TRANSACTIONS, ILL. STATE ACAD. SCI.
Vol. 71, No. 4 (1978)

SIMILARITIES BETWEEN TEXTURES OF DEVITRIFIED SYNTHETIC CA-AL-RICH GLASSES AND SOME CA-AL-RICH ALLENDE INCLUSIONS

Paul P. Sipiera, Jr.
Engineering, Mathematics & Physical Sciences
William Rainey Harper College
Palatine, Illinois 60067

Mohan K. Sood
Department of Earth Sciences
Northeastern Illinois University
Chicago, Illinois 60625

Abstract - When synthetic glasses of compositions similar to those found in the Type B Ca-Al-rich Allende chondrules were devitrified by heating, chondrule-like aggregates of diopside formed along with spherulitic and skeletal development of melilite and diopside. Poikilitic and eutectic growths of spinel were also common as an associated phase. These features have a resemblance to textures found in certain Allende chondrules, demonstrating that some Allende chondrules with these textures and of these compositions could also have originated by devitrification of glasses. From the results of this study, these textural similarities suggest a possible liquid → solid origin for some of the Ca-Al-rich Allende chondrules, either directly or by devitrification.

INTRODUCTION

The white Ca-Al-rich chondrules and inclusions present in the Allende Type III carbonaceous chondrite have received considerable attention due to their unusual chemistry and mineralogy and the general belief that they may represent high temperature condensates from the primordial solar nebula. Clarke et al. (1970) recognized three distinct types of white chondrules: type a, consisting of the mineral assemblage melilite-fassaite-anorthite-spinel; type b, composed of anorthite-forsterite-spinel; and type c, characterized by the assemblage nepheline-sodalite-fassaite-olivine. Grossman (1975) later reclassified these Ca-Al-rich chondrules and inclusions into two major types (Types A and B) based

on differences in abundance, morphology and composition of the clinopyroxene present. Clinopyroxene is the major phase in Type B inclusions, but it is usually absent in the Type A.

Type a chondrules, as described by Clarke et al. (1970), are characterized by their occurrence as prominent spherules with melilite (occurring as prismatic crystals) as the most abundant mineral in the assemblage (∿40 percent); pyroxenes represent approximately 30 percent of the remaining minerals, with anorthite (∿10 percent) and spinel (∿20 percent) completing the assemblage. The Type B classification of Grossman (1975) appears to be the equivalent of the Clarke et al. (1970) type a classification, and it better represents the textural results of the present study. Type b chondrules are smaller than those of type a and consist largely of prismatic crystals of anorthite with minor amounts of spinel contained within. Small amounts of forsterite generally occur interstitial to the anorthite. Type c chondrules are rare. They are extremely fine-grained and consist of sodalite, nepheline, clinopyroxene and olivine. In contrast to Clarke et al. (1970), Grossman (1975) does not consider these fine-grained chondrules in his classification scheme because of their rarity and concentrates on the more abundant coarse-grained material.

The origin of these Ca-Al-rich chondrules has been variously interpreted. Controversy exists as to whether they formed as high temperature solid condensates from a gas of solar composition (Grossman, 1972, 1973, 1975; Grossman and Clark, 1973; Grossman and Ganpathy, 1976; Grossman and Larimer, 1974; Lord, 1965; and Larimer, 1967) or by crystallization from either a supercooled liquid or a reheated solid (Blander and Katz, 1967; Blander and Fuchs, 1975; Kurat et al., 1975; Whipple, 1972; Cameron, 1973; and Chou et al., 1976).

Hypotheses such as these are based upon elemental abundance data (Cameron, 1970) and thermodynamic calculations which permit the prediction of a condensation sequence for the primordial solar nebula. These predictions are largely theoretical and lack experimental tests. In the present study we have attempted to produce the observed textures in the Type B allende chondrules as described by Grossman (1975) and discuss some possible implication for their origin.

