

ANHYDROUS ALTERATION OF ALLENDE CHONDRULES
IN THE SOLAR NEBULA III:
ALKALI-ZONED CHONDRULES AND HEATING EXPERIMENTS
FOR ANHYDROUS ALTERATION

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Abstract: The groundmass of some chondrules in Allende shows chemical zonation from alkali-poor and CaO-rich cores to alkali-rich and CaO-poor rims, and the zonation was defined to be original groundmass (zone I), continuous zoning region (zone II), and discontinuously high-Na and low-Ca zone (zone III). The zonation was formed after chondrule solidification and prior to accretion on the Allende parent body, and was probably produced by reactions with an oxidized nebular gas in equilibrium with nepheline, sodalite, high-Ca pyroxene, and ferroan olivine. Heating experiments using synthetic glass beads were conducted, and zonation similar to the alkali-zoned chondrules was formed. The experimental results suggests that the reaction temperature and duration for the Allende alkali-zoned chondrules were about 600°–400°C and 1–10⁴ years, respectively.

1. Introduction

Most Allende chondrules experienced more or less anhydrous alteration, and the groundmass of most Allende chondrules is often black and highly devitrified (IKEDA and KIMURA, 1995; KIMURA and IKEDA, 1995). However, a few Allende chondrules have clear glass or slightly devitrified groundmass, and we found some zoned chondrules which have clear glass or unaltered groundmass in the chondrule cores but highly devitrified ones in the rims. The groundmass in rims of the zoned chondrules is always richer in alkalis and poorer in CaO than that in the chondrule cores. Such zonation of chondrule groundmass was first reported from the ALH-77003 chondrite (CO) (IKEDA, 1982), but is never observed in ordinary and enstatite chondrites with the rare exception of chondrules which are originally enriched in alkalis in their peripheral portions (MATSUNAMI *et al.*, 1993). Thus, the alkali-zonation of chondrules due to anhydrous alteration is apparently characteristic of CV and CO carbonaceous chondrites. Here, we use the term “anhydrous alteration” for all anhydrous chemical reactions which took place in chondrules or inclusions after their solidification and prior to terrestrial alteration. Therefore, the anhydrous alteration may have been either nebular or parent body processes.

In carbonaceous chondrites, there occur many Ca- and Al-rich inclusions (CAI's) and amoeboid olivine inclusions which contain sometimes large amounts of alkalis. The high contents of alkalis in these inclusions and chondrules have always been a controversial point for their origins (McSWEEN, 1977; WARK, 1981; MACPHERSON *et al.*, 1981; KORNACKI, 1981; IKEDA, 1982; HASHIMOTO and GROSSMAN, 1987; TOMEOKA *et al.*, 1992; IKEDA and KIMURA, 1985, 1995). However, experimental studies for introduction of al-

kalies into inclusions and chondrules have not been carried out, and therefore the formational processes of alkali-zoned chondrules remain unsolved.

In this paper, an alkali-zoned chondrule from the Allende chondrite (CV) is briefly described, and we conducted heating experiments using synthetic glass beads in order to clarify the introduction of alkalis into these chondrules.

2. Analytical Method

Chemical compositions of groundmass and minerals in an alkali-zoned chondrule and heated synthetic glass beads were determined with an electron-probe microanalyser (EPMA; JEOL 733 type, an accelerating voltage of 15 kV and probe current of 3–4 nA). The correction method of BENCE and ALBEE (1968) was used.

3. Description of an Alkali-Zoned Chondrule

The Allende chondrule studied here is large, the size being about 1.3 mm in diameter (Fig. 1). It shows typical barred-olivine texture, although some equant olivine grains are included in the chondrule rim. The chemical composition of olivine is $Fe_{0.99}$, although olivine just in contact with black devitrified groundmass or the Allende matrix is more ferrous, being $Fe_{0.95-89}$. In the chondrule rim, several small euhedral grains of high-Ca pyroxene, about a few tens of micrometers across, occur. Their composition is $Wo_{35-41}En_{58-64}Fs_{0.5-1.0}$. Groundmass in the chondrule core is pale brownish under a microscope and cryptocrystalline, while it is opaque and highly devitrified in the chondrule rim (Fig. 1). The boundary between the brownish cryptocrystalline and opaque devitrified groundmass is very sharp, and the latter seems replacing the former. The sharp boundaries are common for altered Allende chondrules and cannot be explained by overgrowth of both types of the groundmass (IKEDA and KIMURA, 1995). The chemical composition of the groundmass changes from the core to the rim (Fig. 2); the Na_2O content of the brownish cryptocrystalline groundmass in the chondrule core is about 2 wt% and increases over the space of 50–150 μm to about 3 wt% toward the rim. At the rim, the Na_2O content of

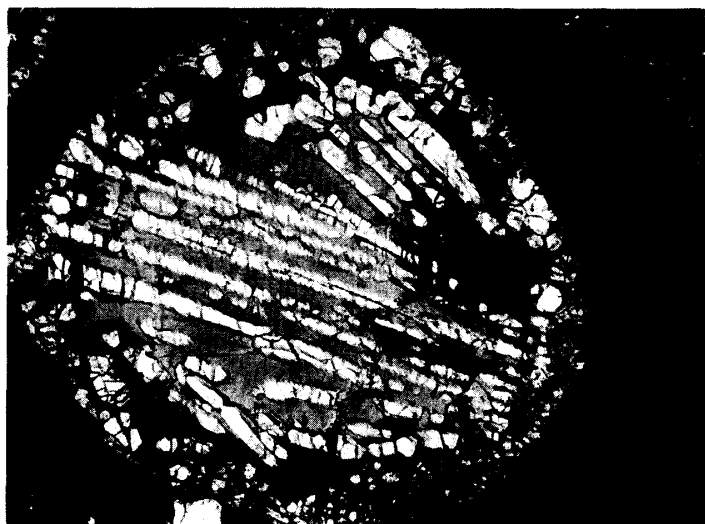


Fig. 1. Photomicrograph of the Allende zoned chondrule (transmitted light). Note that the groundmass is brownish in the central part and opaque in the peripheral part. Width of figure is 2.0 mm.

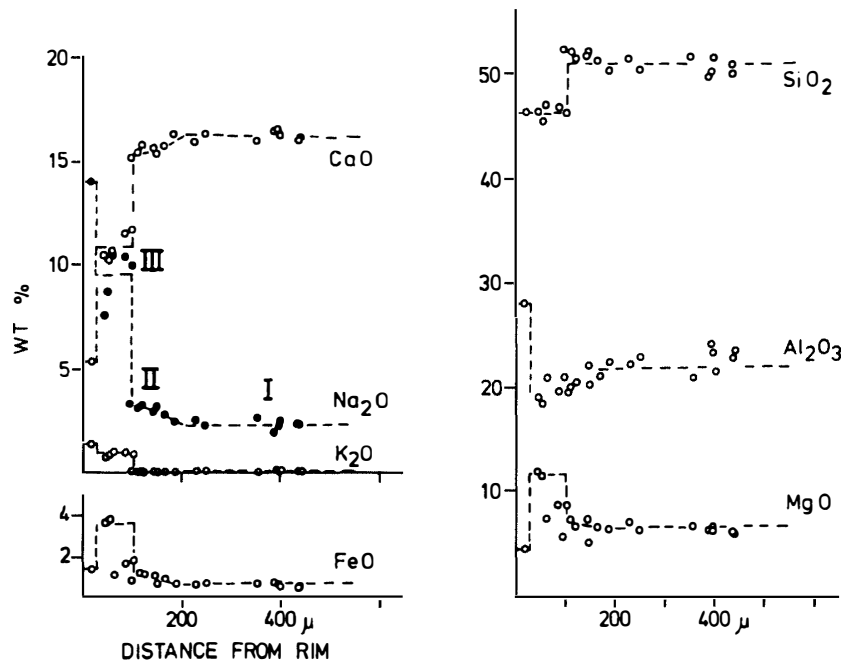


Fig. 2. Chemical compositions of groundmass of the Allende zoned chondrule are plotted against distance from the chondrule rim in μm . Dashed lines show a typical zonal pattern, and each zone is shown by I, II, and III.

