaction at 0 wt.% spinel in the precursor. Also shown is a curve for melilite calculated from the line for SPINEL assuming that  $X_{Ak} = 0.167$  and wt. % (spinel + melilite) in the precursor = 100. The calculated line and curve are intended to be illustrative since  $X_{Ak}$  for melilite in the precursor phase assemblage is variable. Two basic points can be made on the basis of Fig. 3. First, most of the spinel in those type C precursors with the lowest spinel contents reacted with the gas. Since comparable spinel contents are found in some Allende type A's, this suggests that if type C precursors were as coarse grained as these type A's and if both groups were exposed to the gas when it was reacting with type C precursors, then the type A's would also have reacted to form anorthite plus diopside. Therefore, if Allende type A's originated in the same gas as type C precursors, then either reactions (1) and (2) were kinetically inhibited due to coarse grain sizes or the type A's were removed from that gas before reactions (1) and (2) took place. Anorthite and grossularite are common but Ti-poor clinopyroxene relatively rare in the alteration products of Allende type A's [5]. Some spinel-rich, fine-grained inclusions from Efremovka [32,33], Leoville and Vigarano (G.J. MacPherson, personal communication, 1988), however, consist mostly of spinel and melilite

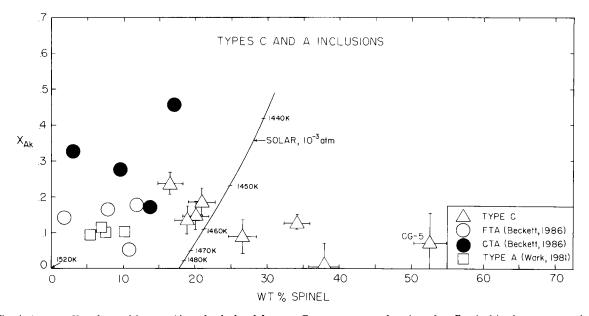


Fig. 4. Average  $X_{Ak}$  observed in type A's and calculated for type C precursors as a function of wt.% spinel in the precursor phase assemblage.

altered partially to pyroxene and anorthite. Such inclusions could be partially reacted type C precursors. A second point based in Fig. 3 is that, if all type C precursors had reacted for the same amount of time in the same gas, the extent of reaction should have been proportional to the spinel—melilite surface area and hence the amount of SPINEL. This is exactly opposite to what is observed in Fig. 3. One possible interpretation is that average grain sizes in type C precursors increased systematically with increasing spinel content. Alternatively, precursors with high spinel contents were exposed to the reacting gas for shorter times or at lower temperatures than were spinel-poor precursors.

In Fig. 4,  $X_{AK}$  of melilite in type C precursors is plotted against wt.% SPINEL assuming only melilite, spinel and perovskite were present. The possible presence of hibonite and/or CaAl<sub>4</sub>O<sub>7</sub> is considered later. Also shown in Fig. 4 are observed values for primary phase assemblages of type A inclusions [11,12] and calculated values for equilibrium condensates from a cooling gas of solar composition (W. Tangren, personal communication, 1984). Calculated  $X_{AK}$  of type C precursors decreases with increasing SPINEL content from  $\sim 0.25$  at 17 wt.% SPINEL to  $\sim 0.07$  at 50 wt.% SPINEL. The type C trend is clearly distinct from that of calculated equilibrium condensates from a solar gas. Prior to reactions (1) and (2), primary phase assemblages of type C inclusions had more than 17 wt.% spinel. With the exception of one CTA, all type A inclusions shown in Fig. 4 have less than 15 wt. % spinel. Thus, bulk compositions of type C precursors are consistent with their being a spinel-rich class of type A's. It is not clear whether the type C precursors are more closely related to FTA's or CTA's.