EXPERIMENTAL PROCEDURE

The experiment was designed to observe the textures and mineralogies resulting from the subliquidus heating and later cooling of glass spherules with a range of compositions encompassing those of the Type B (Grossman, 1975) Allende chondrules (see Table 1). Due to the complexity of the system CaO-MgO-Al_2O_3-SiO_2 (Prince, 1954), only those compo-

TABLE 1. Chemical compositions of experimental glass spherules and of Ca-Al-rich Allende inclusions.

Glass Compositions	Glass Spherules Weight percent oxides SiO_2	Al_2O_3	CaO	MgO	Refractive Index
A	20.0	37.1	32.9	10.0	1.629
B	21.5	25.5	43.0	10.0	1.613
C	23.5	23.5	43.0	10.0	1.615
D	25.1	35.7	29.2	10.0	1.628
E	30.0	30.8	29.2	10.0	1.607
F	30.0	31.5	28.5	10.0	1.613
G	34.9	18.4	36.7	10.0	1.627
H	35.0	17.0	38.0	10.0	1.629
I	40.0	25.6	24.4	10.0	1.603
J	40.0	26.5	23.5	10.0	1.602
K	42.0	19.0	29.0	10.0	1.603
L	44.0	17.0	29.0	10.0	1.606
M	45.0	20.0	25.0	10.0	1.601

Sample Number	Allende inclusions Weight percent oxides SiO_2	Al_2O_3	CaO	MgO
10/5[1]	28.2	27.7	33.0	8.7
3529G[2]	29.8	31.6	26.8	10.8
31[2]	29.9	26.7	30.3	9.0
3658[2]	30.9	29.8	26.0	10.4
10/2[1]	32.8	27.8	24.4	10.4

[1] Courtesy of Louis H. Fuchs, Argonne National Laboratory

[2] Courtesy of Brian Mason, National Museum of Natural History, Washington, D. C.

sitions corresponding to the 10 percent MgO plane were examined (figure 1). Only glass compositions E and F (see Table 1) closely resemble those of actual Allende chondrules.

The experiment started with homogeneous glass spherules prepared according to a modification of the procedure described by Nelson et al. (1972). The CaO, MgO, Al_2O_3, SiO_2 used in manufacturing the glass spherules were of 99.9 percent purity and were combined in the desired proportions into rolled rods which were melted by a continuous-wave carbon dioxide laser (spot diameter ∿1mm; beam power 5-300w; wavelength 10.6 um). The use of this laser was generously supplied by Dr. Lloyd S. Nelson of Sandia Laboratories. The operation of the laser and manufacture of the glass spherules was performed by Dr. Milton Blander of Argonne National Laboratory. A rapidly rotating oxide rod was placed into the focused beam of the laser; molten droplets, ranging in size from 0.3 to 3mm, were spun off and solidified into glass during freefall in air at one atmosphere pressure.

The homogeneity of the glass spherules used in this study was determined by immersion in refractive index liquid utilizing a technique described by Sood, 1969. Determination for glass purity was made optically and, in test cases, by powder camera x-ray diffraction and electron microprobe examination. The specimens selected for devitrification were uniform in size (∿1mm) and contained no evidence of any crystallization. Nelson et al. (1972), using a similar method of forming spherules, recognized partial crystallization can occur during freefall. This was also noted in this study by the presence of "frosted" spherules.

To prevent volatilization or contamination during devitrification, the glass spherules were sealed in platinum envelopes and placed in an alundun boat in the center of the furnace to insure minimal temperature variation. The majority of the glass spherules were devitrified at temperatures of 1000° and 1100°C for periods of 10 days. Additional experimental runs were conducted on select compositions at lower temperatures (820°C) and higher (1200° to 1300°C) for comparison (see Table 2). Quenching of the devitrified spherules was instantaneous producing disequilibrium features. Many of the glass spherules flowed into irregular-shaped masses.

The furnaces used for devitrification were equipped with built-in thermocouples. To verify the accuracy of the instrumentation, measurements were taken and compared to a Pt-10 Rh thermocouple previously calibrated at the melting point of sodium chloride (800.4°C) and gold (1064.4°C). An ice bath was used as a reference junction to standardize the temperature measurements which were recorded on a millivolt potentiometer. Temperature measurements were determined to be accurate to within ±10°C of the stated values.

