

ORIGIN OF SPINEL-RICH CHONDRULES AND INCLUSIONS IN CARBONACEOUS AND ORDINARY CHONDRITES

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**Abstract.** Our evaluation of three models of the origin of spinel-rich chondrules and inclusions includes new calculations of the major-element refractory mineral condensation sequence from a gas of solar composition over a wide pressure interval. Our condensation calculations show that spinel-rich chondrules did not crystallize from metastable liquid condensates, and that spinel-rich inclusions are not aggregates of refractory nebular condensates. We propose that spinel-rich objects are fractionated distillation residues of small aggregates of primitive dust that lost Ca,Si-rich partial melts by evaporation, ablation, or splashing during collisions. This model also explains why spinel-rich chondrules and inclusions: (1) are usually smaller than melilite-rich chondrules and inclusions; (2) often have highly fractionated trace-element compositions; and (3) usually do not contain Pt-metal nuggets even when they are more enriched in the Pt-group metals than nugget-bearing melilite-rich objects.

Introduction

Two types of spinel-rich objects occur in chondrites: (1) spinel chondrules, which consist primarily of spinel (and lesser amounts of hibonite); and (2) spinel inclusions, which consist primarily of spinel and clinopyroxene (and whose irregular shape demonstrates that they were never molten). Spinel-rich inclusions are usually interpreted to be aggregates of refractory nebular condensates, and spinel-rich chondrules are usually interpreted to have formed by the melting of such aggregates [Macdougall, 1979, 1981; MacPherson and Grossman, 1982; MacPherson et al., 1983]. Therefore, the origins of these objects are at least indirectly related, especially since some of the inclusions have recently been interpreted to be complex aggregates of smaller, rounded spinel-rich objects that, like spinel-rich chondrules, may be igneous [Kornacki and Cohen, 1983a; Cohen et al., 1983].

In this paper, we review the mineralogy and chemistry of spinel-rich chondrules and inclusions in carbonaceous and ordinary chondrites, and discuss selected aspects of their chemistry and petrology. We then examine the condensation of major-element refractory phases in the solar

nebula, since recent thermodynamic data for calcium aluminates have allowed us to calculate new stability fields for highly refractory condensates in a gas of solar composition [Fegley, 1982a] and the roles of hibonite (which is common in spinel-rich objects) and calcium dialuminate (which is rare in these objects) during condensation can now be investigated for the first time. Finally, we use these data to evaluate three models of the origin of spinel-rich objects: (1) condensation of metastable liquids; (2) aggregation and melting of refractory nebular condensates; and (3) melting and differentiation of primitive dust aggregates.

Occurrence, Mineralogy, and Chemistry of  
Spinel-rich Chondrules and Inclusions

Spinel-rich chondrules are one of three mineralogical varieties of Ca,Al-rich chondrules (the other two varieties are melilite-rich chondrules and 'basaltic' chondrules). Spinel-rich chondrules are small (usually < 0.5 mm), rounded objects that contain spinel, perovskite, and (usually) hibonite; they are rimmed by layers of Fe-rich phyllosilicate and Al-clinopyroxene. In hibonite-bearing spinel-rich chondrules, sprays of hibonite crystals radiate into an aggregate of spinel and perovskite [Macdougall, 1981; MacPherson et al., 1983].

Spinel-rich chondrules are the most common variety of refractory inclusion in C2 chondrites. They have not been reported in type 3 carbonaceous or ordinary chondrites, but similar objects are constituents of several kinds of irregular, spinel-rich inclusions in chondritic meteorites. These inclusions have been variously classified as spinel-hibonite (SH) inclusions and spinel-pyroxene aggregates (in C2 chondrites), and as 'fine-grained' CAI's and rimmed/unrimmed complex CAI's (in C3 chondrites). Cohen et al. [1983] called these rimmed, rounded constituents of refractory inclusions 'concentric objects.' The 'nodular' spinel-(clino)pyroxene inclusions in C2 chondrites [MacPherson et al., 1983] are aggregates of rounded, rimmed spinel-rich objects; similar aggregates occur in Allende (Figure 1a) [Kornacki and Cohen, 1983b] and Mokoia (Figure 1b). Many refractory inclusions in CV3 chondrites that are traditionally classified as 'fine-grained' CAI's are complex aggregates of even smaller rounded spinel-rich objects (Figure 1c) that could have an igneous origin [Wark and Lovering, 1977; Kornacki and Cohen, 1983a]. Bischoff and Keil [1983] have described spinel-rich inclusions in ordinary chondrites. Finally, small, rounded, spinel-rich objects (and aggregates of these) form refractory nodules in oli-