Possible minor phases: hibonite,  $CaAl_4O_7$  and Nabearing minerals. If type C inclusions were originally a spinel-rich class of type A's, then they may have contained some hibonite. If it was present, then SPINEL contents of type C's shown in Fig. 4 were overestimated and  $X_{Ak}$  in melilite underestimated because:

$$11AK + 4HIB = 13GE + 11SP + 9SiO_{2}$$
 (3)

The amount of hibonite that could have been

present in type C precursors is limited by  $X_{Ak}$  in the resulting phase assemblage. Compact type A inclusions can have rather variable melilite compositions, but hibonite is usually restricted to inclusion rims. On the other hand, fluffy type A inclusions, which do contain hibonite included in melilite, have  $X_{Ak} < \sim 0.25$ . If it is assumed for type C precursors that the average  $X_{Ak} < 0.3$ , then maximum hibonite contents of 4-9 wt.% are obtained using equation (3). This is consistent with hibonite contents of unaltered portions of fluffy type A inclusions (2-5 wt.%; [11]). The presence of hibonite has little effect on calculated spinel/ melilite ratios of the type C precursors. For example, in the precursor of CG-5, the spinel/melilite weight ratio would have been 1.04 if no hibonite were present and 0.98 if there were 9 wt.% hibonite. The effect on calculated spinel and melilite contents for other type C inclusions is even smaller. Bulk compositions of type C inclusions are consistent with an origin as a spinel-rich class of type A inclusions that reacted with SiO<sub>2</sub> in a coexisting gas. It is unclear whether or not these inclusions ever contained hibonite.

There is some controversy over whether  $CaAl_4O_7$  is [24,34] or is not [5,35] a stable condensate in a cooling gas of solar composition. It has been found in three CAIs, one each from Allende [36], Leoville [37] and Vigarano [38] and as two isolated grains in Adelaide (I. Hutcheon, personal communication, 1987). The original provenance of the grains from Adelaide is unknown, but within the inclusions CaAl<sub>4</sub>O<sub>7</sub> is a trace to minor constituent. Type C precursors did not contain major amounts of CaAl<sub>4</sub>O<sub>7</sub> because their bulk compositions do not lie near a line containing the composition CaAl<sub>4</sub>O<sub>7</sub> in Fig. 1. The presence of minor amounts of CaAl<sub>4</sub>O<sub>7</sub> in type C precursors cannot, however, be rejected on the basis of major element bulk compositions.

The sodic phases nepheline and sodalite are often found in alteration products of Allende inclusions and it is possible that these phases were also present in type C precursors prior to melting. If so, volatilization during the melting event must have been sufficient to remove any alkalies and halogens without affecting the Mg-isotope systematics. This sort of process may, as discussed below, have occurred in Al-rich chondrules from ordinary and enstatite chondrites. There is, how-

ever, no evidence for the introduction of sodium into type C's prior to the melting event.

Summary. To summarize, a scenario for the formation of type C inclusions consistent with the above observations is:

- (1) Condensation of melilite + spinel + perovskite  $\pm$  hibonite  $\pm$  CaAl<sub>4</sub>O<sub>7</sub>.
- (2) Reaction of melilite + spinel with  $SiO_{2(g)}$  to form anorthite + diopside. The reaction goes 40-90% of the way towards completion.
- (3) Removal of inclusions from further interaction with the reacting gas.
  - (4) Melting with little or no volatilization.
  - (5) Crystallization.
  - (6) Alteration.
- (7) Incorporation of inclusions into host meteorite.

#### 3. Discussion

## 3.1. Relationships of type C's to other CAIs

Type B inclusions. It was stated above that type C inclusions did not form directly from type B's. Similar processes may, however, have been involved in the origin of both groups. To a first approximation, bulk compositions of type B inclusions can be explained by the stable [39] or metastable [20] reaction of nebular gases with pre-existing melilite-rich phase assemblages to form titaniferous pyroxene. The approximate compositions of melilite in a melilite-rich precursor can be determined by extrapolating the bulk composition trend for type B inclusions in Fig. 1 back to the melilite binary which plots along the FOR-STERITE-GEHLENITE side of the triangle. The melilite compositions thus inferred are more åkermanitic than for type C precursors. Moreover, if the condensing pyroxene were similar in composition to the fassaite CaMg<sub>0.67</sub>Ti<sub>0.21</sub>Al<sub>0.66</sub>Si<sub>1.46</sub>O<sub>6</sub> proposed in [39], then the compositions of type B precursors can be obtained by projecting the bulk compositions of type B inclusions from the pyroxene onto the plane GE-AK-SP. The resulting SPINEL contents are comparable to those of type C precursors but higher than for type A inclusions.