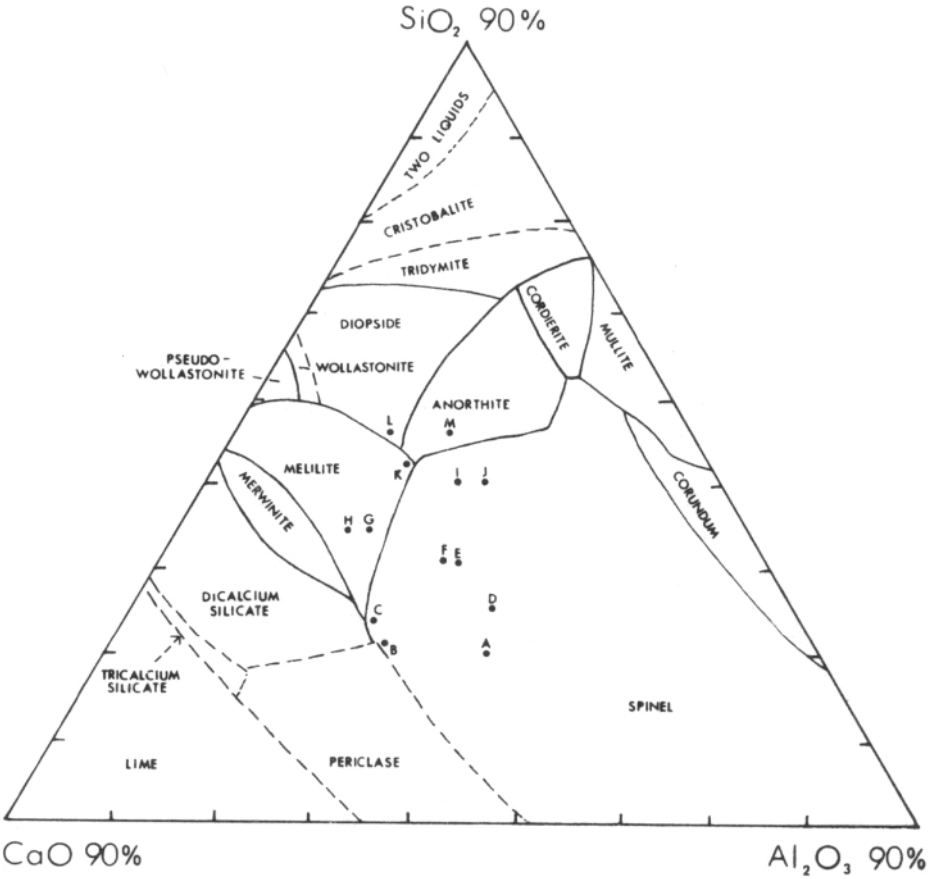

Figure 1. The 10 percent plane of the system $CaO-MgO-Al_2O_3-SiO_2$ showing the location of glass compositions (see Table 1) and their primary fields of crystallization (after Prince, 1954).

TABLE 2. Devitrification Data (Mel = melilite; Sp = spinel; Di = diopside; An = anorthite; Mer = merwinite; DCS = dicalcium silicate; Qz = quartz; Gl = glass)

Glass Comp.	Run No.	Temp C	Duration Days	Phases
A	0037	1100	10	Mel + Sp + Gl
	0016	1000	10	Mel + Sp + Di
	0055	820	60	Mel + Sp + Di
B	0033	1100	10	Mel + Sp + Di + Gl
	0020	1000	10	Mel + Sp + Mer + Gl
	0053	820	60	Mer + Mel + Sp + Gl
C	0044	1300	2	Mel + Sp + DCS + Mer + Gl
	0040	1200	1	Mel + Mer + Sp + DCS + Gl
	0035	1100	10	Mel + Sp + Mer + Gl
	0052	820	60	Mer + Mel + Sp + Gl
D	0003	1100	3	Mel + Sp + Di
	0009	1100	14	Mel + Sp + Di
	0023	1000	7	Mel + Sp + Di
E	0030	1100	10	Mel + An + Di + Sp + Gl
	0015	1000	10	Mel + An + Sp + Di + Gl
	0050	820	60	Mel + An + Di
F	0036	1100	10	Mel + Di + Sp + Gl?
	0026	1000	10	Mel + Sp + An + Di
	0056	820	60	Mel + Sp + An?
G	0006	1100	3	Mel + An + Sp + Di? + Gl
	0010	1000	4	Mel + Di + Sp? + Gl

(cont.)