the opaque devitrified groundmass increases discontinuously up to 7–14 wt%. In contrast, the CaO content decreases from the core to the rim, reversely correlated with the Na₂O content as shown in Fig. 2. However, the Al₂O₃ content of the groundmass is nearly constant through both types of groundmass except at the outermost rim, where it increases locally and discontinuously by about 5 wt% compared to the inner part (Fig. 2).

We define here three zones of groundmass, I, II, and III, from the core to the rim. Zone I is the original groundmass which occurs in the central part of the zoned chondrule. Zone II is defined to be a zone which shows a continuous chemical zonation with increasing Na₂O and decreasing CaO contents from zone I. Zone III is a Na₂O-rich zone in which Na₂O content increases discontinuously from zone I or II up to more than 7 wt%. The chemical compositions and the widths of each zones in the groundmass are shown in Table 1.

In the zoned chondrule, the inner brownish cryptocrystalline and outer opaque devitrified groundmasses correspond to zones I-II and zone III, respectively. In zone II, components other than Na₂O and CaO show no particular zonation (Fig. 2). In zone III, K₂O, FeO and MgO increase discontinuously from zone II, while the SiO₂ content decreases discontinuously (Fig. 2). In the outermost rim of zone III, the Al₂O₃ and alkali contents locally increase discontinuously, and CaO, FeO and MgO contents decrease considerably. Although Cl content is below the detection limit (0.1%) in zones I and II, zone III contains variable amounts of Cl (Table 1).

Table 1. Compositional ranges, normative compositions, MgO/(MgO+FeO) mole ratios (mg), Na/(Na+K) atomic ratios, and widths of zones I, II, and III of the Allende zoned chondrule studied. Numbers in parentheses for zone I are arithmetic means, and those for zone III are arithmetic means which are normalized to Al₂O₃=23.2 wt% (the original arithmetic mean of Al₂O₃ is 24.5). The differences of normative compositions between zones I and III are also shown with the parentheses in the column of zone III.

	I	II	III
SiO ₂	48.8–51.4 (49.7)	50.7–52.6 (51.1)	38.7–47.8 [42.1]
TiO ₂	0.9–1.2 (1.0)	0.8–1.1 (1.0)	0.2–1.1 [0.7]
Al ₂ O ₃	22.0–24.3 (23.2)	20.2–23.5 (21.7)	17.9–30.9 [23.2]
Cr ₂ O ₃	0.2–0.6 (0.4)	0.2–0.7 (0.5)	0.0–0.7 [0.4]
FeO	0.2–0.8 (0.5)	0.4–1.3 (0.7)	0.5–4.7 [1.7]
MnO	0.0–0.2 (0.1)	0.0–0.3 (0.1)	0.0–0.3 [0.1]
MgO	5.5–7.3 (6.2)	5.4–7.9 (6.6)	2.1–13.1 [6.5]
CaO	15.4–17.4 (16.0)	14.7–16.3 (15.4)	1.8–12.1 [7.7]
Na ₂ O	1.9–2.5 (2.3)	2.6–3.3 (2.8)	8.3–23.0 [11.3]
K ₂ O	0.0–0.1 (0.0)	0.0–0.1 (0.0)	0.0–1.6 [0.9]
Cl	0.0–0.0 (0.0)	0.0–0.0 (0.0)	0.0–5.9 [0.7]
Total	99.6	100.1	
Ab+Or	0.0740		0.0083 <–0.0657>
An	0.1908		0.0446 <–0.1462>
Ne+Kp	–		0.1513 <+0.1513>
Sd	–		0.0185 <+0.0185>
Di+Hd	0.0952		
En+Fs	0.0077		– <–0.0077>
Fo+Fa	0.0257		0.0422 <+0.0165>
Cm	0.0030		0.0024
Il	0.0035		0.0084
Ru	0.0095		–
mg	0.959	0.942	0.870
Na/Na+K	0.998	0.997	0.951
Width	–	50–150	100–200

Ab+Or=(Na+K)Si₃AlO₈, An=CaSi₂Al₂O₈, Ne+Kp=(Na+K)₂Si₂Al₂O₈, Sd=Na₄Al₃Si₃O₁₂Cl,
 En+Fs=(Mg+Fe)SiO₃, Fo+Fa=(Mg+Fe)₂SiO₄, Di+Hd=Ca(Mg+Fe)Si₂O₆,
 Cm=FeCr₂O₄, Il=FeTiO₃, Ru=TiO₂

4. Heating Experiments and the Results

4.1. Heating experiments

In order to clarify the origin of alkali-zoned chondrules, we performed heating experiments, using synthetic glass beads, about 2–3 mm in diameter. The chemical composition of the glass is a mixture of normative anorthite and diopside components in nearly equal amounts (Table 2, zone I), being similar to those of the original groundmasses of zoned chondrules except for the absence of alkali and FeO contents in the glass beads. The beads were heated isothermally in an electric furnace with reagents. The reagents used are pure powders of NaCl, Na₂CO₃, or Amelia albite. They were used

Table 2. Chemical and normative compositions, and width (microns) of each zone of heated synthetic glass beads. The composition of zone I is the mean values of all runs. The compositions of zone II are the mean values, and are those just in contact with zone III. The total wt% and normative compositions (mole%) of zone III were calculated using the mean values of each zone. Abbreviations of normative components are the same as those in Table 1, and Wo and Cs are CaSiO_3 and Ca_2SiO_4 , respectively. The widths of zone III of runs 11 and 12 are too narrow to determine the compositions.