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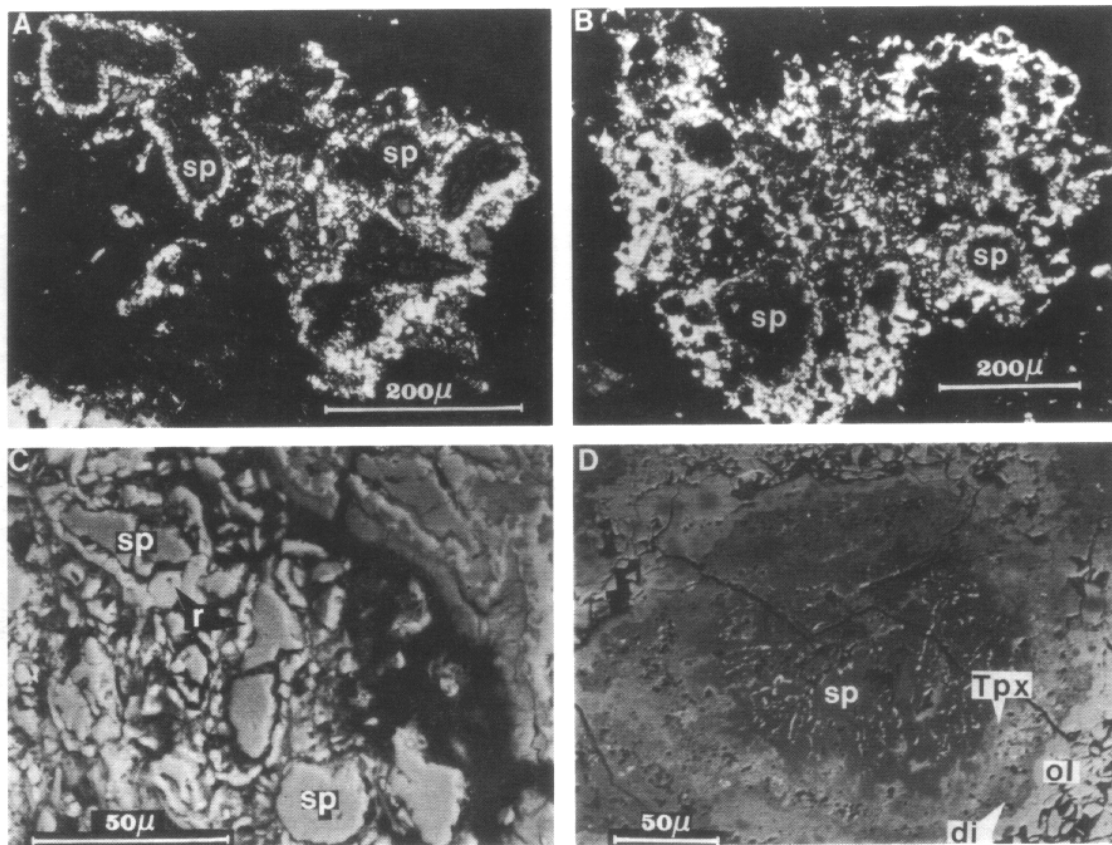


Fig. 1. Spinel-rich objects in Allende (a,d) and Mokoia (b,c); (a,b) Transmitted light photomicrographs (crossed nicols); (c,d) Back-scattered electron images. (a,b) These inclusions are botryoidal aggregates of rounded spinel-rich bodies (sp) rimmed primarily by Al-clinopyroxene and olivine (bright). (c) 'Fine-grained' inclusions are aggregates of smaller spinel-rich bodies (sp) rimmed primarily by Al-clinopyroxene (r). (d) This refractory nodule in an olivine-rich inclusion (ol) has a core of spinel (sp) and perovskite (bright blebs) rimmed by Ti-Al-pyroxene (Tpx) and Al-diopside (di).

vine-rich inclusions in carbonaceous chondrites (Figure 1d) [Ikeda, 1982; Kornacki, 1983] and ordinary chondrites [Noonan et al., 1978].

There are only a few trace-element analyses of spinel-rich chondrules. BB-3, a spinel-hibonite chondrule, has a Group III REE pattern (i.e., the volatile REE Eu and Yb are depleted relative to the other REE). Refractory lithophile and siderophile trace elements are enriched to ~30X chondritic abundances, but trace phases enriched in Pt-group metals have not been observed [Tanaka et al., 1980]. Spinel-rich concentric objects probably have Group II REE patterns, associated refractory trace-element fractionations, and  $^{16}\text{O}$  and  $^{50}\text{Ti}$  isotopic anomalies (since these chemical features characterize spinel-rich inclusions of which concentric objects are the major constituent [Grossman and Ganapathy, 1976b; Mason and Martin, 1977; Clayton et al., 1977; Niederer et al., 1981]). Mg isotopic anomalies due to the decay of  $^{26}\text{Al}$  occur in some spinel-hibonite chondrules (e.g., BB-1 and BB-4), but not in others (e.g., BB-6) [Hutcheon et al., 1980].