TABLE 2 (cont.)

Glass Comp.	Run No.	Temp C	Duration Days	Phases
H	0019	1100	10	Mel + Sp + Gl
	0034	1000	10	Mel + Di + Sp? + Gl
	0047	820	60	Mel + Sp + Gl
I	0032	1100	10	Mel + An + Di + Gl
	0018	1000	10	Mel + Di + An + Gl?
	0054	820	60	Mel + An
J	0017	1100	10	Mel + An + Di + Sp? + Gl
	0031	1000	10	Mel + An + Di + Gl
	0057	820	60	An + Di + Mel
K	0041	1250	1	Mel + An + Di + Sp? + Gl
	0039	1200	1	Mel + An + Di + Sp + Gl
	0038	1100	10	Mel + An + Di + Sp
L	0029	1100	10	Mel + Di + An + Sp + Gl
	0014	1000	10	Mel + An + Di + Sp + Gl
	0049	820	60	Mel + An + Di + Gl
M	0028	1100	10	An + Di + Mel + Sp? + Gl
	0013	1000	10	An + Di + Mel + Gl
	0048	820	60	An + Mel + Di + Gl?

Mineral phases were identified generally by the powder camera X-ray diffraction method. Textures and certain mineral phases were determined using standard optical microscopy techniques. Some minor phases were determined by individual X-ray analyses.

EXPERIMENTAL RESULTS

Mineralogy

The mineralogies observed are presented in Table 2 along with the initial glass composition letter designation (see Table 1) and temperatures of the various runs. In the majority of the experimental runs melilite appears as the principal phase and generally assumes a tabular elongated or blade-like habit surrounded by lighter colored clusters or stringers of diopside (figure 2). Spinel occurs in most specimens as euhedral to subhedral crystals of highest refractive index (see figure 3). Anorthite is generally interstitial between the melilite and diopside and is easily distinguishable by its relatively lower refractive index. Although melilite, diopside, spinel and anorthite were observed as the principal phases in most runs, merwinite and di-calcium silicate occurred as significant minor phases in many runs of "B" and "C" compositions (Table 2). Their order of crystallization was not determined.

Texture

In most runs melilite, diopside, spinel and anorthite display eutectic, poikilitic and spherulitic textures, along with ovoid, tight-fitting aggregates and skeletal textures with and without the presence of a glassy matrix. All of these textures are consistent with their known origin in this case by crystallization from a glass. Some of the textures evident in the present study are also consistent with crystallization from a liquid. The textural relations of selected experimental runs are discussed below in order to evaluate a possible crystallization origin for similar textures found in some Allende chondrules and inclusions.

DISCUSSION

The origin of chondrules centers around two accepted hypotheses. First, that chondrules may represent "primary" objects which condensed from the relatively slow cooling of a gaseous nebula of solar composition as either a liquid (Blander and Katz, 1967) or as a solid (Grossman, 1972) condensate. The second suggests the chondrules may be "secondary" objects formed by the chemical alteration of pre-existing solids, or as a product of a reheating process (see Fredriksson, 1963; Whipple, 1966; and Lange and Larimer,

1973). If chondrules prove to be "primary" condensates, then they may represent the original planetesimals from which the planets are believed to have accreted.

A major controversy centers around the temperature regimes (high vs. low) and formational mechanism of either gas → solid or liquid → solid transitions for the origin of the Ca-Al-rich Allende inclusions. Grossman (1973), on the basis of large enrichments of refractory trace elements (La, Sm, Eu, Yb, Sc and Ir), favors high temperature gas → solid condensation. This, to some extent, conforms to Lord's (1965) calculations on high temperature condensates of solar nebula composition.