Among many possible scenarios by which type B and type C inclusions could be related is the following. Consider a population of spinel-rich aggregates composed mostly of melilite + spinel which differ primarily in terms of melilite grain size. All of the aggregates are exposed to a cooling gas in which products of reactions (1) and (2) are more stable than melilite + spinel. The finergrained aggregates react to produce anorthite + diopside and eventually become type C inclusions. In contrast, the coarser-grained aggregates have little or no spinel-melilite interfaces exposed to the gas and so they do not react substantially according to reactions (1) and (2). Instead, progressively more åkermanitic melilite condenses. Eventually, at lower temperatures, the melilite itself becomes unstable and reacts with the gas to form pyroxene. These coarse-grained aggregates are parental to type B inclusions. The survival of type A inclusions would presumably be due to a fractionation event which removed these relatively coarsegrained melilite-rich aggregates prior to the reaction which produced type B's.

Al-rich chondrules. Ca-, Al-rich inclusions are relatively rare in ordinary [40-44] and enstatite [45] chondrites. Bischoff and Keil [44] classified these objects as "irregularly-shaped inclusions" and "Al-rich chondrules". They did not attempt to correlate Al-rich chondrules with any specific group of inclusions from Allende although some Allende inclusions described in [3,46] are similar. Al-rich chondrules tend to be finer-grained than coarse-grained inclusions from carbonaceous chondrites. Since Na<sub>2</sub>O is quite volatile in silicate melts [13,47,48], the frequent presence of glass and skeletal fassaite [44] together with Na<sub>2</sub>O contents usually in excess of 1 wt.% [44,45], suggests that cooling rates were faster for Al-rich chondrules than for Allende coarse-grained inclusions [49].

Average  ${\rm CaO/Al_2O_3}$  ratios of type C's  $(0.7\pm0.2)$  and Al-rich chondrules from ordinary chondrites  $(0.7\pm0.1)$  for data of [41,43]) are within error of each other and that of the solar value (0.77; [31]).  ${\rm CaO/Al_2O_3}$  ratios of Al-rich chondrules from enstatite chondrites  $(0.5\pm0.1)$  are lower than the solar value but still within error of those in type C inclusions. Thus,  ${\rm CaO/Al_2O_3}$  ratios are consistent with the possibility that type C's are precursors to Al-rich chondrules. On the

other hand,  $\text{CaO/Al}_2\text{O}_3$  ratios in types A and B inclusions  $(1.1 \pm 0.1; [11,12,50])$  are generally much higher than in Al-rich chondrules, suggesting that these inclusions are not the direct precursors of Al-rich chondrules.

Relationships between the Al-rich chondrules and CAIs in Allende are obscured by the significant amounts of iron and sodium that are present in most of these inclusions. In Al-rich chondrules from ordinary chondrites, iron occurs in olivine, spinel and alteration phases [42,44]. Since it is not known how Fe is distributed among these phases, choosing any particular iron-bearing component is likely to introduce some distortion into the projection. It was found for most inclusions from ordinary chondrites, however, that the choice of Fe-bearing component has little effect on the resulting projection if there is less than 5 wt.% FeO in the bulk composition. In contrast, iron in Al-rich chondrules from enstatite chondrites is mostly in Fe-sulfides. Since it is essentially absent from the primary phase assemblage, iron can be ignored without distorting possible chemical relationships to CAIs. Indeed, it is when iron is not ignored that distortions are introduced. Sodium is present in

plagioclase phenocrysts in Al-rich chondrules and is quite volatile in silicate melts. If significant amounts of sodium were volatilized during melting, then projecting bulk compositions from AL-BITE could lead to predicted primary phase assemblages that are badly in error. In addition, small analytical errors in sodium concentrations can lead to large errors in calculated contents of Na-bearing components. Bulk compositions of Na-bearing inclusions are, therefore, projected from Na<sub>2</sub>O rather than ALBITE. The disadvantage to this approach is that variations in the amount of the Na-bearing component will show up as variations in the amount of components that contain no sodium. This can increase the complexity of the resulting projections.