#### Condensation of Aluminates in the Solar Nebula

Although hibonite is commonly found in many varieties of refractory chondrules and inclusions in primitive meteorites, no comprehensive chemi-

cal equilibrium calculations for hibonite and other calcium aluminates were made until those of Fegley [1982a], despite their potential importance for deciphering the history of these objects. Grossman [1972] suggested that hibonite is the first major-element condensate in a cooling solar composition gas (because of the relative rarity of corundum in refractory inclusions), but lack of thermodynamic data prevented him from calculating condensation temperatures. Blander and Fuchs [1975] used activity coefficients measured in slags to estimate free energy values for hibonite and calcium dialuminate ( $\text{CaAl}_2\text{O}_7$ ), and to calculate their condensation temperatures at  $p = 10^{-3}$  bar. However, accurate and internally consistent thermodynamic data for all five calcium aluminates and  $\text{CaO-Al}_2\text{O}_3$  melts were not available until the study by Allibert et al. [1981], which Fegley [1982a] used to calculate the stability of corundum and the calcium aluminates in a solar composition gas over wide temperature and pressure ranges. These calculations have been extended and slightly revised in the present paper.

#### Method of Calculation

Element abundances are from Cameron [1973]. Stability fields of the various aluminates were

calculated using standard methods described by Fegley [1980]. Thermodynamic data from several sources were used: JANAF tables [1971 and supplements] for gases, corundum, liquid  $\text{Al}_2\text{O}_3$ , and spinel; Allibert et al. [1981] for calcium aluminates; Haas et al. [1981] for gehlenite; and Robie et al. [1978] for perovskite. (The use of thermodynamic data from different compilations is undesirable if different element reference states and Gibbs energy functions are used by the different compilers. Since the same element reference states and virtually identical Gibbs energy functions were used in all of the above references, however, there are no errors due to internally inconsistent data. Uncertainties in the condensation curves due to uncertainties in the thermodynamic data were calculated, and they are too small to reverse the condensation sequence for any of the phases considered.)

### Condensation Sequences

The results of the condensation calculations for the calcium aluminates and other refractory phases are shown in Figure 2 and Table 1. Hibonite and  $\text{CaAl}_4\text{O}_7$  are the only two stable calcium

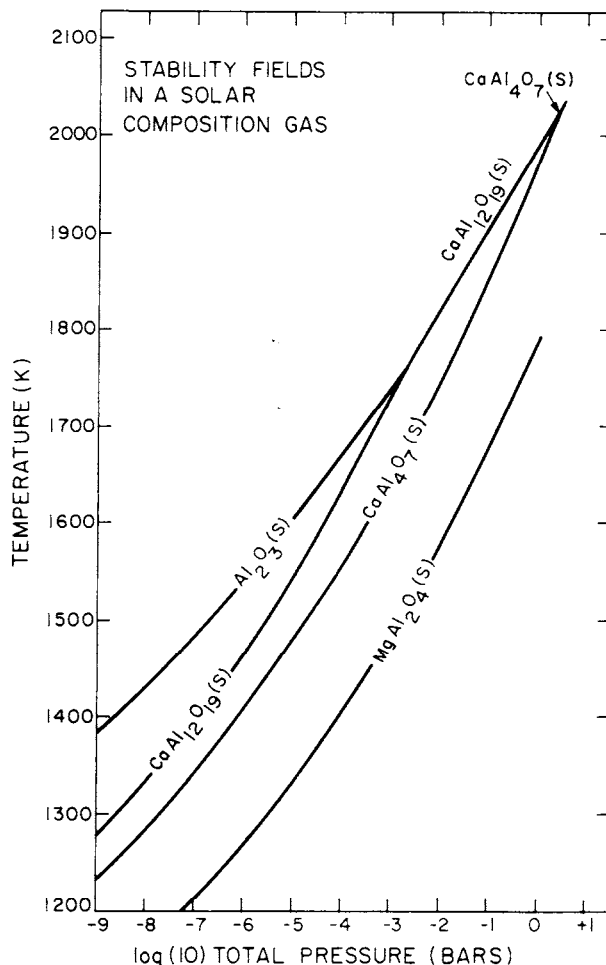


Fig. 2. Stability fields of aluminate minerals in a solar composition gas. The curves labelled  $\text{Al}_2\text{O}_3(\text{s})$ ,  $\text{CaAl}_{12}\text{O}_{19}(\text{s})$ ,  $\text{CaAl}_4\text{O}_7(\text{s})$ , and  $\text{MgAl}_2\text{O}_4(\text{s})$  are the condensation curves for corundum, hibonite, calcium dialuminate, and spinel, respectively.

TABLE 1. Refractory Mineral Condensation Temperatures (K)

Mineral	p(bars)				
	$10^{-9}$	$10^{-7}$	$10^{-5}$	$10^{-3}$	$10^{-1}$
$\text{Al}_2\text{O}_3$	1386	1487	1605	1741	†
$\text{CaAl}_{12}\text{O}_{19}$	1280	1401	1548	1730	1903
$\text{CaTiO}_3$	1301	1404	1529	1677	1856
$\text{CaAl}_4\text{O}_7$	1233	1345	1480	1646	1856
$\text{Ca}_2\text{Al}_2\text{SiO}_7$	1228	1333	1457	1608	1790
$\text{MgAl}_2\text{O}_4^*$	1113	1214	1337	1488	1678

\*Upper limit only (see text).