Run	All		3		7		9		11		12			
Temp. (°C)			700		800		800		700		750			
Time (hours)			320		5		20		80		20			
Reagent			Na_2CO_3		NaCl		NaCl		NaCl		NaCl			
Zone	I		II		III		II		III		II		III	
SiO_2	48.6		48.5	48–49	47.5	48	48.5	47–49	48.0	–	48.0	–		
Al_2O_3	20.9		19.0	19–20	20.0	20	20.0	20–21	20.5	–	21.5	–		
MgO	8.1		8.0	7–8	7.5	8	8.0	9	7.5	–	8.0	–		
CaO	22.9		19.5	12–18	19.5	16	19.5	10–16	19.0	–	18.5	–		
Na_2O	0.0		4.5	6–13	5.0	8.5	4.5	8–11	4.5	–	4.5	–		
Total	100.5		99.5	100.0	99.5	100.5	100.5	99.0	99.5	–	100.5	–		
Ab	0.0		0.2	1.1	0.0	0.0	0.0	2.7	0.0	–	0.0	–		
An	50.0		27.1	9.0	28.3	14.4	30.0	12.1	31.2	–	34.1	–		
Ne	0.0		17.2	35.7	19.8	33.6	17.6	37.2	17.6	–	17.9	–		
Wo	0.5		8.4	10.3	1.4	0.0	2.5	0.0	5.9	–	0.0	–		
Di	48.0		47.2	44.0	45.6	47.6	48.1	46.2	45.2	–	44.8	–		
Fo	0.7		0.0	0.0	0.0	0.5	0.0	1.8	0.0	–	2.0	–		
Cs	0.7		0.0	0.0	4.9	3.9	1.9	0.0	0.0	–	1.2	–		
Width	–		5–10	5–15	15–25	0–5	40–60	5–15	4–8	<2	10	<2		

Run	14		21		22		24		25		26	
Temp. (°C)	700		800		800		800		800		800	
Time (hours)	320		160		330		500		260		50	
Reagent	NaCl		NaCl		NaCl		NaCl		NaCl		NaCl	
Zone	II		III		II		III		II		III	
SiO_2	47.5	46–47	47.7	44–49	47.5	46–48	47.8	47–49	47.2	47	46.9	46–47
Al_2O_3	20.0	19–20	20.1	19–23	20.3	21–22	21.0	21–22	22.0	22–22	22.5	22–23
MgO	9.5	9	7.6	5–10	7.6	5–9	7.9	5–10	7.6	7–8	7.5	5–6
CaO	19.0	16–17	20.6	13–19	20.7	16–19	20.4	14–19	20.1	16	19.5	18–19
Na_2O	4.5	8	3.9	6–12	4.7	6–11	3.7	7–9	3.9	8	4.4	8
Total	100.5	99.5	99.9	99.8	100.9	100.9	100.8	100.8	100.8	100.8	100.8	100.3
Ab	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
An	29.3	14.8	32.7	17.0	29.9	22.5	35.5	17.9	36.8	18.4	36.5	20.2
Ne	17.2	30.8	15.5	32.8	18.0	27.7	14.4	32.3	15.4	32.7	17.0	30.0
Wo	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8.1
Di	40.9	39.1	46.2	41.8	42.1	38.8	42.8	43.0	37.9	38.9	35.3	33.8
Fo	7.5	7.1	0.1	0.5	1.5	3.1	2.4	2.4	3.9	3.2	4.9	0.0
Cs	5.0	8.1	5.4	7.7	8.4	7.8	4.9	4.5	6.0	6.6	6.2	7.9
Width	10	5–15	70–110	0–15	90–150	2–25	190–350	10–30	60–90	2–20	50–130	0–5

to fill a Pt-crucible (diameter and depth are 2 cm and 3 cm, respectively, with a cap) to the top, and a synthetic glass bead was buried in the central part of the reagents. The reagents were compacted by hand as tightly as possible, and the experiments were performed in air. The heating times ranged from 5 hours to 500 hours. After the heating, the glass beads were cut through the center, and thin sections were produced for observation under a microscope and chemical analyses with an EPMA.

In the heating experiments with albite powder, conducted under two conditions, (800°C and 80 hrs) and (700°C and 320 hrs), no compositional change in the heated glass beads were detected. Therefore, we report the results of the heating experiments with NaCl and Na₂CO₃. Heating experiments using an NaCl reagent were performed at temperatures of 800°, 750°, and 700°C, which are lower than the melting point (800.4°C) of NaCl crystals. Temperatures and durations of these runs are shown in Table 2. One heating experiment, run 3, using Na₂CO₃ was conducted at 700°C for 320 hours.

4.2. Zonation of heated glass beads

In Fig. 3, an example of chemical zonation of run 9 with NaCl reagent (800°C, 20 hrs) is shown. The Na₂O content increases continuously from zero in the central part to about 5 wt% in zone II, and the CaO content decreases concomitantly with the Na₂O content. The Na₂O content in zone III increases discontinuously up to 8–11 wt%, while the CaO content decreases. The other components are nearly constant except for the

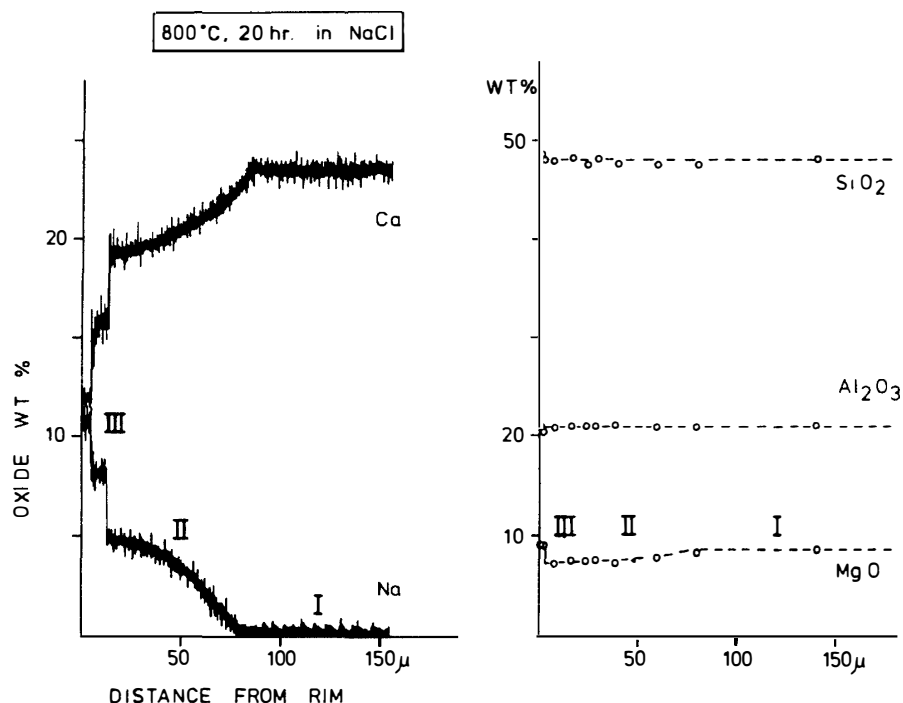


Fig. 3. Chemical zoning patterns of a heated synthetic glass bead (run 9 800°C, 20 hrs, in NaCl). The figure on the left-hand side shows X-ray (K-alpha) intensity of Na and Ca obtained by an EPMA with approximate wt% of Na₂O and CaO. The figures on the right hand side are the contents of each oxide (in wt%) plotted against the distance from the rim.

MgO which decreases gradually in zone II; the MgO content of the inner part of zone III is low in comparison to that in zone I, although it increases in the outer part of zone III (Fig. 3).