In Fig. 5, the bulk compositions of Al-rich chondrules [3,41,42–45] with more than 5 wt.% CaO and less than 5 wt.% each of FeO and Na<sub>2</sub>O are projected from olivine (FORSTERITE-FAY-ALITE), PEROVSKITE and Na<sub>2</sub>O onto the plane AK16.7 melilite-QUARTZ-SPINEL. Also shown are projected composition fields for primary phase assemblages in types A, B and C inclusions [3,11,12]. Bulk compositions of most Al-rich

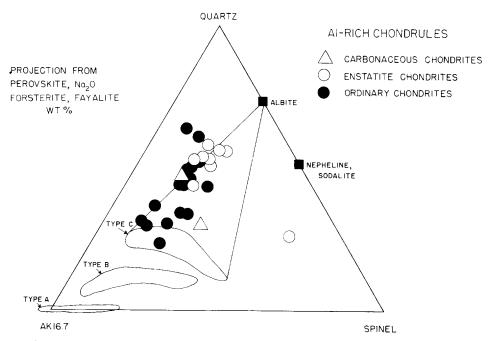


Fig. 5. Bulk compositions of Al-rich chondrules projected from olivine (FORSTERITE-FAYALITE), PEROVSKITE and Na<sub>2</sub>O onto the plane defined by AK16.7 melilite-QUARTZ-SPINEL. Also shown are fields for primary bulk compositions of type A, B [11,12] and C [3] inclusions.

chondrules plot within error of a triangle with a vertex at ALBITE and a base defined by the bulk compositions of type C inclusions. This is consistent with the formation of Al-rich chondrules by the addition of olivine and albite to type C's. A similar triangle could be drawn using bulk compositions of type B's at a base. Differences in CaO/Al<sub>2</sub>O<sub>3</sub> ratios between bulk compositions of type B's and Al-rich chondrules, however, suggest that these inclusions are not directly related to each other. Bulk compositions of most Al-rich chondrules do not plot in a triangle defined by SODALITE or NEPHELINE and type C precursors. This implies that prior to melting of the inclusions, sodium was in albite rather than in nepheline or sodalite. This conclusion is independent of whether or not sodium was significantly volatilized during melting.

Bulk compositions of Al-rich chondrules from carbonaceous chondrites and all but two from ordinary chondrites plot within error of a triangle with a vertex at ALBITE and a base defined by the bulk compositions of type C's. The two aberrant points represent the inclusions with the lowest CaO contents (< 6 wt.%) of those plotted so they are the most likely to be in error. In Fig. 6, wt. % FORSTERITE component is plotted against wt.% QUARTZ for those Al-rich chondrules shown in Fig. 5. Bulk compositions of Al-rich chondrules from ordinary and carbonaceous chondrites plot within the triangle defined by FORSTERITE, AL-BITE and the bulk compositions of type C inclusions. Hence, Al-rich chondrules from ordinary chondrites are consistent with their formation by the addition of olivine and albite to type C precursors.

In Figs. 5 and 6, bulk compositions of most Al-rich chondrules from enstatite chondrites are consistent with being mixtures of olivine, albite and type C precursor. These figures were constructed, however, assuming that FeO was primary. Since the primary phases in Al-rich chondrules from enstatite chondrites are Fe-free, Fe should be ignored. When this is done, about half of the bulk compositions project outside the ALBITE-type C triangle in Fig. 5. Thus, the presence of Al-rich chondrules from enstatite chondrites in the ALBITE-type C triangle is partly an artifact of the projection. These objects probably did not form by the addition of olivine and albite to type C's.