†Does not form.

aluminates; the other three calcium aluminates ( $\text{CaAl}_2\text{O}_4$ ,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ , and  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ ) do not form. Corundum is also stable. Blander [personal communication, 1982] reports that  $\text{CaAl}_2\text{O}_4$  is stable over a small temperature interval. Our results do not confirm this, and the discrepancy is unexplained. However, only this work and that of Fegley [1982a] have included all five calcium aluminates, used internally consistent thermodynamic data, and have covered such a wide range of temperature and pressure.

The nature of the initial condensate varies with pressure: corundum for  $p < 10^{-2.63}$  bar, hibonite for  $p < 10^{+0.4}$  bar,  $\text{CaAl}_4\text{O}_7$ , and (at highest pressures) a  $\text{CaO}\text{-Al}_2\text{O}_3$  melt. Uncertainties in the temperature and pressure at the corundum-hibonite intersection are  $10^{\pm 0.5}$  bar and  $\pm 64$  K (at  $T = 1769$  K). The hibonite- $\text{CaAl}_4\text{O}_7$  intersection has uncertainties of  $10^{+0.75}$  bar and  $10^{-0.44}$  bar, and  $+75$  K and  $-40$  K (at  $T = 2023$  K). Our results for corundum, hibonite, and  $\text{CaAl}_4\text{O}_7$  agree qualitatively with those of Blander and Fuchs [1975] at  $p = 10^{-3}$  bar.

The effect of the prior condensation of the calcium aluminates on the condensation of other refractory minerals is shown in Figure 2 and Table 1. The condensation sequence melilite  $\rightarrow$  spinel is not reversed by the use of more accurate thermodynamic data, or by the prior condensation of hibonite and  $\text{CaAl}_4\text{O}_7$ . (The spinel condensation curve is only an upper limit, since it is calculated assuming that the activity of  $\text{Al}_2\text{O}_3$  is unity; the actual spinel condensation curve is probably 5-10 K lower at any pressure.)

### Discussion

#### Condensation of Metastable Liquids

Several factors lead us to consider the condensation of metastable liquids as a model for the origin of spinel-rich chondrules. First, it is possible that the parent liquids condensed directly from a gas, rather than forming by the melting of pre-existing solids. Second, the nucleation constraints on liquids and solids indicate that metastable liquids and amorphous solids, not crystalline solids, probably condense from low-pressure vapors [Blander and Katz, 1967; Blander and Fuchs, 1975; Cohen, 1981a; Cameron and Fegley, 1982]. Third, several authors have recently calculated the composition of metastable liquids in the solar nebula.

Blander and Fuchs [1975] found that the first liquid to condense is  $\text{Al}_2\text{O}_3$ -rich and contains

~15 wt % CaO. As the temperature decreases, the amount of CaO and SiO<sub>2</sub> in the liquid condensate increases. Only small amounts of MgO are present in the initial liquid condensate: at an SiO<sub>2</sub> concentration of ~1-2 wt %, the SiO<sub>2</sub>/MgO ratio (in wt %) is ~150 (compared to the cosmic ratio of ~1.4). Wagner and Larimer [1978] found that the initial liquid condensate is Al<sub>2</sub>O<sub>3</sub>- and TiO<sub>2</sub>-rich. Substantial amounts of SiO<sub>2</sub>, CaO, and MgO become incorporated in the liquid at lower temperatures. Fegley and Kornacki [1982] (using data from Allibert et al. [1981] and Fegley [1982b]) found that the initial liquid condensate in the CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system is Al<sub>2</sub>O<sub>3</sub>-rich. They also found a high SiO<sub>2</sub>/MgO ratio in the initial liquid condensate (~210), and observed that the amount of MgO in the liquid condensate increases very slowly at lower temperatures.

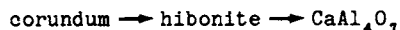
The results of these three studies agree on an important point: the most refractory metastable liquid condensates contain abundant normative corundum, hibonite, and CaAl<sub>4</sub>O<sub>7</sub>, but only small amounts of spinel. Their bulk compositions are significantly different than those of spinel-rich chondrules, which therefore probably did not crystallize from metastable liquid condensates.

#### Aggregation and Melting of Refractory Nebular Condensates

Macdougall [1981] and MacPherson et al. [1983] concluded that spinel-hibonite chondrules in C2 meteorites formed by the melting of spinel-rich aggregates of nebular condensates, and that the irregular spinel-hibonite inclusions in C2 chondrites are their likely precursors. If the spinel-rich concentric objects that are constituents of botryoidal inclusions, 'fine-grained' CAI's, and some olivine-rich inclusions are also igneous objects, they could have a similar origin. If they are not igneous, they may also be precursor material from which spinel-rich chondrules formed.

Condensation calculations lead to specific predictions about the bulk composition, mineralogy, and textural relationships that aggregates of condensates should exhibit. The concept that highly refractory phases formed by equilibrium condensation reactions should be carefully evaluated to determine how well that model explains the compositions, mineralogy, and textures of the likely precursors of spinel-rich chondrules.