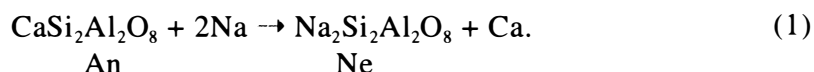
In other runs with NaCl, chemical zonations ranging from zone I to zone III were similar to those produced in run 9. The chemical compositions and widths of each zone of those runs are shown in Table 2. Zone III is always devitrified, whereas zones I and II are always clean glass. Becke' lines (which are bright lines between two phases having different refractive indices under open Nicols) are observed between zones II and III under a microscope. The width of zone II is nearly constant within a factor of 3 in each heated glass bead, whereas the width of zone III is variable (Table 2). For example, in run 7, the width of zone III at some peripheral parts of the heated bead is 4–5 μm , but at other peripheral parts it is thinner than one μm and sometimes cannot be clearly detected. The zone III for runs 11 and 12 is too narrow (less than a few microns in width) to determine the chemical composition by EPMA.

For the heating experiment run 3 with Na_2CO_3 , the zonal pattern is nearly the same as that of run 9 with NaCl, and the widths of zones II and III are 5–10 μm and 5–15 μm , respectively.

4.3. Interpretation of heating experiments

The chemical compositions of each zone produced in runs 9, 14, and 3 are plotted in Al-Na-Ca and Al-Na-(Ca+Mg) diagrams in atomic ratios in Fig. 4. Zones II and III, except for the outermost part of zone III of run 9, are plotted on a line extending from zone I towards the direction indicating the substitution of one Ca atom by two Na atoms. The outermost part of the zone III of run 9 deviates slightly from the 2Na-Ca substitution line (Fig. 4a). However, as shown in Fig. 4b, all compositions including the outermost part of the zone III of run 9 are plotted on the 2Na-(Ca+Mg) substitution line. This means that small amounts of Mg in addition to Ca are replaced by Na exactly with the ratio of 1 to 2, although this substitution of Mg by 2Na is minor in comparison to the main substitution of Ca by 2Na.

The main substitution proceeds from zone I to zone III, but never extends beyond the tie line between nepheline (Ne) and diopside (Di) as shown in Fig. 4. This indicates that, although Na and Ca are the main mobile components in zones I, II and III, only Ca atoms corresponding to the anorthite component can be replaced by 2Na to form the nepheline component in zone III. This interpretation is supported by the systematic change of normative compositions from zone I to zone III as shown in Table 2; normative anorthite component decreases from zone I to zone III, while the normative nepheline component increases inversely with the anorthite component. This substitution is expressed by the following equation, ignoring the minor substitution of Mg by 2Na,



The Na atoms of the left-hand side of eq. (1) come from NaCl or Na_2CO_3 reagent during the heating experiments, and the Ca atoms of the right-hand side precipitate as CaCl_2 or CaCO_3 , which are observed at the surface of the heated glass beads and/or in the reagents

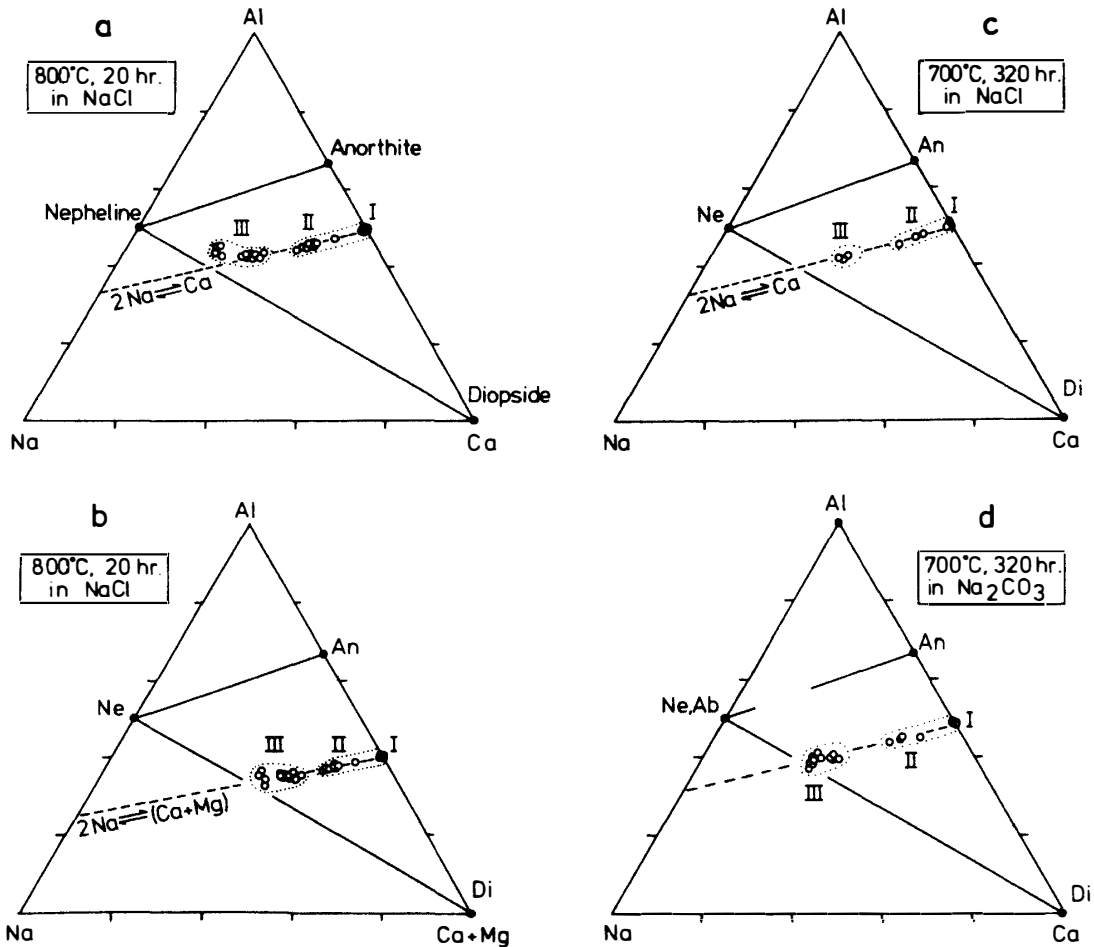


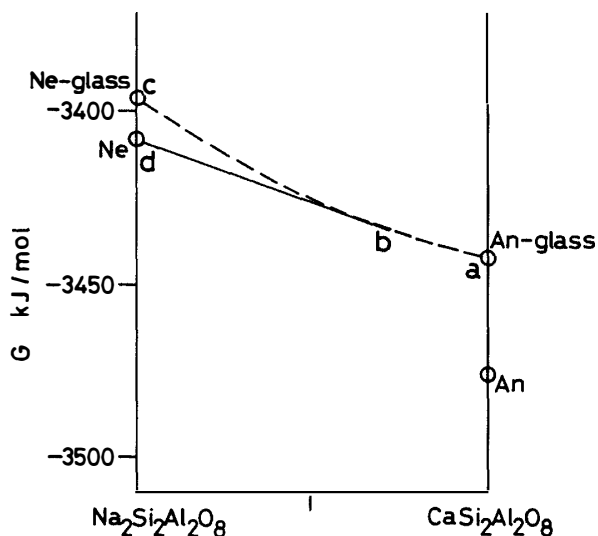
Fig. 4. Chemical compositions of each zone in heated glass beads are plotted in Al-Na-Ca diagrams (a, c and d) and Al-Na-(Ca+Mg) diagram (b) in atomic ratios. Each zone is surrounded by dotted lines. Dashed lines show a substitution of Ca or (Ca+Mg) atoms by Na atoms in the ratio of 1 to 2, drawn from zone I. An, Ab, Ne, and Di are anorthite, albite, nepheline, and diopside, respectively.

far from the glass beads.