Blander and Fuchs (1975) favor the crystallization of analogous mineral assemblages from a liquid phase based on textural (spherical, ovoid aggregate shapes, eutectic and poikilitic textures in Allende inclusions), thermodynamic and chemical considerations. Also, they cite the presence of glass and the fine grain size of these inclusions as additional evidence for a liquid → solid transition. They further suggest that such a transition could take place from a "metastable subcooled liquid" 500°K below the liquidus temperatures of $CaO-Al_2O_3$ (15% CaO) mixtures. This is contrary to the proposal of Grossman (1972, 1973). The present study provides experimental data which corresponds to the thermal calculations of both Grossman (1972) and Blander and Fuchs (1975). It offers support for Blander and Fuchs' (1975) theory that Allende chondrules could have crystallized a Ca-Al-rich assemblage at considerably lower temperatures than predicted by Grossman (1972).

In the Ca-Al-rich Allende inclusions, there is considerable evidence suggestive of a liquid → solid transition. A coarse-grained inclusion, specimen 10/2 (see Blander and Fuchs, 1975) with a mineral assemblage characteristic of the Type B chondrules of Grossman (1975), has spinel occurring as small rounded euhedral grains tightly situated between the enclosing phases. This textural feature indicates that spinel formed first but was partially resorbed, presumably by a liquid, before being enclosed by the latter phases. The fact that the enclosing phases do not have euhedral textures supports rapid growth.

Experimental run 0026 (figure 3) of the present study offers support for a liquid → solid transition for inclusion 10/2. In this devitrified spherule, the poikilitic growth of spinel is evident within the surrounding melilite and diopside phases. In this experimental run (see Table 2) spinel was observed to crystallize first, with the appearance of melilite, diopside and interstitial anorthite as the later phases. If inclusion 10/2 is considered to be a solid condensate originating from a vapor, then the crystallization of spinel should have followed melilite and not preceded it. It is also noted that under the gas → solid condensate model,

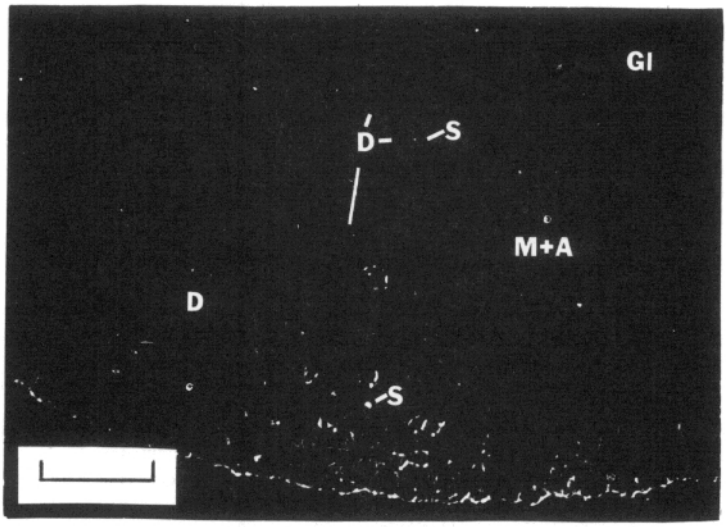

Figure 4. Spherulitic growth of melilite (M) and anorthite (A) in glass (center right). Chondrule-like growths of diopside (D) with spinel (S) are also present. (scale = 100 μm)