At  $p < 10^{-2.6}$  bar, the initial aluminate condensation sequence is:

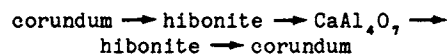


Perovskite also forms at comparable temperatures and can coexist with hibonite and lower temperature phases. If reactions were incomplete, condensate assemblages from this stage that became isolated from further reactions would consist of relict corundum surrounded by hibonite, or relict hibonite surrounded by CaAl<sub>4</sub>O<sub>7</sub>. Perovskite crystals would occur on the surface of hibonite (which forms at a higher temperature) or enclosed in CaAl<sub>4</sub>O<sub>7</sub> (which forms at a lower temperature).

At lower temperatures, CaAl<sub>4</sub>O<sub>7</sub> reacts to form gehlenite and then spinel; CaAl<sub>4</sub>O<sub>7</sub> is consumed during spinel formation. Condensate assemblages

from this stage would consist of relict CaAl<sub>4</sub>O<sub>7</sub>, surrounded by melilite, or melilite and relict CaAl<sub>4</sub>O<sub>7</sub>, surrounded by spinel. At higher pressures, first corundum and then hibonite become unstable and do not condense (Figure 2); similar reasoning can be applied to predict the mineralogy and texture of condensate assemblages under those conditions.

The mineralogy and textural features of condensate assemblages formed during more complex pressure-temperature excursions in the solar nebula can also be predicted. Under these conditions, it is possible to produce condensate assemblages with more refractory minerals enclosing less refractory ones. For example, an isobaric cooling path at 10<sup>-3</sup> bar from 1800 K to 1600 K followed by an isothermal pressure drop to 10<sup>-5</sup> bar would produce the following condensation sequence:



Cameron and Fegley [1982] and Morfill [1983] discussed the feasibility of such complex pressure-temperature histories in the solar nebula; they independently concluded that grain and vapor transport mechanisms may be important processes for producing the various types of refractory chondrules and inclusions.

How well do the observed compositions, mineralogies, and textural features of the most highly refractory chondrules and inclusions compare with those predicted by condensation calculations? Fegley [1982a] concluded that BB-5, a corundum-bearing Murchison inclusion described by Bartholomew et al. [1982], and the 'coarse-grained' hibonite inclusions in Murchison described by Macdougall [1979] could be aggregates of condensates that were isolated before the onset of CaAl<sub>4</sub>O<sub>7</sub> condensation. But Fegley [1982a] and Kornacki and Cohen [1983a] concluded that spinel and spinel-hibonite objects, which account for the majority of refractory inclusions in C2 chondrites and which are common constituents of CAI's in C3 chondrites, do not have compositions, mineralogies, or textural features consistent with the predictions of condensation calculations.

Hibonite occurs in many spinel-rich chondrules and inclusions, but CaAl<sub>4</sub>O<sub>7</sub> is very rare in CAI's [Christophe Michel-Lévy et al., 1982]. More importantly, the temperature at which spinel forms by condensation (~1490 K at 10<sup>-3</sup> bar) is >100 K into the stability field of melilite (Table 1). Although these two minerals ought to coexist during condensation, spinel-rich chondrules and inclusions seldom contain melilite (or its alteration products). There is no inherent reason why spinel and melilite should fractionate in the solar nebula: melilite-rich chondrules and inclusions contain both minerals in abundance [Grossman, 1975]. Finally, perovskite is enclosed in hibonite in some hibonite-bearing inclusions [MacPherson et al., 1983], although hibonite condenses before perovskite at  $p > 10^{-6.6}$  bar (Table 1).

Spinel-rich chondrules and inclusions are not simply aggregates of crystalline condensates from an unfractionated gas of solar composition. They must have formed by more complex processes. The simplest explanation, that there are major errors

in the calculated condensation sequence, can be easily dismissed. Using the best available thermodynamic data, we find that melilite condenses at a significantly higher temperature than spinel. Thermodynamic uncertainties are not large enough to reverse the condensation sequence. There is no reason to suppose that the unintentional neglect of another phase will reverse the condensation sequence of melilite and spinel: such a hypothetical phase would have to condense before melilite to depress the condensation temperature of that mineral, and this still leaves the problem of the absence of the more stable phase in spinel-rich inclusions. The solid solution of  $\text{Al}_2\text{O}_3$  in spinel recently observed by El Goresy et al. [1983] in an Essebi ultra-refractory inclusion will raise the spinel condensation temperature, but this mechanism is not applicable to most spinel-rich chondrules and inclusions because they contain nearly pure  $(\text{Mg,Fe})\text{Al}_2\text{O}_4$  [MacPherson et al., 1983; Kornacki, 1983].