4.4. Formation of zone II

Zone II of the heated glass beads shows continuous zoning from zone I, and was produced by the reaction (1) in the glass state. The chemical zonation of zone II shows a characteristic pattern as shown in Fig. 3; the Na_2O content increases abruptly but continuously from zone I, and the rate of the Na_2O increase becomes smaller towards zone III, forming a plateau at 5 wt% just before the boundary with zone III. This pattern is the same for all heating experiments reported here, and the Na_2O content at the plateau is always 4 to 5 wt%, which corresponds to 14–20 mole% of normative nepheline (Table 2). Zone III always includes a discontinuously-high (more than 25 mole%) content of normative nepheline (Table 2). Thus, the Na_2O plateau of zone II may correspond to a “metastable solubility limit” of nepheline component in the zone-II glass at the temperature range of 700°–800°C on the assumption that nepheline easily nucleates and grows in zone III. As shown in Fig. 5, the nepheline component in zone-II glass continuously

Fig. 5. Schematic diagram showing "metastable solubility limit" of nepheline component in glass (see text). Vertical and horizontal axes are Gibbs free energy at the temperature of about 1000 K and mole fraction in the binary system, respectively. The Gibbs free energy of anorthite-glass (An-glass, -3441 kJ/mole), anorthite (An, -3475 kJ/mole) and nepheline (Ne, -3408 kJ/mole) at 1000 K are quoted from ROBIE et al. (1978). That of nepheline glass (Ne-glass, about -3400 kJ/mole) was estimated from the devitrification of nepheline at 985 K ($H_{985}=5951$ cal/mole; NAVROTSKY et al., 1980). The curve a-b-c was obtained on the assumption that the binary glass is an ideal solution. The line d-b is tangential with the curve a-b-c through d. The point b corresponds to 6-7 wt% of Na_2O .



increases under a metastable condition from point a to point b by the substitution of eq. (1), and when nepheline nucleates and grows at point b to form devitrified glass of zone III, the Na_2O content in zone-II glass cannot increase any more than point b. This hypothesis can explain the discontinuity in Na_2O content between zones II and III; zone II consists merely of glass of a-b composition, whereas zone III is a mixture of nepheline crystallites and the glass of point b in Fig. 5. If a large amount of nepheline crystallites was produced in zone III the Na_2O content would increase discontinuously from zone II to zone III.

Zone II shows continuous chemical zonation, which was produced in the clean glass during the heating experiments by body diffusion according to the Ca-2Na substitution. Here, we use equation, $x=(Dt)^{1/2}$, to obtain the apparent diffusion coefficient D for the Na_2O concentration at half of the maximum Na_2O content in zone II, where t is the time in seconds and x is the distance in cm from the chondrule rims to the point of $\text{Na}_2\text{O}=2$ wt% in zone II. The distance x for run 24 (800°C, 500 hrs) and run 14 (700°C, 320 hrs) are about 170 and 15 μm , respectively. Thus we obtain the apparent diffusion coefficient;

$$D=6.95 \times 10^8 \exp(-46 \times 10^3/T) \text{ cm}^2/\text{s}, \quad (2)$$

where T is temperature in Kelvin.

Self diffusion coefficients of Na in obsidian glass, albite glass, and orthoclase glass are about $10^{-6} \text{ cm}^2/\text{s}$ at a temperature of 800°C (JAMBON and CARRON, 1976; MARGARITZ and HOFMANN, 1978), which is larger by a factor of 10^4 than our apparent coefficient of $1.7 \times 10^{-10} \text{ cm}^2/\text{s}$. This discrepancy may be explained by the reason that in our heating experiments the diffusion took place by two Na atoms substituting exactly for one Ca atom in zone-II glass, whereas the self diffusion above stated takes place only by substitution of Na atoms.

4.5. Reaction velocity of zone III

Zone III in heated glass beads is always devitrified and shows a discontinuous change in chemical composition. The discontinuity between zones II and III is the front of devitrification which proceeds from the rim of the heated glass beads towards the interior. The reaction velocity, which is here defined as the velocity of the advancing front, may be controlled by the reaction rate at the boundary to form zone III from zone II and/or by the material supply through the zone III from outside of the beads to the reaction front.

The mean width (y in cm) of zone III seems to be proportional to the heating duration (t in s) at constant temperature. On the assumption that the temperature dependence of the reaction velocity is expressed by an Arrhenius-type equation, the following equation can be obtained; $y = t \times A \exp(-B/T)$, where T is temperature in Kelvin, and A and B are constants. Applying this equation for runs of 800°C and 700°C with the least square fitting method, we obtain,

$$y = t \times 1.05 \times 10^{-8} \exp(-2464/T). \quad (3)$$

5. Discussion

5.1. Mass balance for zoning formation of Allende chondrules

In Fig. 6, the chemical compositions of groundmass of the Allende zoned chondrule studied here are plotted in (Na+K)-Al-Ca diagrams, where zonation of the chondrule shows chemical trends roughly similar to those of heated glass beads. The chemical zonation of the Allende zoned chondrule from zone I to zone III is apparently controlled by substitution according to eq. (1). However, the substitution in the zoned chondrule is more complicated than that in heated glass beads. The following discussion is based on

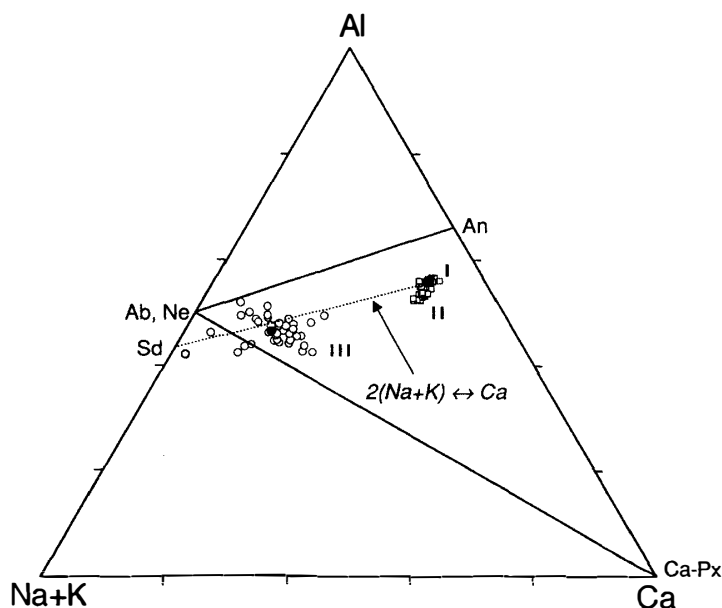
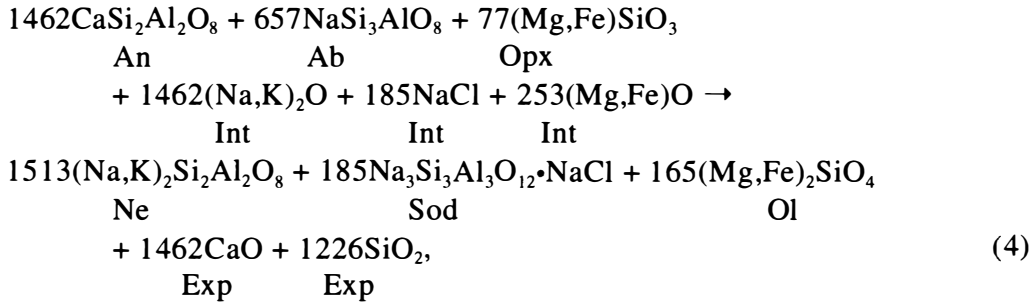