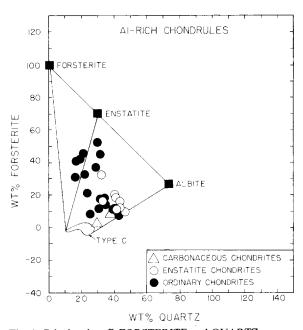


Fig. 6. Calculated wt.% FORSTERITE and QUARTZ components for bulk compositions of Al-rich chondrules in the system AK16.7-QUARTZ-SPINEL-PEROVSKITE-FOR-STERITE-FAYALITE.

In Fig. 7, bulk compositions for the Al-rich chondrules shown in Fig. 5, are projected from EN-STATITE, PEROVSKITE, FeO and Na2O onto the plane AK16.7 melilite-QUARTZ-SPINEL. With the exception of ALHA77295 [45], Al-rich chondrules from enstatite chondrites plot within error of a triangle defined by ALBITE and the bulk compositions of type C's. They are consistent with the addition of enstatite and albite to type C precursors as are most Al-rich chondrules from ordinary chondrites. On the other hand, bulk compositions of several Al-rich chondrules from ordinary chondrites plot outside the ALBITE-type C triangle. They are inconsistent with an origin by combining enstatite and albite with type C's. A simple model for the formation of Al-rich inclusions is that those from ordinary chondrites formed by the addition of olivine and albite to type C precursors while those from enstatite chondrites formed by the addition of enstatite and albite to type C precursors.

In the above discussion, addition of components was presented on the basis of mass balance relationships without attempting to explore just how they were added to type C's. Reactions which produced type C inclusions themselves are strongly

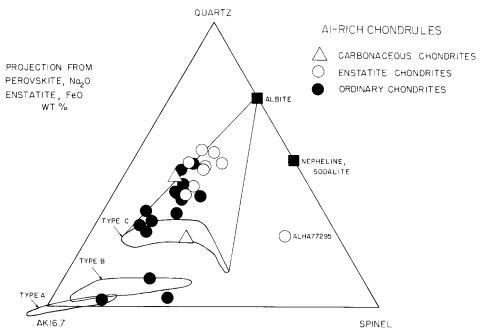


Fig. 7. Bulk compositions of Al-rich chondrules projected from ENSTATITE, PEROVSKITE, FeO and Na<sub>2</sub>O onto the plane defined by AK16.7 melilite-QUARTZ-SPINEL. Also shown are fields for primary bulk compositions of type A, B [11,12] and C [3] inclusions.

constrained because the reactant and product phase assemblages are uniquely determined for each inclusion by its major element bulk composition. In contrast, major element bulk compositions are insufficient to uniquely determine primary albite/forsterite or albite/enstatite ratios for Alrich chondrules because of analytical uncertainties and the possibility that substantial amounts of sodium were volatilized during melting. Hence the mechanisms by which these components were introduced into Al-rich chondrules are not as well constrained as they are for type C's. If, however, it is assumed that reactions to form albite in Al-rich chondrules did not involve the exchange of Ca or Al from the coexisting gas, then a likely reaction would be:

$$AN + SP + 2Na_2O_{(g)} + 12SiO_{2(g)} = 4AB + DI$$
 (4)

Since ALBITE contains Al, reaction (4) or something similar must have occurred in order for bulk Al/Ca ratios to be conserved. In contrast, neither FORSTERITE nor ENSTATITE contains any Ca or Al. Hence it is not known if olivine and/or enstatite were direct vapor-to-solid condensates which were mechanically mixed in with type C

material or if these phases formed by reaction of the gas with pre-existing solids [21].

The most likely source region for the refractory component in Al-rich chondrules is similar to the one that gave rise to type C inclusions. There is, therefore, at least one population of CAIs that is a reasonable precursor for Al-rich chondrules. Since type C's and Al-rich chondrules have average Ca/Al ratios that are near chondritic, they may represent the high-temperature component accessed by most chondrites.