A second possibility can be explored. Some spinel forms by equilibrium condensation at a lower temperature ( $\sim 1450$  K) by the reaction [Grossman, 1972]:



Spinel-rich chondrules and inclusions contain clinopyroxene, but the above reaction should produce spinel and clinopyroxene intergrown with a reaction texture (sometimes rimming relict cores of melilite), since they form together from condensed melilite. Instead, we see mineralogically zoned objects with cores of spinel and (sometimes) hibonite that are rimmed by Al-clinopyroxene (Figure 1). Furthermore, since Ca and Al should be completely condensed by 1450 K (primarily as intimately intergrown spinel and clinopyroxene), it is again difficult to understand the low Ca/Al ratios in spinel-rich chondrules and inclusions, which now require the separation of spinel and clinopyroxene.

The third possibility involves the transport of grains in the solar nebula. An implication of this model is that a wide variety of condensate assemblages (e.g., corundum- $\text{CaAl}_2\text{O}_7$ , corundum-spinel, hibonite-melilite) would be produced by grain condensation, transport, and isolation. It is also reasonable to expect that the relative abundance of different condensate assemblages would be related to the size of their stability fields, since phases stable over a wide temperature interval will also be stable over large distances in the solar nebula. However, although hibonite has a smaller stability field than  $\text{CaAl}_2\text{O}_7$ , spinel-hibonite assemblages are the most common variety of refractory inclusion in C2 chondrites. Although a grain transport model is qualitatively appealing, it does not explain the almost perfect selectivity in producing spinel and spinel-hibonite chondrules and inclusions.

The final possibility is condensation of spinel-rich material from a fractionated gaseous reservoir with a noncosmic chemical composition. Many spinel-rich inclusions have Group II REE patterns [Grossman and Ganapathy, 1976b; Mason and Martin, 1977] that can be explained by the loss of highly refractory condensates prior to their formation, but the separation of highly refractory trace phases alone (e.g., perovskite)

probably caused the trace-element depletions and fractionations in Group II inclusions [Davis and Grossman, 1979]. The major-element chemistry of any region of the nebula should not have been greatly altered by the loss of trace phases. Indeed, the occurrence of Group II REE patterns in melilite-rich CAI's (e.g., the Ca,Al-rich chondrule A-2 of Conard et al. [1975], CG-5 of Grossman and Ganapathy [1976a], CG-12 of Davis and Grossman [1979], 3643 of Wark [1980], 4691 of Mason and Taylor [1982], and the FUN inclusion EK 1-4-1 [Nagasawa et al., 1982]) suggests that Group II REE patterns were caused by the loss of trace phases that did not significantly alter the local chemistry of the nebula: the mineralogy and Ca/Al ratios in these Group II CAI's approximate those predicted for cosmic systems at high temperatures. The loss of Ca-rich major phases seems necessary for isolated spinel condensation, but it is difficult to explain how to deplete Ca (but not Al) from nebular gas, since gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) is the major Ca sink and the two elements occur in subequal amounts in gehlenite and in cosmic systems [Cameron, 1973].

Because it is difficult to produce spinel-rich aggregates of crystalline nebular condensates, we conclude that spinel-rich chondrules and inclusions did not form from such material.

#### Melting and Differentiation of Primitive Dust Aggregates

The interpretation that refractory inclusions formed by the distillation and melting of primitive dust aggregates, rather than by the aggregation of refractory nebular condensates, has been a persistent (albeit a minority) one [Kurat, 1970; Chou et al., 1976; Clayton, 1977; Cohen et al., 1983]. Experimental results [Notsu et al., 1978; Hashimoto et al., 1979; King, 1982] and an analysis of oxygen isotope anomalies [Wood, 1981] support this model, as do recent models of solar nebula physics (which suggest that the solar nebula was not heated to a high enough temperature to completely vaporize interstellar dust) [Cameron, 1978; Cameron and Fegley, 1982]. Distillation models have been applied primarily to the origin of melilite-rich chondrules [Kurat et al., 1975; Wark and Lovering, 1982a], which have relatively unfractionated major- and trace-element chemical compositions [Mason and Taylor, 1982].

The formation of spinel-rich chondrules and inclusions by any mechanism required the physical separation of one or more Ca-rich phases from spinel. Cohen [1981b] and Kornacki [1981] first suggested that spinel-rich objects could form from undifferentiated material by the separation of partial melts from residual crystals during evaporative metamorphism: since spinel is the liquidus phase for CAI-composition material [Stolper, 1982], partial melting of cosmic material at high temperatures ( $>1600$  K) will produce a Ca,Si-rich melt and a spinel-rich residue as the diopside, anorthite, and gehlenite components sequentially melt in preference to spinel. There are several mechanisms that could separate Ca,Si-rich liquids from residual spinel crystals in the nebula to produce the chemical and mineralogical fractionation necessary to form spinel-rich chondrules and inclusions. These include evaporation, ablation, and splashing during collisions.