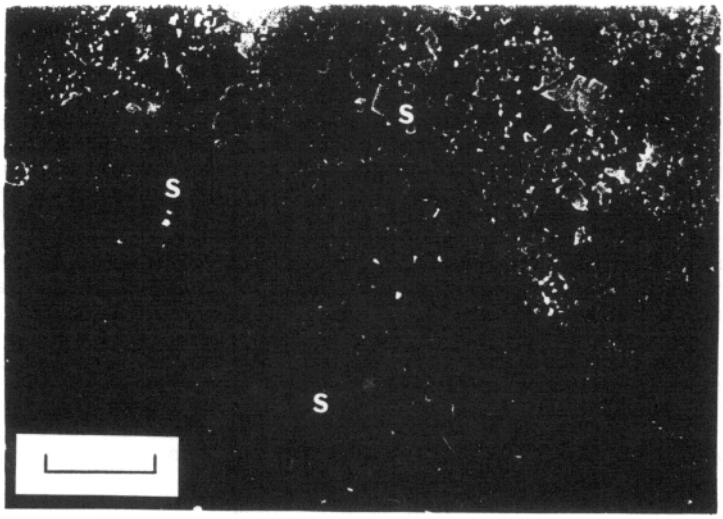

Figure 5. Characteristic Allende Type B chondrule exhibiting euhedral grains of spinel (S) in a glassy matrix. (scale = 100 μm) Courtesy of Louis H. Fuchs.

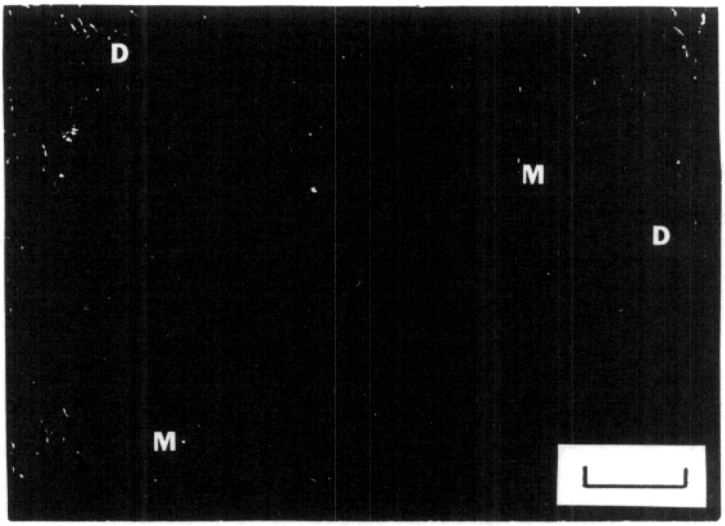

Figure 2. Microphotograph of run 0009 showing long blades of melilite (M) and skeletal diopside (D). (scale = 70 µm)

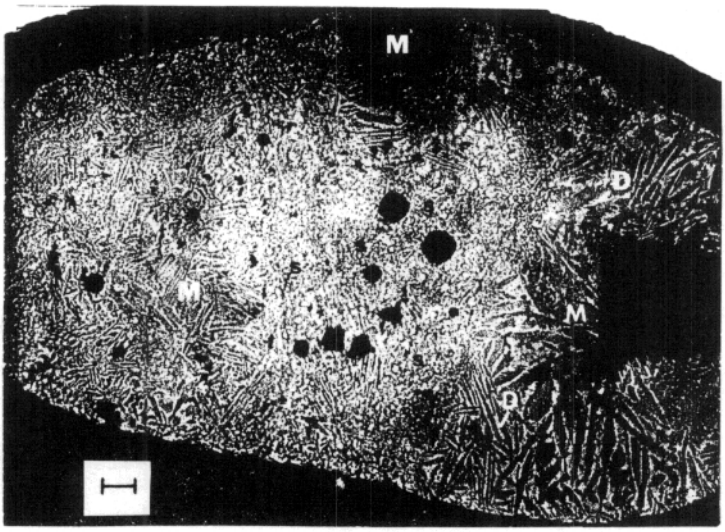

Figure 3. Microphotograph of run 0026 exhibiting numerous subhedral spinel (S) crystals scattered throughout the major phases: melilite (M) and diopside (D). (scale = 100 µm)

melilite and anorthite are incompatable. The observations on run 0026 combined with the crystallization data found in inclusion 10/2 disfavors a gas → solid transition as proposed by Grossman (1972, 1973) and others.

In one Allende inclusion (figure 4), the presence of spinel in spherical aggregates is evident. This type of aggregate closely resembles chondrules in their basic shape and structure. Similar aggregates have been synthesized in many of the devitrified spherules of the present study. This similarity (of figures 4 and 5) combined with the related mineralogy between the experimental spherules and the bulk inclusions, indicate that these sphere-like aggregates are primary crystallization features characteristic of liquid → solid transition.