Chondrules. Based on major, minor and trace element bulk compositions, it is likely that the common ferromagnesian chondrules of ordinary and enstatite chondrites were originally random mixtures of various complex components which were later melted [5]. Al-rich chondrules [44,45] and hence type C inclusions may have been the dominant refractory component.

Other inclusion types. Marvin et al. [26] gave glass analyses for several glass-spinel inclusions from Allende. The composition of one of these, glass G, is shown in Fig. 1 projected from SPINEL and

PEROVSKITE. It plots near the intersection of the AN-DI and C3A-SiO<sub>2</sub> joins, consistent with being a type C inclusion whose melilite had completely reacted away. If inclusion G was a type C inclusion, then it cooled more rapidly than other type C's, possibly due to a high velocity impact, as suggested by [52].

Possible genetic relationships of type C's to other inclusion types are tenuous. Fine-grained inclusions for which analyses are available have substantially lower  $CaO/Al_2O_3$  ratios (< ~ 0.2 [53,54]) than do type C's. It is, however, possible that prior to open system alteration, these inclusions had bulk compositions similar to those expected for type C precursors. Spinel-, hibonite-rich inclusions from Murchison have been described by Macdougall [55,56] and MacPherson et al. [57]. These inclusions have variable amounts of spinel, hibonite and perovskite and conceivably represent an extension of type C precursors to more spinelrich compositions. Spinel/melilite ratios and hibonite contents are, however, much higher than in type C precursors. There is a large gap in composition between the two groups.

## 3.2. Origin of type C inclusions as liquid condensates

It was shown above that bulk compositions of type C inclusions are consistent with an origin by vapor-to-solid condensation followed by melting. Thus, the principal argument used by Wark [3] against such a model is no longer compelling. If type C inclusions formed as liquid condensates, then their relationship to types A or B inclusions is obscure. As solid condensates, type C's are related to type A's. Condensation of solids to form type C's can take place at the low total pressures  $(10^{-6}-10^{-4})$  atm) thought to have existed in the primitive solar nebula [58,59]. Forming liquids in the protoatmosphere of giant gaseous planets has been proposed [60], but this leads to the difficult dynamic problem of how to extract such condensates from the gravity field of a giant planet. One possibility [6,61] is that melts condensed metastably at lower nebular pressures, but this requires substantial supersaturation of the vapor with respect to the stable solid condensates. High supersaturations have been achieved experimentally [63,64] but they are very specific to the particular systems and experimental conditions studied. The experiments also clearly indicate that there are conditions for which supersaturation would be negligible. Moreover, meaningful quantitative calculations for the nucleation behavior of relevant solids in the solar nebula are not possible at this time. Neither sticking efficiencies nor surface energies, which are essential for such calculations, are accurately known for Ca-, Al-rich phases. Thus, metastable nucleation of type C's as liquids must be regarded as speculative. In summary, although none of the objections raised above is fatal to a liquid condensation model, we consider the formation of type C's as solid condensates to be less contrived.

## 3.3. Implications for gas-solid reactions in the solar nebula

Reactions (1) and (2) are not predicted by condensation calculations for a cooling gas of solar composition [21,24,25,34]. Instead, spinel and gehlenitic melilite react to form anorthite and åkermanitic melilite. This is followed at lower temperatures by reaction of åkermanitic melilite to form diopside. Reactions (1) and (2) probably occurred metastably after the initial melilite decomposition reaction had been overstepped. The high spinel contents of type C precursors relative to those of type A's or equilibrium condensates from a cooling gas of solar composition could be due to mestatable condensation of spinel after the gehlenite reaction had been overstepped. Similar overstepping of stable reactions may be responsible for the formation of type B inclusions.

### 4. Conclusions

Type C inclusions are probably a spinel-rich class of type A's that reacted with silica from a coexisting gas to produce anorthite plus diopside. The reaction melilite + spinel +  $SiO_{2(g)} \rightarrow$  anorthite + diopside occurred instead of reactions predicted by equilibrium condensation calculations, probably due to overstepping of melilite decomposition reactions. Type C's are possible precursors to Al-rich chondrules in ordinary and enstatite chondrites.

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