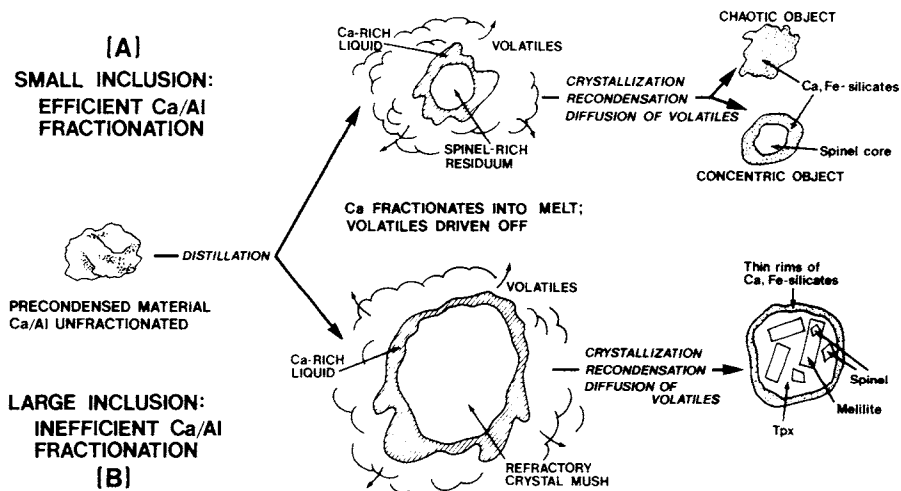


Fig. 3. Origin of spinel-rich and melilite-rich chondrules. Ca could have fractionated from Al during partial melting and differentiation of unfractionated precondensed material. (a) Fractionation was efficient in small inclusions. Ca,Si-rich 'chaotic objects' [Cohen et al., 1983] formed from melt that was physically separated from residual spinel. (Chaotic objects and small concentric objects are common in 'fine-grained' inclusions.) (b) Fractionation was inefficient in large inclusions, which retained typical CAI compositions. Spinel, melilite, and Ti-Al-pyroxene crystallized slowly from the partial melt, forming 'coarse-grained' melilite-rich chondrules.

Liquids are metastable under low-pressure nebular conditions and would probably evaporate more rapidly than residual spinel would sublimate [Cohen et al., 1983; MacPherson et al., 1983]. Wood [1983] has argued that chondrules and CAI's were formed from interstellar dust aggregates as they fell into the solar nebula during the collapse of the interstellar cloud fragment that became the solar system. The high initial kinetic energy of the infalling solid material was dissipated by aerodynamic drag in the nebular gases, which converted it to heat. Aggregates that fell into the nebula sufficiently near the protosun would be heated to peak temperatures capable of distilling them to CAI compositions. During this process, partial melts could be ablated from the surface of proto-CAI's.

Finally, partially molten proto-CAI's involved in energetic collisions would be disrupted into their liquid and solid constituents. Individual spinel crystals and small clumps of crystalline spinel that were liberated during these collisions could have formed the individual spinel crystals and spinel-rich concentric objects found in spinel inclusions. They also could have aggregated into the spinel 'palisades' and chains that were eventually incorporated into some melilite-rich chondrules [Wark and Lovering, 1982b].

Several of the mineralogical and chemical properties of spinel-rich objects can be explained if they distilled from relatively small aggregates of primitive dust, which requires not only the loss of a substantial amount (~95 wt %) of precondensed material [Chou et al., 1976], but also the loss of refractory Ca-rich components in a molten state. Both processes would have operated more efficiently in small aggregates of primitive dust than in large ones (which are more likely to have been the precursors of melilite-rich objects). Two factors would have contributed to this effect: diffusion path lengths and surface area/volume ratios.

Since volatile constituents leaving a solid or liquid object must diffuse through the volume to reach the surface, small objects would devolatilize more efficiently than large ones, especially if heating was relatively rapid. The effect of the surface area/volume ratio (which for a sphere is inversely proportional to the diameter) would also be important for efficient differentiation. The importance of the surface area during melting and evaporation is utilized by materials engineers in industrial processes, such as freeze-drying and the fusion of silica (the 'G.E. Process'), in which raw materials are reduced to small size to facilitate devolatilization and melting. A more familiar analogy involves the flow of heat rather than the flux of volatile materials, but the reasoning is similar. Tsuchiyama et al. [1981] experimentally verified that the volatilization rate of Na from liquid silicate spheres is a function of their size.

Spinel-rich chondrules (and concentric objects in spinel-rich inclusions) are typically ~10-100X smaller than melilite-rich chondrules. In a 0.1 mm spinel-rich chondrule, the diffusion path length from the core is 100X smaller and the surface area/volume ratio is 100X larger than in a 1 cm melilite-rich chondrule. Both factors contribute to the efficiency with which the smaller precursor of the spinel-rich chondrule could have lost Ca,Si-rich melt by either evaporation or ablation from its surface (Figure 3).