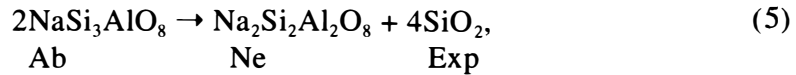
Fig. 6. Chemical compositions of each zone in the Allende zoned chondrule are plotted in Al-(Na+K)-Ca diagrams in atomic ratios. Zones I and II (open squares) with the average of zone I (solid square) and zone III (open circles) with the average (solid circle) are along a dotted line which shows the substitution of one Ca atom by two (Na+K) atoms, drawn through zone I. Abbreviations are the same as those in Fig. 4, and CaPx and Sd are high-Ca pyroxene and sodalite.

the assumption that the Al_2O_3 component was immobile during the zoning formation.

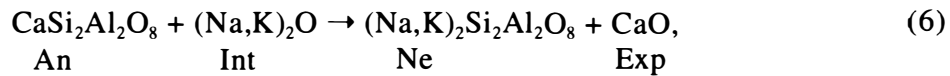
As shown in Table 1, the difference in average normative composition between zones I and III (Table 1) may be represented as a decrease of 0.1462 mole anorthite +0.0657 mole albite +0.0077 mole orthopyroxene, which is compensated by an increase of 0.1513 mole nepheline +0.0185 mole sodalite +0.0165 mole olivine. This is shown by the following equation;



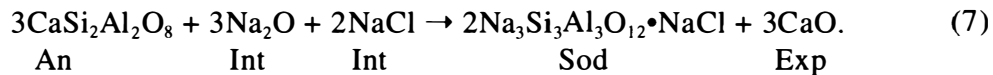
where Int and Exp are introduced and expelled components, respectively, and the total Al molecules are the same between the right- and left-hand sides of the equation. The reactants of the equation are normative albite (albite+orthoclase), anorthite, and orthopyroxene components in addition to the introduced components. The normative albite component in zone I reacts to form nepheline component in zone III;



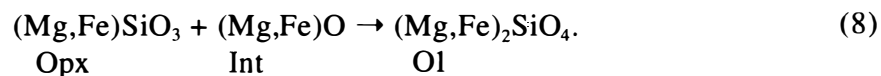
where, SiO_2 in the right-hand side is expelled from zone III or used to form other phases such as ferroan olivine which is stable in zone III (see following eq. (9)). The normative anorthite component in zone I reacts to form nepheline and sodalite in zone III as follows (IKEDA and KIMURA, 1995);



and

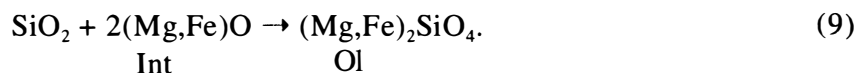


The normative orthopyroxene component in zone I forms olivine component in zone III;



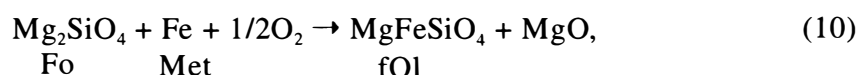
Some fractions of SiO_2 and CaO , which are expelled by reactions (5), (6), and (7), may be used to form Ca-bearing phases such as ferroan Ca-pyroxene, grossular, etc. elsewhere in chondrules or outside of chondrules (KIMURA and IKEDA, 1995), and a fraction

of the expelled SiO_2 component of reaction (5) reacts to form ferroan olivine in zone III;



Equations (5) to (9) are elementary reactions for producing zone III, and eq. (4) for zone III of the Allende zoned chondrule is obtained by a combination of eqs. (5) to (9) as follows; eq. (4) = $328.5 \times (5) + 1184.5 \times (6) + 92.5 \times (7) + 77 \times (8) + 88 \times (9)$. Equation (6) is essentially equal to eq. (1) for heating experiments, but reactions (5), (7), (8), and (9) did not take place in the heating glass beads because the heating experiments were free of FeO component and the synthetic glass beads contain no normative albite and orthopyroxene components. Sodalite was not detected in our heating experiments; perhaps Cl molecules reacted with oxygen molecules to form some Cl-O species which prevented sodalite formation in our experiments carried out in air.

Equation (4) indicates that some fraction of CaO and SiO_2 was expelled from the Allende zoned chondrule, and this could have formed CaO-bearing phases in the matrix. Equation (4) also indicates that (Mg,Fe)O must be introduced into zone III to form ferroan olivine by reactions (8) and (9). The FeO component can be produced by oxidation of Fe metal within or outside of chondrules (IKEDA and KIMURA, 1995). The MgO/(MgO+FeO) mole ratio (mg ratio) of each zone in the Allende zoned chondrule continuously decreases from 0.96 for zone I to 0.87 for zone III (Table 1), meaning that the ambient gas or solution could coexist with ferromagnesian minerals with the mg ratios equal to, or smaller than, 0.87. This suggests that the MgO component may be supplied from olivines (which are suspended in the solar nebula prior to the accretion, or occur in the Allende matrix after the accretion) by the following reaction;



where Fo and fOl are forsterite and ferroan olivine components. The MgO produced by eq. (10) may have been the main source of Mg introduced in zone III of Allende zoned chondrules.

In summary, there are two fundamental potential factors to produce the zonation in Allende chondrule groundmasses, high oxygen pressure of the ambient gas or solution, and high alkali pressure. Under conditions of high oxygen pressure, Fe metals in or outside of chondrules were oxidized and consumed SiO_2 by eq. (9) to form silica-under-saturated products in or outside of chondrules, resulting in expulsion of the excess SiO_2 from zone III. Conditions of high alkali pressure produced nepheline and/or sodalite, resulting in the high Na and K contents of zone III.