The presence of appreciable amounts of glass in many of the experimental runs indicates a liquid phase at temperatures around 1100°C, conforming to many of the earlier thermal calculations (see Blander and Fuchs, 1975) from which the Ca-Al-rich inclusions may have crystallized. Such a liquid may be generated either by a reheating or through the existence of a "metastable subcooled liquid", or both.

Evidence presented by Fuchs (1974) offers additional support for a liquid → solid transition. The presence of grossular with melilite within an Allende inclusion indicates that the grossular formed from a pre-existing liquid phase. Melilite cannot co-exist with grossular under equilibrium conditions because the upper stability limit of grossular is way below that of melilite. Considering the solid condensate model of Grossman (1972), melilite would condense at temperatures 500°C above the stability of grossular. If grossular did originate from a liquid, it occurred as a condensate from a "metastable liquid" or as a reheating product. Fuchs (1974) suggests on this basis of texture, mode of occurrence and equilibrium considerations, grossular probably formed as a devitrification product from glass at temperatures below 800°-850°C. Taking into account the unfavorable reaction kinetics of grossular (Yoder, 1950), condensation from a "metastable liquid" would require a heating period up to a maximum of 20 days at temperatures lower than the probable 800°-850°C. Conditions meeting these requirements can be found if the inclusion was buried in a thermal blanket (Fuchs, 1974). The textural features in many of the experimental runs support "secondary" solid → liquid systems, giving rise to the Ca-Al-rich chondritic inclusions. The crystallization sequences (Table 2) obtained in the present study further suggest that the chondritic materials may be only somewhat chemically differentiated and not fully primitive as previously believed.

Considering the evidence, the possibility that crystallization of Ca-Al-rich inclusions took place from the residual

low temperature melting fraction of the primitive chondritic material is suggested here. The low pressure (10^{3} - 10^{-5} atms.) proposed for the initial condensation conditions of these Ca-Al-rich materials may have resulted in the loss of Na and other volatile elements which might have been responsible for the low temperature nature of the residual liquids. Such escape or loss must have taken place rather slowly, because some of the inclusions do show the presence of nepheline (Clarke et al., 1970; Blander and Fuchs, 1975).

CONCLUSION

The mineralogies and textures of chondrules are dependent upon their bulk compositions, physical conditions of formation (including equilibrium vs. non-equilibrium states), initial state of the parent material (solid, glass or liquid) and stability relations of the crystallizing phases. The mineral assemblage (melilite-spinel-diopside-anorthite) and the textural relations observed in the devitrified spherules in the compositions of the present study are suggestive of a liquid rather than a solid origin for the Ca-Al-rich Allende chondrules.

Assuming that liquids were present in the meteoritic parent body, once generated they could be isolated and then crystallize. Considering the variety of igneous textures found in chondrites: the reported zoned structure in the Bali chondrite (Kurat et al., 1975); the general shape of chondrules and the presence of glass; and the presence of low temperature phases (i.e. grossularite), origin could then be attributed to non-equilibrium crystallization of the liquids.

Alternatively, if thermal conditions permitted, such liquids (or "residual liquid" derivations of initial liquid condensates) could subcool to metastable glasses which then may undergo non-equilibrium devitrification through secondary energy impact reheating or reheating under thermal blanket conditions. This would tend to explain the textures and mineralogies observed by Blander and Fuchs (1975).

ACKNOWLEDGEMENTS

The authors wish to thank Mr. Louis H. Fuchs and Dr. Milton Blander of Argonne National Laboratory for their assistance and direction during the course of this study and to our reviewers for their very valuable comments.

One of us (PPS) also acknowledges his Thesis Parts Fellowship from Argonne National Laboratory which made this study possible.

LITERATURE CITED

BLANDER, M. and L. H. Fuchs, 1975. Calcium-aluminum-rich inclusions in the Allende meteorite: evidence for a liquid origin. Geochim. Cosmochim. Acta, 39: 1605-1619.