The relationship between the initial size and the final chemistry of primitive dust aggregates can also explain why highly-fractionated Group II REE patterns and refractory noble metal depletions are usually found in spinel-rich inclusions. Wood [1981] noted that Group II inclusions could have distilled from primitive dust aggregates that were already depleted in super-refractory trace elements; Fegley and Kornacki [1983] identified Fremdlinge (or their precursors) as specific candidates for the trace phase

that was fractionated in the presolar interstellar cloud or the solar nebula to produce Group II REE patterns. Small primitive dust aggregates, which could fractionate efficiently during evaporative metamorphism to form spinel-rich objects, would have incorporated a smaller number of dust grains than large aggregates did. Thus spinel-rich objects are more likely to display chemical anomalies due to the absence of a particular variety of refractory element-enriched primitive dust grain.

Finally, this model can explain a puzzling mineralogical feature of spinel-rich objects: the absence of microscopic Pt-metal nuggets. Cameron and Fegley [1982] and Fegley and Kornacki [1983] interpret micron-sized Pt-metal nuggets that occur in melilite-rich chondrules and inclusions as evaporation residues, rather than as refractory crystalline condensates. When volatiles that are likely to have been present in primitive dust aggregates fluxed through a distilling proto-CAI, they would have enhanced the formation of metallic beads from smaller grains (as do volatile fluxes during the fire-assaying of terrestrial Pt-metal ores [Crocket and Cabri, 1981]). If these microscopic nuggets formed from submicroscopic grains, the absolute abundance of refractory noble metals may simply have been too low in small dust aggregates to have formed many micron-sized nuggets (even though their relative abundance is ~2X greater in some spinel-rich objects than in nugget-bearing melilite-rich chondrules [Tanaka et al., 1980]).

The formation of Pt-metal nuggets during evaporative metamorphism also may have required the presence of a slowly cooled silicate melt in which immiscible metal droplets had sufficient time to coalesce into larger nuggets. Pt-metal nuggets in melilite-rich chondrules are usually enclosed in melilite and Ti-Al-pyroxene (minerals that probably crystallized from slowly cooled Ca,Si-rich melts [Paque and Stolper, 1983]), but they only adhere to spinel [El Goresy et al., 1978]. Since many spinel-rich objects may consist of residual material from which partial melts were rapidly lost by evaporation or ablation, and the cooling rate of spinel-rich chondrules could have been faster than the cooling rate of melilite-rich chondrules (since spinel chondrules are usually smaller than melilite chondrules), spinel-rich objects may not have been suitable systems in which Pt-metal nuggets could form.

Many spinel-rich inclusions have highly irregular shapes that range from botryoidal aggregates of nodules to sinuous sheets [MacPherson et al., 1983]. These unusual contorted, convoluted morphologies can be explained if spinel-rich concentric objects aggregated into complex botryoidal or sheeted inclusions that subsequently deformed plastically (during sintering) into their present shapes [Kornacki and Cohen, 1983a]. Unlike the semimolten objects that could merge into rounded melilite-rich chondrules [Wark and Lovering, 1982b], spinel-rich objects consisted largely of crystalline material and thus retained unusual aggregational textures. (The contorted, convoluted shapes of 'fluffy' Type A CAI's can also be explained by this model, except that they are complex, welded aggregates of melilite-rich objects [Wark and Lovering, 1982b; Kornacki and Cohen, 1983b].) Spinel-rich chondrules, on the

other hand, formed by the nearly total melting of spinel-rich residual material.

Spinel-rich objects are rimmed by a layer of Al-clinopyroxene that could have crystallized either from a residual film of Ca,Si-rich melt that coated the crystalline, spinel-rich core of the proto-CAI, or from a liquid or amorphous solid condensate that nucleated on the spinel substrate [Cohen et al., 1983].

### Conclusions

We conclude that the mineralogy, composition, and textural features of spinel-rich inclusions are inconsistent with the simple interpretation that they are aggregates of crystalline equilibrium condensates, and that more complex models involving only vapor-solid condensation do not adequately explain their formation. We also doubt that spinel-rich chondrules crystallized from refractory metastable liquid condensates (which are enriched in CaO and Al<sub>2</sub>O<sub>3</sub> and contain only small amounts of normative spinel).

Instead, we propose that spinel-rich objects are distillation residues of small aggregates of primitive dust that lost Ca,Si-rich partial melts by evaporation, ablation, or splashing in the solar nebula (processes that could have been widespread due to nebular turbulence or shocks at the nebular accretion front). Furthermore, we propose that the initial size of precondensed dust-balls influenced their final chemistry and mineralogy, since small dust aggregates have large surface area/volume ratios and small diffusion path lengths, and thus can differentiate efficiently by the removal of liquids from their surface. Since they sampled fewer grains, small objects preferentially preserved chemical anomalies caused by the absence of trace phases. We believe that these combined effects explain why Group II inclusions are also usually spinel-rich. We note that the absolute abundance of refractory noble metals in small, spinel-rich objects may simply be too low to have formed many microscopic Pt-metal nuggets during distillation and melting, especially if nugget formation occurred in slowly cooled melts. Finally, we propose that spinel-rich chondrules formed from molten spinel-rich distillation residues, not from molten spinel-rich aggregates of crystalline condensates. The contorted, convoluted morphologies that characterize spinel-rich inclusions may result from the sintering of complex aggregates of smaller spinel-rich objects.

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