5.2. Environment of zoning formation

Zonation was formed after the solidification of chondrules, and then solid chondrules were transported to a condition under which the zonation was produced by reaction with the ambient gas or solution. Two hypotheses are considered for the formation of Allende zoned chondrules. (A) Zonation was formed during metamorphism which

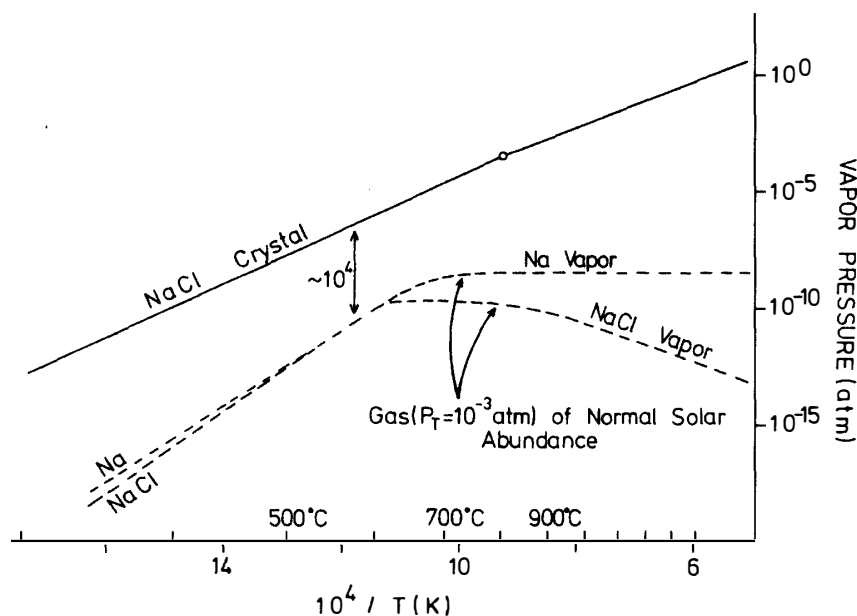


Fig. 7. Vapor pressures of NaCl crystals (quoted from Landolt-Bornstein Zahlenwerte und Funktionen, solid line with an open circle at NaCl melting point) and vapor pressures of Na and NaCl vapors having for the canonical solar gas (total pressure = 10^{-3} atm, FEGLEY and LEWIS, 1980, dashed curves) are plotted against $10^4/T$ (in Kelvin). The difference in vapor pressure of NaCl between the two is about 10^4 atm at the temperature range from 500°C to 700°C.

took place in the parent body under a dry or wet condition, and (B) zonation was formed by reaction with a nebular gas before accretion of the carbonaceous chondrite parent bodies.

Hypothesis (A) is not plausible for the following reasons. Chemical zonation is restricted to unbroken chondrules in carbonaceous chondrites, and fragmented planes of broken chondrules seem not to show such a zonation. Clean glass which is included in silicate fragments in ALH-77003, is directly in contact with the chondrite matrix, and shows no zonation (IKEDA, 1982). These observations mean that the zonal structures in round-shaped chondrules were produced prior to the final agglomeration with the matrix and the metamorphism in the carbonaceous chondrite parent body. If zone III was produced under a wet condition in the Allende parent body, hydrous minerals should occur commonly, but they are in fact very rare. If the formation of zone III took place under a dry condition, nepheline and sodalite in the Allende matrix surrounding the zoned chondrules should decompose to supply alkali components to zone III. This is not observed.

The second hypothesis (B) seems to be most plausible. A solar nebular gas having the canonical solar abundances cannot coexist in equilibrium with NaCl or Na_2CO_3 crystals at any temperature. Instead, it precipitates nepheline and/or sodalite at temperatures lower than about 900 K under the condition of total gas pressure of 10^{-3} atm (FEGLEY and LEWIS, 1980). In Fig. 7, vapor pressures of Na and NaCl species for the canonical solar gas (FEGLEY and LEWIS, 1980, total pressure of 10^{-3} atm) are shown together with the vapor pressure of pure NaCl crystals. The difference between the two is about 10^4 in

temperature range from 500°C to 700°C (Fig. 7).

The nebular gases which reacted with chondrules in some carbonaceous chondrites were extremely oxidized in comparison to the canonical solar gas (IKEDA and PRINZ, 1993; MURAKAMI and IKEDA, 1994). Thus, the nebular gas which produced Allende zoned chondrules may have been also oxidized; it was depleted in H₂ and He, whereas the other components could have been present in solar abundances. Under these oxidizing conditions the stable mineral assemblage of the Allende zoned chondrule should comprise those phases present in zone III; these are nepheline, sodalite, fayalite (Table 1), and high-Ca pyroxene. Therefore, the gas which produced zone III of Allende zoned chondrules should have been in equilibrium with the mineral assemblage (nepheline + sodalite + high-Ca pyroxene + ferroan olivine). According to PALME and FEGLEY (1990), gases enriched in H₂O compared to H₂ by a factor more than 10³ precipitate ferroan olivine directly from the gas at high temperatures. On the other hand, alkalis condense at lower temperatures, around 1000 K, from nebular gases, over a considerable range of H₂O/H₂ ratios (LATTIMER *et al.*, 1978; WOOD and HASHIMOTO, 1993). These suggest that gases depleted in H₂ and He by a factor more than 10³ in comparison to the canonical solar gas can coexist with the above-stated mineral assemblage of zone III at temperatures around 1000 K.

Our scenario is as follows. The nebular gas depleted in H₂ and He could be produced in the solar nebula; for an example, if sedimentation of chondritic or cometary materials took place at the ecliptic plane in low temperatures, shock heating or radiation heating could produce gases which are depleted in H₂. Evaporation of these materials could produce gases in which the vapor pressure of Na is higher by 10³ than the canonical solar gas, on the assumption that the total gas pressure is about 10⁻³ atm. The gas would have a high oxygen and water-vapor pressure, as demonstrated by the mineralogy of some carbonaceous chondrites (IKEDA and PRINZ, 1993; MURAKAMI and IKEDA, 1994).

On the other hand, zoned chondrules such as the Allende zoned chondrule studied here have not yet been found in unequilibrated ordinary chondrites. This suggests that chondrules in ordinary chondrites have never experienced such high Na-vapor and oxygen pressures and that the nebular gases which were in equilibrium with chondrules in ordinary chondrites had a composition similar to the canonical solar gas or at least had some other composition.

5.3. Diffusion in zone II and reaction duration of zone III

The Na₂O content of the Allende zoned chondrule studied here increases continuously from 1.5–2.5 wt% in zone I to 2.5–3.5 wt% in zone II (Table 1). However, zone II cannot be clearly detected in some Allende zoned chondrules having glassy groundmass, which may be due to low diffusivity of glassy groundmass in comparison to the cryptocrystalline groundmass of the Allende zoned chondrule studied here.

We can estimate the constraints for the anhydrous reactions by applying the diffusion coefficient of eq. (2). In Fig. 8, the curve denoted by $x=1 \mu\text{m}$ shows the relation between time and temperature using the equation $1 \times 10^{-4} \text{ cm} = (Dt)^{1/2}$ where D is diffusion coefficient obtained by eq. (2). Distance x may be smaller than $1 \mu\text{m}$ for glassy groundmasses of Allende chondrules. The groundmass of the Allende zoned chondrule studied here, which has zone II of about $100 \mu\text{m}$ width (Table 1), is cryptocrystalline, and the