BLANDER, M. and J. L. Katz, 1967. Condensation of primordial dust. Geochim. Cosmochim. Acta, 31: 1025-1034.

CAMERON, A. G. W., 1970. Abundances of the elements in the solar system. Space Sci. Rev., 15: 121-146.

CAMERON, A. G. W., 1973. Accumulation processes in the primitive solar nebula. Icarus, 18: 407-450.

CHOU, C. L., P. A. Baedecker and J. T. Wasson, 1976. Allende inclusions: volatile-element distribution and evidence for incomplete volatilization of presolar solids. Geochim. Cosmochim. Acta, 40: 85-94.

CLARKE, R. S. Jr., E. Jarosewich, B. Mason, J. Nelen, M. Gomez, and J. R. Hyde, 1970. The Allende, Mexico, meteorite shower. Smithson. Contrib. Earth Sci., 5.

FREDRIKSSON, K., 1963. Chondrules and the meteorite parent bodies. Trans. N.Y. Acad. Sci., 25: 756-769.

FUCHS, L. H., 1974. Grossular in the Allende (type III carbonaceous) meteorite. Meteoritics, 9: 11-18.

GROSSMAN, L., 1972. Condensation in the primitive solar nebula. Geochim. Cosmochim. Acta, 36: 597-619.

GROSSMAN, L., 1973. Refractory trace elements in Ca-Al-rich inclusions in the Allende meteorite. Geochim. Cosmochim. Acta, 37: 1119-1140.

GROSSMAN, L., 1975. Petrography and mineral chemistry of Ca-rich inclusions in the Allende Meteorite. Geochim. Cosmochim. Acta, 39: 433-454.

GROSSMAN, L. and S. P. Clark, Jr., 1973. High-temperature condensates in chondrites and the environment in which they formed. Geochim. Cosmochim. Acta, 37: 635-649.

GROSSMAN, L. and R. Ganpathy, 1976. Trace elements in the Allende meteorite - I. Coarse grained Ca-rich inclusions. Geochim. Cosmochim. Acta, 40: 331-344.

GROSSMAN, L. and J. W. Larimer, 1974. Early chemical history of the solar system. Rev. Geophys. Space Phys., 12: 71-101.

KURAT, G., G. Hoinkes and K. Fredriksson, 1975. Zoned Ca-Al-rich chondrule in Bali: new evidence against the primordial condensation model. Earth Planet. Sci. Lett., 26: 140-144.

LANGE, D. E. and J. W. Larimer, 1973. Chondrules: an origin by impacts between dust grains. Science, 182: 920-922.

LARIMER, J. W., 1967. Chemical fractionation in meteorites - I. Condensation of elements. Geochim. Cosmochim. Acta, 31: 1215-1238.

LORD, H. C. III, 1965. Molecular equilibria and condensation in a stellar nebula and cool stellar atmospheres. Icarus, 4: 279-288.

NELSON, L. S., M. Blander, S. R. Skaggs and K. Keil, 1972. Use of a CO_2 laser to prepare chondrule-like spherules from supercooled molten oxide and silicate droplets. Earth Plan. Sci. Lett., 14: 338-344.

PRINCE, A. T., 1954. Liquidus relationships on 10% MgO plane of the system lime-magnesia-alumina-silica. J. Amer. Ceram. Soc., 37: 402-409.

SOOD, M. K., 1969. The join diopside ($CaMgSi_2O_6$)-albite ($NaAlSi_3O_8$)-leucite ($KAlSi_2O_6$) in the system diopside ($CaMgSi_2O_6$)-nepheline ($NaAlSiO_4$)-kalsilite ($KAlSiO_4$)-silica (SiO_2) and its petrological implications. University of Western Ontario (unpublished Ph.D. thesis).

WHIPPLE, F. L., 1966. A suggestion as to the origin of chondrules. Science, 153: 54-56.

WHIPPLE, F. L., 1972. On certain aerodynamic processes for asteroids and comets. In From Plasma to Planet, Ed. by A. Elvius, 211-232. Almqvist & Wiksell.

YODER, H. S., 1950. Stability relations of grossularite. J. Geol., 58: 221-253.