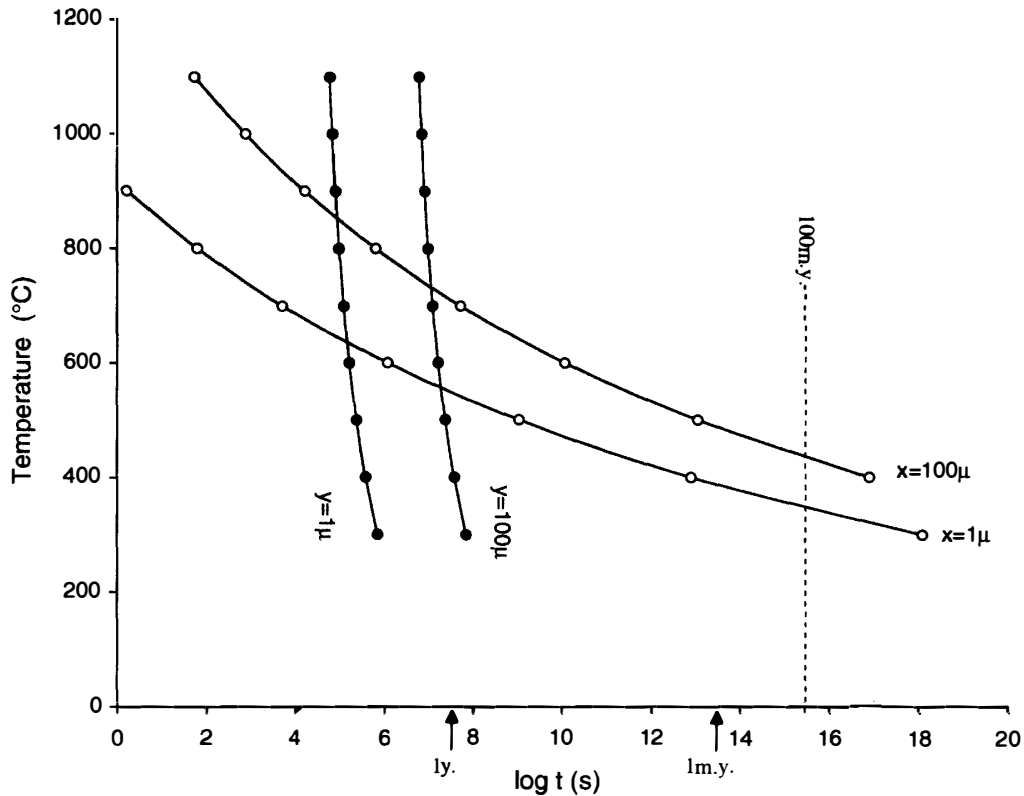


Fig. 8. Temperature-time relations for zone-II diffusion (curves with open circles) calculated from equation $x=(Dt)^{1/2}$ with the diffusion coefficients of eq. (2) and for zone-III formation (curves with solid circles) obtained from eq. (3).

diffusion must have been faster than the diffusion coefficients of eq. (2) because of boundary diffusion due to the cryptocrystalline texture. Therefore, the temperature and duration to produce zone II for Allende chondrules should be lower and shorter than at least the curve denoted by $x=100 \mu\text{m}$ and probably than the curve denoted by $x=1 \mu\text{m}$.

In Fig. 8, the curve denoted by $y=100 \mu\text{m}$ was obtained from eq. (3) with an average width of $100 \mu\text{m}$ for zone III of the Allende zoned chondrule studied here, suggesting that the reaction duration might have been about 1 year. As already discussed in Section 5.2, the Na or NaCl pressure which produced the Allende zoned chondrules might have been higher by 10^3 than the canonical solar gas. If so, the Na or NaCl gas pressure may be slightly lower than the vapor pressure of pure NaCl for the heating runs. If the NaCl gas pressure was lower by 1/10 than that of the pure NaCl, the reaction rate to produce zone III would be smaller by 1/10 than that obtained for the heating experiments. In this situation the reaction duration might have been about 10 years on the assumption that the reaction rate is in proportion to the gas pressure. However, if the gas which produced Allende zoned chondrules was the canonical solar gas, the NaCl gas pressure might have been lower by an order of 10^4 in comparison to that of our heating runs (Fig. 7) and the reaction duration might have been about 10^4 years. Therefore, the reaction duration for Allende zoned chondrules is estimated to have been between 1 and 10^4 years. Taking the absence of zone II in glassy Allende chondrules into consideration, the $T-t$ relation for the reactions should be on the right-hand side of the curve

denoted by $y=100 \mu\text{m}$ and in the lower portion of the curve denoted by $x=1 \mu\text{m}$. Therefore, the reaction temperature should be lower than 600°C as shown in Fig. 8, and this is consistent with the reaction temperature estimated by KIMURA and IKEDA (1995), who suggested the temperatures were lower than 800°C based on mineral assemblages in altered groundmasses of Allende chondrules. It is unlikely that the reaction to form zone III took place at temperatures lower than 400°C , because alkalis condense at temperatures higher than 500°C (FEGLEY and LEWIS, 1980; LATTIMER *et al.*, 1978) and the NaCl pressure decreases rapidly at temperatures lower than 400°C (Fig. 7). In summary, the temperature and duration for Allende zoned chondrules were about $400\text{--}600^\circ\text{C}$ and $1\text{--}10^4$ years, respectively.

5.4. *Correlation between zoned chondrules and alkali-bearing inclusions in carbonaceous chondrites*

Many fine-grained CAI's and amoeboid olivine inclusions occur in type 3 carbonaceous chondrites. These contain variable amounts of alkalis and FeO components (McSWEEN, 1977; WARK, 1981), although they are considered to have had a high-temperature origin (MARTIN and MASON, 1974; WARK, 1979; KORNACKI, 1981; COHEN, 1981; ARMSTRONG and WASSERBURG, 1981). According to IKEDA (1982), alkalis and FeO components were introduced into fine-grained CAI's at lower temperatures by the reaction of fassaite and minor melilite with an ambient nebular gas. These reactions expelled excess CaO, SiO₂, and minor MgO components of the fassaite to produce nepheline, spinel, and minor high-Ca pyroxene within the inclusions. This reaction is similar to that for the formation of zone III in Allende zoned chondrules. However, the oxygen isotopic compositions of highly-altered Allende chondrules are different from those of CAI's or amoeboid olivine inclusions in Allende (IKEDA and KIMURA, 1995), and the gas for Allende zoned chondrules might be different from the gas for Allende inclusions.

6. Conclusion

1) Round-shaped large chondrules show zonal structures (denoted I, II, III), which were produced by reaction with a nebular gas after chondrule formation and prior to the accretion on the parent body, although the intermediate zone is sometimes lacking in zoned chondrules having glassy groundmasses.

2) Similar zonations were produced in isothermally heated experiments under the condition of high vapor pressure of NaCl or Na₂CO₃.

3) In zones II and III, the main reaction is substitution of one Ca atom of a normative anorthite component by two Na atoms to produce normative nepheline components both in heating experiments and Allende zoned chondrules. In addition, in Allende chondrules the introduction of FeO, MgO, Cl, and alkalis and expulsion of excess CaO and SiO₂ produced nepheline, sodalite, and ferroan olivine components in zone III.

4) The temperatures of the zoning formation are around $600\text{--}400^\circ\text{C}$ for Allende. The duration to form the zonation is calculated to have been 1 to 10^4 years.

Acknowledgments

We thank to Prof. R.H. HEWINS of Rutgers University for a critical reading of the manuscript and discussion. We also thank Dr. M. ZOLENSKY and an anonymous referee for constructive reviews. This work was supported partly by a Grant for the Japan-Korea Cooperative Science Program (IKEDA).

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(Received September 8, 1995; Revised manuscript accepted October 23, 1995)